

**MIL-HDBK-691B**

**12 March 1987**

**SUPERSEDING**

**MIL-HDBK-691A**

**17 May 1965**

# **MILITARY STANDARDIZATION HANDBOOK**

## **ADHESIVE BONDING**



**NO DELIVERABLE DATA REQUIRED BY THIS DOCUMENT**

**AMSC N/A**

**FSC 8040**

DISTRIBUTION STATEMENT A Approved for public release; distribution unlimited.

Department of Defense  
Washington, D.C.

MIL-HDBK-691B

Adhesive Bonding

Date

1. This standardization handbook was developed by the Department of Defense in accordance with the established procedures.
2. This publication was approved on \_\_\_\_\_ for printing and inclusion in the military standardization handbook series.
3. This handbook provides basic and fundamental information on adhesives and related bonding processes for the guidance of engineers and designers of military materiel. It should provide valuable information on most of the factors that must be considered in adhesive bonding, and should be of value in the preparation of specifications, including process specifications. The handbook is not intended to be referenced in purchase specifications, except for informational purposes, nor shall it supersede any specification requirements.
4. Every effort has been made to reflect the latest information on adhesives and adhesive bonding and closely related techniques. It is the intent to review this handbook periodically to insure its completeness and accuracy. Beneficial comments (recommendations, additions, or deletions) and any pertinent data which may be of use in improving this document should be addressed to: Director, Army Materials Technology Laboratory ATTN: SLCMT-MSE, Watertown, MA 02172-0001, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document, or by letter.

## MIL-HDBK-691B

### FOREWORD

This handbook is one of a group which covers metallic and nonmetallic materials used in the design and construction of military equipment. The purpose of these handbooks is to provide up-to-date information and design data of direct usefulness to engineers and designers of military equipment.

The intent of this handbook is to provide detailed information useful to engineers and designers concerned with adhesive bonding of military materiel. The earlier versions of this document concentrated on fundamental guidelines, but it was felt that such information was too general to be useful. Consequently, the handbook has been completely rewritten and expanded. Even with the considerable amount of information given in this handbook and in other sources, it is nevertheless recommended that designers and engineers with adhesive bonding problems seek the assistance of a qualified adhesives technologist.

The properties and data presented in this handbook come from many sources and are not intended to be used for purposes of providing manufacturing or procurement specifications. Such requirements are adequately covered by applicable specifications.

Comments on this handbook are invited. This document was prepared for the U.S. Army Materials Technology Laboratory, (MTL), by the DoD Plastics Technical Evaluation Center, (PLASTEC), U.S. Army Armament Research, Development and Engineering Center (ARDEC) at Dover, NJ 07801-5001

## MIL-HDBK-691B

## CONTENTS

		<u>Page</u>
	Foreword	ii
Paragraph	INTRODUCTION TO ADHESIVE BONDING . . . . .	1
1.		
1.1	Definition of adhesive bonding. . . . .	1
1.2	Functions of adhesives . . . . .	1
1.3	Advantages and disadvantages of adhesive bonds	2
1.3.1	Advantages. . . . .	2
1.3.2	Disadvantages . . . . .	4
1.4	Theories of adhesion . . . . .	5
1.4.1	Mechanical theory. . . . .	5
1.4.2	Adsorption theory . . . . .	6
1.4.3	Electrostatic theory. . . . .	6
1.4.4	Diffusion theory. . . . .	6
1.4.5	Weak-boundary layer theory. . . . .	7
1.5	Requirements for a good bond. . . . .	7
1.5.1	Cleanliness . . . . .	7
1.5.2	Wetting . . . . .	8
1.5.3	Solidification. . . . .	8
1.5.4	Adhesive choice . . . . .	8
1.5.5	Joint design. . . . .	9
1.6	Mechanism of bond failure . . . . .	9
1.7	Basic adhesive materials classification . .	11
1.7.1	Function. . . . .	11
1.7.2	Major types . . . . .	11
1.7.2.1	Thermosetting adhesives . . . . .	11
1.7.2.2	Thermoplastic adhesives . . . . .	11
1.7.2.3	Elastomeric adhesives . . . . .	14
1.7.2.4	Adhesive alloys . . . . .	14
1.7.3	Mode of application and setting . . . . .	14
1.7.4	Physical form . . . . .	14
1.7.5	Cost. . . . .	14
1.7.6	Specific adherends or applications. . . . .	17
1.8	Adhesive composition . . . . .	17
1.8.1	Base or binder. . . . .	17
1.8.2	Hardener. . . . .	17
1.8.3	Catalyst. . . . .	17
1.8.4	Solvents. . . . .	17
1.8.5	Diluent . . . . .	17
1.8.6	Fillers . . . . .	17
1.8.7	Carriers or reinforcements. . . . .	18
1.9	Adhesive bonding process . . . . .	18
	References. . . . .	19
2.	JOINT DESIGN. . . . .	20
2.1	Basic principles . . . . .	20
2.2	Types of stress . . . . .	20
2.2.1	Compression . . . . .	20



## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
2.2.2	Shear . . . . .	20
2.2.3	Tensile . . . . .	20
2.2.4	Peel. . . . .	21
2.2.5	Cleavage. . . . .	21
2.3	Methods of improving joint efficiency . . .	21
2.3.1	Joint design criteria . . . . .	24
2.4	Typical joint designs . . . . .	26
2.4.1	Joints for flat adherends . . . . .	27
2.4.1.1	Butt joints . . . . .	27
2.4.1.2	Lap joints. . . . .	27
2.4.1.3	Strap joints. . . . .	29
2.4.1.4	Peeling of adhesive joints. . . . .	29
2.4.2	Stiffening joints . . . . .	29
2.4.3	Cylindrical joints . . . . .	29
2.4.4	Angle and corner joints . . . . .	29
2.4.5	Plastic and elastomer joints . . . . .	33
2.4.5.1	Flexible plastic and elastomers . . . . .	33
2.4.5.2	Rigid plastics. . . . .	33
2.4.5.3	Wood joints . . . . .	34
2.4.6	Metal joints. . . . .	36
2.4.7	Joints combining different adherend types . .	36
2.4.7.1	Joints with adherends differing in rigidity .	36
2.4.7.2	Joints with adherends differing in coefficient of thermal expansion. . . . .	36
2.5	Stress analysis . . . . .	36
2.5.1	General principles. . . . .	36
2.5.1.1	Theoretical analyses of stresses and strains.	36
2.5.1.2	Experimental analyses . . . . .	39
2.5.1.3	Failure analyses. . . . .	40
2.5.2	Methods . . . . .	40
2.5.2.1	Volkersen . . . . .	40
2.5.2.2	Goland and Reissner . . . . .	41
2.5.2.3	Forest products laboratory review . . . . .	41
	References. . . . .	42
3.	ADHEREND TYPES. . . . .	44
3.1	General discussion. . . . .	44
3.2	Similar substrates. . . . .	44
3.2.1	Porous materials. . . . .	44
3.2.2	Nonporous materials . . . . .	45
3.3	Dissimilar substrates . . . . .	45
3.3.1	Porous materials. . . . .	45
3.3.2	Nonporous materials . . . . .	45
	References. . . . .	46

## MIL-HDEK-691B

## CONTENTS - Continued.

		<u>Page</u>
4.	STRUCTURAL ADHESIVE TYPES & SELECTION GUIDELINES	47
4.1	General discussion . . . . .	47
4.2	Classification of SME handbook. . . . .	47
4.2.1	Chemically reactive types . . . . .	47
4.2.1.1	Catalytic plural components - chemical cure . . . . .	47
4.2.1.1.1	Epoxy adhesives . . . . .	47
4.2.1.1.2	Phenolic adhesives . . . . .	48
4.2.1.1.3	Resorcinol-formaldehyde . . . . .	49
4.2.1.1.4	Polylesters . . . . .	49
4.2.1.1.5	Polysulfides . . . . .	49
4.2.1.1.6	Polyurethanes . . . . .	49
4.2.1.1.7	Silicones . . . . .	50
4.2.1.2	Catalytic plural components - moisture cure . . . . .	51
4.2.1.2.1	Silicones . . . . .	51
4.2.1.2.2	Urethanes . . . . .	52
4.2.1.2.3	Other adhesives . . . . .	52
4.2.1.3	Heat-activated system (one-part system) . . . . .	52
4.2.1.3.1	Polybenzimidazoles (PBI) and polyimides (PI) . . . . .	52
4.2.1.3.2	Epoxies . . . . .	54
4.2.1.3.3	Nylon . . . . .	55
4.2.1.3.4	Phenolics . . . . .	56
4.2.1.3.5	Polyvinyl acetals . . . . .	56
4.2.1.3.6	Urethanes . . . . .	56
4.2.2	Evaporation or diffusion adhesives . . . . .	56
4.2.2.1	Solvent-based systems . . . . .	56
4.2.2.1.1	Natural rubber . . . . .	57
4.2.2.1.2	Reclaimed rubber . . . . .	57
4.2.2.1.3	Synthetic rubbers. . . . .	57
4.2.2.1.3.1	Nitrile rubber . . . . .	57
4.2.2.1.3.2	Neoprene or polychloroprene. . . . .	58
4.2.2.1.3.3	Butyl rubber . . . . .	58
4.2.2.1.3.4	Styrene-butadiene rubber . . . . .	58
4.2.2.1.4	Phenolics. . . . .	58
4.2.2.1.5	Urethanes. . . . .	58
4.2.2.1.6	Vinyl resins . . . . .	59
4.2.2.1.7	Acrylics . . . . .	59
4.2.2.1.8	Miscellaneous resins . . . . .	60
4.2.2.2	Water-based systems. . . . .	60
4.2.2.2.1	Natural rubber . . . . .	60
4.2.2.2.2	Reclaimed rubber . . . . .	61
4.2.2.2.3	Synthetic rubbers. . . . .	61
4.2.2.2.4	Vinyl Resins . . . . .	61
4.2.2.2.5	Acrylics . . . . .	61
4.2.2.2.6	Miscellaneous Resins . . . . .	61

## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
4.2.3	61
4.2.3.1	62
4.2.3.2	63
4.2.3.3	64
4.2.4	65
4.2.5	65
4.2.5.1	69
4.2.5.2	69
4.2.5.3	69
4.2.5.4	70
4.2.5.5	71
4.2.5.6	71
4.2.6	71
4.3	72
4.3.1	72
4.3.1.1	72
4.3.1.2	72
4.3.1.3	73
4.3.1.4	73
4.3.1.5	73
4.3.1.6	74
4.3.1.7	75
4.3.1.8	75
4.3.1.9	75
4.3.1.10	75
4.3.1.11	76
4.3.1.12	78
4.3.2	78
4.3.2.1	78
4.3.2.2	79
4.3.2.2.1	79
4.3.2.2.2	79
4.3.2.2.3	79
4.3.2.2.4	80
4.3.2.2.5	80
4.3.2.3	80
4.3.2.3.1	80
4.3.2.3.1.1	80
4.3.2.3.1.2	81
4.3.2.3.2	84
4.3.2.4	84
4.3.2.4.1	84
4.3.2.4.2	84
4.3.2.4.3	84
4.3.2.5	84
4.3.3	85

## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
4.4	Additional classifications . . . . . 86
4.4.1	Adhesive/sealants . . . . . 86
4.4.1.1	Types of sealants . . . . . 86
4.4.1.1.1	Hardening types . . . . . 86
4.4.1.1.2	Non-hardening types . . . . . 87
4.4.1.2	Primers . . . . . 87
4.4.2	Microencapsulated adhesives . . . . . 87
4.4.3	Electrically and thermally conductive adhesives . . . . . 88
4.4.3.1	Electrically-conductive adhesives . . . . . 88
4.4.3.2	Thermally-conductive adhesives. . . . . 89
4.4.4	Premixed frozen adhesives . . . . . 89
4.4.5	Anaerobic adhesives . . . . . 89
4.4.6	Fast setting adhesives. . . . . 92
4.4.7	Elastomeric adhesives . . . . . 92
4.4.8	Natural glues . . . . . 95
4.4.8.1	Vegetable glues . . . . . 95
4.4.8.1.1	Starch. . . . . 95
4.4.8.1.2	Dextrins. . . . . 95
4.4.8.1.3	Soyabean glue . . . . . 96
4.4.8.1.4	Rosin . . . . . 96
4.4.8.2	Glues of animal origin. . . . . 96
4.4.8.2.1	Casein glue . . . . . 97
4.4.8.2.2	Blood albumen (blood glues) . . . . . 97
4.4.8.2.3	Animal glues. . . . . 97
4.4.8.2.4	Fish glues. . . . . 98
4.4.8.2.5	Shellac . . . . . 98
4.4.9	Inorganic glues . . . . . 98
4.4.9.1	Soluble silicates . . . . . 99
4.4.9.2	Phosphate cements . . . . . 99
4.4.9.3	Basic salts (Sorel cements) . . . . . 100
4.4.9.4	Litharge cements. . . . . 100
4.4.9.5	Sulphur cements . . . . . 100
4.4.9.6	Hydraulic cements . . . . . 100
4.5	Factors to be considered in adhesive selection . . . . . 101
4.5.1	Adhesive substrates (adherends) . . . . . 101
4.5.2	Service requirements. . . . . 101
4.5.3	Assembly requirements . . . . . 101
4.5.4	Cost requirements . . . . . 102
4.5.5	Time-related requirements . . . . . 102
4.5.5.1	Storage life (shelf life) . . . . . 102
4.5.5.2	Working life (pot life). . . . . 102
4.5.5.3	Tack range (open time) (open tack time) (tack time) (tack-free time). . . . . 102
4.5.5.4	Assembly time . . . . . 103
4.5.5.5	Curing time . . . . . 103

## MIL-HDEK-691B

## CONTENTS - Continued.

		<u>Page</u>
4.5.5.6	Drying time . . . . .	103
4.5.5.7	Joint conditioning time (joint aging time). .	103
4.5.5.8	Setting time. . . . .	103
4.5.5.9	Earliest handling time. . . . .	103
4.6	Adhesives for metals. . . . .	103
4.7	Adhesives for plastics. . . . .	105
4.7.1	Solvent cementing . . . . .	105
4.7.2	Adhesive bonding. . . . .	105
4.7.3	Thermal welding techniques. . . . .	105
4.7.3.1	Direct heating methods. . . . .	105
4.7.3.1.1	Hot-plate welding . . . . .	106
4.7.3.1.2	Hot-gas welding . . . . .	106
4.7.3.1.3	Heated-tool welding . . . . .	106
4.7.3.1.4	Radiant-heat welding. . . . .	106
4.7.3.1.5	Resistance-wire welding . . . . .	107
4.7.3.1.6	Molten-polymer (extruded bead) sealing. . . .	107
4.7.3.2	Indirect heating methods. . . . .	107
4.7.3.2.1	Dielectric bonding (high frequency bonding) . . . . .	107
4.7.3.2.2	Induction heating (electromagnetic bonding). . . . .	107
4.7.3.2.3	Ultrasonic welding. . . . .	107
4.7.3.2.4	Ultrasonic adhesive bonding . . . . .	107
4.7.3.2.5	Spin or friction welding. . . . .	107
4.8	Adhesives for elastomers. . . . .	108
4.8.1	Vulcanized elastomers . . . . .	108
4.8.2	Unvulcanized elastomers . . . . .	108
4.9	Adhesives for wood. . . . .	108
4.10	Adhesives for glass . . . . .	109
4.11	Checklist for adhesives selection . . . . .	109
	References . . . . .	111
5.	ADHEREND SURFACE PREPARATION. . . . .	115
5.1	General discussion. . . . .	115
5.2	Primers . . . . .	115
5.3	Surface preparation . . . . .	116
5.3.1	Importance of surface preparation . . . . .	116
5.3.2	General cleaning methods. . . . .	118
5.3.2.1	Solvent wiping. . . . .	118
5.3.2.2	Vapor degreasing. . . . .	118
5.3.2.3	Abrasive cleaning . . . . .	119
5.3.2.4	Chemical cleaning (alkaline cleaning) . . . .	119
5.3.2.4.1	Water purity. . . . .	119
5.3.2.5	Other cleaning methods. . . . .	120
5.3.2.6	Chemical etch . . . . .	120

## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
5.3.2.7	Combined cleaning methods. . . . . 120
5.3.2.8	Activated-gas surface treatment of polymer . . 122
5.3.3	Evaluation of cleaned parts before and after bonding. . . . . 124
5.3.3.1	Water-break test . . . . . 124
5.3.3.2	Contact angle test . . . . . 124
5.3.3.3	Mode of failure of adhesive joint. . . . . 125
5.3.4	Surface exposure time. . . . . 125
5.3.5	Specific surface treatments. . . . . 126
5.3.5.1	Metals . . . . . 126
5.3.5.1.1	General discussion . . . . . 126
5.3.5.1.2	Aluminum and alloys. . . . . 126
5.3.5.1.3	Beryllium. . . . . 131
5.3.5.1.4	Brass. . . . . 135
5.3.5.1.5	Bronze . . . . . 135
5.3.5.1.6	Cadmium. . . . . 135
5.3.5.1.7	Copper and alloys. . . . . 136
5.3.5.1.8	Magnesium and alloys . . . . . 138
5.3.5.1.9	Nickel and alloys. . . . . 140
5.3.5.1.10	Steel (mild carbon), iron. . . . . 140
5.3.5.1.11	Steel (stainless). . . . . 142
5.3.5.1.12	Tin. . . . . 144
5.3.5.1.13	Titanium and alloys. . . . . 144
5.3.5.1.14	Tungsten and alloys. . . . . 146
5.3.5.1.15	Zinc and alloys. . . . . 146
5.3.5.1.16	Plated metals. . . . . 147
5.3.5.1.17	Weldbonding. . . . . 148
5.3.5.1.17.1	Aluminum . . . . . 148
5.3.5.1.17.2	Titanium . . . . . 149
5.3.5.2	Plastics . . . . . 150
5.3.5.2.1	General discussion . . . . . 150
5.3.5.2.2	Thermoplastics . . . . . 150
5.3.5.2.2.1	Acetal copolymer . . . . . 150
5.3.5.2.2.2	Acetal homopolymer . . . . . 151
5.3.5.2.2.3	Acrylonitrile-butadiene-styrene. . . . . 152
5.3.5.2.2.4	Cellulosics. . . . . 153
5.3.5.2.2.5	Ethylene-tetrafluoroethylene copolymer . . . . 153
5.3.5.2.2.6	Ethylene-vinylacetate. . . . . 153
5.3.5.2.2.7	Fluorinated ethylene propylene . . . . . 154
5.3.5.2.2.8	Ionomers . . . . . 154
5.3.5.2.2.9	Nylon (polyamide). . . . . 154
5.3.5.2.2.10	Perfluoroalkoxy resin. . . . . 155
5.3.5.2.2.11	Phenylene oxide-based resins . . . . . 155
5.3.5.2.2.12	Polyaryl ether . . . . . 155
5.3.5.2.2.13	Polyaryl sulfone . . . . . 156
5.3.5.2.2.14	Polycarbonate. . . . . 157
5.3.5.2.2.15	Polychlorotrifluoroethylene. . . . . 158

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
5.3.5.2.2.16	Polyester (thermoplastic) . . . . .	158
5.3.5.2.2.17	Polyethylene . . . . .	158
5.3.5.2.2.18	Poly(ethylene-chlorotrifluoroethylene) . . . . .	161
5.3.5.2.2.19	Polymethylmethacrylate . . . . .	161
5.3.5.2.2.20	Polymethylpentene . . . . .	161
5.3.5.2.2.21	Polyphenylene sulfide . . . . .	163
5.3.5.2.2.22	Polypropylene . . . . .	163
5.3.5.2.2.23	Polystyrene . . . . .	164
5.3.5.2.2.24	Polysulfone . . . . .	165
5.3.5.2.2.25	Polytetrafluoroethylene . . . . .	167
5.3.5.2.2.26	Polyvinyl chloride . . . . .	167
5.3.5.2.2.27	Polyvinyl fluoride . . . . .	167
5.3.5.2.2.28	Polyvinylidene fluoride . . . . .	168
5.3.5.2.2.29	Styrene-acrylonitrile . . . . .	169
5.3.5.2.3	Thermosets . . . . .	169
5.3.5.2.3.1	Diallylphthalate . . . . .	169
5.3.5.2.3.2	Epoxies . . . . .	169
5.3.5.2.3.3	Melamine-formaldehyde . . . . .	170
5.3.5.2.3.4	Phenol-formaldehyde . . . . .	170
5.3.5.2.3.5	Polyester . . . . .	170
5.3.5.2.3.6	Polyimide . . . . .	171
5.3.5.2.3.7	Polyurethane . . . . .	171
5.3.5.2.3.8	Silicone-resins . . . . .	172
5.3.5.2.3.9	Urea-formaldehyde . . . . .	172
5.3.5.2.4	Reinforced plastics/composites . . . . .	173
5.3.5.2.4.1	Reinforced thermosets (laminates) . . . . .	173
5.3.5.2.4.2	Reinforced thermoplastics (glass reinforced) . . . . .	176
5.3.5.2.5	Plastic Foams . . . . .	177
5.3.5.3	Rubbers . . . . .	177
5.3.5.3.1	General discussion . . . . .	177
5.3.5.3.2	Neoprene . . . . .	181
5.3.5.3.3	Ethylene-propylene-diene terpolymer . . . . .	183
5.3.5.3.4	Silicone rubber . . . . .	183
5.3.5.3.5	Butyl rubber . . . . .	184
5.3.5.3.6	Chlorobutyl rubber . . . . .	184
5.3.5.3.7	Chlorosulfonated polyethylene . . . . .	185
5.3.5.3.8	Nitrile rubber (butadiene-acrylonitrile) . . . . .	186
5.3.5.3.9	Polyurethane elastomers . . . . .	188
5.3.5.3.10	Synthetic natural rubber (polyisoprene) . . . . .	188
5.3.5.3.11	Styrene-butadiene rubber . . . . .	188
5.3.5.3.12	Polybutadiene (butadiene rubber) . . . . .	189
5.3.5.3.13	Fluorosilicone elastomers . . . . .	189
5.3.5.3.14	Epichlorohydrin rubber . . . . .	189
5.3.5.3.15	Polysulfide rubber . . . . .	189
5.3.5.3.16	Polypropylene oxide . . . . .	190
5.3.5.3.17	Fluorocarbon elastomers . . . . .	190
5.3.5.3.18	Polyacrylate (polyacrylic rubber) . . . . .	190
5.3.5.3.19	Thermoplastic rubber . . . . .	191

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
5.3.5.4	Miscellaneous materials. . . . .	191
5.3.5.4.1	Asbestos . . . . .	191
5.3.5.4.2	Brick and fired non-glazed building materials. . . . .	192
5.3.5.4.3	Carbon and graphite. . . . .	192
5.3.5.4.4	Glass (non-optical). . . . .	192
5.3.5.4.5	Glass (optical). . . . .	192
5.3.5.4.6	Ceramics (unglazed). . . . .	193
5.3.5.4.7	Ceramics (glazed). . . . .	193
5.3.5.4.8	Concrete . . . . .	193
5.3.5.4.8.1	Portland cement type . . . . .	193
5.3.5.4.8.2	Bituminous type. . . . .	193
5.3.5.4.9	Wood, plywood. . . . .	194
5.3.5.4.10	Painted surfaces . . . . .	194
	References . . . . .	195
6.	THE CONVENTIONAL ADHESIVE BONDING PROCESS. . . . .	199
6.1	General discussion . . . . .	199
6.2	Adhesive storage and preparation . . . . .	199
6.2.1	Adhesive storage . . . . .	199
6.2.2	Adhesive preparation . . . . .	199
6.2.2.1	Small-portion mixer-dispensers . . . . .	200
6.3	Methods of adhesive application. . . . .	200
6.3.1	General. . . . .	200
6.3.2	Liquid adhesives . . . . .	200
6.3.2.1	Brushing . . . . .	201
6.3.2.2	Flowing. . . . .	201
6.3.2.3	Spraying . . . . .	201
6.3.2.4	Roll coating . . . . .	201
6.3.2.5	Knife coating. . . . .	201
6.3.2.6	Silk screening . . . . .	202
6.3.2.7	Oil can and squeeze bottle . . . . .	202
6.3.2.8	Hand dipping . . . . .	202
6.3.3	Pastes . . . . .	202
6.3.3.1	Spatulas, knives, trowels. . . . .	202
6.3.4	Powders. . . . .	202
6.3.5	Films. . . . .	203
6.3.6	Hot melt . . . . .	203
6.3.6.1	Melt-reservoir systems . . . . .	203
6.3.6.2	Progressive-feed systems . . . . .	204
6.4	Joint assembly methods . . . . .	205
6.4.1	Wet assembly . . . . .	205
6.4.2	Pressure-sensitive and contact bonding . . . . .	205
6.4.3	Solvent activation . . . . .	206
6.4.4	Heat activation. . . . .	206
6.5	Bonding equipment. . . . .	206



## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
6.5.1	General. . . . .	206
6.5.2	Pressure equipment . . . . .	207
6.5.3	Heating equipment. . . . .	208
6.5.3.1	Direct heat curing . . . . .	209
6.5.3.1.1	Oven heating . . . . .	209
6.5.3.1.2	Liquid baths . . . . .	209
6.5.3.1.3	Hot presses or platens . . . . .	209
6.5.3.2	Radiation curing . . . . .	209
6.5.3.3	Electric resistance heaters. . . . .	209
6.5.3.4	High-frequency dielectric (radio frequency heating) . . . . .	210
6.5.3.5	Induction heating. . . . .	211
6.5.3.6	Low-voltage heating. . . . .	211
6.5.3.7	Ultrasonic activation. . . . .	211
6.5.4	Adhesive thickness . . . . .	212
	References . . . . .	213
7.	SOLVENT CEMENTING OF PLASTICS (Solvent Welding)	214
7.1	Introduction . . . . .	214
7.2	Types of plastics solvent-cemented . . . . .	215
7.2.1	Cellulosics. . . . .	215
7.2.2	Acrylonitrile-butadiene-styrene. . . . .	217
7.2.3	Polyvinyl chloride . . . . .	217
7.2.3.1	PVC-ABS joints . . . . .	217
7.2.4	Polyamide (nylon). . . . .	217
7.2.5	Polymethylmethacrylate . . . . .	220
7.2.6	Polycarbonate. . . . .	220
7.2.7	Polystyrene. . . . .	220
7.2.8	Acetal homopolymer . . . . .	221
7.2.9	Acetal copolymer . . . . .	221
7.2.10	Polysulfone. . . . .	221
7.2.11	Polyphenylene oxide, polystyrene-modified. . . . .	222
7.2.12	Structural foams (thermoplastic) . . . . .	223
7.3	Methods of application . . . . .	224
7.3.1	Dip method . . . . .	224
7.3.2	Capillary method . . . . .	224
7.3.3	Precautions. . . . .	225
	References . . . . .	226
8.	RECOMMENDED ADHESIVES FOR SPECIFIC ADHERENDS	228
8.1	General discussion . . . . .	228
8.2	Metals . . . . .	228
8.2.1	Aluminum and alloys. . . . .	228
8.2.2	Beryllium. . . . .	228
8.2.3	Brass. . . . .	231
8.2.4	Bronze . . . . .	231

## MIL-HDEK-691B

## CONTENTS - Continued.

	<u>Page</u>
8.2.5	Cadmium. . . . . 231
8.2.6	Copper and alloys. . . . . 231
8.2.7	Magnesium and alloys . . . . . 232
8.2.8	Nickel and alloys. . . . . 232
8.2.9	Steel (Mild)(Carbon)(Iron) . . . . . 232
8.2.10	Steel, stainless . . . . . 233
8.2.11	Tin. . . . . 233
8.2.12	Titanium and alloys. . . . . 233
8.2.13	Tungsten and alloys. . . . . 233
8.2.14	Zinc and alloys. . . . . 233
8.2.15	Plated metals. . . . . 233
8.3	Plastics . . . . . 235
8.3.1	Thermoplastics . . . . . 235
8.3.1.1	Acetal copolymer (CELCON). . . . . 235
8.3.1.2	Acetal homopolymer (DELIN). . . . . 235
8.3.1.3	Acrylonitrile - butadiene - styrene (ABS). . . . . 236
8.3.1.4	Cellulosics. . . . . 236
8.3.1.5	Ethylene-tetrafluoroethylene copolymer (ETFE) (TEFZEL) . . . . . 236
8.3.1.6	Ethylene-vinyl acetate (EVA) . . . . . 236
8.3.1.7	Fluorinated ethylene propylene (FEP) . . . . . 236
8.3.1.8	Ionomer. . . . . 236
8.3.1.9	Nylon (polyamide). . . . . 236
8.3.1.10	Perfluoroalkoxy resins (PFA). . . . . 237
8.3.1.11	Phenylene oxide - based resins (NORYL) . . . . . 237
8.3.1.12	Polyaryl ether (ARYLON T). . . . . 237
8.3.1.13	Polyaryl sulfone (ASTREL 360). . . . . 237
8.3.1.14	Polycarbonate (LEXAN) (MERLON) (TUFFAK). . . . . 238
8.3.1.15	Polychlorotrifluoroethylene (PCTFE) (KEL-F). . . . . 239
8.3.1.16	Polyester (Thermoplastic). . . . . 239
8.3.1.17	Polyethylene . . . . . 240
8.3.1.18	Polyethylene - chlorotrifluoroethylene (E-CTFE)(HALAR). . . . . 240
8.3.1.19	Polymethylmethacrylate (PMMA) (Plexiglas) (Lucite) . . . . . 240
8.3.1.20	Polymethylpentane (TPX). . . . . 240
8.3.1.21	Polyphenylene sulfide (RYTON). . . . . 240
8.3.1.22	Polypropylene (PP) . . . . . 240
8.3.1.23	Polystyrene (PS) . . . . . 241
8.3.1.24	Polysulfone (UDEL) . . . . . 241
8.3.1.25	Polytetrafluoroethylene (PTFE) . . . . . 242
8.3.1.26	Polyvinyl chloride (PVC) . . . . . 242
8.3.1.27	Polyvinyl fluoride (PVF)(TELAR). . . . . 242
8.3.1.28	Polyvinylidene fluoride (PVF <sub>2</sub> )(KYNAR). . . . . 242
8.3.1.29	Styrene-acrylonitrile (SAN)(LUSTRAN) . . . . . 242
8.3.2	Thermosets . . . . . 242
8.3.2.1	Diallylphthalate (DAP) . . . . . 242

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
8.3.2.2	Epoxies. . . . .	243
8.3.2.3	Melamine-Formaldehyde (Melamines). . . . .	243
8.3.2.4	Phenol-Formaldehyde (Phenolics). . . . .	243
8.3.2.5	Polyesters . . . . .	243
8.3.2.6	Polyimide. . . . .	243
8.3.2.7	Polyurethane . . . . .	244
8.3.2.8	Silicone resins. . . . .	244
8.3.2.9	Urea-formaldehyde. . . . .	244
8.3.3	Reinforced plastics/composites . . . . .	244
8.3.4	Plastic foams. . . . .	244
8.3.4.1	Thermoplastic foams. . . . .	244
8.3.4.2	Thermosetting foams. . . . .	245
8.4	Rubbers. . . . .	246
8.5	Wood . . . . .	246
8.6	Glass. . . . .	246
	References . . . . .	247
9.	THERMALLY AND ELECTRICALLY CONDUCTIVE ADHESIVES	250
9.1	Introduction . . . . .	250
9.2	Filler choice. . . . .	250
9.3	Filler content . . . . .	250
9.4	Silver migration . . . . .	250
9.5	Storage problems . . . . .	250
9.6	Oxide coatings . . . . .	250
9.7	Curing schedules . . . . .	250
9.8	Hardener/resin ratio . . . . .	253
9.9	Mixing time. . . . .	253
9.10	Time delay between mixing and use. . . . .	253
9.11	Surface preparation and solvent cleaning . . . . .	253
9.12	Interfacial resistance . . . . .	254
9.13	Aging. . . . .	254
9.14	Elevated-temperature testing . . . . .	255
9.15	Humidity environment . . . . .	256
9.16	Salt spray . . . . .	257
9.17	Water immersion. . . . .	258
9.18	Outgassing . . . . .	258
9.19	Pot life . . . . .	259
9.20	Maximum service temperature. . . . .	259
9.21	Flexibility. . . . .	259
	References . . . . .	260
10.	BONDING OF HONEYCOMB STRUCTURES . . . . .	261
10.1	Introduction . . . . .	261
10.2	Adhesive types . . . . .	263
10.3	Filleting. . . . .	263
10.4	Adhesive application techniques. . . . .	265

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
10.4.1	Films and tapes. . . . .	265
10.4.2	Solutions/emulsions. . . . .	265
10.4.3	Pastes . . . . .	266
	References . . . . .	267
11.	REPAIR OF ADHESIVE-BONDED STRUCTURES . . . . .	268
11.1	Introduction . . . . .	268
11.1.1	General application. . . . .	268
11.1.2	Factors to be considered . . . . .	268
11.2	Field repair . . . . .	268
11.3	Depot repair . . . . .	269
11.4	Materials. . . . .	269
11.5	Repair techniques. . . . .	270
11.5.1	General procedures for FRP . . . . .	270
11.5.2	Small cracks . . . . .	270
11.5.3	Delamination . . . . .	270
11.5.4	Small holes. . . . .	270
11.5.5	Radomes and antenna housing. . . . .	270
11.5.6	Polyester-glass. . . . .	271
11.5.7	FRP/metal. . . . .	271
11.5.8	Pressure application . . . . .	271
11.5.9	Air exclusion. . . . .	271
11.5.10	Repair of metals . . . . .	271
11.5.11	Phosphoric acid anodize. . . . .	271
11.5.12	Large-area composites. . . . .	273
11.5.13	Army aircraft weapons systems honeycomb structures . . . . .	274
11.5.14	Air Force repair guide . . . . .	274
11.5.15	Command airline practice . . . . .	274
	References . . . . .	276
12.	WELDBONDING. . . . .	277
12.1	Introduction . . . . .	277
12.1.1	Weldbond configuration . . . . .	277
12.2	Advantages and limitations . . . . .	282
12.3	Surface preparation. . . . .	282
12.4	Adhesive selection . . . . .	283
12.5	Tooling for weldbonding. . . . .	284
12.6	Weldbonding techniques . . . . .	285
12.7	Quality control. . . . .	285
	References . . . . .	286
13.	TEST METHODS . . . . .	288
13.1	Organization . . . . .	288
13.2	ASTM Standards . . . . .	288

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
13.2.1	ASTM D816-82 . . . . .	288
13.2.2	ASTM D896-84 . . . . .	288
13.2.3	ASTM D897-78 (1983) . . . . .	288
13.2.4	ASTM D898-69 (1980) . . . . .	289
13.2.5	ASTM D899-51 (1984) . . . . .	289
13.2.6	ASTM D903-49 (1983) . . . . .	289
13.2.7	ASTM D904-57 (1981) . . . . .	289
13.2.6	ASTM D905-49 (1981) . . . . .	289
13.2.9	ASTM D906-82 . . . . .	289
13.2.10	ASTM D950-82 . . . . .	290
13.2.11	ASTM D1002-72 (1983) . . . . .	290
13.2.12	ASTM D1062-78 (1983) . . . . .	290
13.2.13	ASTM D1084-63 (1981) . . . . .	290
13.2.14	ASTM D1144-84 . . . . .	291
13.2.15	ASTM D1146-53 (1981) . . . . .	291
13.2.16	ASTM D1151-84 . . . . .	291
13.2.17	ASTM D4299-83 . . . . .	292
13.2.18	ASTM D1183-70 (1981) . . . . .	292
13.2.19	ASTM D1184-69 (1980) . . . . .	292
13.2.20	ASTM D4300-83 . . . . .	292
13.2.21	ASTM D1304-69 (1983) . . . . .	293
13.2.22	ASTM D1337-56 (1984) . . . . .	293
13.2.23	ASTM D1338-56 (1982) . . . . .	293
13.2.24	ASTM D1344-78 . . . . .	293
13.2.25	ASTM D1382-64 (1981) . . . . .	294
13.2.26	ASTM D1383-64 (1981) . . . . .	294
13.2.27	ASTM D1488-60 (1981) . . . . .	294
13.2.28	ASTM D1489-69 (1981) . . . . .	294
13.2.29	ASTM D1490-82 . . . . .	295
13.2.30	ASTM D1579-60 (1981) . . . . .	295
13.2.31	ASTM D1581-60 (1984) . . . . .	295
13.2.32	ASTM D1582-60 (1981) . . . . .	296
13.2.33	ASTM D1583-61 (1981) . . . . .	296
13.2.34	ASTM D1584-60 (1984) . . . . .	296
13.2.35	ASTM D1713-65 (1981) . . . . .	296
13.2.36	ASTM D1780-72 (1983) . . . . .	296
13.2.37	ASTM D1781-76 (1981) . . . . .	297
13.2.38	ASTM D1828-70 (1981) . . . . .	297
13.2.39	ASTM D1875-69 (1980) . . . . .	298
13.2.40	ASTM D1876-72 (1983) . . . . .	298
13.2.41	ASTM D1877-77 . . . . .	298
13.2.42	ASTM D1879-70 (1981) . . . . .	298
13.2.43	ASTM D1916-69 (1980) . . . . .	299
13.2.44	ASTM D2095-72 (1983) . . . . .	299
13.2.45	ASTM D2182-72 (1978) . . . . .	300
13.2.46	ASTM D2183-69 (1982) . . . . .	300
13.2.47	ASTM D2293-69 (1980) . . . . .	301
13.2.48	ASTM D2294-69 (1980) . . . . .	301

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
13.2.49	ASTM D2295-72 (1983) . . . . .	301
13.2.50	ASTM D2239-82. . . . .	302
13.2.51	ASTM D2556-69 (1980) . . . . .	302
13.2.52	ASTM D2557-72 (1983) . . . . .	302
13.2.53	ASTM D2558-69 (1984) . . . . .	302
13.2.54	ASTM D2739-72 (1984) . . . . .	303
13.2.55	ASTM D2918-71 (1981) . . . . .	303
13.2.56	ASTM D2919-71 (1981) . . . . .	304
13.2.57	ASTM D2979-71 (1982) . . . . .	304
13.2.58	ASTM D3111-76 (1982) . . . . .	305
13.2.59	ASTM D3121-73 (1984) . . . . .	305
13.2.60	ASTM D3163-73 (1979) . . . . .	305
13.2.61	ASTM D3164-73 (1979) . . . . .	305
13.2.62	ASTM D3165-73 (1979) . . . . .	306
13.2.63	ASTM D3166-73 (1979) . . . . .	307
13.2.64	ASTM D3167-76 (1981) . . . . .	307
13.2.65	ASTM D3236-73 (1983) . . . . .	308
13.2.66	ASTM D3310-74 (1983) . . . . .	308
13.2.67	ASTM D3482-76 (1981) . . . . .	308
13.2.68	ASTM D3528-76 (1981) . . . . .	308
13.2.69	ASTM D3632-77 (1982) . . . . .	309
13.2.70	ASTM D3658-78 (1984) . . . . .	309
13.2.71	ASTM D3762-79 (1983) . . . . .	310
13.2.72	ASTM D3807-79. . . . .	310
13.2.73	ASTM D3808-79. . . . .	310
13.2.74	ASTM D3929-80. . . . .	311
13.2.75	ASTM D3931-80. . . . .	311
13.2.76	ASTM D3983-81. . . . .	311
13.2.77	ASTM D4027-81. . . . .	312
13.2.78	ASTM E229-70 (1981). . . . .	312
13.3	Federal Test Methods . . . . .	313
13.3.1	Federal Test Method Standard No. 175B. . . . .	313
13.3.1.1	Method 1081 Flexibility of Adhesives . . . . .	313
13.3.1.2	Method 4032.1 Ash Content of Adhesives . . . . .	313
13.3.1.3	Method 4041.1 Grit or Lumps.(or Undissolved Matter) in Adhesives . . . . .	313
13.3.1.4	Method 4051.1 Odor Test for Adhesives. . . . .	314
	References . . . . .	315
14.	QUALITY CONTROL. . . . .	316
14.1	Introduction. . . . .	316
14.2	Incoming material control . . . . .	318
14.2.1	Containers. . . . .	318
14.2.2	Adhesives . . . . .	319
14.3	Surface preparation control . . . . .	320
14.4	Process control of bonding. . . . .	320



## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
14.4.1	Prefit. . . . .	321
14.4.2	Adhesive application. . . . .	321
14.4.3	Assembly. . . . .	321
14.4.4	Curing. . . . .	322
14.4.5	Standard test specimen. . . . .	322
14.5	Final inspection. . . . .	322
14.5.1	General . . . . .	322
14.5.2	Nondestructive tests. . . . .	322
14.5.2.1	Visual inspection . . . . .	322
14.5.2.2	Sonic methods . . . . .	323
14.5.2.2.1	Tap test. . . . .	323
14.5.2.2.2	Sonic resonator . . . . .	323
14.5.2.2.3	Eddy-sonic test method. . . . .	323
14.5.2.2.4	Pulsed eddy-sonic test method/shurtronic harmonic bond tester. . . . .	323
14.5.2.2.5	Arvin acoustic analysis system. . . . .	323
14.5.2.3	Ultrasonic methods. . . . .	325
14.5.2.3.1	Ultrasonic pulse echo and contact impedance testing . . . . .	326
14.5.2.3.2	Sweep frequency resonance method. . . . .	326
14.5.2.4	Liquid crystals . . . . .	326
14.5.2.5	Holography. . . . .	327
14.5.2.6	Thermal image inspection. . . . .	327
14.5.2.7	Thermal infra-red inspection (TIRI) . . . . .	328
14.5.2.8	Radiography . . . . .	328
14.5.2.8.1	X-ray techniques. . . . .	328
14.5.2.8.2	Radioisotope methods. . . . .	328
14.5.2.8.3	Neutron radiography . . . . .	328
14.5.2.9	Penetrant inspection. . . . .	329
	References. . . . .	330
15.	ENVIRONMENTAL EFFECTS (Durability of Adhesive Joints in Adverse Environments). . . . .	331
15.0	Environmental effects . . . . .	331
15.1	Introduction. . . . .	331
15.2	High temperature. . . . .	334
15.2.1	General . . . . .	334
15.2.2	Epoxies . . . . .	336
15.2.3	Modified phenolics. . . . .	336
15.2.3.1	Nitrile phenolics . . . . .	336
15.2.3.2	Epoxy-phenolics . . . . .	337
15.2.4	Polysulfone . . . . .	337
15.2.5	Silicones . . . . .	338
15.2.6	Polyaromatics . . . . .	338
15.2.6.1	Polyimides. . . . .	338
15.2.6.2	Polybenzimidazole (PBI) . . . . .	339
15.3	Low temperatures and cryogenic temperatures. . . . .	339

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
15.4	Humidity and water immersion. . . . .	342
15.4.1	Effects of surface preparation on moisture exposure. . . . .	343
15.4.2	Stressed temperature/humidity test. . . . .	343
15.4.3	Hot water soak test . . . . .	346
15.4.4	Fatigue life data . . . . .	346
15.5	Salt water and salt spray . . . . .	351
15.5.1	Introduction. . . . .	351
15.5.2	Seacoast weathering environment . . . . .	351
15.5.3	Salt water immersion. . . . .	356
15.5.4	Nitrile-phenolic adhesives. . . . .	357
15.5.5	Boeing/Air Force studies. . . . .	357
15.6	Weathering. . . . .	358
15.6.1	General . . . . .	358
15.6.2	Simulation weathering/accelerated testing . . .	358
15.6.3	Outdoor weathering. Picatinny Arsenal studies . . . . .	360
15.6.4	Australian studies. . . . .	365
15.7	Chemicals and solvents. . . . .	366
15.8	Vacuum. . . . .	367
15.8.1	Higher temperature and vacuum . . . . .	368
15.9	Radiation . . . . .	368
15.10	Biological. . . . .	373
15.10.1	General . . . . .	373
15.10.2	Test methods. . . . .	374
	References. . . . .	374
	AN OUTLINE FOR A BONDING PROCESS SPECIFICATION .	378
16.1	Introduction. . . . .	378
16.2	Outline for bonding process specification . . .	378
	Reference . . . . .	382
	SPECIFICATIONS . . . . .	383
17.1	Organization. . . . .	383
17.2	ASTM Specifications . . . . .	383
17.2.1	ASTM C557-73 (1978) . . . . .	383
17.2.2	ASTM F656-80. . . . .	383
17.2.3	ASTM E865-82. . . . .	383
17.2.4	ASTM E866-82. . . . .	384
17.2.5	ASTM D1580-60 (1984). . . . .	384
17.2.6	ASTM D1779-65 (1983). . . . .	384
17.2.7	ASTM D1874-62 (1981). . . . .	384
17.2.8	ASTM D2235-81 . . . . .	384
17.2.9	ASTM D2559-82 . . . . .	385
17.2.10	ASTM D2560-80 . . . . .	385
17.2.11	ASTM D2564-80 . . . . .	385



## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
17.2.12	ASTM D2851-70 (1981). . . . . 385
17.2.13	ASTM D3024-83 . . . . . 385
17.2.14	ASTM D3110-82 . . . . . 386
17.2.15	ASTM D3122-80 . . . . . 386
17.2.16	ASTM D3138-83 . . . . . 386
17.2.17	ASTM D3498-76 (1981). . . . . 386
17.2.18	ASTM D3930-82 . . . . . 386
17.3	General Services Administration . . . . . 387
17.3.1	MMM-A-100D. . . . . 387
17.3.2	MMM-A-105 . . . . . 387
17.3.3	MMM-A-110B. . . . . 387
17.3.4	MMM-A-115C. . . . . 388
17.3.5	MMM-A-121 . . . . . 388
17.3.6	MMM-A-122C. . . . . 388
17.3.7	MMM-A-125C. . . . . 388
17.3.8	MMM-A-130B. . . . . 389
17.3.9	MMM-A-131A. . . . . 389
17.3.10	MMM-A-132A. . . . . 389
17.3.11	MMM-A-134 . . . . . 390
17.3.12	MMM-A-137D. . . . . 390
17.3.13	MMM-A-138A. . . . . 390
17.3.14	MMM-A-139A. . . . . 391
17.3.15	MMM-A-00150B (GSA-FSS). . . . . 391
17.3.16	MMM-A-179B. . . . . 392
17.3.17	MMM-A-180C. . . . . 392
17.3.18	MMM-A-181D. . . . . 392
17.3.19	MMM-A-182A. . . . . 393
17.3.20	MMM-A-185 . . . . . 393
17.3.21	MMM-A-187B. . . . . 393
17.3.22	MMM-A-188C. . . . . 394
17.3.23	MMM-A-189B. . . . . 394
17.3.24	MMM-A-250C. . . . . 394
17.3.25	MMM-A-260B. . . . . 395
17.3.26	A-A-342A. . . . . 395
17.3.27	A-A-529 . . . . . 395
17.3.28	MMM-A-1058A . . . . . 395
17.3.29	MMM-A-1617. . . . . 396
17.3.30	MMM-A-1754. . . . . 396
17.3.31	MMM-A-1931. . . . . 396
17.3.32	MMM-A-001993 (GSA-FSS). . . . . 397
17.3.33	MMM-A-002015 (GSA-FSS). . . . . 397
17.3.34	MMM-A-002408 (GSA-FSS). . . . . 397
17.4	Department of Defense (DOD) . . . . . 398
17.4.1	MIL-G-413B. . . . . 398
17.4.2	MIL-C-2399B (2) . . . . . 398
17.4.3	MIL-A-3167A (OS). . . . . 398
17.4.4	MIL-A-3316B (6) . . . . . 399
17.4.5	MIL-A-3562B . . . . . 399

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
17.4.6	MIL-A-5540B . . . . .	399
17.4.7	MIL-A-8576 (2). . . . .	400
17.4.8	MIL-A-9117D . . . . .	400
17.4.9	MIL-A-13374D. . . . .	400
17.4.10	MIL-A-14064C. . . . .	401
17.4.11	MIL-A-17682E. . . . .	401
17.4.12	MIL-A-21016E. . . . .	401
17.4.13	MIL-A-21366A (SHIPS). . . . .	401
17.4.14	MIL-A-22397 (SHIPS) . . . . .	402
17.4.15	MIL-A-22434A (WEP). . . . .	402
17.4.16	MIL-S-22473E. . . . .	402
17.4.17	MIL-A-22895 (1) (SHIPS) . . . . .	403
17.4.18	MIL-C-23092B (SHIPS). . . . .	403
17.4.19	MIL-A-23940 (1) (AS). . . . .	403
17.4.20	MIL-A-23941A (AS). . . . .	403
17.4.21	MIL-A-24179A (SHIPS). . . . .	403
17.4.22	MIL-A-24456 (3) (SHIPS) . . . . .	404
17.4.23	MIL-A-25463E. . . . .	404
17.4.24	MIL-A-43316A (1) (GL) . . . . .	405
17.4.25	MIL-A-45059C. . . . .	405
17.4.26	MIL-G-46030D (MR) . . . . .	405
17.4.27	MIL-A-46050C (2). . . . .	405
17.4.28	MIL-A-46091B. . . . .	406
17.4.29	MIL-A-46106A (2). . . . .	406
17.4.30	MIL-A-46146A (2). . . . .	407
17.4.31	MIL-A-46864A (MI) . . . . .	407
17.4.32	MIL-A-47040 (1) (MI). . . . .	408
17.4.33	MIL-C-47072 (MI). . . . .	408
17.4.34	MIL-A-47074A (MI) . . . . .	408
17.4.35	MIL-A-47089 (MI). . . . .	409
17.4.36	MIL-P-47125 (1) (MI). . . . .	409
17.4.37	MIL-A-47126 (MI). . . . .	409
17.4.38	MIL-P-47170 (1) (MI). . . . .	409
17.4.39	MIL-L-47274 (1) (MI). . . . .	409
17.4.40	MIL-P-47275 (MI). . . . .	410
17.4.41	MIL-P-47276 (1) (MI). . . . .	410
17.4.42	MIL-P-47279 (1) (MI). . . . .	410
17.4.43	MIL-A-47280 (MI). . . . .	410
17.4.44	MIL-A-47284 (1) (MI). . . . .	410
17.4.45	MIL-A-48611A (2). . . . .	411
17.4.46	MIL-B-48612 (MU). . . . .	411
17.4.47	MIL-A-50926A (PA) . . . . .	412
17.4.48	MIL-A-52194A (MR) . . . . .	412
17.4.49	MIL-A-52685 . . . . .	412
17.4.50	MIL-A-60091 (1) (AR). . . . .	412
17.4.51	MIL-A-81236 (2) (OS). . . . .	413
17.4.52	MIL-C-81247 (WP). . . . .	413
17.4.53	MIL-A-81253 (1) (OS). . . . .	413

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
17.4.54	MIL-A-81270 (1) (OS) . . . . .	413
17.4.55	MIL-A-81786/11 (AS) . . . . .	414
17.4.56	MIL-K-81786A (AS) . . . . .	414
17.4.57	MIL-A-82484 . . . . .	414
17.4.58	MIL-A-82569 (OS) . . . . .	415
17.4.59	MIL-A-82636A (OS) . . . . .	415
17.4.60	DOD-A-82720 (OS) . . . . .	415
17.4.61	MIL-A-83376A (USAF) . . . . .	415
17.4.62	MIL-A-83377B. . . . .	415
17.4.63	MIL-S-83432 (USAF) . . . . .	416
17.4.64	MIL-A-87134 (USAF) . . . . .	416
17.4.65	MIL-A-87135 (USAF) . . . . .	416
17.5	Society of Automotive Engineers (SAE) . . . . .	417
17.5.1	Aerospace Materials Specifications (AMS) . . . . .	417
17.5.1.1	AMS 2491C . . . . .	417
17.5.1.2	AMS 3106A . . . . .	417
17.5.1.3	AMS 3107. . . . .	417
17.5.1.4	AMS 3107/1. . . . .	418
17.5.1.5	AMS 3107/2. . . . .	418
17.5.1.6	AMS 3107/3. . . . .	418
17.5.1.7	AMS 3107/4. . . . .	418
17.5.1.8	AMS 3681B . . . . .	418
17.5.1.9	AMS 3685A . . . . .	419
17.5.1.10	AMS 3686. . . . .	419
17.5.1.11	AMS 3687. . . . .	419
17.5.1.12	AMS 3688A . . . . .	420
17.5.1.13	AMS 3689A . . . . .	420
17.5.1.14	AMS 3690. . . . .	420
17.5.1.15	AMS 3691. . . . .	421
17.5.1.16	AMS 3692. . . . .	421
17.5.1.17	AMS 3693B . . . . .	421
17.5.1.18	AMS 3695. . . . .	421
17.5.1.19	AMS 3695/1. . . . .	422
17.5.1.20	AMS 3695/2. . . . .	422
17.5.1.21	AMS 3695/3. . . . .	422
17.5.1.22	AMS 3695/4. . . . .	422
17.5.1.23	AMS 3698. . . . .	422
	References. . . . .	424
	Appendix. . . . .	425
	References. . . . .	438

## FIGURES

Figure 1.	Common methods of structural fastening. . . . .	3
2.	Illustration of wetting by adhesive spread. . .	7
3.	Cohesive and adhesive bond failure. . . . .	10
4.	Basic steps in the adhesive bonding process . .	18
5.	Types of stress on adhesive joints. . . . .	20

## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
6. Types of joints for flat adherends. . . . .	22
7. Tensile force on lap joint. . . . .	23
8. Single lap joint. . . . .	23
9. Effect of overlap and width on strength of typical joint . . . . .	24
10. Correlation diagram between shear strength and L/T resins. . . . .	25
11. L/T curves for modified epoxy adhesive. . . . .	25
12. Specific design curves single-lap shear joint .	26
13. Interrelation of failure loads for lap joints with a specific adhesive/adherend. . . . .	27
14. Designs that minimize peel. . . . .	28
15. Minimizing peel for stiffening sections . . . .	30
16. Recommended designs for rod and tube adhesive-bonded joints . . . . .	31
17. Angle joints. . . . .	32
18. Corner joints . . . . .	33
19. Joints for rubber (under stress). . . . .	34
20. Joints for flexible materials . . . . .	35
21. Straight joints for laminated wood. . . . .	37
22. Joints for solid and laminated wood assembly. .	38
23. High-temperature adhesive performance . . . .	53
24. Typical tensile shear strength data for paste and liquid adhesives . . . . .	67
25. Typical tensile shear strength data for tape-film and solvent based adhesives . . . . .	68
26. Checklist for adhesive selection. . . . .	110
27. Voltage increases for aluminum anodizing. . . .	132
28. Structural reinforced plastic laminate with a tear ply. . . . .	175
29. Principle of adhesive bonding in an autoclave .	207
30. Resistivity of flexible 85% silver conductive adhesive as a function of curing temperature. .	251
31. Volume resistivity of silver-epoxy adhesive (E-SOLDER 3012) as a function of temperature and time of curing. . . . .	252
32. Tensile adhesion vs cure time and temperature for hysol K8-4238 conductive cement . . . . :	252
33. Relationship between volume resistivity, operating temperature and aging for hysol K20 epoxy conductive cement . . . . .	255
34. Typical honeycomb sandwich construction . . . .	262
35. Methods of manufacturing honeycomb. . . . .	262
36. Honeycomb bonded to face sheet showing location location of adhesive fillet . . . . .	265
37. Set-up for non-tank phosphoric acid anodizing of aluminum . . . . .	272

## MIL-HDBK-691B

## CONTENTS - Continued.

	<u>Page</u>
38. Polarized light test-verification of anodic oxide film. . . . .	273
39. Schematic description of a spotweld in a single-lap wellbonded joint . . . . .	278
40. Comparable single-lap and double-lap weldbonded joint. . . . .	279
41. Axial load fatigue strength of aluminum alloy weldbond, as compared to rivets . . . . .	279
42. Static joint strength of weldbond as compared to other types of joints. . . . .	280
43. Comparative joining technique on typical aircraft structure. . . . .	280
44. Comparative joint strength, butt shear double row, for 0.025" to 0.063" titanium alloy (Ti-6Al-4V) . . . . .	281
45. Flow chart of a quality control system for adhesive bonding. . . . .	317
46. Tensile strength vs temperature of adhesives. . . . .	335
47. Shear strength vs temperature for HYSOL EA 934 RT-cure two-part paste epoxy adhesive . . . . .	335
48. Heat resistance and thermal aging of high-temperature structural adhesives. . . . .	337
49. Comparison of cryogenic and low temperature adhesive types. . . . .	341
50. Stressing jig used in loading test fixture. . . . .	347
51. Stressing jigs used at ARRADCOM with automatic failure recording device. . . . .	348
52. Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH . . . . .	349
53. Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH (log plot). . . . .	350
54. Hot water soak data with epoxy-nitrile film adhesive on aluminum joints . . . . .	352
55. Comparison of stressed durability data and unstressed hot water soak data with epoxy-nitrile film adhesive on anodized aluminum joint . . . . .	353
56. Environmental S-log N curves for nitrile-epoxy film adhesive - bonded aluminum joints. . . . .	354
57. Effect of surface treatment and intermittent immersion in salt water under stress on the durability of aluminum alloy. . . . .	358
58. Effect of nuclear radiation dosage on structural adhesive. . . . .	368
59. Effect of gamma radiation on overlap shear strength of structural adhesive bonds . . . . .	371
60. Effect of gamma radiation on structural adhesive bonds over temperature range . . . . .	372

## MIL-HDBK-691B

## CONTENTS - Continued.

		<u>Page</u>
<b>TABLES</b>		
I.	Factors influencing adhesive selection. . . . .	8
II.	Adhesive classified by major types. . . . .	12
III.	Thermosetting adhesive classified by activation and cure requirements. . . . .	15
IV.	Adhesives classified by form. . . . .	16
V.	Comparison of typical urethane adhesive with other adhesives on aluminum. . . . .	50
VI.	Properties of a cured one-component epoxy polymer. . . . .	55
VII.	Strength characteristics of SCOTCH-WELD thermoplastic adhesive film. . . . .	65
VIII.	Most important tape and film adhesives. . . . .	68
IX.	Range of bond strengths of tape and film adhesives at room temperature . . . . .	69
X.	Comparison of properties of acrylic and other adhesive types (room temperature curing). . .	77
XI.	Shear strengths of various substrates bonded with methyl 2-cyanoacrylate adhesive. . . . .	83
XII.	Properties of new and old anaerobic structural adhesives . . . . .	91
XIII.	Properties of elastomeric adhesives on nonstructured applications. . . . .	93
XIV.	Available forms and processing requirements for adhesives. . . . .	102
XV.	Properties of structural adhesives used to bond metals . . . . .	104
XVI.	Effect of metal substrate surface treatment on adhesive-bonded joints . . . . .	117
XVII.	General requirements for water used on cleaning solutions and rinsing . . . . .	120
XVIII.	Surface preparation of aluminum vs lap-shear strength. . . . .	121
XIX.	Typical adhesive-strength improvement for aluminum-plastic lap-shear sandwich specimens bonded with EPON-VERSAMID 140 epoxy adhesive . . . . .	123
XX.	Results of lap-shear tests in various polymers showing advantage of plasma processing. . . .	124
XXI.	Wettability of various plastics . . . . .	125
XXII.	Effects of various surface treatments on lap-shear strength of adhesive bonded HD polyethylene. . . . .	162
XXIII.	Comparison of vulcanization and post-vulcani- zation bonding. . . . .	178

## MIL-HDEK-691B

XXIV.	Effect of surface treatment of rubbers on rubber to metal adhesive-bonded butt joints. . . . .	180
XXV.	Effects of modified cyclization on neoprene/aluminum bonds. . . . .	182
XXVI.	Peel strength of epoxy-polyamide resin adhesive to chlorobutyl rubber pretested by various methods . . . . .	185
XXVII.	Effect of surface preparation on T-peel strength of Hypalon rubber. . . . .	185
XXVIII.	Effects of surface preparation on adhesive bonding of BUNA N rubber. . . . .	187
XXIX.	Solubility parameter of solvents and resins . .	216
XXX.	Solvents and solvent mixtures used in solvent cementing plastics. . . . .	218
XXXI.	Solvents recommended for cementing polystyrene.	222
XXXII.	Solvent cements (GE) for cementing NORYL modified PPO resins . . . . .	223
XXXIII.	Selection guide for general aluminum bonding applications. . . . .	229
XXXIV.	Lap shear strength and durability of acrylic and epoxy adhesives bonded to 4340 steel, using two different surface preparations. . .	234
XXXV.	Effect of cure in conditions of resistivity . .	250
XXXVI.	Effect of hardener/resin ratio on tensile adhesion and conductivity . . . . .	253
XXXVII.	Resistivity of copper-filled epoxy adhesive after elevated-temperature testing . . . . .	255
XXXVIII.	Characteristics of Becon Industries epoxy/silver electrically conductive adhesive . . .	256
XXXIX.	Bond-tensile-shear strengths of conductive adhesives . . . . .	257
XL.	Volume resistivity of silver-filled conductive epoxy adhesives . . . . .	258
XLI.	Classifications of honeycomb adhesive systems .	264
XLII.	Adhesive selection matrix for honeycomb . . . .	264
XLIII.	Faults in adhesive-bonded joints revealed by mechanical tests. . . . .	324
XLIV.	Faults in adhesive-bonded joints revealed by visual inspection . . . . .	325
XLV.	Relative resistance of synthetic adhesives to common service environments. . . . .	332
XLVI.	Environmental failure resistance of different adhesive-aluminum joints. . . . .	333
XLVII.	Effect of temperature variation on tensile lap shear strength of hot-melt polysulfone adhesive. . . . .	338
XLVIII.	Comparison of "tough" cryogenic adhesives at liquid hydrogen and ambient temperatures. . .	340
XLIX.	Effect of water (liquid and vapor) on tensile shear strength of structural adhesive bonds on aluminum . . . . .	344



## MIL-HDBK-691B

L.	Effects of surface treatment on the durability of 6061-T6 aluminum alloy joints exposed to inversion in RT water in the unstressed condition (nitrile-modified epoxy paste adhesive) . . . . .	345
LI	Effects of surface treatment on the durability of 6061-T6 aluminum alloy joints exposed to 100% RH (condensing humidity) at 125°F (52°C) in the unstressed condition (nitrile-modified epoxy paste adhesive) . . . . .	345
LII	Effect of surface treatment and exposure to salt water intermittent spray on the durability of 6061-T6 aluminum alloy joints exposed in the unstressed condition (nitrile-modified epoxy paste adhesive) . . . . .	355
LIII	Effect of surface treatment and exposure to seacoast environment on the durability of 6061-T6 aluminum alloy joints exposed in the unstressed condition (nitrile-modified epoxy paste adhesive) . . . . .	355
LIV	Effect of salt spray- 5% NaCl at 95°F (35°C) on bonded aluminum alloy joints with different surface preparation . . . . .	359
LV	Effect of MIL-STD-304 conditioning (JAN cycle) on strength of bonded aluminum alloy 2024-T3 joints. . . . .	361
LVI	Percent retention of original adhesive joint strength after weathering one year . . . . .	362
LVII	Percent retention of original adhesive joint strength after weathering three years. . . . .	363
LVIII	Effect of $10^{-7}$ Torr on commercial adhesives/sealants . . . . .	368
LIX	Effect of gamma radiation on T-peel strength of elastomer-phenolic film adhesives. . . . .	372



## MIL-HDBK-691B

## Chapter 1. INTRODUCTION TO ADHESIVE BONDING

**1.1 Definition of adhesive bonding.** Adhesive bonding is the process of uniting materials with the aid of an adhesive, a substance capable of holding such materials together by surface attachment.<sup>(1)</sup> There are two principal types of adhesive bonding, structural and non-structural. Structural adhesive bonding is bonding where elements of a structure are fastened together with an adhesive. Structural adhesive bonds must be capable of transmitting structural stress without loss of structural integrity within design limits. Resistance to the service environment is a corollary property. Because this handbook is intended for military users, the emphasis in it will be on structural adhesive bonding.<sup>(2)</sup>

Important types of non-structural adhesive bonding will include adhesives/sealants and conductive adhesives, both of which will be discussed below.

**1.2 Functions of adhesives.** The major function of adhesives is to fasten parts together. They do this by transmitting stresses from one member to another in a manner that distributes the stresses much more uniformly than can be achieved with conventional, mechanical fasteners. Consequently, adhesives often permit the fabrication of structures that are mechanically equivalent to, or stronger than, conventional assemblies, at lower cost and weight. For example, thin adherends can be adhesively bonded to thick sections so that the full strength of the thin member is utilized. In mechanical fastening or spot-welding, the strength of the structure is limited to that of the areas of the members in contact with the fasteners or welds.

Smooth surfaces are an inherent advantage of adhesively joined structures and products. Exposed surfaces are not defaced, and contours are not disturbed as with other types of fastening systems. This feature is important, both in function and in appearance. Aerospace structures require such external smoothness for minimum drag and for keeping temperatures as low as possible. Helicopter rotor blades, for example, are assembled entirely with adhesives.

Close-fitting electronic or electrical components also benefit from the lack of projections offered by adhesive bonding. Home appliances can have smooth, uninterrupted exterior surfaces when adhesives are used for assembly. Lighter-weight materials can often be used with adhesive bonding rather than with conventional fastening, simply because the uniform stress distribution in the joint permits full utilization of the strength and rigidity of the adherends. Payloads in aircraft can be increased, gas mileage in automobiles raised, and shipping costs for adhesively bonded items reduced.

Dissimilar materials are easily joined by many adhesives, provided that proper surface treatments are used. Metal adherends that would ordinarily corrode because of their electromotive series relationship can be protected from this form of destruction by a layer of nonconductive adhesive that not only joins but isolates them. (Adhesives can also be formulated to be conductive, as will be shown below). Adhesives are also used to join metals to plastics, ceramics, cork, rubber, glass, wood, or combinations of materials. Where temperature variations are expected in the service of an item containing dissimilar materials, adhesives perform another service. A flexible adhesive

## MIL-HDBK-691B

can accommodate differences in the thermal-expansion characteristics among the adherends and thereby prevent damage that might occur if a stiff fastening system were used. Flexible adhesives are used to bond windows to metal frames in motor vehicles and spacecraft, for example, to allow adequate movement between the dissimilar materials during the temperature extremes to which they are exposed.

Sealing is another important function of adhesive joining. The continuous bond easily seals against liquids or gases that do not attack the adhesive (or, in this case, adhesive/sealant). Some adhesives are used in place of solid or cellular gaskets to seal gearbox housings, valve covers, and other automotive and industrial components. Other types of sealing operations performed by adhesives are encapsulation and potting of circuit boards, motors, and other electrical and electronic assemblies. These materials are not strictly adhesives, however, and are often called potting and encapsulating compounds.

Mechanical damping can be imparted to a structure through the use of adhesives formulated for that purpose. A related characteristic, fatigue resistance, can be improved by the ability of such adhesives to withstand cyclic strains and shock loads without cracking. In a properly designed joint, the adherends generally fail in fatigue before the adhesive fails. Thin or fragile parts can be adhesive bonded. Adhesive joints do not usually impose heavy loads on the adherends, as in riveting, or localized heating, as in welding. The adherends will also be relatively free from heat-induced distortion.(3).

**1.3 Advantages and disadvantages of adhesive bonds.** A number of advantages of adhesive bonds have been discussed above under 1.2 from a functional viewpoint. However, the advantages and disadvantages will be discussed here in the interest of completeness.

**1.3.1 Advantages.(4)(5)(6)**

- o Provide uniform distribution of stress and larger stress-bearing area
- o Join thin or thick materials of any shape
- o Join similar or dissimilar materials
- o Minimize or prevent electrochemical (galvanic) corrosion between dissimilar materials
- o Resist fatigue and cyclic loads
- o Provide joints with smooth contours
- o Seal joints against a variety of environments
- o Insulate against heat transfer and electrical conductance
- o Heat required to set the joint is usually too low to reduce the strength of metal parts
- o Damp vibration and absorbs shock
- o Provide attractive strength/weight ratio
- o Frequently faster or cheaper than mechanical fastening

The most common methods of structural fastening are shown in Figure 1. Welding or brazing, useful in heavy-gage metal, is expensive and requires great heat. Many light-weight metals such as aluminum, magnesium, and titanium are difficult to weld and are weakened or distorted by the heat of welding.

## MIL-HDBK-691B

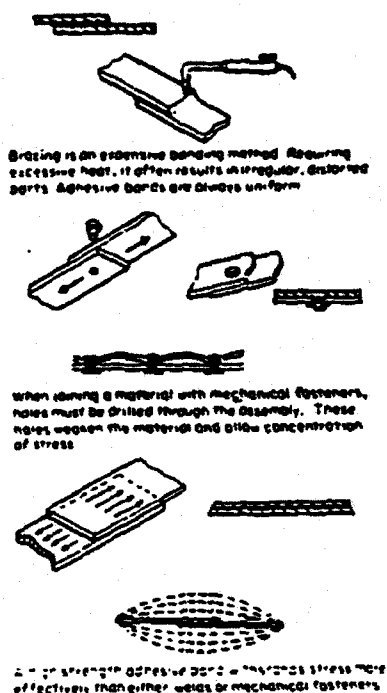


FIGURE 1. Common methods of structural fastening.(6)(7)

High-strength, reliable joints can be made on these metals with adhesives. Holes, needed for rivets or other mechanical fasteners, are not required for an adhesive bond, thereby allowing the stresses to be uniformly distributed over the entire bonded area.(6)

The stress-distribution characteristics and inherent toughness of adhesives provide bonds with superior fatigue resistance. Generally, in well-designed joints, the adherends fail in fatigue before the adhesive. With the proper selection and use of adhesives, shear strengths as high as 7,000 psi (48.3 MPa) are available.(6)

In the presence of vibration, a bonded structure usually has a longer life than a riveted assembly. In addition, because adhesives of different moduli, (stiffnesses), are available, damaging resonant frequencies can be modified or even eliminated by proper analysis and selection of the adhesive. In the manufacture of aircraft and motor vehicles, adhesive bonding may be used to advantage instead of riveting and welding, since (a) riveted structures add

## MIL-HDBK-691B

weight and drag, (b) rivets and welds are unsightly and difficult to conceal, and (c) holes and welds may facilitate the start of corrosion. Adhesives in film form are particularly desirable for this type of application, since they facilitate close control of weight distribution and total weight of adhesive used.(6)

Some applications, such as bonded honeycomb structures, rely totally for their success on the use of adhesives. One example of this type of structure, thin nonmetallic honeycomb core bonded to thin metal facings, could not be constructed without adhesives. Adhesives often perform important functions as sealants. Since the adhesive in a properly prepared joint provides full contact with the mating surfaces of the joint, it forms a barrier to the passage of fluids which do not attack or soften the adhesive. Most adhesives are organic polymeric materials, however, and therefore do not form hermetic seals. They may perform well in containing liquids, but gases can diffuse through them. Diffusion is generally slow, however, and adhesives perform as acceptable gas seals in all but the most critical applications. An adhesive may also function as an electrical and/or thermal insulator in a joint. Its thermal insulating efficiency can be increased, if necessary, by foaming the adhesive in place.(4)

On the other hand, the electrical and/or thermal conductivity of an adhesive can be raised appreciably by adding metallic fillers. Oxide fillers, such as alumina or beryllia, increase only thermal conductivity.(4)

### 1.3.2 Disadvantages(4)(6)(6)

- o The bond does not permit visual examination of the bond area
- o Require careful surface preparation, often with corrosive chemicals
- o Long cure times may be needed, particularly where high cure temperatures are not used
- o Holding fixtures, presses, ovens and autoclaves, not usually needed for other fastening methods, are necessities for adhesive bonding
- o There is a limitation on the upper service temperature to approximately 350°F (177°C), but special adhesives are available for limited use to 700°F (371°C)
- o Rigid process control, including emphasis on cleanliness, is required for most adhesives
- o The useful life of the joint depends on the environment to which it is exposed
- o Natural or vegetable-origin materials are subject to attack by bacteria, mold, rodents, or vermin

Adhesive bonding is not a panacea for assembling all products. The very fact that there are so many variations in available adhesive formulations, for example, makes selection of the best adhesive for a particular application more difficult than choosing a mechanical fastening system. These variations also complicate control procedures on incoming materials, assembly processing, and testing of the finished product. Also, even though adhesive-bonding operations can be automated, they usually require higher skilled personnel than do other methods.(3)

## HIL-HDLK-691B

Although adhesives are capable of producing structures which are more reliable than those fastened by conventional means, adhesive-bonded structures must be carefully designed and used under conditions which do not exceed the known operational limitations of the adhesive. Limitations include types and magnitudes of stresses and whether static or dynamic, and environmental factors such as temperature, humidity, salt environment, or other vapors or liquids. The effects of salt spray, simulating a marine environment, are particularly corrosive in aluminum bonded joints.<sup>(4)</sup>

Probably all organic adhesives are adversely affected by simultaneous application of moisture and stress. Some adhesives (even including those containing components obviously water-soluble) perform particularly poorly under these conditions. Joints made with such materials may sustain constant loads that produce no greater than 10% of their normal ultimate failing stress for only short periods. Joints made with other materials may sustain 50% of failing stress for extended periods of time. The mechanisms which determine this behavior are still not completely clear at the present time. The recognition that such behavior exists, however, should influence joint design in proportion to the anticipated severity of stress and environment in service. Permanence of an adhesive joint is influenced not only by the properties of the adhesive, but also by the method of preparing the surfaces of the adherends. More precisely, it is the surface layers present on the adherends at the time of joining, and how they are affected by stress and environment that is important. If the surface layers are weak and susceptible to moisture, the adhesive joint will be weak and susceptible to moisture. Surface condition of adherends often determines the utility of a structure, both initially and in service. Thorough surface preparation is a necessary part of the price paid for the performance and reliability of a bonded joint.<sup>(4)</sup>

**1.4 Theories of adhesion.** The actual mechanism of adhesive attachment is not yet fully understood. No single theory can explain adhesion in a general, all-encompassing way. A knowledge of various adhesion theories can assist in understanding the basic requirements for good bonding.<sup>(6)</sup>

**1.4.1 Mechanical theory.** At one time adhesion was thought to occur by the adhesive flowing and filling microcavities on the substrate. When the adhesive hardens, the substrates are held together mechanically. The surface of a solid material is never completely smooth, although it may appear so microscopically. Rather, it consists of a maze of peaks and valleys. According to this theory, in order to function properly, the adhesive must penetrate the cavities on the surface and displace the trapped air at the interface.

Mechanical anchoring of the adhesive appears to be a prime factor in bonding many porous substrates, such as plastic foams (cellular plastics). Adhesives also frequently bond better to nonporous abraded surfaces than to natural surfaces. This advantageous effect of mechanical roughening may be due to:

1. Mechanical interlocking
2. Formation of a clean surface
3. Formation of a highly reactive surface
4. Increasing surface area

HIL-HDBK-691B

While the surface does become rougher because of abrasion, it is believed that a change in both physical and chemical properties of the surface layer produces an increase in adhesive strength. While some enhanced adhesive applications can be explained by mechanical interlocking, mechanical effects are not always the cause.(6)

**1.4.2 Adsorption theory.** The adsorption theory states that adhesion results from molecular contact between two materials and the surface forces which develop. The process of establishing continuous contact between an adhesive and the adherend is known as "wetting". For an adhesive to wet a solid surface, the adhesive should have a lower surface tension ( ) than the critical surface tension of the solid. Figure 2 illustrates good and poor wetting of an adhesive spreading over a surface. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting results when the adhesive bridges over the valley and results in a reduction in actual area of contact between the adhesive and the adherend, causing a lower overall joint strength.(6)

Most organic adhesives easily wet metallic solids. However, many solid organic substrates have surface tensions less than those of common adhesives. The fact that good wetting requires the adhesive to have a lower surface tension than the substrate explains in part why organic adhesives such as epoxies have excellent adhesion to metals, but offer weak adhesion on untreated polymeric substrates such as polyethylene, polypropylene, and the fluorocarbons.(6)

After intimate contact is achieved between adhesive and adherend through wetting, it is believed that permanent adhesion results primarily through forces of molecular attraction. Four general types of chemical bonds are recognized as being involved in adhesion and cohesion, as follows:

#### Primary bonds

- o Electrostatic bonds
- o Covalent bonds
- o Metallic bonds

#### Secondary bonds

- o Van der Waal's forces

**1.4.3 Electrostatic theory.** This theory states that electrostatic forces in the form of an electrical double layer are formed at the adhesive-adherend interface. These forces account for resistance to separation. This theory gains support from the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate.(6)

**1.4.4 Diffusion theory.** This theory postulates that adhesion comes about through the interdiffusion of molecules in the adhesive and the adherend. The diffusion theory is primarily applicable when both the adhesive and the adherend are polymeric, having long-chain molecules capable of movement. The solvent cementing or heat welding of thermoplastics is considered to be due to diffusion of molecules.(6)



## MIL-HDBK-691B

**1.4.5 Weak-boundary layer theory.** According to this theory, first described by Bikerman, when bond failure seems to be at the interface, usually a cohesive break or a weak boundary layer is the real event.<sup>(10)</sup> Weak boundary layers can originate from the adhesive, the adherend, the environment, or a combination of any of the three. Weak boundary layers can occur in the adhesive or adherend if an impurity concentrates near the bonding surface and forms a weak attachment to the substrate. When failure occurs, it is the weak boundary layer that fails, although failure seems to occur at the adhesive-adherend interface.<sup>(6)</sup>

Polyethylene and metal oxides are examples of this effect. Polyethylene has a weak, low-molecular-weight constituent that is evenly distributed throughout the polymer. This weak boundary layer is present at the interface and contributes to low failing stress when polyethylene is used as an adhesive or adherend. Some metallic oxides are weakly attached to their base metals. Failure of adhesive joints made with these materials occurs cohesively within the oxide. Some oxides, such as aluminum oxide, are very strong and do not significantly impair joint strength. Weak boundary layers, such as polyethylene and metal oxides, can be removed or strengthened by various surface treatments. Weak boundary layers formed from the bonding environment, generally air, are very common. When the adhesive does not wet the substrate, as shown in Fig. 2, a weak boundary layer of air is trapped at the interface, causing a reduction in joint strength.<sup>(6)</sup>

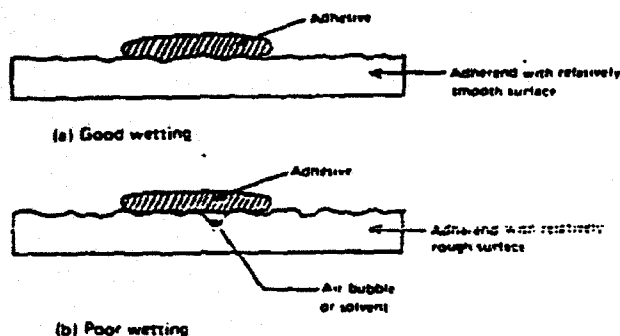


FIGURE 2. Good and poor wetting by an adhesive spreading over a surface.

**1.5 Requirements for a good bond.** The basic requirements for a good adhesive bond are cleanliness, wetting, solidification, proper choice of adhesive, and good joint design.<sup>(6)</sup>

**1.5.1 Cleanliness.** To obtain a good adhesive bond it is essential to start with a clean surface. Foreign materials, such as dirt, oil, moisture, and weak oxide layers, must be removed from the substrate surface, or else the adhesive will bond to these weak boundary layers rather than the substrate. There are various surface treatments that remove or strengthen the weak boundary layer. Some of these will be discussed below. These treatments generally involve physical or chemical processes, or a combination of both.<sup>(6)</sup>

## MIL-HDBK-691B

**1.5.2 Wetting.** While in the liquid state, the adhesive must "wet" the substrate. The term "wetting" refers to a liquid spreading over and intimately contacting a solid surface. Examples of good and poor wetting are shown in Fig. 2. The result of good wetting is greater contact area between adherend and adhesive over which the forces of adhesion may act.<sup>(6)</sup>

**1.5.3 Solidification.** The liquid adhesive, once applied, must be capable of being converted into a solid in any one of three ways:

- o Chemical reaction by any combination of heat, pressure, and curing agents
- o Cooling from a molten liquid to a solvent
- o Drying due to solvent evaporation

The method by which solidification occurs depends on the choice of adhesive.<sup>(6)</sup>

**1.5.4 Adhesive choice.** A number of important considerations must be taken into account when determining which adhesive is to be used for a particular application. Many of the factors are listed in Table 1. With regard to the controlling factors involved, the many adhesives available can usually be narrowed to a few most promising candidates. The general areas of concern to the design engineer when selecting adhesives should be the material to be bonded, service requirements, production requirements, and cost.<sup>(6)</sup>

**TABLE 1. Factors influencing adhesive selection. (Modified after Ref. 11)**

1. Capability of bonding specific adherends (see "Internal Chemical Factors" below).

2. Service requirements:

Stress (Tension, Shear, Impact, Peel, Cleavage, Fatigue)

Chemical factors:

External (effect of chemical agents, including solvents, acids, alkalies, etc)

Internal (effect of adherend on adhesive, e.g., exuded plasticizers on certain plastics and rubbers; effect of adhesive on the adherend, e.g., crazing, staining, etc.)

3. Environmental factors:

Weathering

Light (important only with translucent adherends)

Oxidation

Moisture

Salt Spray

Temperature extremes (including temperature cycling)

Biological factors

Bacteria

Fungi

Vermin

Rodents



## MIL-HDBK-691B

4. Specialized functional requirements (thermally or electrically conductive, etc.)

5. Production requirements:

- Application method
- Bonding range
- Blocking
- Curing rate (time vs temperature)
- Storage stability (life)
- Working life
- Coverage

6. Cost

7. Health and Safety hazards

1.5.5 Joint design. The adhesive joint should be designed to take advantage of the desirable properties of adhesives and to minimize their shortcomings. Such design considerations will be discussed in detail in Chapter 2. Although adequate adhesive-bonded assemblies have been made from joints designed for mechanical fastening, the maximum benefits of the adhesive can be obtained only in assemblies specially designed for adhesive bonding.(6)

1.6 Mechanism of bond failure. Adhesive joints may fail adhesively or cohesively. Adhesive failure is interfacial bond failure between the adhesive and adherend. Cohesive failure occurs when fracture allows a layer of adhesive to remain on both substrates. When the adherend fails before the adhesive, it is known as a cohesive failure of the substrate. The various modes of failure are shown in Fig. 3. Cohesive failure within the adhesive or one of the adherends is the ideal type of failure, because the maximum strength of the materials in the joint has been reached. In analysis of a joint that has been tested to destruction, the mode of failure is expressed as a certain percentage cohesive or adhesive failure. The ideal failure is a 100% cohesive failure.(6)(12)

Failure mode should not be used as a criterion for a useful joint, however. Some adhesive-adherend combinations may fail in adhesion, but exhibit greater strength than a similar joint bonded with a weaker adhesive that fails cohesively. The ultimate strength of a joint is a more important criterion than the mode of joint failure. However, an analysis of failure mode can be an extremely useful tool to determine if the failure was due to a weak boundary layer or improper surface preparation.

The exact cause of premature adhesive failure is very difficult to determine, because so many factors in adhesive bonding are interrelated. However, there are certain common factors at work when an adhesive bond is made that contribute to the weakening of all bonds. If the adhesive does not wet the surface of the substrate, the joint will be inferior. It is also important to allow the adhesive sufficient time to wet the substrate effectively before gelation occurs.(6)

## MIL-HDBK-691B

Internal stresses occur in the adhesive joint during production because of natural tendency of the adhesive to shrink during setting, and because of differences in physical properties between adhesive and substrates. The coefficient of thermal expansion of adhesive and adherend should be as close as possible to limit stresses that may develop during thermal cycling or after cooling from an elevated-temperature cure. Polymeric adhesives generally have a thermal-expansion coefficient an order of magnitude greater than metals. Fillers can be used to formulate adhesives to modify their thermal-expansion characteristics and limit internal stresses. A relatively elastic adhesive capable of accommodating internal stress may also be useful when thermal expansion differences are of concern.(6)

Once an adhesive bond is made and placed in service, other forces are at work tending to weaken the bond. The type of stress involved, its orientation to the adhesive, and the rate in which the stress is applied are important. Sustained loads can cause premature failure in service, even though similar unloaded joints may exhibit adequate strength when tested after aging. Some adhesives show very little resistance to dead load, especially during exposure to heat or moisture. The possibility of constant loads should be looked for in every application, and the adhesive should be tested accordingly. Most adhesives have poor strength when the stresses are acting to peel or cleave the adhesive from the substrate. Many adhesives are sensitive to the rate in which the joint is stressed. Rigid, brittle adhesives sometimes have excellent tensile or shear strength, but do very poorly under impact.(6)

Operating environmental factors, such as those shown in Table I, are capable of degrading an adhesive joint in various ways. If more than one environmental factor is acting, their combined effect would cause a catastrophic decline in adhesive strength. The possible combinations of adhesive, adherends, stresses and environments are so many that reliable adhesive strength and durability data are rarely available to the design engineer. Where time and funds permit, the candidate adhesive joints should always be evaluated under simulated operating loads in the intended environment.(6)

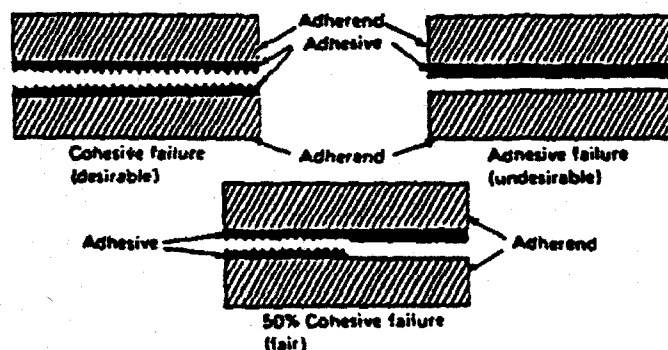


FIGURE 3. Cohesive and adhesive bond failure.(6)(12)

## MIL-HDBK-691B

**1.7 Basic adhesive materials classification.** Adhesives may be classified by many methods. The most common methods are by function, chemical composition, mode of application and setting, physical form, cost and end use.(6)

**1.7.1 Function.** The functional classification defines adhesives as being structural or nonstructural. Structural adhesives are materials of high strength and permanence. Their primary function is to hold structures together and be capable of resisting high loads. The emphasis in this handbook, as might be expected, is on structural adhesives. Nonstructural adhesives are not required to support substantial loads, but merely hold lightweight materials in place. Nonstructural adhesives are sometimes referred to as holding adhesives. Sealing adhesives (adhesives/sealants) usually have a nonstructural function. They are primarily used to fill a gap between adherends to provide a seal without having high degrees of strength.(6)

**1.7.2 Major types.** The major type classification describes synthetic adhesives as thermosetting, thermoplastic, elastomeric, or combinations of these. They are described generally in Table II.

**1.7.2.1 Thermosetting adhesives.** Thermosetting adhesives are materials that cannot be heated and softened repeatedly after the initial cure. Adhesives of this type are cured by chemical reaction at room or elevated temperatures, depending on the type of adhesive. Substantial pressure may also be required with some thermosetting adhesives, and others are capable of providing strong bonds with only contact pressure. This type of adhesive is sometimes provided in a solvent medium to facilitate application. They are also commonly available as solventless liquids, pastes, and solids. Thermosetting adhesives may be supplied as multiple and single-part systems. Generally, the single-part adhesives require elevated-temperature cure, and they have a limited shelf life. Multiple-part adhesives have longer shelf lives, and some can be cured at room temperature, or more rapidly at elevated temperature. However, they must be metered and mixed before application. Once the adhesive is mixed, the working life is limited. Because molecules of thermosetting resins are heavily cross-linked, they have good resistance to heat and solvents, and they show little elastic deformation under load at elevated temperatures.(6)

**1.7.2.2 Thermoplastic adhesives.** Thermoplastic adhesives do not cross-link during cure, so they can be resoftened after heating. They are single-component systems that harden upon cooling from a melt, or by evaporation from a solvent or water vehicle. Hot-melt adhesives commonly used in packaging applications are examples of a solid thermoplastic that is applied in a molten state, and develops adhesive properties as it solidifies on cooling. Some wood glues, such as polyvinyl acetate emulsions, are thermoplastic emulsions that are common household items. They harden by evaporation of water from an emulsion, but are capable of resoftening at high temperatures. Thermoplastic adhesives have a more limited temperature range than thermosetting types. They should not be used at temperatures over 150°F. Their physical properties vary over a wide range because many polymers are used in a single adhesive formulation.(6)

TABLE II. Adhesives classified by major types. (13)

Classification	Thermoplastic	Thermosetting	Elastomeric	Alloys
Types within group	Cellulose acetate, cellulose acetate butyrate, cellulose nitrate, polyvinyl acetate, vinyl vinylidene, polyvinyl acetate, polyvinyl alcohol, polyamide, acrylic, phenoxy	Cyanoacrylate, polyester urea formaldehyde, melamine formaldehyde, resorcinol and phenol-resorcinol formaldehyde, epoxy, polyimide, polybenzimidazole acrylic, acrylate acid diester	Natural rubber reclaimed rubber, butyl, polyisobutylene, nitrile, styrene-butadiene, polyurethane, polysulfide, silicone, neoprene	Epoxy-phenolic, epoxy-polysulfide, epoxy-nylon nitrile-phenolic, neoprene-phenolic, vinyl-phenolic
Most used form	Liquid, some dry film	Liquid, but all forms common	Liquid, some film	Liquid, paste, film
Common further classifications	By vehicle (most are solvent dispersion or water emulsions)	By cure requirements (heat and/or pressure most common but some are catalyst types)	By cure requirements (all are common); also by vehicle (most are solvent dispersions or water emulsions)	By cure requirements (usually heat and pressure except some epoxy types); by vehicle (most are solvent dispersions or 100% solids); and by type of adherends or end-service conditions
Bond Characteristics	Good to 150-200°F; (66-430°C) poor creep strength; fair peel strength	Good to 200-500°F; (93-260°C) good creep strength; fair peel strength	Good to 150-400°F; (66-204°C) never melt completely; low strength; high flexibility	Balanced combination of properties of other chemical groups depending on formulation; generally higher strength over wide temp. range

MIL-HDBK-691B

TABLE II. Adhesives classified by major types (continued). (13)

Classification Major type of use	Thermoplastic	Thermosetting	Elastomeric	Alloys
	Unstressed joints; designs with caps, over- laps, stiffeners	Stresses joints at slightly elevated temp	Unstressed joints on lightweight materials; joints in flexure	Where highest and strictest end-service conditions must be met; sometimes regardless of cost, as military uses
Materials most commonly bond- ed	Formulation range covers all materials, but em- phasis on nonmetallics - especially wood, leather, cork, paper, etc.	For structural uses of most materials	Few used "straight" for rubber, fabric, foil, paper, leather, plastics films; also as tapes. Most modified with syn- thetic resins	Metals, ceramics, glass thermosetting plastics; nature of adherenda often not as vital as design or end-service conditions (i.e., high strength, temp)

MIL-HDBK-691B

## NIL-HUBK-691B

**1.7.2.3 Elastomeric adhesives.** These are based on synthetic or naturally occurring polymers with outstanding toughness and elongation. They may be supplied as solvent solutions, latex cements, dispersions, pressure-sensitive types, and single-or multiple part solventless liquids or pastes. The curing requirements vary with the type and form of elastomeric adhesive. These adhesives can be formulated for a wide variety of applications, but they are generally noted for their high degree of flexibility and good peel strength.(6)

**1.7.2.4 Adhesive alloys.** Adhesive alloys are made by combining thermosetting, thermoplastic, and elastomeric adhesives. This type of adhesive utilizes the most useful properties of each constituent type. However, the adhesive alloy is usually as weak as its weakest constituent. Thermosetting resin additions provide a very strong cross-linked structure. Impact, bending, and peel strength are provided by the addition of thermoplastic or elastomeric materials. Adhesive alloys are commonly available in solvent solutions and as supported or unsupported film.(6)

**1.7.3 Mode of applications and setting.** Adhesives are often classified by their mode of application. Depending on viscosity, adhesives are sprayable, brushable, or trowelable. Heavily bodied adhesive pastes and mastics are considered extrudable. They are applied by syringe, caulking gun, or pneumatic pumping equipment. Another distinction between adhesives is the manner in which they flow or solidify. As shown in Table III, some thermosetting adhesives solidify simply by losing solvent, while others harden as a result of heat activation or chemical reaction. Pressure-sensitive systems flow under pressure and are stable when pressure is absent.(6)

**1.7.4 Physical form.** Adhesives can also be distinguished by their physical form. The physical state of the adhesive generally determines how it is to be applied. Liquid adhesives lend themselves to easy handling by mechanical spreaders or spray and brush. Paste adhesives have high viscosities to allow application on vertical surfaces with little danger or drip. These bodied adhesives also serve as gap fillers between mated substrates. Tape and film adhesives are poor gap fillers, but offer a uniform bondline thickness, no need for metering, and easy dispensing. Adhesive films are available in a pure sheet of adhesive, or with cloth or paper reinforcement. Another form of adhesive is powder or granules which must be heated or solvent-activated to be made liquid and applicable(6). A rather unique form of adhesive is found in plastic powder coatings in which powder particles are thermally fused on the two metal substrate surfaces, which are then joined together while the powder particles are still in the molten state before cooling and/or curing. Adhesives for labels and packaging applications are not considered here. The characteristics and advantages of the various adhesive forms are summarized in Table IV. Hot-melt adhesives are not listed in this table.

**1.7.5 Cost.** The cost of fastening with adhesives must include the material cost of the adhesive, the cost of labor, the time required to cure the adhesive, and the economic loss due to rejects of defective joints. Adhesive price is dependent on development costs and volume requirements. Adhesives that have been specifically formulated to be resistant to adverse requirements are more expensive than "general-purpose adhesives". Adhesive prices range from pennies a pound for inorganic and animal-based systems to over \$20/lb for some heat-resistant types. Adhesives in film or powder form require more processing than liquid or paste types and are more expensive.



TABLE III. Thermosetting adhesives classified by activation and cure requirements. (13)

Requirement	Types Available	Forms Used	Remarks
Heat	Room temp to 450°F (232°C) types available; 250 to 350°F (121 to 177°C) types most common for structural adhesives	Formulated in all forms; liquid most common	Applying heat will usually increase bond strength of any adhesive, even room temp types
Pressure	Contact to 500 psi (3.4 MPa) types available 25 to 200 psi (0.17 MPa) lb/in <sup>2</sup> types most common for structural adhesives	Formulated in all forms; liquid or powder most common	Pressure types usually have greater strength (not true of modified epoxies)
Time	Types requiring a few seconds to a week available; 1/2 to 24-h types most common for structural adhesives	Formulated in all forms; solvent solutions common	Time required varies with pressure and temp applied and immediate strength
Catalyst	Extremely varied in terms of chemical catalyst required; may also contain thinners, etc.	Two components - paste (or liquid) + liquid	Sometimes catalyst types may require elevated temp ( 212°F) ( 100°C) and/or pressure instead of, or in addition to a chemical agent

MIL-HDBK-691B



MIL-HDBK-691B

TABLE IV. Adhesives classified by form. (13)

Type	Remarks	Advantages
Liquid	Most common form; practically every formulation available. Principally solvent-dispersed	Easy to apply. Viscosity often under control of user. Major form of hand application.
Paste	Wide range of consistencies. Limited formulations; principally 20% solids modified epoxies	Lends itself to high-production setups because of less time wait. High shear and creep strengths
Powder	Requires mixing or heating to activate curing	Longer shelf life; mixed in quantities needed
Mastic	Applied with trowel	Void-filling nonflowing
Film, tape	Limited to flat surfaces, wide range of curing ease	Quick and easy application. No waste or run-over; uniform thickness
Other	Rods, supported tapes, precoated cop-per for printed circuits, etc.	Ease of application and cure for particular use.

## MIL-HDEK-691B

Adhesive-materials costs should be calculated on a cost-per-bonded-area basis. Since many adhesives are sold as dilute solutions, a cost per unit weight or volume basis may lead to erroneous comparisons<sup>(6)</sup>.

**1.7.6 Specific adherends or applications.** Adhesives may also be classified according to their end use. Thus, metal adhesives, wood adhesives, and vinyl adhesives refer to the substrates they bond, and acid-resistant adhesives, heat-resistant adhesives, and weatherable adhesives indicate the environments for which each is suited.<sup>(6)</sup> Another common classification is aerospace adhesives for high-performance applications on aircraft or space vehicles. Many of these adhesives may also be heat-resistant.

**1.8 Adhesive composition.** Modern adhesives are often fairly complex formulations of components that perform specialized functions.<sup>(6)</sup>

**1.8.1 Base or binder.** The adhesive base or binder is the primary component of an adhesive that holds the substrates together. The binder is usually the component from which the name of the adhesive is derived. For example, an epoxy adhesive may have many components, but the primary material is epoxy resin.<sup>(6)</sup>

**1.8.2 Hardener.** A hardener is a substance added to an adhesive to promote the curing reaction by taking part in it. Two-part adhesive systems generally have one part which is the base and a second part which is the hardener. Upon mixing, a chemical reaction takes place which causes the adhesive to solidify.<sup>(6)</sup>

**1.8.3 Catalyst.** (Activator) A catalyst is sometimes incorporated into an adhesive formulation to speed-up the reaction between the base and the hardener.<sup>(6)</sup> Sometimes an activator is used to speed-up the reaction. The activator is not mixed into the adhesive but is applied in a thin layer to one substrate, while a thicker layer of the base system is applied to the other substrate, and the two are joined.

**1.8.4 Solvents.** Solvents are sometimes needed to thin the adhesive to a spreadable consistency. Solvents used with synthetic resins and elastomers are generally organic, and often a mixture of solvents is required to achieve the desired properties.<sup>(6)</sup>

**1.8.5 Diluent.** An ingredient added to an adhesive to reduce the concentration of binder is called a diluent. Diluents are primarily used to reduce the viscosity and modify the processing conditions of some adhesives. Reactive diluents react with the binder during cure, become part of the product, and do not evaporate, as does a solvent.<sup>(6)</sup>

**1.8.6 Fillers.** Fillers are relatively nonadhesive substances added to the adhesive to improve its working properties, strength, permanence, conductivity or other qualities. Fillers are also used to reduce material cost. By selective use of these materials, the properties of an adhesive can be changed to a considerable extent. Thermal expansion, electrical and thermal conductivity, shrinkage, viscosity, and thermal resistance are only a few of the properties that can be modified by use of fillers.<sup>(6)</sup>

## MIL-HDDK-691B

**1.8.7 Carriers or reinforcements.** A carrier or reinforcement is usually a thin fabric or paper used to support the semicured adhesive compositions, to provide a tape or film. The carrier also serves as a bond-line spacer and reinforcement for the adhesive.(6)

**1.9 Adhesive bonding process.** A typical flow chart for the adhesive bonding process is shown in Fig. 4. The bonding process is as important as the adhesive itself for a successful end product.

**FIGURE 4. Basic steps in the adhesive bonding process.(14)**



Many of the adhesive problems that develop are not due to a poor choice of material or joint design, but are directly related to faulty production techniques. The adhesive user must obtain the proper processing instructions from the manufacturer and follow them closely and consistently to ensure acceptable results. Adhesive production involves four basic steps:

- o Design of joints and selection of adhesives
- o Preparation of adherends
- o Applying and curing the adhesive
- o Inspection of bonded parts

These steps will be discussed in considerable detail in chapter 6.(6)

## MIL-MDBK-691B

## REFERENCES

- (1-1) Modified from ASTM D907-82, "Standard Definitions of Terms Relating to Adhesives", published in Volume 15.06, Annual Book of ASTM Standards.
- (1-2) (Modified from Chapter 1. "Introduction, Scope, Exclusions, Methodology,") STRUCTURAL ADHESIVES, WITH EMPHASIS ON AEROSPACE APPLICATIONS, TREATISE ON ADHESION AND ADHESIVES, Vol. 4, A Report of the ad hoc Committee on Structural Adhesives for Aerospace Use, National Materials Advisory Board, Marcel Dekker, 1976.
- (1-3) Anonymous, "Joining Techniques", Section 4, Machine Design, (Fastening and Joining Reference Issue,) 48 (26): 155-162, November 18, 1976.
- (1-4) L.H. Sharpe, "The Materials, Processes and Design Methods for Assembly with Adhesives", Machine Design, 38 (19): 179-200 (August 18, 1966).
- (1-5) ADHESIVES IN MODERN MANUFACTURING, Society of Manufacturing Engineers, edited by E.J. Bruno, 1970.
- (1-6) E.H. Petri, Chapter 10, "Plastics and Elastomers as Adhesives", in HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A. Harper, McGraw-Hill, New York, N.Y., 1975.
- (1-7) 3M Company, Adhesives, Coatings and Sealers Division, "Structural Adhesives", Technical Bulletin.
- (1-8) H.J. DeLollis, ADHESIVES FOR METAL - THEORY AND TECHNOLOGY, Industrial Press, N.Y., 1970.
- (1-9) G.L. Schneberger, "Chemical Aspects of Adhesive Bonding - Part II - Physical Principles", Adhesives Age, 13 (3): 28-31 (March 1970).
- (1-10) J.J. Bikerman, "Causes of Poor Adhesion", Industrial and Engineering Chemistry, 59 (9): 40-44 (Sept. 1967).
- (1-11) G.W. Koehn, "Design Manual on Adhesives", Machine Design, April 1954).
- (1-12) C.V. Cagle, ADHESIVE BONDING, TECHNIQUES AND APPLICATIONS, McGraw-Hill, N.Y., 1968.
- (1-13) J.C. Merriam, "Adhesive Bonding", Materials in Design Engineering, 50 (3): 113-128 (Sept. 1959).
- (1-14) D.K. Rider, "Which Adhesives for Bonded Metal Assembly?", Product Engineering, May 25, 1964.

## MIL-HDBK-691B

## Chapter 2. JOINT DESIGN

**2.1 Basic principles.** The first and most important principle of joint design is that joints for adhesive bonding must be designed specially for the use of adhesives. An all-too-common practice has been to start with a design used for another method of fastening, alter it slightly, and bond. This practice can lead to disastrous results. When one well-known civilian aircraft was first designed, adhesive bonding was used extensively; the adhesive chosen was rigid and the joint design was essentially that used for riveting. With riveted joints (as with specially designed bonded joints), enough slippage can take place for the normal vibrating stresses to be relieved. However, the joint design used in the aircraft did not allow slippage, and the vibrating stresses acted to fatigue the metal in the aircraft structure. After a relatively short time, two of the airplanes disintegrated in mid air.<sup>(1)</sup>

In designing joints specifically for adhesive bonding, the basic characteristics of adhesives must dictate design planning. An adhesive bond acts over an area, not at a single point. The joint should, therefore, be designed to minimize concentration of stress.<sup>(1)</sup>

**2.2 Types of stress.** Figure 5 shows five types of stress found in adhesive joints. Any combination of these stresses may be encountered in adhesive application. These conditions are described briefly as follows:

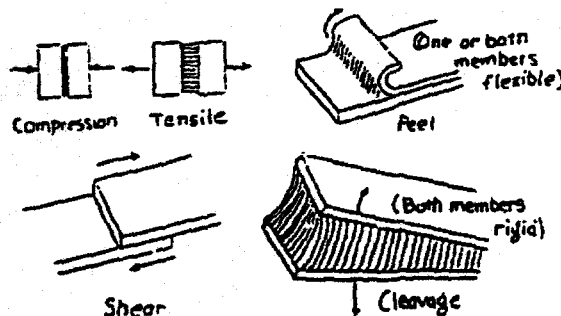


FIGURE 5. Types of stress on adhesive joints (modified after Ref. 4).

**2.2.1 Compression.** When loaded in pure compression, a joint is less likely to fail than when loaded in any other fashion, but such joints are limited in application.

**2.2.2 Shear.** Shear loading imposes an even stress across the whole bonded area. This type of loading utilizes the joint area to the best advantage, providing an economical joint that is most resistant to joint failure. Whenever possible, joints should be formed in such a way that most of the load is transmitted through the joint as a shear load.<sup>(2)</sup>

**2.2.3 Tensile.** The strength of joints when loaded in tension or shear are comparable. Tensile stress develops when forces acting perpendicular to the plane of the joint are distributed uniformly over the entire bonded area.

## MIL-HDBK-691D

Adhesive joints show good resistance to tensile loading because all the adhesive contributes to the strength of the joint. If the applied load is at all offset, then the benefit of an evenly distributed stress is lost and the joint is more likely to fail. Joints designed to load the adhesive in tension should have physical restraints to ensure axial loading.(2)(3)

**2.2.4 Peel.** For this type of loading to be present, one or both of the adherends must be flexible. The effect of peel is to place a very high stress on the boundary line of the joint, and unless the joint is wide or the load small, failure of the bond will occur. This form of loading should be avoided whenever possible.(2)

**2.2.5 Cleavage.** This type of loading is usually the result of an offset tensile force or a moment. Unlike the other types of stress, cleavage stress is not evenly distributed, but concentrated at one side of the joint. A sufficiently large bonded area is needed to accommodate this type of stress, in which case the joint will be less economical. Cleavage stress is, in general, undesirable.(2)

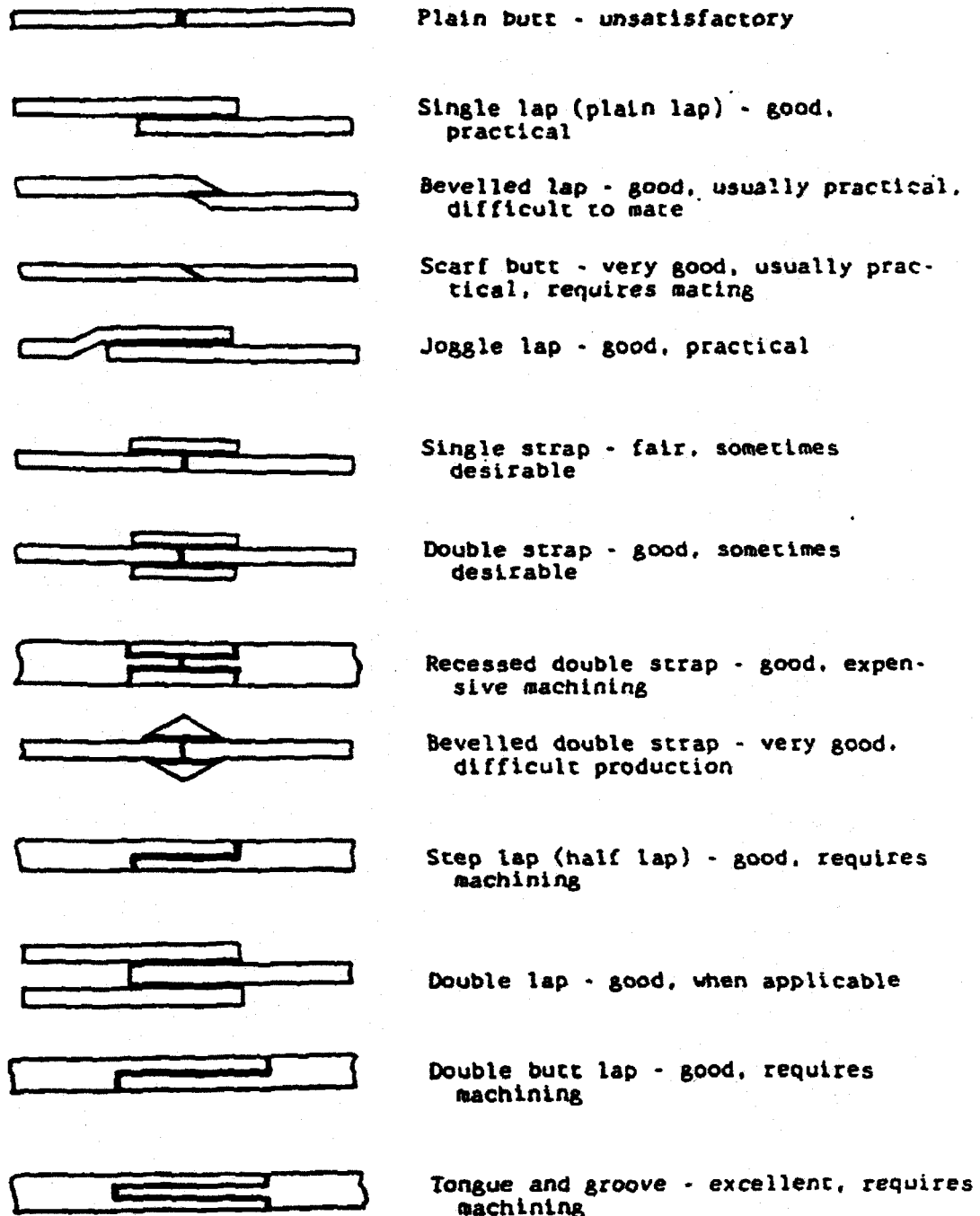
**2.3 Methods of improving joint efficiency.** To realize maximum efficiency from adhesives, joints should be specifically designed for adhesive bonding. Fig. 6 shows various types of adhesive joints for flat adherends. For maximum effectiveness and confidence, adhesive bonds should be designed in accordance with the following general principles:(5)

- o The bonded area should be as large as possible within allowable geometry and weight constraints.
- o A maximum percentage of the bonded area should contribute to the strength of the joint.
- o The adhesive should be stressed in the direction of its maximum strength.
- o Stress should be minimized in the direction in which the adhesive is weakest.

Thermosetting adhesives are relatively rigid and exhibit high tensile and shear strength independent of whether the load is applied at a rapidly varying rate (dynamic loading) or is relatively constant (static loading). These adhesives also demonstrate good fatigue characteristics. However, rigid, brittle adhesives possess relatively poor bonding qualities when stressed in peel or cleavage. Rubber-based (elastomeric) adhesives, however, have low tensile or shear strength, but because of the effects of film elasticity, these adhesives develop high peel or cleavage strength. Some adhesives demonstrate high tensile and shear strength when bonds are applied for short time periods, but have poor resistance to loads applied for sustained periods, or to vibrating stresses.

Generally, good design practice requires the avoidance of loads and joints which concentrate stresses in small areas or on edges. Since adhesives generally possess considerable strength under shear loading, joints which stress the adhesive in shear are preferable. Regardless of the direction of stress in relation to the bond line, if the load is suddenly applied, such as during impact, the adhesive must be sufficiently elastic or resilient to absorb such a shock without failure.(7)

MIL-HDBK-691B

FIGURE 6. Types of joints for flat adherends.(3)(6)(7)



HIL-MDBK-691B

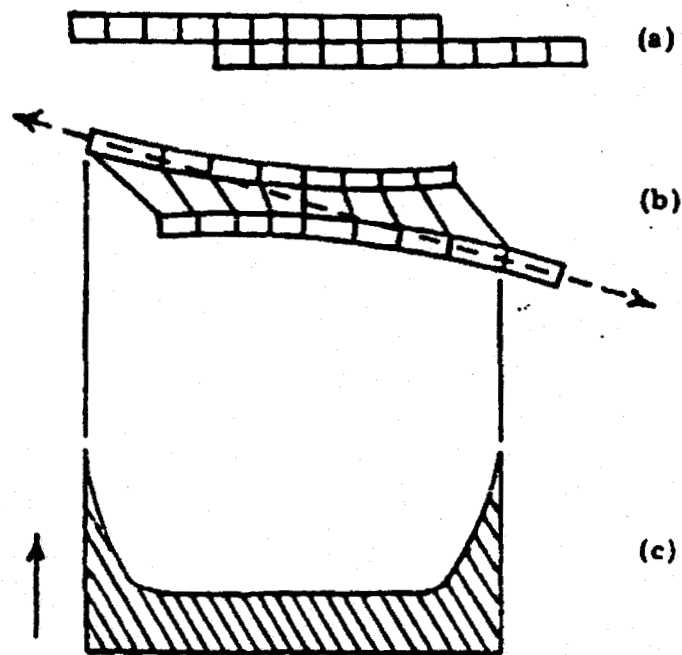


FIGURE 7. Tensile force on lap joint showing: (a) unloaded joint, (b) joint under stress, and (c) stress distribution in adhesive.<sup>(2)</sup>

The lap joint (Figure 8) is typical of most adhesive joints

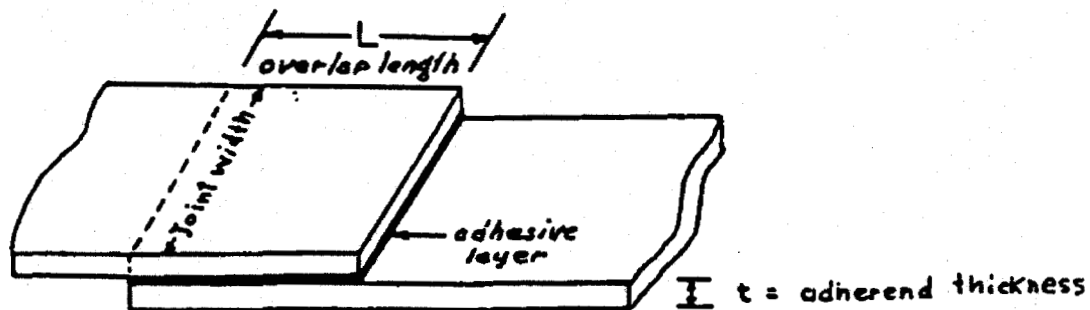


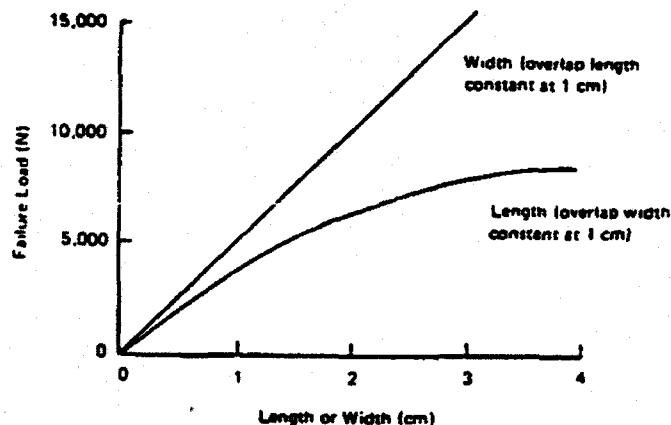
FIGURE 6. Single lap joint.

## MIL-HDBK-691B

**2.3.1 Joint design criteria.** The bonded area should be large enough to resist the greatest force that the components are expected to withstand in service. Using the principles of good joint design outlined above, this will normally be achieved, provided the load does not have a large mechanical advantage. The calculation of stress in the adhesive joint is not a reliable method of determining the exact dimensions required. It is not a simple matter to decide on an allowable stress. The adhesive strength is affected by environmental conditions, age, temperature of cure, material and size of adherends, and the thickness of the adhesive layer.<sup>(2)</sup>

The stress in the adhesive is rarely a pure one, but rather a combination of various stresses. The relative flexibility of the adhesive to that of the adherends greatly affects the stress distribution. Fig. 7 is a typical example of a tensile-lap joint under tensile loading. It will be observed from the stress distribution curve (Fig. 7-C) that most of the stress is concentrated at the ends of the lap. The greater part of the overlap, (adjacent to the center), carries a comparatively low stress. If the overlap length is increased by 100%, the load-carrying capability is increased by a much lower percentage. The most effective way to increase the bond strength is to increase the joint width.<sup>(2)</sup>

Increasing the width of the joint has the effect of giving a proportionate increase in strength, while increasing the overlap (length) beyond a certain limit has very little effect. This is illustrated in Fig 9.<sup>(2)</sup>



**FIGURE 9. Effect of overlap and width on strength of a typical joint.**<sup>(2)</sup>

In addition to overlap length and width, the strength of the lap joint is dependent on the yield strength of the adherend. The modulus and thickness of adherend determine its yield strength, which should not be greater than the joint strength. The yield strength of thin metal adherends can be exceeded where an adhesive with a high tensile strength is employed with a relatively small joint overlap. Figs 9 and 10 show the relationship between shear strength, adherend thickness, and overlap length.<sup>(2)</sup>

The fall-off in the effective load-carrying capacity of the overlap joint is usually expressed as a correlation between shear strength and the  $L/t$  ratio, where  $L$  = overlap length and  $t$  = adherend thickness. Many variables that greatly affect the strength of an adhesive are related by the simple  $L/t$  curve (sometimes  $L/t^{1/2}$ ).

## HIL-HDBK-691B

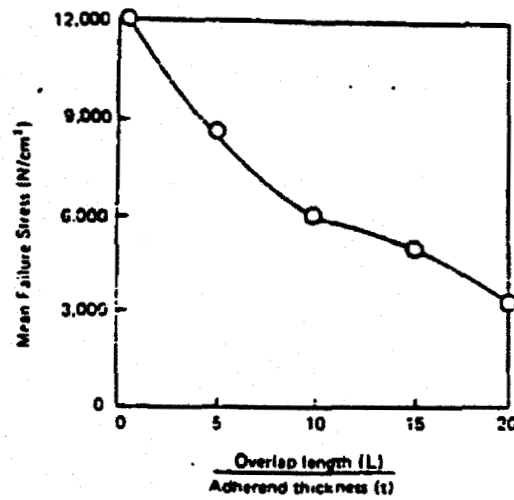


FIGURE 10. Correlation diagram between shear strength and L/t ratio. (2)

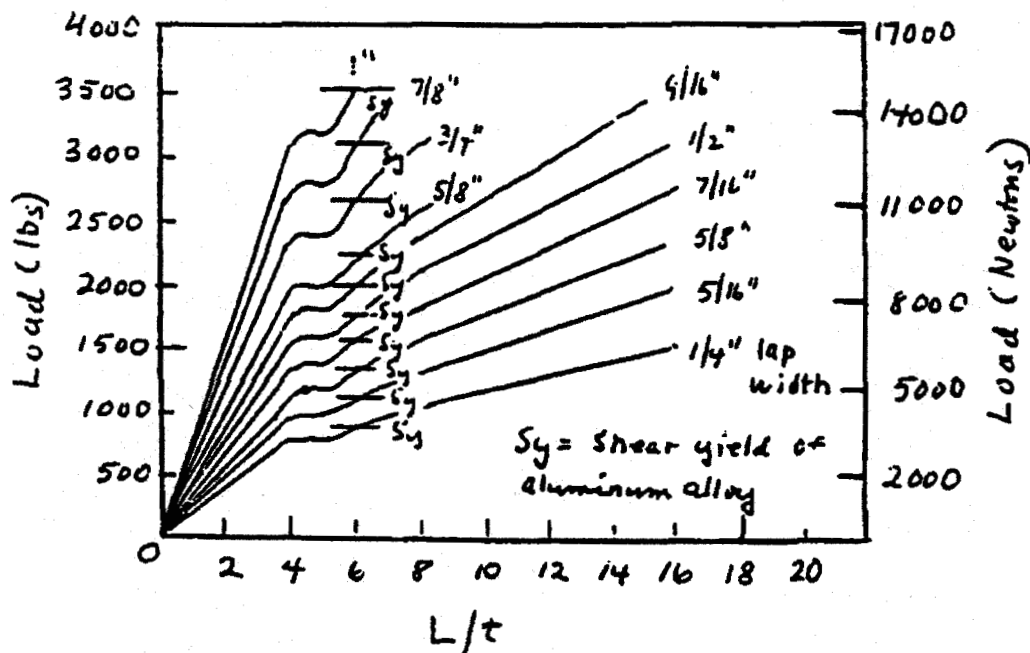


FIGURE 11. L/t curves for modified epoxy adhesive on 0.125\"/>

MIL-HDBK-691B

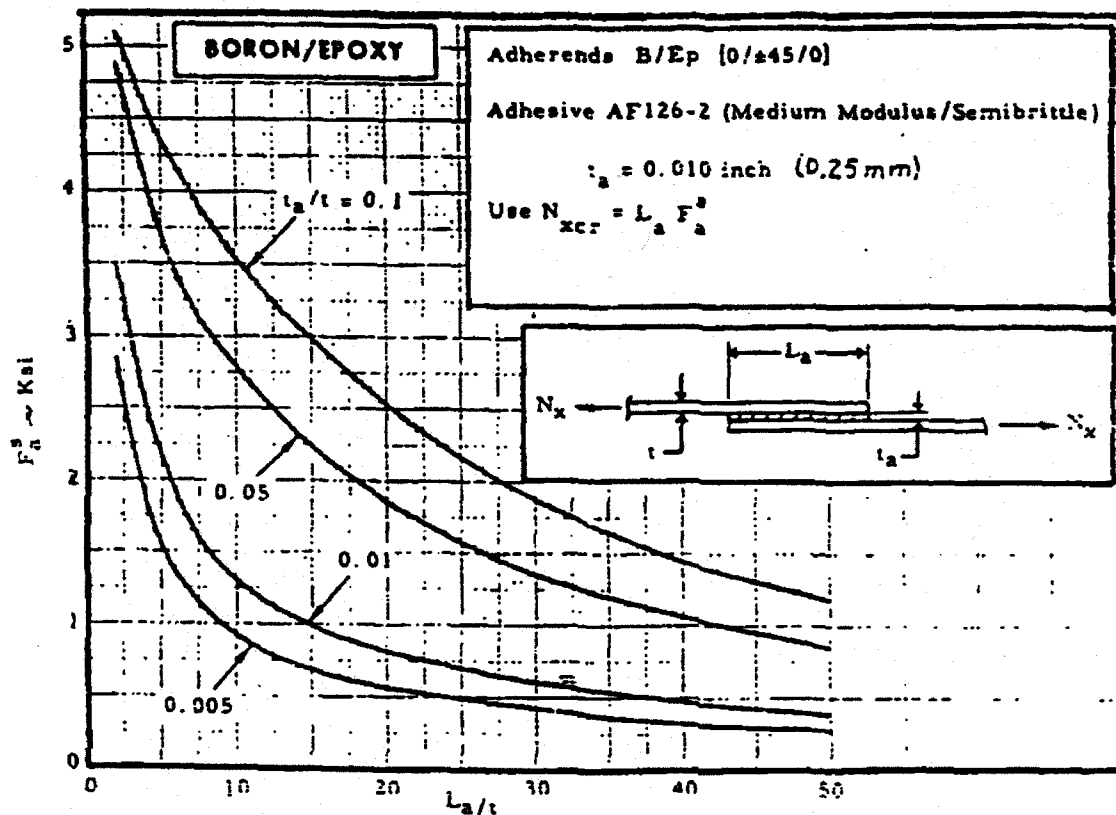


FIGURE 12. Specific design curves, single-lap shear joint, boron/epoxy to boron/epoxy AF 126-2 epoxy nitrile film adhesive.<sup>(5)</sup>

Some of these are: adherend modulus, adhesive, test temperature, bondline thickness, and joint configuration. The  $L/t$  curve is generally used for each and every variable that may enter the design, and data are presented to the designer as families of  $L/t$  curves.<sup>(6)</sup> An example of one type of  $L/t$  curve is shown in Figure 11 where load is plotted against  $L/t$  factor, for a modified epoxy adhesive 250°F (121°C) curing, supported film on 0.125 inch (3.2 mm) thick 2024-T3 aluminum alloy. These curves were plotted for various bond widths from 1/4 inch (6.3 mm) to 1 inch (25.4 mm).<sup>(9)</sup> Perhaps a more useful way for presenting data to the design engineer is plotting stress against  $L/t$ , as shown in Figure 12.

**2.4 Typical joint designs.** The ideal adhesive-bonded joint is one in which, under all practical loading conditions, the adhesive is stressed in the direction in which it most resists failure. A favorable stress can be applied to the bond by using proper joint design. Some joint designs may be impractical, expensive to make, or hard to align. The design engineer will often have to weigh these factors against optimum adhesive performance.<sup>(3)</sup>

## MIL-STD-691B

2.4.1 Joints for flat adherends. This type of joint has already been discussed above briefly, and a number of examples are shown in Fig. 6.

2.4.1.1 Butt joints. Butt joints cannot withstand bending forces because the adhesive would undergo cleavage stress. If the adherends are too thick to design simple overlap joints, the butt joint can be improved by redesigning a number of ways, as shown in Fig. 6. All the modified butt joints reduce the cleavage effect caused by side loading. Tongue-and-groove joints also have an advantage in that they are self-aligning and act as a reservoir for the adhesive. The scarf butt joint keeps the axis of loading in line with the joint and does not require a major machining operation.<sup>(3)</sup>

2.4.1.2 Lap joints. Lap joints are the most commonly used adhesive joints because they are simple to make, are applicable to thin adherends, and stress the adhesive primarily in its strongest direction. Tensile loading of a lap joint causes the adhesive to be stressed in shear. However, the simple lap joint is offset and the shear forces are not in line. (Fig. 7) This factor results in cleavage stress at the ends of the joint, which seriously impairs its efficiency. Modifications of lap-joint design include:<sup>(3)</sup>

- o Redesigning the joint to bring the load on the adherends in line
- o Making the adherends more rigid (thicker) near the bond area (see Figure 13)
- o Making the edges of the bonded area more flexible for better conformance, thus minimizing peel.

Modifications of lap joints are shown in Figure 6.

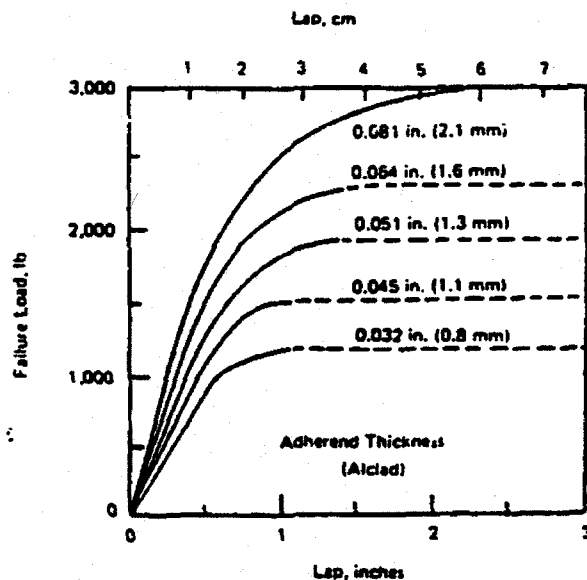


FIGURE 13. Interrelation of failure loads, depth of lap, and adherend thickness for lap joints with a specific adhesive and adherend.<sup>(3)(10)</sup>

MIL-HDBK-691B

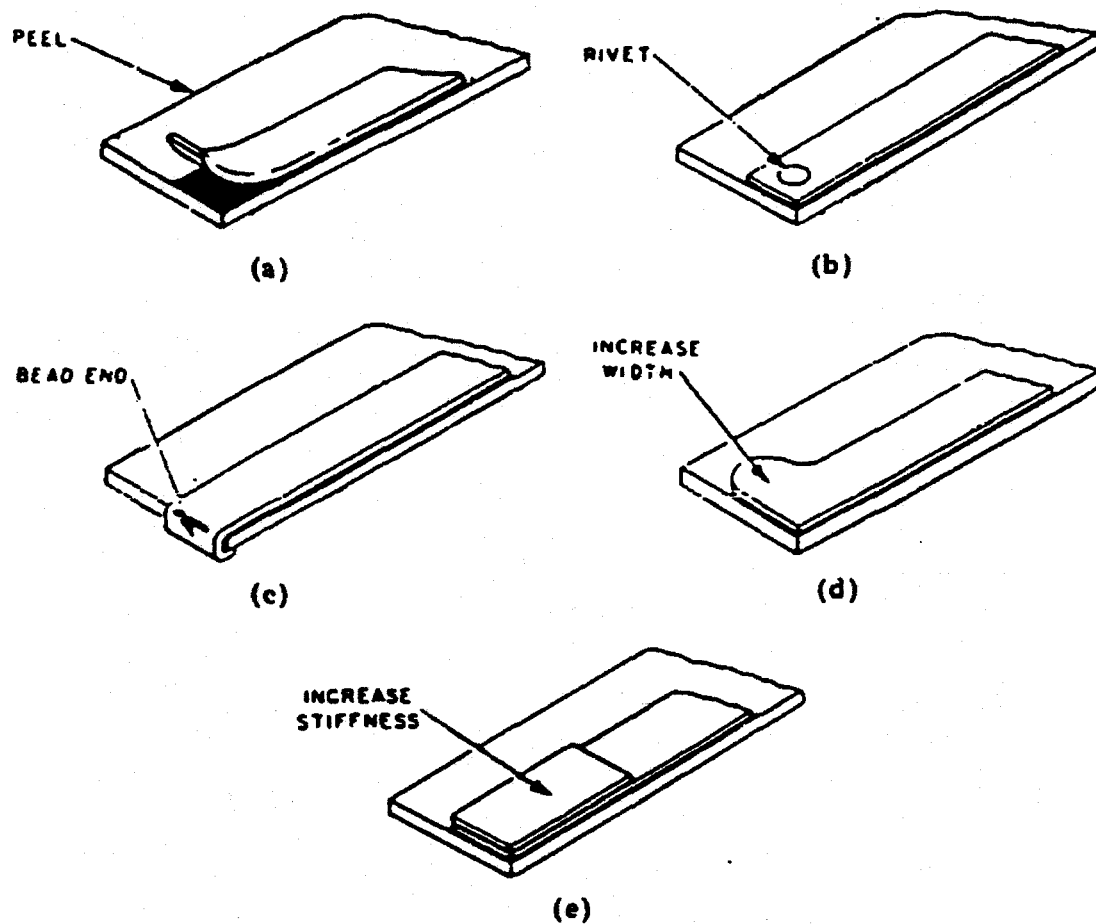


FIGURE 14. Designs that minimize peel.(1)

## MIL-HDBK-691B

The joggle-lap joint design is the easiest method of aligning loads. This joint can be made by simply bending the adherends. It also provides a surface to which it is easy to apply pressure. The double-lap joint has a balanced construction which is subjected to bending only if loads on the double side of the lap are not balanced. The beveled-lap joint is also more efficient than the plain lap joint. The beveled edges allow conformance of the adherends during loading, with a resultant reduction of cleavage stress on the ends of the joint.<sup>(3)</sup>

**2.4.1.3 Strap joints.** Strap joints keep the operating loads aligned and are generally used where overlap joints are impractical because of adherend thickness. As in the case of the lap joint, the single strap is subjected to cleavage stress under bending forces. The double-strap joint is superior when bending stresses are encountered. The beveled double strap and recessed double strap are the best joint designs to resist bending forces. They both require expensive machining, however.<sup>(3)</sup>

**2.4.1.4 Peeling of adhesive joints.** When thin members are bonded to thicker sheets, operating loads generally tend to peel the thin member from its base, as shown in Fig. 14<sup>(3)</sup>. Riveting may provide extra strength at the ends of the bond, but rivets often produce stress concentrations. Beading the end of the joint is good, but not always possible. Increasing the width of the end of the joint will increase its peel strength. Finally, increasing the stiffness of the adherends is often quite effective. The stiffer the adherends, the smaller the deflection of the joint for a given force, and the smaller the peel stresses.<sup>(1)</sup>

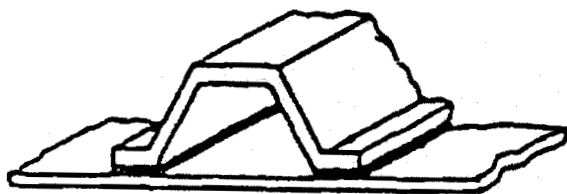
**2.4.2 Stiffening joints.** Often thin sheets of a material are made more rigid by bonding stiffening members to the sheet. When such sheets are flexed, the bonded joints are subjected to cleavage stress. Some design methods for reducing cleavage stress on stiffening joints are illustrated in Figure 15. Resistance of stiffening members to bending forces is increased by 1) extending the bond area, 2) providing greater flange flexibility, and 3) increasing the stiffness of the base sheet.<sup>(3)</sup>

**2.4.3 Cylindrical joints.** Several recommended designs for rod and tube joints are illustrated in Figure 16. These designs should be used instead of the simple butt joint because of their resistance to bending forces and subsequent cleavage and their increase in bonding area. With tubular forms, unless the tube walls are very thick, the bonding area is also quite small. Unfortunately, most of these joint designs require a machining operation.<sup>(3)</sup>

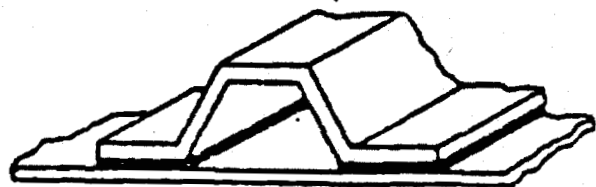
**2.4.4 Angle and corner joints.** Angle and corner joints for flat adherends are shown in Figure 17 and 18. In both, the butt joint is again susceptible to cleavage under bending stress. Among the angle joints (Figure 13), the dado joint is probably the best, provided that the reduction in section required for the recess is acceptable. This design is less subject to cleavage than the right-angle butt joints (also called "L" angle joints), and is generally easier to produce. The double right-angle butt joint is also called the "T" angle joint. Corner joints (Figure 14) for flat adherends are best designed to use fixtures. For solid rods and tubular forms fixtures are always required.



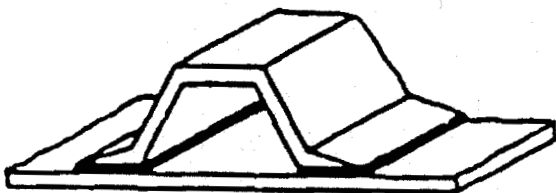
MIL-HDBK-691B



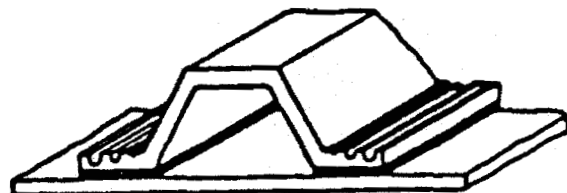
ORIGINAL DESIGN



INCREASED BOND AREA



INCREASED FLANGE FLEXIBILITY



INCREASED SHEET STIFFNESS

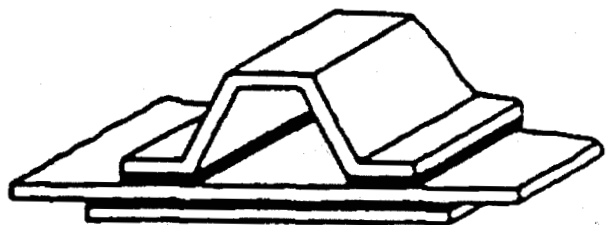
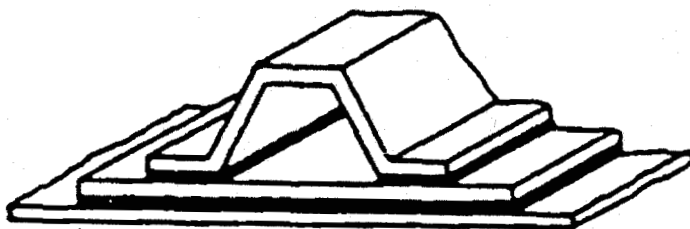
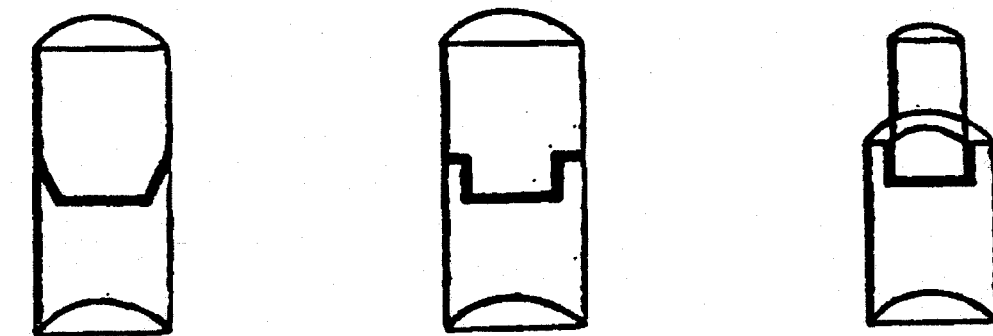


FIGURE 15. Minimizing peel for stiffening sections.(1)

MIL-HDBK-691B

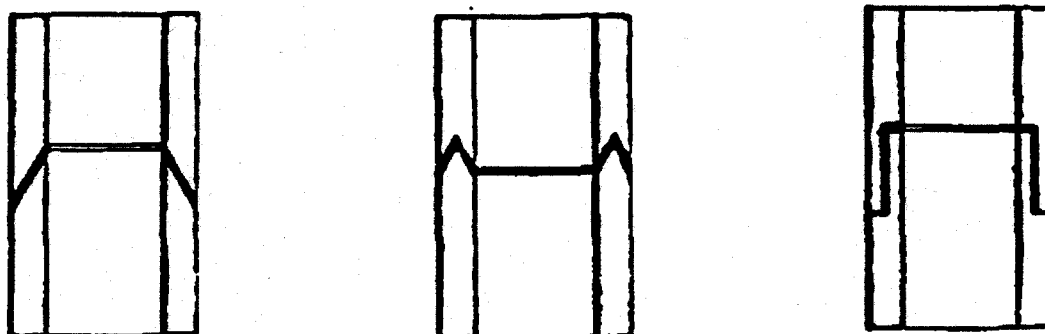


Tapered socket

Landed socket

Socket

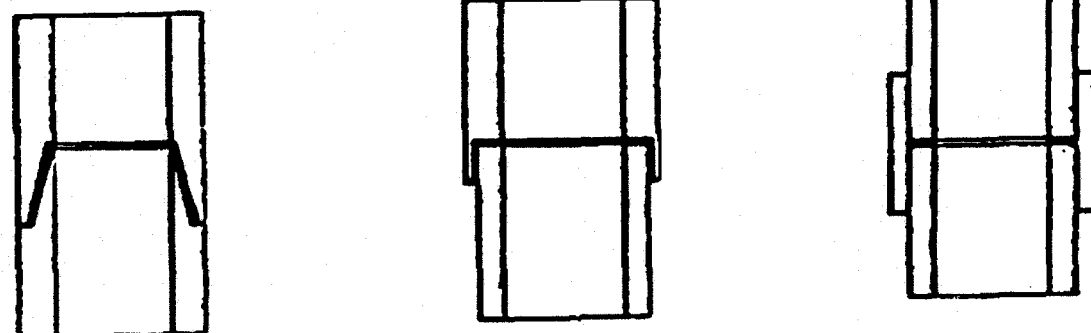
(a) Designs for solid bars



Taper

V-groove

Half-lap



Landed taper

Landed lap

Sleeve-reinforced butt

(b) Designs for cylinders or tubes

FIGURE 16. Recommended designs for rod and tube adhesive-bonded joints. (1)(11)

MIL-HDBK-691B

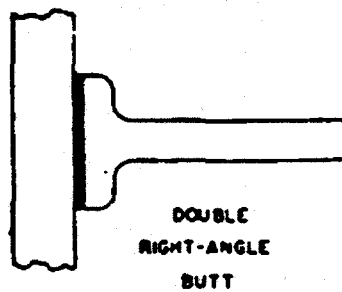
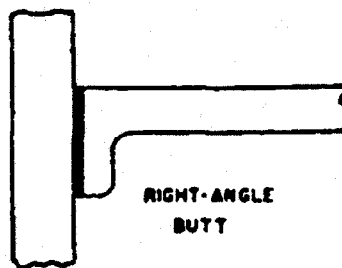
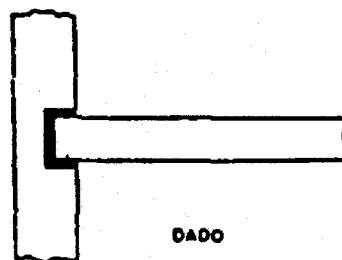
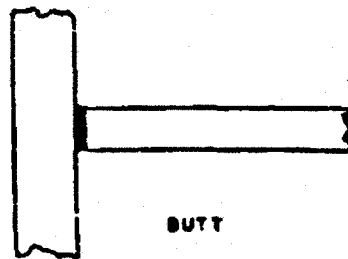
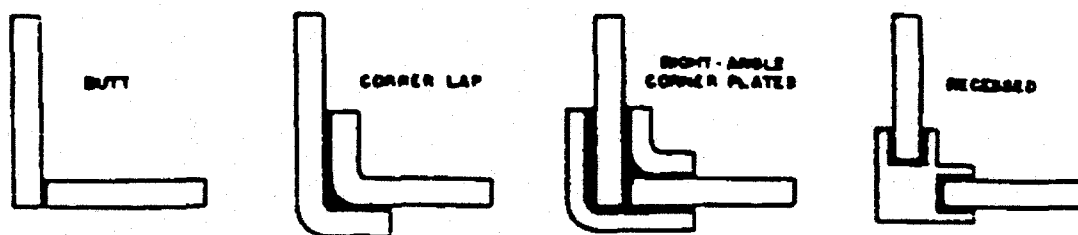


FIGURE 17. Angle joints.(1)

MIL-HDBK-691B

FIGURE 18. Corner joints.(1)

**2.4.5 Plastic and elastomer joints.** Designing of joints for plastics and elastomers usually follows the same practice as for metals. However, the designer should be aware of certain characteristics of these materials that require special consideration.(3)

**2.4.5.1 Flexible plastics and elastomers.** Thin or flexible polymeric substrates may be joined using a simple or modified lap joint. The double-strap joint (Fig. 6) is best, but also the most time-consuming to fabricate. The strap material should be made out of the same material as the parts to be joined, or at least, have approximately equivalent strength, flexibility, and thickness. The adhesive should have the same degree of flexibility as the adherends. If the sections to be bonded are relatively thick, a scarf joint is acceptable. The length of the scarf should be at least four times the thickness; sometimes larger scarfs may be needed.(3)

Figure 19 shows several types of joints for rubber under tension. The horizontal white lines are equidistant when joints are unstressed. Clearly, the scarf joint is least subject to stress concentration with materials of equal modulus, and the double scarf joint is the best for materials of unequal modulus. These designs provide the best resistance to peel, and, all other factors being equal, would represent the best choice.(1)

When bonding elastic material, forces on the elastomer during cure should be carefully controlled, since excess pressure will cause residual stresses at the bond interface. Stress concentrations may also be minimized in rubber-to-metal joints by elimination of sharp corners and by using metal thick enough to prevent peel stresses that may arise with thinner-gage metals. As with all joint designs, polymeric joints should avoid peel stress. Fig. 20 illustrates methods of bonding flexible substrates so that the adhesive will be stressed in its strongest direction.(1)

**2.4.5.2 Rigid plastics.** Reinforced plastics are often anisotropic materials, meaning that their strength properties may not be the same in all directions. Joints made from anisotropic substrates should be designed to stress both the adhesive and the adherend in the direction of greatest

## MIL-HDBK-691B

strength. Laminates, for example, should be stressed parallel to the laminations. Stresses normal to the laminate may cause the substrate to delaminate. Single- and joggle-lap joints are more likely to cause delamination than scarf or beveled lap joints. The strap-joint variations are useful when bending loads may be imposed on the joint.<sup>(3)</sup>

**2.4.5.3 Wood joints.** Wood presents special problems in joint design. It is anisotropic; both shrinkage and strength will vary with grain direction and with angle of cut. For example, tangential shrinkage in wood is generally double the radial shrinkage, and shrinkage perpendicular to the grain is usually greater than shrinkage in the direction of the grain. Therefore, for maximum durability, wood should be bonded to similar types and cuts. Two other characteristics of wood place severe limitations on the types of joints that may be used. First, the tensile strength of wood perpendicular to the grain is approximately one-tenth that of wood in the direction of the grain. Second, end-grain butt joints can transmit no tensile stress, and can transmit compressive stress only after considerable deformation. Thus, most of the designs discussed above are ruled out. The scarf-joint, however, remains as the best type of joint for bonding wood end-to-end. For solid wood, the straight scarf joint permits very high joint efficiencies. For most

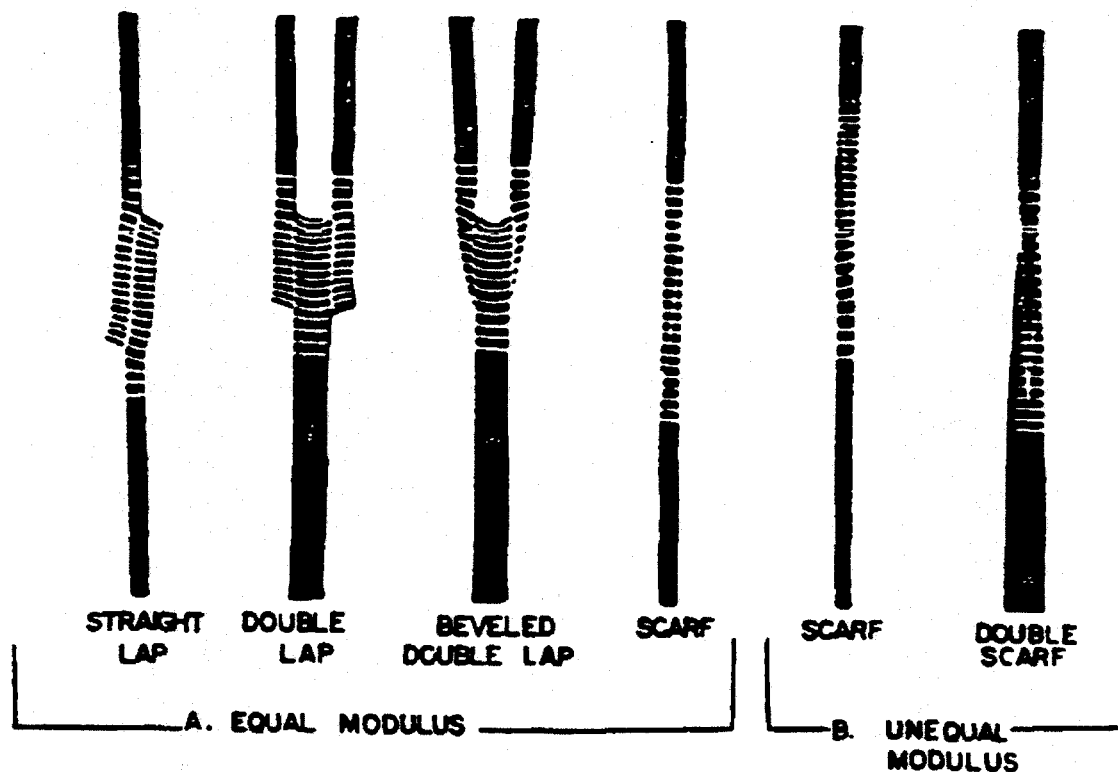


FIGURE 19. Joints for rubber (under stress).<sup>(1)</sup>

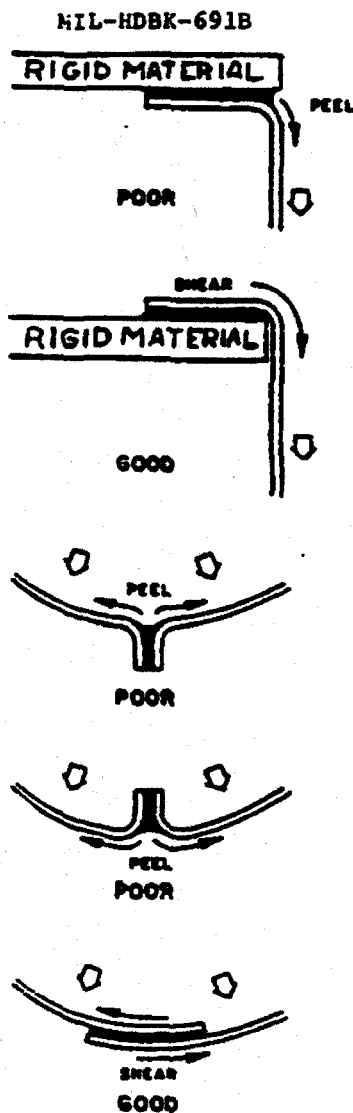


FIGURE 20. Joints for flexible materials.(1)

↻ = stress direction  
 → = resultant force

applications, a slope of 1 in 12 is used. The slope should never be steeper than 1 in 5. Such joints require the application of lateral or transverse pressure during the time the adhesive hardens.

For laminated wood, several other types of scarf joints have been developed. These joints are shown in Fig. 21. In tension, none of these joints is as efficient as a straight scarf joint with a slope of 1 in 8 or flatter. In compression, however, all exhibit efficiencies approaching 100%. For both solid and laminated wood, a number of joints generally useful in assembly are shown in Fig. 22. These joints are more commonly used in combination rather than alone. The principles of wood-joint design, and not the specific designs illustrating these principles, should be considered first at all times. The joints shown in both Figs. 21 and 22 are self-aligning, and require no pressure.(1)

## MIL-HDBK-691B

**2.4.6 Metal joints.** Information on bonding metals is found in the general discussions under 2.1 - 2.4.4. Indeed, the emphasis in this handbook will be on metal-to-metal bonds.

**2.4.7 Joints combining different adherend types.**

**2.4.7.1 Joints with adherends differing in rigidity.** When adherends differ in rigidity, their thicknesses should be adjusted so that they will be equally rigid; that is, their thicknesses should be in inverse proportion to their moduli. The most efficient type of joint for such materials is probably the double scarf-lap joint, with the adherends tapered in proportion to their moduli of elasticity (shown for rubber in Fig. 19). Naturally, when the difference in rigidity is very large, as in rubber-to-steel bonds, this practice is not feasible.(1)

**2.4.7.2 Joints with adherends differing in coefficient of thermal expansion.** Differences in the coefficients of thermal expansion of the adherends may cause, among other things, warpage of the final assembly. Such differences may also cause thermal breakage of the joints. The use of an elastic adhesive is often valuable here. However, in some instances, such an adhesive would be unusable for other reasons. Careful joint design can also prevent warpage. The best procedure is to balance the construction. For most common straight joints, this would mean that a double-lap or double-strap joint (Figures 6 and 19) would be desirable. When sheets are being laminated, balance can be best achieved by making a "sandwich", so that one of the adherends is bonded to both sides of the other. Alternatively, the continuity of the sheet having the lower coefficient of expansion may be broken. In bonding wood to metal, for example, the wood could be made into several smaller panels before fabrication.

**2.5 Stress analysis.** This is an extremely complex subject and will only be touched upon briefly in this discussion.

**2.5.1 General principles.** Recognizing that present aerospace design practice has not caught up with newer analytical techniques, present analysis efforts in aerospace structural adhesive bonding can be separated into three categories: (1) theoretical analysis of stresses and strains, (2) experimental analysis, (3) failure analysis. Most of the analysis work in all three categories has been concentrated on bonded lap joints, and the original pioneer work of Volkersen (1938) and Goland and Reissner (1944) has been continued and expanded during the past 30 years by other investigators. The ultimate objective of these analyses has been to develop a design method for bonded construction; based on the principles of mechanics and rational engineering design, so that joint behavior could be predicted.(12)

**2.5.1.1 Theoretical analyses of stresses and strains.** Most theoretical analyses have been on the single or double lap type joint, because these are the most common types occurring in adhesive-bonded assemblies. The analyses of scarfed and stepped-lap joints are very different from lap joints, and have rarely been attempted. Lap joints are also the primary type of joint used for determining the strength of adhesive joints. There is a good reason for this reliance on a lap-type configuration. If the joint is properly designed, the primary stress in the adhesive is a shear stress, toward which adhesives



NIL-HDBK-691B

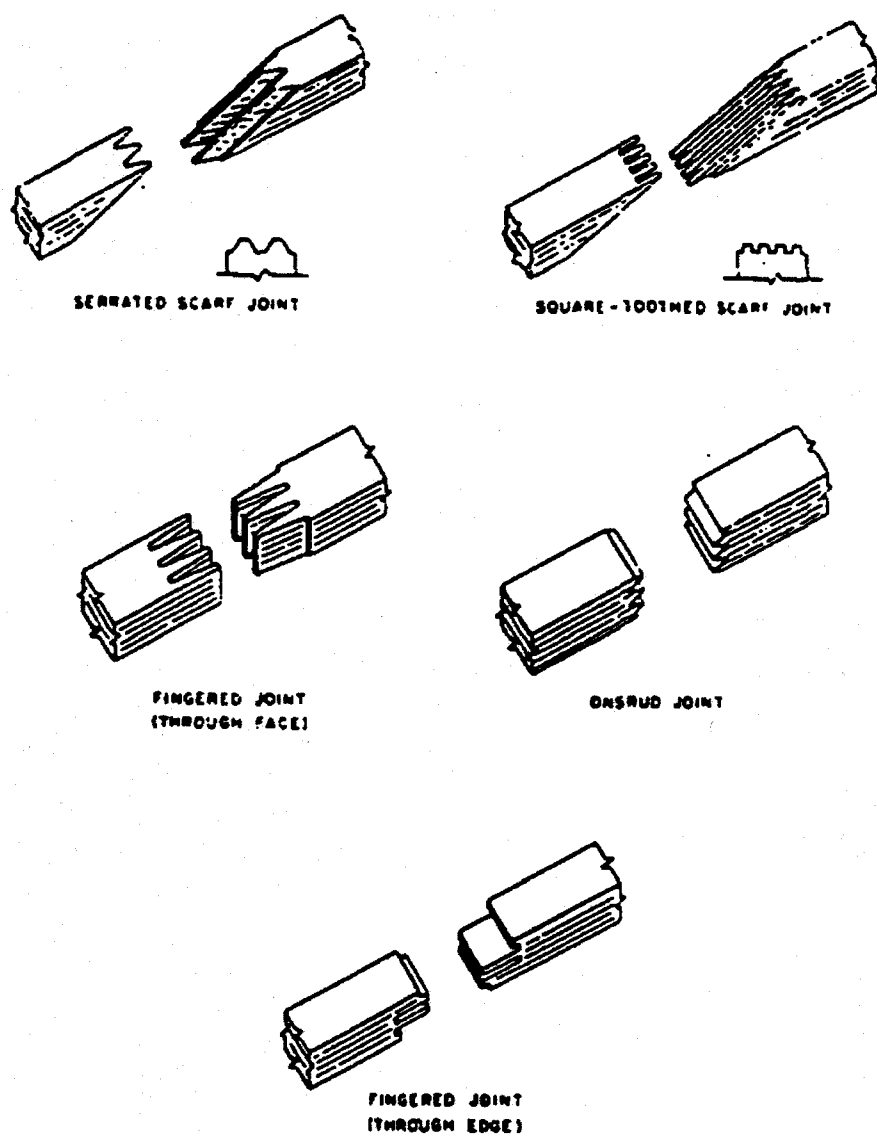


FIGURE 21. Straight joints for laminated wood.(1)

NIL-HDBK-691B

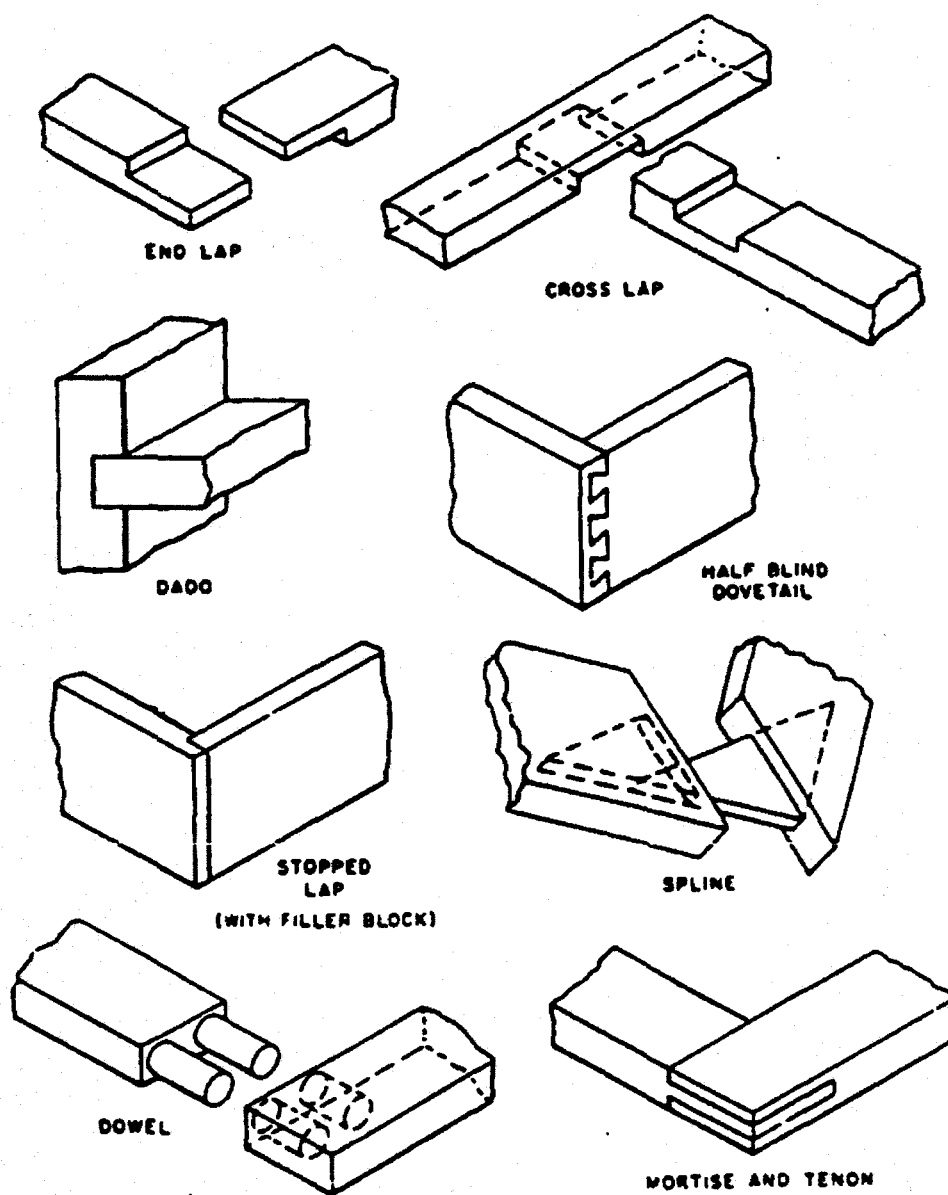


FIGURE 22. Joints for solid and laminated wood assembly. (1)

## HIL-HDBK-691B

oppose their greatest strength. Adhesive joints are notoriously weak in peel, and are also weak under tensile loads applied normal to the plane of the joint. The need for strong adhesives with high peel strength is still very acute.

The earliest theoretical lap-joint work involved the most simplifying assumptions, i.e., the joint was a simple overlap type, both adherends were made of the same metal and had the same geometry, the adherends and the adhesive behaved elastically, bending or peeling stresses were not included, thermal expansion or residual stresses were ignored, deflections were small, etc. Furthermore, the stress-strain distributions that were derived were "closed form" solutions of various differential equations.

Present theoretical efforts have become much more sophisticated. New computer-assisted techniques have introduced the application of finite-element-matrix theory type approaches. Parametric studies are being conducted to determine the effects of important variables. Double-lap joints, scarf joints, jogged joints, and stepped-lap joints have been added to the original simple-overlap joint, and nonlinear closed-form solutions are available.

New adherend materials, especially the advanced filamentary composites, are now being considered, and various bonded combinations of materials with different stiffnesses and various geometries have become common. The elastic, low-deflection, constant-temperature behavior of scarf and stopped-lap joints has been replaced by elastic-plastic, large-deflection behavior combined with thermal expansion differences, or curing shrinkage induced residual stresses. Many new considerations arise and promise to continue to complicate the analysis picture. Now the theoretical expert is supposed to handle fatigue, creep, impact, varying elevated or very low service temperatures, continued heating, deleterious environmental effects, corrosion of the metal substrates, crack propagation, yielding of the adherend, and many other variables. (12)

**2.5.1.2 Experimental analyses.** Whether a theoretical analysis is successfully completed, or whether the practical complications outstrip the capabilities of even the most sophisticated approach, today the only conclusive progress has not been nearly as great because the labor and materials costs associated with laboratory experiments greatly surpass theoretical efforts, hence provide a very effective economic deterrent to significant progress in relating theory, laboratory test, and real-life performance. Typically, the yardstick for qualitatively measuring the internal resistance of an adhesive bond to an external load has been the determination of the strain distributions in the adhesive and the adherends. This is no small task. Even in the simplest lap joints, the actual stress-strain distributions under load are extremely complex combinations of shear and tensile stresses and are very prone to disturbance by nonuniform material characteristics, stress concentrations or localized partial failures, creep and plastic yielding, etc. The fact that the adhesive gage length (glue-line thickness) is very small and that the adhesive is so completely encapsulated between the adherends that it is practically inaccessible means that the strains are both hidden and small, and, hence, extremely difficult to measure accurately. The usual techniques of extensometers, strain gages, and photoelasticity are being used with limited success. (12)

## MIL-HDBK-691B

**2.5.1.3 Failure analyses.** The function of a structural adhesive joint is to transmit an external load to the structural members. If the joint fails to function properly, it will undergo damage or failure. The damage could be actual fracture of the structure, excessive elastic deformation, or excessive inelastic flow. The criteria for what constitutes structural failure depend on the performance requirements of the joint. The fundamental problem in the mechanics of adhesives and of joints is to obtain some relationship between the loads applied to the joint and a parameter that will adequately describe the criteria for structural failure. For example, if a joint is considered to have failed when its elastic deflection reaches a certain limit, a relationship is necessary between applied load and elastic deflection. Similarly, relationships may be necessary between joint strength and applied load or creep and applied load. The most common criterion for structural failure of lap-type joints is actual fracture of the joint. For a given combination of adherend and adhesive, the stress analyst has to make a decision as to what the mode or theory of failure of the joint would be if the applied loads become large enough to cause failure. The decision as to which theory would realistically determine the mode of failure is usually based on past experience, or some form of experimental evidence.

The selection of a failure theory for a particular adhesive joint then leads to the determination of a relationship between the applied load, and a parameter (stress, strain, strain energy, etc.) that will describe the failure of the joint. Assuming, for example, that the joint will fail when the principle stress in the adhesive perpendicular to the plane of the joint (tensile stress) reaches a level sufficient to cause fracture, it is necessary to know the strength of the adhesive under tension in this direction when constrained by the adjacent adherends. Finally, when maximum tolerable stresses have been obtained, the allowable stress values or factors of safety are decided upon to allow for factors such as long-and short-term loading, fatigue loading, special environmental conditions, and other special considerations. This step is usually based on experience, engineering judgement, and legal, government, or commercial specifications.(12)

## 2.5.2 Methods.

**2.5.2.1 Volkersen.** Volkersen, (1938), analyzed the distribution of shearing stresses on the adhesive layer of a lap joint. His model is valid only for the special case of very stiff adhesives, which do not bend on loading the joint. A dimensionless stress concentration factor is found to depend on the geometry and on physical parameters of the joint. By introducing further simplifications, certain reasonable geometric conditions and identical adherends, a simple formula is obtained as follows:

$$\Delta = \frac{GL^2}{Etd}$$

where  $\Delta$  is the stress concentration in elastic theory and is a dimensionless coefficient, G is the shear modulus of the adhesive, E is the Young's modulus of the adherend, d is the thickness of the adhesive, t is the thickness of the adherend, and L is the length of the overlap. DeBruyne has suggested that, when all other variables are kept constant, the  $t/L$ , the "joint factor" derived from the above equation, is useful in correlating joint strength. (See also 2.3.1)

## NHL-HDBK-691B

Enlarged models of lap joints can be made by sealing a plate of photo-elastically-sensitive resin, the "adhesive", between steel plates, the adherends. It follows from the principles of geometric similarity that the stress concentrations observed on loading this composite are comparable to those in an actual lap joint of the same geometry. Volkersen's theory predicts that the shear stresses in the adhesive layer reach a maximum at each end of the overlap when the bonded plates are in pure tension. Photoelastic analysis of these composite structures revealed that stresses are uniform in the central part of the model adhesive, but high near the edges of the steel plates. Stress distributions at the end were found to be independent of the length of the overlap when its length was at least three times the thickness of the adhesive layer. (13)(14)

**2.5.2.2 Goland and Reissner.** In the theory of Volkersen, the so-called "tearing" or "peeling" stresses were neglected. Goland and Reissner took the bending deformation of the adherends into account, as well as the transverse strains in the adhesive and the associated tearing stresses. They considered two cases, (1) where the adhesive layer is extremely thin and of similar elastic stiffness to the adherends, so that its deformations are of little importance, as, for example, in well-fitting glued wooden joints, and (2) where the adhesive layer is thin, but its deformation makes a significant contribution to the stress pattern in the joint, as in bonded metal-to-metal joints. These workers pointed out that the maximum tearing and shear stresses reach asymptotic values for large overlap lengths. Hence, provided the system remains linearly elastic, the joint strength reaches a limiting value with increasing length of overlap. In practice, a limiting strength is obtained for a different reason, namely that the adherends are loaded to their ultimate strength. (13)(14)(15)(16)

**2.5.2.3 Forest Products Laboratory Review.** A critical review in the field of the design of adhesive-bonded lap type joints was prepared by FPL for the Air Force Materials Laboratory in 1964. This study included a comprehensive survey and analysis of the literature pertaining to the theoretical and experimental analysis of lap joints, mechanical properties of adhesive film in joints, failure criteria for joints, and empirical methods of joint design. Based on the results of this survey, recommendations are given for further research in this area. (17)

(WP# ID-6598A/DISC-0514A. FOR HTL USE ONLY.

## MIL-HDBK-691B

REFERENCES

- (2-1) Military Handbook (MIL-HDBK-691A), "Adhesives", 17 May 1965.
- (2-2) J. Shields, ADHESIVES HANDBOOK, London, Hwnes-Butterworth, 1976.
- (2-3) E.N. Petrie, Chapter 10, "Plastics and Elastomers as Adhesives", in HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A. Harper, McGraw-Hill, New York, N.Y., 1975.
- (2-4) B. Fader, "Adhesive Bonding of Lead", Chapter 13 in HANDBOOK OF ADHESIVE BONDING, edited by C.V. Cagle, McGraw-Hill, New York, N.Y.
- (2-5) J.T. Kubo, Chapter 1.3 - "Joints", Sept. 1976, in ADVANCED COMPOSITES DESIGN GUIDE, Vol. 1 - Design, 3rd edition, 2nd revision. Prepared for Air Force Flight Dynamics Laboratory, WPAFB, OH, by Rockwell International Corp.
- (2-6) L.H. Sharpe, "The Materials, Process and Design Methods for Assembling with Adhesives", Design Guide, Machine Design, 38 (19): 179-200 (August 18, 1966).
- (2-7) J.T. Kubo, Chapter 2.4 - "Joints", Rev. Jan 1977, in ADVANCED COMPOSITES DESIGN GUIDE, Vol. 2 - Analysis, 3rd edition, 3rd revision. Prepared for Air Force Flight Dynamics Laboratory, WPAFB, OH, Rockwell International Corp.
- (2-8) L.R. Lunsford, "Stress Analysis of Bonded Joints", Applied Polymer Symposia No. 3, "Structural Adhesive Bonding, presented at symposium sponsored by Picatinny Arsenal, held at Steven Institute of Technology, Sept. 14-16, 1965, pp. 57-73. Wiley-Interscience (1966).
- (2-9) K.F. Wegman et al., "Adherend Mechanical Properties Limit Adhesive Bond Strength", SAMPE Journal, 3 (2): 68-72 (April/May 1968).
- (2-10) H.A. Perry, Room Temperature Setting Adhesives for Metals and Plastics", in ADHESION AND ADHESION FUNDAMENTALS AND PRACTICE, edited by J.E. Kutzler and R.L. Savage, Society of the Chemical Industry, London, 1954.
- (2-11) Aluminum Company of America (ALCOA), ADHESIVE BONDING ALCOA ALUMINUM, 1967.
- (2-12) Chapter 8, "Design, Analysis, and Test Methods", in STRUCTURAL ADHESIVES; WITH EMPHASIS ON AEROSPACE APPLICATIONS, TREATISE ON ADHESION AND ADHESIVES, Vol. 4, A Report of the ad hoc Committee on Structural Adhesives for Aerospace Use, National Materials Advisory Board, Marcel Dekker, 1976.
- (2-13) G. Salomon, "Introduction", Chapter 1, ADHESION AND ADHESIVES, edited by R. Houvink and G. Salomon, 2nd edition, Vol. 2, Applications, Elsevier Publishing Co., 1967.
- (2-14) N.K. Benson, "Influence of Stress Distribution on Joint Strength", Chapter 3 in Part IV. Joint Design. ADHESION - FUNDAMENTALS AND PRACTICE, A Report of an International Conference held at the

**MIL-MDBK-691B**

**University of Nottingham, England, 20-22 Sept. 1966 by the Ministry of Technology (UK), Gordon and Breach, 1969.**

- (2-15) H. Goland and E. Reissner, "The Stresses in Cemented Joints", Journal of Applied Mechanics, 2 (1): A-17 - A-27 (March 1944).**
- (2-16) L. Greenwood, T.R. Boag and A.S. McLaren, Chapter 5, "Stress Distribution in Lap Joints", in Part V, Methods of Test, ADHESION - FUNDAMENTALS AND PRACTICE, A Report of an International Conference held at the University of Nottingham, England, 20-22 Sept. 1966, by the Ministry of Technology (UK), Gordon and Breach, N.Y., 1967.**
- (2-17) D. Kutscha (U.S. Forest Products Laboratory), "Mechanics of Adhesive Bonded Lap-Type Joints: Survey and Review," Air Force Materials Laboratory Report HL-TDR-64-298, December 1964.**



## MIL-HDBK-691B

## Chapter 3. ADHEREND TYPES

**3.1 General discussion.** A wide variety of materials are currently available for the construction of bonded assemblies. Some of these materials are relatively thin and fragile and adhesive bonding is the only way they can be joined. A number of high-strength materials can be joined with adhesives more economically and can out-perform assemblies fabricated by other joining techniques. Adhesive bonding is particularly desirable for joining porous materials and nonmetallics and for bonding dissimilar substances. Often adhesives provide the only satisfactory method for joining materials. Several general points should be kept in mind when bonding with adhesives:(1)

- o All parts must be meticulously clean and structurally sound
- o The adhesive should not significantly degrade either substrate

**3.2 Similar substrates.** Ordinarily, it is easier to select an adhesive and design a bonded joint when the adherends are identical or similar. It is easier, for example, to bond two pieces of wood than to bond wood and polyethylene. In all cases, however, the nature of the surface, porosity, cleanliness, and surface preparation must be carefully considered before attempting to join materials or components with adhesives.(1)

**3.2.1 Porous materials.** Porous materials that are frequently bonded with adhesives to the same or similar substrates are wood, paper, rubber, fabrics, leather, foamed plastics, some ceramics, and some metals. The porosity of a substrate or a surface may vary considerably with any type of material. Wood, for example, is a relatively porous material, and adhesives for bonding wood must be formulated to prevent excessive absorption into the adherend. When selecting adhesives for wood, consideration must be given to such variables as moisture content, percent extractables, surface effects, density, hardness and strength. The denser hardwoods, such as oak, maple, and walnut, form somewhat stronger adhesive joints than can be obtained with the less dense softwoods, such as cedar, pine, and fir. As porosity increases, the possibility of forming "starved" glue lines increases because the adhesive tends to be absorbed into the pores. Bonding of porous surfaces requires special handling to prevent absorption of the adhesive and formation of weak joints. Some preventive measures that are usually effective are:(1)

- o Use of high-viscosity adhesives
- o Formulations with high-molecular-weight resins and polymers
- o Maintenance of high-solids content
- o Bonding or curing with minimum-pressure application
- o Incorporation of fillers into the adhesive
- o Partial reaction of adhesives before application to substrate and before application of pressure

Residual solvents or volatiles produced during cure are easily eliminated with porous adherends. Frequently, paper is bonded with adhesives based on polyvinyl acetate dispersed in water. The porous paper absorbs the water and the adhesive remains on top of the paper ready for bonding. Adhesives based on phenol-formaldehyde, resorcinol-formaldehyde, urea, or melamine resins produce volatiles during the curing reaction. These volatiles escape easily through most wood adherends, but could cause blisters in metal-to-metal bonding unless special precautions are taken.(1)

## HIL-HDEK-691B

**3.2.2 Nonporous materials.** In general, most metal substrates, except for a few materials such as compressed metal powders or metal foams, can be considered as nonporous materials. Other examples of nonporous materials would include laminates of various types such as epoxy-glass fabric, phenolic-canvas, melamine-paper, cast, extruded or molded plastic sheets, molded polyester fiberglass, and glass. Ordinarily, the designer, in bonding materials of this sort, selects an adhesive as nearly like the substrate as possible. Modified epoxy adhesives are frequently employed on reinforced thermosetting resinous materials. Most thermoplastic substrates require special adhesives and/or special surface treatments in order to produce satisfactory bonds. Since the elimination of volatiles is often a problem in bonding nonporous materials, many fabricators include glass fabric, chopped glass or other fillers in the adhesive to provide an escape path for the volatiles, to enhance bond strength and to control bondline thickness.(1)

**3.3 Dissimilar substrates.** Particular attention must be given to the design of bonded joints of dissimilar materials. When different metals are involved, the surface preparation for each metal must be carefully followed. Consideration must be given to the different coefficients of thermal expansion of all three materials involved - the two substrates and the adhesive. Often, a single adhesive system will not bond two dissimilar substrates, and various primers may have to be applied to each adherend before bonding with adhesives. A duplex adhesive film can also be used to bond two dissimilar adherends.(1)

**3.3.1 Porous materials.** Special bonding systems are frequently required to join dissimilar porous surfaces such as rubber and porous metal, or rubber and wood. Modified rubber adhesives can also be used on both substrates, depending upon the application. Wood may have to be filled, sealed, or primed before application of the adhesive, and the rubber may require cyclizing. Wood can be bonded to metal with a neoprene adhesive. Polystyrene foam can be bonded to metals with a modified epoxy, to metal foils with polyvinyl acetate, or to paper or plywood with vinyl or rubber-base adhesives. In all cases, the formulation and application of the adhesive must be such that it does not flow off the surface and/or into the pores.(1)

**3.3.2 Nonporous materials.** Typical examples of the bonding of dissimilar nonporous materials are the bonding of metal to rubber, metal foils to laminates or plastics, or different metals. A strong bond can be formed between rubber and metals, using isocyanate and rubber-base adhesives. In some cases, with vulcanized rubbers, the rubbers must be cyclized with acids, or the rubber surface prepared by chlorination. Metal foils such as copper are readily bonded to phenolic-paper and epoxy-glass fabric laminates through the use of polyvinyl acetate adhesives. Even some rubber-base adhesives have performed satisfactorily in this application. Thin metal foils have been bonded for many years to plastics using hot-melt and polyvinyl acetate-type adhesives.(1)

**NIL-HDLK-691B**

**REFERENCE**

- (3-1) Society of Manufacturing Engineers, Chapter 2, "Design Considerations, ADHESIVES IN MODERN MANUFACTURING, edited by E. J. Bruno, 1970.**

**(WP# ID 6759A/DISC 0530A. FOR HTL USE ONLY)**

NIL-MDBK-691B

## Chapter 4. STRUCTURAL ADHESIVE TYPES & SELECTION GUIDELINES

**4.1 General discussion.** There are a number of different classification systems in use, all of which offer certain advantages. Two of these classifications will be given below, although there may be some overlapping of information on the specific adhesive materials. The first classification, based on an SME publication, is based primarily on physical or chemical form and is largely concerned with how the adhesive is used. The second classification is based on the usual separation into the physical forms of thermoplastic, thermosetting and alloyed adhesives; and, within each of these groups, details are given on the particular chemical types of adhesives listed. There follows a discussion of additional classifications commonly encountered, along with a discussion of the factors to be considered in adhesive selection.

**4.2 Classification by SME handbook.** Currently there are about 25 basic types of synthetic adhesives useful to the design engineer. New types are appearing at the rate of about one per year. Each of these may have from 10 to 20 modifications. When it is considered that frequently two or more individual adhesives are combined to provide special properties, this lends to a vast array of specific products from which to choose. One source divides the adhesives into six major types:(1)

- o Chemically reactive types
- o Evaporation or diffusion types
- o Hot-melt types (cooling)
- o Delayed-tack adhesives
- o Film adhesives
- o Pressure-sensitive types

The discussion below will give a descriptive evaluation of each type and place it in its proper category so that the designer can narrow his choice of adhesive for a specific application.(1)

### 4.2.1 Chemically reactive types.

**4.2.1.1 Catalytic plural components - chemical cure.** Adhesives of this type are normally provided in twin tubes or cans and are mixed immediately before use. In large operations, the components may be mixed in bulk to supply an 8-hour shift or may be mixed directly in the application nozzle. Chemically reactive adhesives will harden at room temperature, although the application of heat gives a better quality bond and a faster cure.(1)

**4.2.1.1.1 Epoxy Adhesives** are familiar to the reader in the form of twin-tube household adhesive kits. They are relatively simple to use and produce reliable bonds. Industrial epoxy adhesives may be similar to the household adhesive, or they may be quite different. Epoxies are versatile, and there are a number of different formulations. They are particularly useful in joining dissimilar materials. Epoxies are usually chosen for specialized service where high strength is required and a moderately high cost is acceptable. Peel strength and flexibility are low for unmodified epoxies. The most common epoxy resin is the diglycidyl ether of bisphenol A. This and other types will be discussed below under 4.3.1.5.

## MIL-HDBK-691B

To form a permanent adhesive bond, the epoxy resins must be reacted with a hardener (also called catalyst, curing agent or "Part B"). The hardener chemically converts the liquid epoxy resin into a solid resin. If the epoxy is in a solid form, it must be heated to melt and be able to wet the surfaces being bonded. Generally, only resins that are liquids at room temperature are used for adhesives. The epoxy bond will set or cure faster if the bonded surfaces are heated. The most important advantage of the epoxy class of adhesives is that they solidify without evolution of volatile materials and with minimal shrinkage. Materials of this type may serve as "gap-filling" adhesives.

The major classes of hardeners will be discussed below under 4.3.1.5. In the catalytic plural-component system, resin and hardener are packaged separately and, thus, are stable until mixed. The user mixes the component just prior to application.

The following list of uses demonstrates the versatility of epoxy adhesives in bonding a large variety of substrates.<sup>(1)</sup>

- o Metal - Automobile repair, lamination of (oily) steel sheet and foil, joining of steel pipe, underwater protective coatings;
- o Concrete - bonding new concrete to old, patching of cracks (gap filling);
- o Glass - TV tube safety lamination, stained-glass window assembly and filament-wound structures;
- o Plastic - repair of polyester-fiberglass boats, bonding of treated nylon, joining of plastic pipe;
- o Wood - wood-to-metal bonding (doors, architectural panels, etc.);
- o Ceramic - binder for ceramic powders (molded, machined, then fired at 1725°C (3137°F))
- o Composites - metal-plastic sandwich construction, cement board.

**4.2.1.1.2 Phenolic adhesives.** Phenol-formaldehyde resins were the earliest synthetic plastics to attain commercial prominence. Although they are mainly used to mold plastic products, they also dominate the wood-adhesives (plywood) field. For this reason, they represent one of the largest volumes of any synthetic adhesive. They are also among the lowest-cost adhesives. Phenolics may be formulated as water dispersions, which have advantages in bonding wood, where penetration into the cell structure is important for the formation of permanent bonds. Since phenolics have a high temperature stability, they are used in blends with other resins ("alloys" - see 4.3.3.1.1) for bonding to metals. These bonds are exceptionally stable to their environment (moisture, temperature, microorganisms, etc.) Limited shelf stability before usage and the release of volatiles during cure are potential disadvantages.<sup>(1)</sup>

## NIL-HDBK-691B

Beyond the wood and wood products area, the uses for unmodified phenolic adhesives are mainly as:

- o Primers, to prepare metal surfaces for bonding;
- o Binders, for such varied products as glass-wool insulation mats, foundry sand, abrasive wheels and brake lining composites.

Phenolics are provided either as a one-component, heat-curable liquid solution or powder, or as a liquid solution to which a catalyst must be added. The curing mechanism differs for these two types.(1)

4.2.1.1.3 Resorcinol-formaldehyde. This resin, closely related to phenol-formaldehyde, is used in tiecoating tire cord fabric to rubber and is also used as an extremely durable marine-plywood adhesive. It is curable at room temperature in 8 to 12 hours, while the phenolic wood adhesives require elevated-temperature cure.(1)

4.2.1.1.4 Polyesters. Polyester resins may be divided into two distinct groups, saturated and unsaturated. The saturated polyesters are reaction products of difunctional acids plus difunctional alcohols or glycols. The adhesive uses of the saturated polyesters are minor. The unsaturated polyesters which require a catalytic cure have few uses as adhesives. They usually involve the bonding of polyester substrates. Uses include polyester patching kits for repair of fiberglass boats, automobile bodies and concrete flooring. Other minor uses are in bonding polyester laminates to polyester or to metal and as an adhesive for optical equipment. For the majority of other applications where the properties of good adhesion, low shrinkage and solvent resistance are required, a different type of adhesive such as epoxy should be used.(1)

4.2.1.1.5 Polysulfides. Polysulfides are flexible materials that belong to the synthetic rubber family. Although they are principally used as sealants for automotive, construction and marine uses, they are used to some extent as flexibilizing hardeners for epoxy adhesives. Their sulfur linkages combine good strength with the ability to rotate freely, thus giving a strong, flexible polymer. (See 4.3.2.5.6.) Polysulfides and epoxies are mutually soluble in all proportions. As the percentage of polysulfide increases, the cured product changes in properties from an adhesive to a sealant. They are also often used to bond new to old concrete. In addition, steel-to-glass bonds using this combination have good properties, but the cost is relatively high. For adhesive sealants, curing agents such as lead dioxide or an isocyanate are used. Among other techniques, a three-component system is available that is mixed directly in the applicator head for metal-to-glass bonding.(1)

4.2.1.1.6 Polyurethanes. Urethane polymers, developed in Germany in World War II, have been used frequently in flexible and rigid foams, cryogenic sealants and abrasion-resistant coatings. As adhesives, their principal use is bonding "difficult-to-bond" plastics, usually to a dissimilar material or to metals. The use of urethanes for adhesives is expanding but is still quite small. Urethane adhesives resemble epoxies in three respects: cost, method of handling and ability to bond to most surfaces. The differences from epoxy



## MIL-HDBK-691B

may be illustrated by considering the cured urethane as a very lightly crosslinked thermoset resin, almost a thermoplastic. This gives a flexible, rubbery characteristic, in contrast to the hard and rigid epoxies. This flexibility, combined with good adhesion, insures good bonding to flexible plastics where peel strength is important. The outstanding feature of urethanes is strength at cryogenic (extremely low) temperatures, which is better than for any other adhesive. Table V compares strength at -400°F (-240°C).

A potential disadvantage of urethanes is the reactivity of the uncured adhesive with moisture, which may require some handling precautions. This reactivity introduces the concept of a one-component moisture-curing adhesive. Poor lap-shear strength at room or elevated temperature and sensitivity of the cured glue lines to moisture are other limitations. The lap-shear strength for a typical urethane adhesive with aluminum is only 1800 psi (12.4 MPa) at room temperature, but this increases to 5000 psi (34.4 MPa) at -100°F (-73.3°C) and below.<sup>(1)</sup>

Specific uses for urethane adhesives include the following:

- o Rubber to metal - Lap-shear strength of 1000 psi (6.9 MPa);
- o Packaging film lamination - Polyester-to-polyethylene laminates use a two-part urethane adhesive (solution adhesive);
- o Flocking adhesives - The bonding of short fibers (synthetic) to fabric by an electrostatic technique. This is another example of the use of a flexible adhesive to bond dissimilar plastics;
- o Laminating of flexible vinyls to nylon or other plastics. This is a difficult problem for which urethanes work well;
- o Tire-cord bonding - Urethanes may be used to promote adhesion of both nylon and polyester fiber to rubber.

(See Table XLVII and figures 24, 46, 47 and 49 for additional data on polyurethane adhesives.<sup>(1)</sup>)

TABLE V. Comparison of typical urethane adhesive with other adhesives on aluminum at -400°F (-240°C).<sup>(1)</sup>

Adhesive	Lap-Shear Strength		Peel Strength	
	(psi)	(MPa)	(lb/in)	(N/m)
Urethane	8000	55.2	26	4550
Epoxy-Nylon	4600	31.7	(brittle)	(brittle)
Epoxy-Polyamide	1600	11.0	(brittle)	(brittle)



## NIL-HDBK-691B

**4.2.1.1.7 Silicones.** Silicone polymers have unusual properties and are used both to promote and to prevent adhesion. Silicones have good heat stability, chemical inertness and surface-active properties. Adhesive uses fall into four groups:(1)

- o Primers, or coupling agents, used to solve some difficult industrial bonding problems;
- o Adhesives and sealants;
- o Pressure-sensitive adhesives;
- o Heat-cured adhesives.

The use of silicones as adhesives is limited mainly by their high cost. Applications are numerous and varied. In general, silicones are used where organic materials (based on carbon) cannot withstand harsh environmental conditions, where superior reliability is required, or where the durability of silicones gives them economic advantages. As coupling agents, silicones are widely used for surface treatments of fiberglass fabric for glass-reinforced laminates. Epoxy or polyester bonding to glass cloth treated with a silicone "finishing agent" is improved both in strength and in moisture resistance of the cured bond. The retention of flexibility and some degree of strength at a temperature range from cryogenic to over 500°F (260°C) is unusual in the field of polymers. In general, however, the room-temperature-strength properties of silicones are quite low in comparison to the typical polymer.(1)

Joints bonded with silicones are designed to utilize the good peel strength of silicones, rather than the tensile or lap-shear properties. This is discussed in Chapter 2. For example, the peel strength in bonding rubber to aluminum is in the range of 17-20 lb/in (2975-3500 N/m); the peel strength for urethane sealant to aluminum is 3.5 lb/in (612 N/m) without primer and 14 lb/in (2450 N/m) with a silicone coupling agent. The lap-shear strength, metal-to-metal, is 250 to 500 psi (1.72 to 3.44 MPa).(1)

Specific adhesive applications of silicones include:(1)

- o Two-part adhesive for bonding insulating tape to magnet wire (Class H performance);
- o One or two-part adhesive to prepare pressure-sensitive tapes useful from -80°F (-62°C) to +500°F (+260°C). These are used for adhering certain components in electronics or in aerospace assemblies.

The use of silicone as a primer includes:

- o Bond promoters with phenolic binders for foundry sand or abrasive wheels.
- o Filler treatment in filled polyester or epoxy castings (Epoxy concrete patching formulations.)
- o Improved bonding of polysulfide or urethane sealants to metal substrates or to glass.

## HIL-HDBK-691B

In some cases, the silicone is as effective when blended into an adhesive formulation as when applied separately as a primer.<sup>(1)</sup>

**4.2.1.2 Catalytic plural components - moisture cure.** Adhesives of this type are supplied as one-component formulations, usually in collapsible tubes, to insure good protection from atmospheric moisture before use. The second requisite component, moisture, is always available, either from the surrounding air or as adsorbed moisture on the surface of the substrates. The only situation where insufficient moisture may be present is in overlap bonding of nonporous substrates such as metals.<sup>(1)</sup>

**4.2.1.2.1 Silicones.** Organic groups such as acetyl, attached to a silicon atom, are readily hydrolyzed. "Room-temperature vulcanizing" (RTV) sealants use the principle in which the adhesive reacts with atmospheric moisture and releases acetic acid vapor, causing a crosslinking of the viscous paste into an elastomer, such as the silicone rubber adhesives. For silicone coupling agents, moisture adsorbed on the substrate plays an important role in attacking the silicone molecule through hydrolysis.<sup>(1)</sup>

**4.2.1.2.2 Urethanes.** The free isocyanate groups in a urethane adhesive will react with water. This serves as a means of converting the liquid into a crosslinked solid. This technique is used in coatings and sealants. Adhesive use is minor because of slow curing, foaming during cure and variable shelf life.<sup>(1)</sup>

**4.2.1.2.3 Other adhesives.** Polysulfides utilize atmospheric moisture to accelerate cures. However, a two-component system is usually used, consisting of formulated polysulfide and formulated lead dioxide. Moisture converts a portion of the latter to a faster-reacting form. Cyanoacrylate adhesives cure very rapidly through surface moisture and may be used as quick-set cements to bond metal to nonmetal. Lap-shear strengths of 2000 psi (13.7 MPa) have been reported. However, the resistance to moisture of these adhesives is still somewhat low. A one-container epoxy has been developed which utilizes atmospheric moisture to effect the cure by an unusual mechanism. The amine hardener for the epoxy is first adsorbed by molecular sieves. The sieves, in bead form, are then blended into the epoxy formulation. The sieve structure is a porous inorganic matrix that prevents contact of the trapped amine with the surrounding epoxy. Water molecules are preferentially adsorbed by the molecular sieves and will displace the amine from the pores. Thus, upon usage, exposure of the adhesive to atmospheric moisture causes the amine hardener to be released into the epoxy, and the system will cure. Alternately, heating the glue line will also release the epoxy hardener, enabling the system to be used as a one-component, heat-activated epoxy adhesive. One-component urethanes may be formulated, using the same principle. A tertiary amine is the hardener.<sup>(1)</sup>

**4.2.1.3 Heat-activated system (one-part system).** One-part adhesives are desirable because they eliminate the need for careful proportioning and mixing of components. They may be supplied as solid films (see Film adhesives under 4.2.5) for convenient assembly of the joint and a uniform bondline thickness. These systems do require elevated-temperature cure and may have a limited shelf life.<sup>(1)</sup>

## NIL-HDBK-691B

4.2.1.3.1 Polybenzimidazoles (PBI) and polyimides (PI). Benzimidazole polymers were developed as a result of research specifically aimed at producing high-temperature organic polymers. Polyimides are analogous polymers competing for the same applications. Benzimidazole polymers, or polybenzimidazoles, are thermoplastics, although their thermoplastic nature is not evident below 700°F (371°C). They are relatively stable in air to 500°F (260°C) for short-term applications (see Figure 23). Polyimides are superior for long-term strength retention.(1)

PBI and PI have only recently been developed, and further improvements in properties and workability may be expected. The formulations usually contain oxidation inhibitors and aluminum powder as a filler. The adhesive prepolymer cures by a high-temperature condensation reaction involving the loss of water or other volatiles. These adhesives are very expensive and are limited to the bonding of high-temperature metals (stainless steels, beryllium and titanium) that must perform at 500°F (260°C) or higher. PBI's are of greatest interest to the aerospace engineer for use in the adhesive assembly of light-weight honeycomb structures for supersonic aircraft, missiles, and other space systems. There is some moisture sensitivity at room temperature. The lap-shear strength drops gradually on heating to 600°F (316°C), then more rapidly above this temperature.(1)

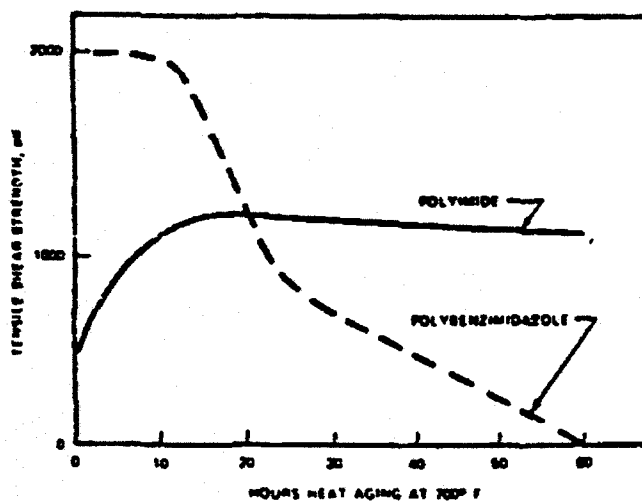


FIGURE 23. High-Temperature Adhesive Performance.(1)(2)

Adhesive binder solutions, such as duPont's NR-150, contain polyimide precursor materials which, upon the application of heat, produce aromatic condensation polyimides. These are linear amorphous polymers free of crystallinity and essentially noncrosslinked. They are sufficiently thermoplastic to permit melt flow when pressure is applied above the polymer softening point or glass transition temperature ( $T_g$ ). Due to this property, voids formed during the condensation polymerization can be eliminated. Single overlap shear-strength of NR-150AG adhesive-bonded titanium joints (unaged) was found to be 3516 psi (24.3 MPa) at RT, 3599 psi (24.8 MPa) at 350°F (177°C) and 2292 psi (15.8 MPa) at 500°F (260°C). The strength increases with aging at either 350°F or 500°F (177°C or 260°C).(3)

## NIL-HDBK-691B

FM-34 is an aluminum-arsenic sulfide-filled glass-scrim-reinforced condensation-type polyimide adhesive supplied by American Cyanamid Company's Bloomingdale Department for use at exposures of 400-600°F (204-316°C) in both metal-to-metal and sandwich constructions. With the application of heat, imidization polymerization begins with this adhesive at temperatures as low as 250°F (121°C). An increase in temperature produces further linear chain extension and crosslinking. The latter induces crystallinity and reduced toughness to the resultant polymer. Because of the crystalline nature of the fully-cured polymer, the gross voids (up to 14% maximum) formed during the initial imidization reaction must be minimized while the polymer still retains some thermoplasticity. This is generally accomplished by pressure application during the linear chain extension stages of polymerization. The exact thermal-time conditions required to accomplish this, however, are difficult to assess without direct knowledge of the degree of polymerization. Improper assessment of these conditions may lead to extensive porosity in the bond joint. Single overlap-shear strength of FM-34 adhesive-bonded titanium joints was found to be 3026 psi (20.9 MPa) at RT and 2192 psi (15.1 MPa) at 500°F (260°C). FM-34 is recommended for use by the manufacturer with their primer BK-34, a polyimide solution of 81% solids which is further diluted in use. (3)(4)

4.2.1.3.2 Epoxies. Hardener systems for epoxies will be discussed below under 4.3.1.5. If the hardener is a meltable solid rather than a liquid, it may, in some cases, be included in a formulation supplied to the user as a latent "one-component" adhesive. Dicyandiamide (DICY) is the standard hardener used in this way and requires a cure temperature of 350°F (177°C) or higher. Recently, accelerators for DICY have been found that reduce the cure schedule to one hour at 250°F (121°C). This is more practical for the bonding of large surface areas where the supply of heat is limited. The boron trifluoride-amine complexes are second to DICY as hardeners in one-component epoxies. They are neither as latent nor as effective in curing as DICY - their final bond strengths are lower - but may fit a given cure schedule to better advantage. A typical one-component paste-form epoxy adhesive supplied to the user will include the following components: (1)

- o Principal epoxy resin;
- o Hardener-accelerator combination;
- o Thixotroping agent. This prevents excessive flow of the resin when heated to the cure temperature;
- o Filler. Aluminum powder of 150 mesh is customary in metal-to-metal adhesives, but other fillers can also be used;
- o Special epoxy-resin additives. These promote specific properties, such as reactivity, high-temperature strength, adhesion, etc.;
- o Modifier, usually a thermoplastic alloying additive. This eliminates brittleness in the cured polymer.

## MIL-HDBK-691B

Physical properties of a cured epoxy polymer of this type are given in Table VI. Major uses for the heat-activated epoxies include:<sup>(1)</sup>

- o Replacement of lead solder or rivets in metal joints;
- o Sandwich panel adhesive bonding of skins to core in heavy-duty, lightweight panels;
- o Lightweight honeycomb structure assembly for aircraft;
- o Replacement for welding in pressure-tight assemblies

In all of these applications, the filleting action of the adhesive formulations is important in producing a strong, thoroughly bonded joint. The situation is analogous to the buildup in welding or soldering.<sup>(1)</sup>

TABLE VI. Properties of a cured one-component epoxy<sup>1</sup> polymer.(1)(5)

PROPERTY	VALUE	
	ENGLISH UNITS	SI UNITS
Tensile Strength	11,000 psi	75.8 MPa
Shear Strength	7,000 psi	8.3 MPa
Flexural Strength	13,000 psi	89.6 MPa
Modulus of Elasticity	$2.5 \times 10^5$ psi	1720 MPa
Heat-Deflection Temperature	240°F	116°C

<sup>1</sup>Resin - Diglycidyl ether of Bisphenol A

Hardener - DICY

Filler - Aluminum Powder

Modifier - Nitrile Rubber

Cure - 30 min at 360°F (660°C)

4.2.1.3.3 Nylon. Nylons form the high-molecular-weight members of the family of polyamide resins. Although these polymers have excellent physical properties, approaching 12,000 psi (83 MPa) tensile strength, combined with 300% maximum elongation, the high softening points and high melt viscosities limit their use as hot-melt adhesives. However, certain specialty nylon resins having lower melting temperatures are used quite successfully by extrusion techniques. Both nylon 11 and high-molecular-weight polyamide resins chemically related to dimer acid-based polyamides are used as high-strength metal-to-metal adhesives and are applied by extrusion.

## NIL-HDBK-691E

Terpolymers and methyl methoxy-modified nylons are soluble in certain organic solvents and can be combined with epoxy resins to form exceptional metal-to-metal adhesives.<sup>(1)</sup> Lap-shear strengths of alloyed nylon adhesives (Epoxy-nylon) are high, as shown in Table IX below.

A latent hardener for the epoxy (dicyandiamide) is included in the epoxy-nylon blend, although reaction of the epoxy with the nylon is also indicated at the cure temperatures used. Epoxies and nylon are not truly compatible at room temperature and must be "forced together" in formulating the adhesive. For this reason, the products are supplied primarily as flexible films.<sup>(1)</sup>

As an alternative to epoxy-nylon blends, a nylon may be used as a powdered filler in an adhesive. As the glue line is cured at high temperature, the filler fuses and contributes its special strength properties to the finished bond. Peel strength in an epoxy/polyamide adhesive may be increased from 12 lb/in (2100 N/m) to 40 lb/in (7000 N/m) by adding 20 parts of nylon powder per hundred parts of resin.<sup>(1)</sup>

**4.2.1.3.4 Phenolics.** Phenolic adhesives have been described in 4.2.1.1.2 above. Phenolics available as one-component heat-activated systems include:<sup>(1)</sup>

- o Melttable powders of the resole type, used as binders for particle board, etc.;
- o Alloys, such as epoxy-phenolic or nitrile-phenolic, used in structural bonding of metals.

**4.2.1.3.5 Polyvinyl acetals.** These resins are derived from polyvinyl acetate. The acetate is hydrolyzed to polyvinyl alcohol (which is also an adhesive) and then reacted with an aldehyde to form the acetal. When reacted with formaldehyde, polyvinyl formal is formed; when reacted with acetaldehyde, polyvinyl acetal is the resultant product. Both of these materials are blended with phenolics to form structural adhesives. When reacted with butyraldehyde, polyvinyl butyral is formed. This material is commonly used in safety-glass laminates. Polyvinyl acetals are useful in flexibilizing thermoset resins to obtain structural adhesives for metals. The vinyl phenolics and vinyl-epoxy alloys are examples.<sup>(1)</sup>

**4.2.1.3.6 Urethanes.** One-component, heat-curable urethane formulations are used chiefly in sealants. Here the "blocked isocyanate" principle is utilized. The free isocyanate groups are all reacted with a temporary blocking agent such as phenol. This allows the isocyanate prepolymer to be blended with the polyglycol curing agent and packaged as a mixture that is stable until heated to 280-300°F (138-149°C). In this reaction, phenol is released and the isocyanate groups are regenerated. At this temperature, the reaction with polyglycol is very rapid to form the cured urethane polymer.<sup>(1)</sup>

#### **4.2.2 Evaporation or diffusion adhesives.**

**4.2.2.1 Solvent-based systems.** Solvent-based adhesives are supplied by coating the resin solution on a substrate or substrates, followed by some combination of solvent evaporation and contact with the second adherend, which may or may not be coated. With porous materials, such as wood or paper, the



## MIL-HDBK-691B

contact usually precedes the final drying step; and the last traces of solvent are absorbed by the substrate. On the other hand, metals and nonporous plastics require essentially complete removal of solvent, so that good contact will be maintained during the bonding process. In the latter case, heat and pressure are used to activate the adhesive coating during bonding. The advantages of solvent systems are good water resistance, high heat strength, and ease of wetting of some substrates. The disadvantages of solvents are their fire hazard and toxicity.<sup>(1)</sup>

**4.2.2.1.1 Natural rubber.** Natural rubber is one of the earliest raw materials used in the preparation of adhesives. Its most important property from an adhesive viewpoint is its tack or stickiness. Natural rubber is also soft and flexible, with relatively low strength values, unless vulcanized (chemically crosslinked). These properties make natural rubber suitable for use in pressure-sensitive applications and in bonding nonmetallics such as leather, textiles and paper.<sup>(1)</sup>

Solutions of natural crepe rubber in solvents comprise the standard household "rubber cement." Again, advantage is taken of the initial tack of the rubber. However, natural rubber loses most of this tack on aging. Natural rubber has good water resistance but is susceptible to attack by solvents, oils and chemicals. Ozone and other oxidizers will gradually reduce flexibility and adhesion, so antioxidants are generally added to formulations. A variety of natural and synthetic resins can be blended with natural rubber in solvent-based adhesives. The chemical structure of natural rubber is best described as a cis-polyisoprene. Important uses of natural rubber solvent-based adhesives are in the building, automotive and shoe industries. Rubber cements are used for adhering nonmetallic trim to metal automobile parts. An example of a major use in construction is in the preparation of mastics for floor tile. In shoes, natural rubber cements provide water-resistant, flexible bonds to leather, rubber and canvas.<sup>(1)</sup>

**4.2.2.1.2 Reclaimed rubber.** Solvent adhesives based on reclaimed rubber have a number of applications which are similar to the natural rubber systems. Reclaimed rubber is usually obtained from used tires and thus contains small amounts of fibers, sulfur and other additives. The reclaiming process must, however, meet certain standards of the rubber industry. Mixtures of natural and synthetic rubber with reclaimed rubber are used in adhesive formulations when a more economical system is required. Although the reclaimed material has a relatively low elongation and tensile strength, the economic advantage will sometimes dominate the choice of an adhesive.<sup>(1)</sup>

**4.2.2.1.3 Synthetic rubbers.** A number of synthetic rubber-like materials have become available during the last several decades with properties that are useful in adhesive applications. Most important are nitrile rubber, neoprene, butyl rubber and styrene-butadiene rubber.<sup>(1)</sup>

**4.2.2.1.3.1 Nitrile rubber.** Nitrile rubber is a copolymer of butadiene and acrylonitrile. Usually the copolymer contains enough acrylonitrile (over 25%) so that good resistance to oil and grease is obtained. The adhesive properties also increase with increasing nitrile content. Nitrile rubbers are used to bond vinyls, other elastomers and fabrics where good wear, oil and water resistance are important. Compatibility with additives, fillers and



## HIL-HDBK-6911

other resins is another advantage of nitrile-rubber adhesives. Phenolic-resin blends with nitrile rubber have many important applications as structural adhesives. In the aircraft industry, aluminum honeycomb construction is fabricated with nitrile-phenolic adhesives. Other uses include bonding of abrasives to metal, brake linings to brake shoes and lamination of aluminum and stainless steel. These adhesives are used in the form of supported or unsupported films and then heat-cured in the bonding operation to give optimum bond strength to the substrate. In bonding metals, tensile-shear strengths up to 4000 psi (26 MPa) at 70°F (21°C) and 1000 psi (7 MPa) at 320°F (160°C) are achieved.<sup>(1)</sup>

4.2.2.1.3.2 Neoprene or polychloroprene. This type of rubber adhesive is used extensively to bond aluminum and is used in organic solvents for convenient application. Although neoprene is similar in properties to natural rubber, it generally provides higher strength, better aging and higher temperature resistance. Neoprene solvent-based cements are also used extensively as shoe adhesives. For structural applications, neoprene is usually combined with a phenolic resin, plus a number of other additives for curing and stabilizing the mixture (neoprene-phenolic). Both cold-setting and heating-curing formulations can be prepared.<sup>(1)</sup>

4.2.2.1.3.3 Butyl rubber. Butyl rubber is a copolymer of isobutylene with small amounts of isoprene. Characterized by relatively low strength levels and a tendency to creep under load, butyl rubber cements are useful in packaging applications where advantage can be taken of the water resistance and low gas permeability of the rubber. Butyl rubber is also used as an adhesive sealant.<sup>(1)</sup>

4.2.2.1.3.4 Styrene-butadiene rubber. This rubber, when properly formulated with reinforcing agents and resins, can provide bond strengths comparable to natural rubber. Commonly available as a copolymer composition of 75% butadiene and 25% styrene, styrene-butadiene (SBR), formerly called GRS, was the first synthetic rubber manufactured in the U.S. Most of the production is used for products other than adhesives, but when a low-cost, synthetic, elastomeric adhesive is required, SBR must be considered. Generally, SBR is not used to bond metal parts because of its inferior tack and film strength compared to natural rubber. However, solvent-based adhesives are used to bond plastics, rubber, wood and fabrics.<sup>(1)</sup>

4.2.2.1.4 Phenolics. As previously discussed under chemically reactive adhesives (4.2.1.1.2), phenolic resins represent the largest-volume commodity among the synthetic adhesives. For many applications, phenolic-based glues are deposited on a substrate from aqueous, alkaline solution or the resin is handled on a 100%-solids basis as an uncured syrup. However, for wood bonding (plywood), dilution of the phenol or resorcinol-derived adhesive with an organic solvent is advantageous for handling, mixing and coating. In addition to plywood manufacture, other uses of solvent solutions of phenolic resins are in the preparation of wood particle boards, the bonding of glass-fiber mats and in aircraft honeycomb construction. Blends with synthetic rubber have already been described. High-strength compositions can be prepared by modification with thermoplastic resins.<sup>(1)</sup>

## NIL-HDBK-651B

**4.2.2.1.5 Urethanes.** While urethane adhesives are normally formulated so that a cured or thermoset product can be obtained, as already described under plural-component reactive systems (4.2.1.1.6), the polyisocyanates are usually diluted with dry solvents such as methylene chloride or chlorobenzene for easy applications. Mixtures with rubber modifiers are also prepared in this manner. The reactive isocyanate can be coated on the substrate and the solvent allowed to evaporate. The cure process begins after exposure to atmospheric moisture. This technique has been used with success for bonding rubber to fibers, rubber to metals and for wood assemblies. For these applications, solutions of triphenylmethane triisocyanate (TTI) or diphenylmethane diisocyanate (MDI) are generally used. Two-part urethane formulations in solution are used to laminate packaging films. Polyester can be bonded to polyethylene films with this system. Thermoplastic urethanes are also available for use in solvent-based adhesives.(1)

**4.2.2.1.6 Vinyl resins.** Several vinyl monomers are used to prepare thermoplastics which are useful in certain adhesive applications. Thermoplastic resins do not "cure" when heated but develop joint strength by solvent evaporation, diffusion or by fusion. The most important vinyl resins for adhesives are polyvinyl acetate, the polyvinyl acetals (butyral and formal) and polyvinyl alkyl ethers. Polyvinyl chloride and copolymers of both vinyl chloride and vinyl acetate with other monomers such as maleic acid esters, alkyl acrylates, maleic anhydride and ethylene are also used for solvent-based adhesives. Polyvinyl acetate resins can be dissolved in alcohols, ketones and esters for coating on substrates. Clear films deposited from solvents can be heat-sealed to substrates for satisfactory adhesion. Metal foil to plastic film or paper laminates can be manufactured in this manner. Polyvinyl acetate and its copolymers are also used extensively in hot-melt adhesive compositions. Copolymers with vinyl chloride are used for bonding vinyl plastic film to metals. The polyvinyl acetal resins represent an important part of the solvent-based vinyl adhesive category. Polyvinyl butyral is employed as the basic resin component for the laminating adhesives in the manufacture of safety glass. Acetal-phenol resin mixtures (more commonly called vinyl phenolics) are used extensively as structural adhesives for metal honeycomb systems and metal-to-wood laminates. Other vinyl resins which are occasionally used as solvent-based adhesives are polyvinyl alkyl ethers and polystyrene. Solutions of the vinyl ethers are used where a high degree of tack is needed; and polystyrene is used for bonding polystyrene to itself and to porous materials such as wood and plaster.(1)

**4.2.2.1.7 Acrylics.** A number of acrylic resins are used for bonding cloth, plastics, leather and, in some cases, metal foils. The acrylic monomers most commonly used in adhesives are ethyl acrylate, methyl acrylate, methacrylic acid, acrylic acid, acrylamide and acrylonitrile. The polymers or copolymers are soluble in common organic solvents such as chloroform or toluene and can be applied in the same manner as other solvent-based adhesives. In addition, the polymers are soluble in the monomers; and, when a catalyst is added, the solvent monomer will polymerize to give good adhesive strength to glass and to plastic surfaces of similar composition (e.g., polymethyl methacrylate).(1)

## MIL-HDBK-691C

The advantages of the acrylics over the vinyls for adhesive use are:(1)

- o They are stable in sunlight;
- o Some are flexible at low temperature;
- o Some of the acrylic copolymers are oil-resistant;
- o They are readily modified with crosslinkable monomers so that heat-cured adhesives with improved solvent resistance can be obtained.

Such systems are useful in textile-laminating applications where resistance to dry-cleaning fluids is important. The acrylic resins are generally more expensive than vinyl resins. One class of acrylic adhesives differs from those already discussed in that solvents are usually not employed in handling; these are the cyanoacrylates (mentioned in 4.2.1.2.3). These materials are activated by pressing into thin films between the substrates. Very rapid curing (10-30 seconds) occurs; and good bonds develop with glass, metal, rubber and wood. The chief disadvantage of this material is its high cost. The major use is in bonding small parts where a quick set is required. The electronics and jewelry industries utilize cyanoacrylates where it is difficult to clamp or hold the assembly. Ethylene glycol dimethacrylate is also used for this kind of quick application.(1)

4.2.2.1.6 Miscellaneous resins. A few materials are used in a more limited way as solvent adhesives. Two natural product-derived materials are the cellulose esters and asphalt. Cellulose esters are used for bonding leather, paper and wood. While not generally used with metals, specific nonporous substrates such as cellophane and glass are occasionally bonded with cellulose nitrate or other cellulose esters applied from solution. Asphaltic materials from petroleum fractionation are inexpensive products which are used for some special adhesive applications. The most important property of asphalt in adhesives is water resistance. It is used in laminating paper and other packing materials where a water-barrier layer is needed. The other important use of asphalt is in roofing and flooring adhesives.(1)

Another class of resins used in solvent adhesives is the polyamides. These high-molecular-weight products are generally referred to as modified nylons. Low-and-intermediate-molecular-weight materials are also available. The latter two are more commonly used in hot-melt formulations; and the modified nylons, are often blended with small amounts of a phenolic resin to improve surface wetting. Solution systems of low-and intermediate-molecular-weight resins can be coated in paper, metal foil or plastics and, when heat-activated, will act as adhesives for these substrates. The modified-nylon polyamides have fair adhesion to metals and have good low-and-high-temperature properties, good resistance to oils and glass but poor resistance to solvents.

Several recently developed thermoplastics are beginning to be used as solution-applied adhesives for selected applications. Examples are phenoxy resin, bisphenol A polycarbonate and polysulfone. These materials are temperature-resistant plastics which require fairly high temperatures for heat activation after solvents have been removed. Phenoxy has been used quite extensively as an adhesive and will develop shear values of 3500 to 4000 psi (24 to 28 MPa) in a few seconds at 600°F (316°C) surface temperatures and in 2 to 3 minutes at 500°F (260°C). Good adhesion is observed with substrates such as copper, brass, steel, aluminum, wood and many other nonmetallic substances.(1)

## HIL-HDBK-691B

**4.2.2.2 Water-based systems.** Water solutions, dispersions or emulsions are widely used for application and bonding of various substrates. Water systems are most frequently used when at least one surface to be bonded is porous so that the water may escape by permeation. The major advantage of water as a vehicle for adhesives is the lower cost compared to organic solvents. Other advantages of water-based adhesives are nonflammability, low toxicity and the wide range of viscosity and solids contents which can be obtained. Disadvantages are generally poor water resistance, slow drying, a tendency to freeze and a shrinkage of fabric substrates.(1)

**4.2.2.2.1 Natural rubber.** As mentioned under solvent systems, natural rubber is isolated as a water dispersion known as latex. Thus, the material can be used directly as a water-based adhesive. Usually the latex is treated with preservatives, such as ammonia, and formulated for specific end use. Natural rubber latex dries to an almost tack-free film which will, however, stick to itself. Generally, however, natural rubber latex is blended with other adhesive raw materials such as phenolics, casein or natural tackifiers such as Kayara gum to obtain better bonding. Portland-cement blends can be used to provide adhesion to metals, glass, and cementitious materials.(1)

**4.2.2.2.2 Reclaimed rubber.** Reclaimed rubber is used in a water-dispersed formulation for a number of adhesive applications. Mixed with natural or synthetic rubber latexes, reclaimed rubber provides a lower-cost adhesive system. Asphalt blends have excellent tack and are used to join textiles to metals, felt to metal and similar applications where an inexpensive adhesive in a nonflammable solvent is required.(1)

**4.2.2.2.3 Synthetic rubbers.** All of the synthetic rubbers discussed under solvent adhesives (4.2.2.1.3) are available as emulsions in water. Generally, butyl rubber is used in solvent solution, but nitrile, neoprene and styrene-butadiene latexes represent an important outlet for synthetic rubber adhesives. Styrene-butadiene rubber latex is used for carpet backing, paper coating and tire cord bonding. Neoprene latex is used in paper treatment to give leather-like properties, in casein blends to laminate metal foil to paper and in shoe adhesives. Nitrile-rubber latex is used as a binder for nonwoven fabrics and in paper treatments.(1)

**4.2.2.2.4 Vinyl resins.** By far the most widely used vinyl resin in water dispersion form is polyvinyl acetate, both as homopolymer and copolymer. Prepared by an emulsion-polymerization technique, polyvinyl acetate latex is the basis for the common household "white glue." Products of this type are good adhesives for paper, wood, leather and cloth. The major end use is as a packaging adhesive for such flexible substrates. Polyvinyl acetate water dispersion is also used as a lagging adhesive to bond insulating fabric to pipe and duct work in steam plants and ships. When satisfactorily formulated, satisfactory adhesion can be developed to plastic surfaces and to metal foil. Among the other vinyl resins, polyvinyl alcohol and polyvinyl methyl ether are the most useful for water-based adhesives.(1).

**4.2.2.2.5 Acrylics.** A variety of acrylic copolymers are prepared commercially by emulsion polymerization. The most common monomers are those listed under 4.2.2.1.5. Advantages and disadvantages of the acrylic latex products are similar to the solvent adhesive properties outlined earlier.(1)

## MIL-HDBK-691B

4.2.2.2.6 Miscellaneous resins. Some other polymeric materials used in water solution or dispersion form as adhesives should be mentioned. Water-sensitive materials derived from natural products include animal glue, starch, soya and blood glue, casein and certain cellulose derivatives. When carboxyl groups are present at sufficient concentrations in synthetic polymers, the resins become soluble in aqueous alkali. Examples are ethylene-acrylic acid and ethylene-methacrylic acid copolymers, vinyl acetate copolymers containing maleic acid or crotonic acid and acrylates modified with unsaturated carboxylic acids. These carboxylic-containing copolymers exhibit enhanced metal adhesion and grease resistance in comparison with the same systems without the acid groups.(1)

4.2.3 Hot-melt types. Several major industries have recently converted to the new hot-melt method of applying adhesives. This method offers the advantage over older techniques of high-speed production rates and simplicity in handling the adhesive itself. The packaging, bookbinding and shoe industries are most involved in hot melts. A hot melt may be defined as a 100%-solids thermoplastic adhesive polymer. The definition appears to include all thermoplastics, which is potentially true. Usually, however, there are roughly ten types. These materials are ideally solid up to 175°F (79°C) or higher, then melt sharply to give a low-viscosity fluid that is easily applied and capable of wetting the adhesive to be bonded, followed by rapid setting upon cooling. When hot melts are used, a new set of polymer properties such as softening point, melt viscosity, melt index, crystallinity, tack, heat capacity and heat stability must be understood and used in addition to the usual physical and strength properties. The adhesives themselves are not necessarily newly developed materials. It is the combination of properly formulated resins and of application equipment to handle these resins that has made the hot-melt technique successful.(1)

Application temperatures of hot melts range from about 300 to 550°F (149 to 288°C). All hot-melt adhesives are based on thermoplastic polymers. Other ingredients are added to improve processing characteristics, bonding characteristics or service properties. For example, stabilizers are used to retard oxidation, tackifiers to improve bond strength, wax to reduce viscosity and to alter surface characteristics and various fillers to increase viscosity, melting point and bond strength. Some hot melts used in potting applications contain asbestos fibers for improved strength and dimensional stability. Despite the fact that all hot melts are based on only a few polymers, available commercial products number in the hundreds. This is because individual producers sell a large number of formulations which may have been developed originally for a specific market. Also, a "black-art" atmosphere seems to prevail - producers sell hot melts only by their own number or name, with no generic identification attached. Thus, making comparisons among competing brands of similar hot-melt adhesives is not easy.(6)

From the design standpoint, one of the most important characteristics of hot-melt adhesives is service temperature. Because the hot melts, being thermoplastics, have relatively low melting temperatures, service temperatures are also low. This has been a limitation for product-assembly applications. Another limitation of the hot melts, also based on their thermoplastic nature,



## MIL-HDBK-691D

is that they creep under load and with time. Thermoplastics have some characteristics of viscous liquids and, with few exceptions, are not dimensionally stable under load. Thus, the hot melts are recommended for hold-in-place operations having negligible load requirements.(6)

The main disadvantages of hot melts are limited strength and heat resistance. Unlike other adhesives, the set-up process of hot melts is reversible and, at about 170°F (77°C), most hot melts begin to lose their strength. Maximum shear-load capacity is usually about 500 psi (3.4 MPa). Currently, the main goal in hot melts is to produce an adhesive that will survive a 180°F (82°C) continuous-service temperature. This is the temperature requirement for a material to be used in or near the engine compartment of an automobile.(7)

Lap-shear strengths up to 630 psi (4.3 MPa) have very recently been reached with hot-melt adhesives in bonding untreated HDPE to HDPE.(8)

**4.2.3.1 Ethylene-vinyl acetate (EVA) and polyolefin resins.** Hot melts based on these resins are the lowest-cost materials. The primary polyolefin type is polyethylene. These are general-purpose, low molecular-weight adhesives for bonding substrates of paper, cardboard, wood, fabric and similar materials. For such uses, their strength is adequate at temperatures from about -30 to +120°F (-34 to +49°C). They are not limited to service at these temperatures, however. Compounded versions are available that are suitable for nonloadbearing applications to about 160°F (71°C). The EVA's and polyethylenes represent the highest volume of hot-melt adhesives used today, principally in packaging and wood-assembly applications.(6)

**4.2.3.2 Polyamide (nylon) and polyester resins.** These compounds represent the next step up in strength and general service. They are currently the fastest-growing materials in product-assembly applications. Compounds of these materials, which are generally referred to as "high-performance" hot melts, are being used to assemble products made from plastics, glass, hardboard, wood, fabric, foam materials, leather, hard rubber and some metals. Successful bonding of plastic foam and oily aluminum panels has also been claimed. Various compounds made from these resins maintain adequate bonding characteristics in the temperature range from -40°F (-40°C) to about 180°F (62°C). A number of formulations are available that can be used at over 200°F (93°C); some can serve in no-load applications at temperatures above 300°F (149°C).(6)

Polyester-based hot melts are generally stronger and more rigid than the nylon compounds. Polyesters have high crystallinity, which gives them sharp melting points, a decided advantage in high-speed bonding and often have a combination of high tensile strength plus elongation. However, so much overlap of properties can be achieved with compounding that selection can only be based on examining specific service recommendations of available hot-melt formulations. Both nylon and polyester hot melts are sensitive to moisture during application, but each in a different manner. Nylon compounds have the advantage of combining good strength with flexibility. If nylon compounds are not stored in a dry area, they may pick up moisture. Then, during application, the absorbed moisture causes foaming in the heated adhesive which, in turn, produces voids in the applied layer, reducing bond strength.

## NIL-HDBK-691L

A corrective measure is to flash off the moisture by holding the adhesive in the fluid state for several minutes in a reservoir-type applicator system. Moisture affects polyester hot melts in a more complex and permanent way. Moisture enters into the molecular structure of these materials; and, the longer the adhesive is heated, the more the molecular weight is reduced and the lower the viscosity becomes. With polyesters, moisture and long-term heat-resistance time are detrimental to bond strength. For this reason, polyesters should not be used in a reservoir-type application system.(6)

Hot-melt adhesives are used for critical applications in military electronic assemblies. Extensive testing on Henkel Corporation's Versalon 1140 polyamide hot-melt adhesive indicates that strong bonds to aluminum can be obtained with minimal degradation resulting from exposure to severe environments. Versalon 1140 has a melting point of 285°F (141°C). The bond strength to unprimed surfaces exhibits some degree of moisture sensitivity which is strongly temperature-dependent. Relatively low-temperature applications seem to present no problems. Salt environments (salt spray) appear to accelerate the effects of moisture on the bond strengths. The adhesive becomes reversibly softened on exposure to moist environments. In addition, it has a tendency to oxidize and become brittle on exposure to heat and light. This effect would generally not affect its use as an adhesive.(9)

4.2.3 3 Other hot-melt materials. Other materials, not yet widely used, are the polyester-amides and those formulated from thermoplastic elastomers.

Polyester-amide compounds are still considered developmental, but are said to have the desirable properties of polyesters, but with improved application characteristics. Thermoplastic elastomer hot melts are another new class of materials. The principal base polymers in these formulations are polyurethanes and styrene-butadiene-styrene and styrene-isoprene-styrene polymers. These thermoplastic elastomers are currently being used mostly in pressure-sensitive applications, replacing other adhesives, such as contact cements, to eliminate the solvent-pollution problem. These are "soft" applications such as for tape products and labels, which require relatively low strength.(6) One particular thermoplastic rubber formulation provides paper tear in the range -10 to +140°F (-23 to +60°C). The adhesive may also be applied by guns for attaching; for example, plastic molding to wooden cabinet doors.(10)

As a class, thermoplastic-elastomer hot melts are not as strong as the polyesters but are stronger than conventional thermosetting rubbers. They offer good flexibility and toughness for applications requiring dynamic endurance, vibration endurance and vibration resistance; and they have good wetting characteristics. These compounds are very viscous, even at 450°F (232°C), because of their high molecular weights. This makes them more difficult to apply than the non-elastomeric materials unless they are formulated with other ingredients.

An example of a 100%-solids, nonflammable, heat-reactivable hot-melt adhesive recommended for structural bonding of aluminum, steel, copper, brass, titanium, fabrics and some plastics is 3M Co.'s SCOTCH-WELD Thermoplastic Adhesive Film 4060. Strength data on this material is given in Table VII.(11)



## MIL-HDBK-691B

Bonding with this clear amber unsupported film adhesive takes place very rapidly. The speed of bonding is limited only by the time required to reach the optimum bonding temperature of 300°F (149°C) at a pressure sufficient to maintain contact between the surfaces to be bonded. The adhesive can also be preapplied to parts days or months in advance of the actual bonding operation. When parts are ready for bonding, the application of heat to the previously applied adhesive quickly reactivates the material for bonding. The adhesive is available in roll form in thicknesses of 3 and 5 mils. Typical applications include non-load-bearing honeycomb panels, application of decorative trim and installation of electronic parts.(11)(12)

TABLE VII. Strength characteristics of SCOTCH-WELD thermoplastic adhesive film used to bond 2024 T3 clad aluminum, FPL-etched.1 (11)

Temperature (°F) (°C)		Overlap Shear Strength (psi) (MPa)		T-Peel Strength (lb/in) (N/m)	
-67	-55	4100	28.2	4	700
0	-18	--	--	5	875
75	24	2200	15.2	30	5250
180	82	400	2.8	20	3500

<sup>1</sup>Bonding cycle 5 min at 300°F (149°C) in a platen press at 100 psi (0.69 MPa). For additional conditions, consult 3M Company Technical Bulletin on this film, Ref. 12.

Foamable hot-melt adhesives have been available commercially since September 1981. The process involves introducing a gas, normally H<sub>2</sub> or CO<sub>2</sub>, into the hot-melt adhesive in a volumetrically metered fashion. The process utilizes a patented two-stage gear pump. Usually an increase in adhesive volume of 20-70% is obtained. Although all adhesives foam, the quality of the foam varies with the individual adhesive. Foamed hot-melt adhesives can be used on the same substrates on which standard hot melts are used. Often a superior bond can be formed on metal, plastic and paper products, as well as heat-sensitive and porous substrates. This is due to the foaming characteristics of increased spreading ability, longer open time, shorter set time, increased penetration and reduced thermal distortion over traditional hot melts. Polyethylene, in particular, gives excellent results. Two examples of this application are in gasketing and sealant applications.(13)

**4.2.4 Delayed-tack adhesives.** A delayed-tack adhesive differs from both a hot-melt adhesive and a heat-seal adhesive. A hot melt will be nontacky when cooled, while a heat-seal adhesive will seal under heat and pressure, but does not remain tacky for any period of time after cooling. On the other hand, after a delayed-tack system is heat-activated and cooled, it will remain tacky for anywhere from several minutes to several days over a wide temperature range. For example, a rubber-based delayed-tack adhesive plasticized with diphenyl phthalate can become heat-activated at 150°F (66°C). The formulation remains adhesive and tacky even as the temperature cools to 50°F (10°C). Below 50°F, the adhesive will set. This type of adhesive is coated on paper for labels such as bread packages and cans. To obtain the

## NIL-HDBK-691B

delayed-tack characteristics of the adhesive system, a solid plasticizer must be used. A solid plasticizer also contributes to nontackiness before heat activation. The most common such plasticizers are dicyclohexyl phthalate, diphenyl phthalate, N-cyclohexyl-p-toluene-sulfonamide and o/p-toluenesulfonamide. Adhesives with different heat-activation temperatures are possible because of the range of melting points. The most commonly used resins are styrene-butadiene copolymers, polyvinyl acetate, polystyrene and polyamides.<sup>(1)</sup>

**4.2.5 Film and tape adhesives.** Bonds produced by a given adhesive will usually have similar properties, whether the adhesive is applied as a one-component paste or as a solid film. The advantages of using the adhesive in film form are:

- (o) Uniform, controlled glue-line thickness;
- (o) Speed and ease of application (a clean, solvent-free operation is permitted);
- (o) Two-sided films can be prepared. These are used in lightweight sandwich construction. The honeycomb side of the adhesive will provide good filleting; the skin side will provide high peel strength. If one side of the film is tacky, it is easier to align the assembly to be bonded.

In some film adhesives, a woven or knitted fabric that may be used to support the polymer film will also carry part of the load and will give improved bond strength by better distribution of the applied forces. Film adhesives are provided in two forms: unsupported or alternately supported on a flexible carrier such as glass cloth, nylon or paper. The carrier will usually have little effect on adhesive properties.<sup>(1)</sup>

Sometimes the term film adhesive is applied to the high molecular-weight polymers, normally elastomers, blended with curing agents, fillers and other ingredients that are extruded, calendered or cast into 5 to 15 mil unsupported thick films. When the mixture is cast or calendered onto a mesh support, such as woven or nonwoven mesh of glass or other fibers, the result is a tape adhesive. Films and tapes may be either soft and tacky or stiff and dry, may be room-temperature storable or may require refrigeration between manufacture and time of usage. Although some film and tape adhesives are designed to cure at room temperature after removal from dry-ice storage, most are cured at elevated temperatures and pressures. Film and tape adhesives differ from paste and liquid adhesives in that the former contain a high proportion of a high-molecular-weight polymer. The "100% solids" paste and liquid adhesives contain only low-molecular-weight resins because this is the only way they can remain fluid and usable. On the other hand, the tape and film adhesives often contain linear polymers with molecular weights of at least 20,000 and with a degree of polymerization (DP) of 600 or more. Such polymers can be very much tougher and more resilient and can provide more recoverable elongation than the more highly branched networks formed by curing the low-molecular-weight resins used in paste adhesives. Figures 24 and 25 compare typical tensile shear data for a variety of adhesive types. The best of the tape and film types have higher peak values and broader service temperature ranges than the best of the "100% solids" types.<sup>(14)</sup>

## NIL-HDBK-691B

Tape and film adhesives now dominate the airframe market for structural adhesives. Several thousand pounds of such adhesives are used per plane on jumbo jet aircraft such as the Boeing 747. High-performance military aircraft such as the B-58 "Hustler" bomber or the swing-wing F-111 fighter use considerable quantities of tape and film adhesives in the wing, tail and fuselage structures. Tape adhesives, for example, generally of the nylon-epoxy type, are used for assembly of helicopter blades and for bonding rotor-blade segments to support spars. Adhesive bonding with tape and film adhesives is often combined with mechanical fastening. For example, the combined riveting and bonding of the Boeing 727 fuselage splices and reinforcements provides better fatigue strength, more uniform load distribution, higher strength-to-weight ratios and smoother skins than the previous all-riveted construction. The fact that film adhesives seal as well as fasten makes possible air-tight and liquid-tight pressure cabins, fuel and hydraulic systems. (14)

Tape and film adhesives have been widely accepted by the airframe industry because they have handling and reliability advantages and are tougher than pastes or other adhesives types. The handling and reliability advantages stem from the fact that they come ready to use, with no need for mixing, no degassing and no possibilities for error in adding catalyst. Both the supplier and the user can test the tapes. Tapes permit a variety of lay-up techniques which facilitate the production of a virtually defect-free structure. The use of a support mesh also serves to control the bond-line thickness with tape adhesives, avoiding thin, adhesive-starved areas where curvature or external pressure is largest. (14)

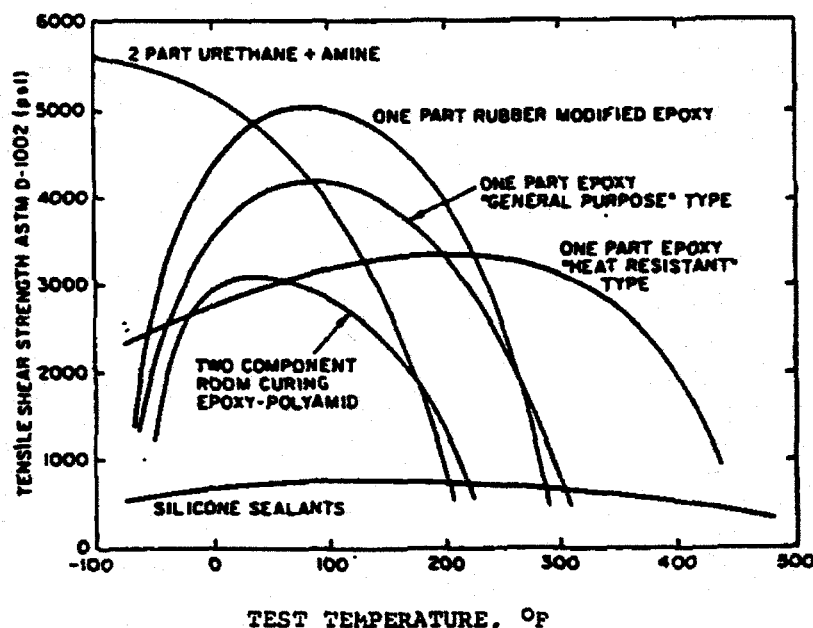


FIGURE 24. Typical tensile shear strength data for paste and liquid (100% solids) adhesives. (14)

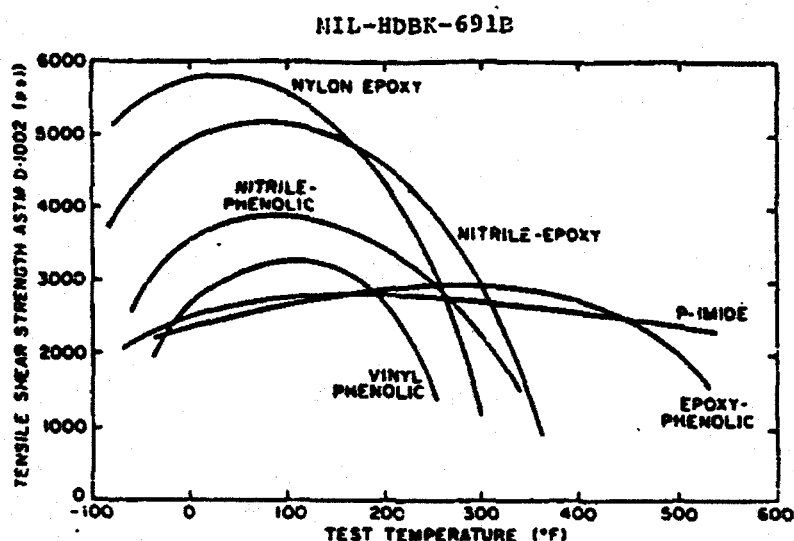


FIGURE 25. Typical tensile shear strength data for tape-, film- and solvent-based adhesives. (14)

In general, tape and film adhesives are composed of the following three components:

- (o) A high-molecular-weight "backbone" polymer, providing the elongation, toughness and peel properties required;
- (o) A low-molecular-weight crosslinking resin, invariably either an epoxy or phenolic type;
- (o) A curing agent for the crosslinking resin.

These adhesives are named according to the identity of components 1 and 2 (e.g., nitrile-phenolic, nylon-epoxy, etc.) and are also frequently referred to as "two-polymer" or "alloyed" adhesives. With very few exceptions, all successful tape and film adhesives are, or have been, one of the five types shown in Table VIII. It should be noted that the adhesives types based on phenolic crosslinking resins liberate volatiles during cure and require high-pressure cures, while the types based on epoxy curing agents need only enough pressure to maintain alignment and compensate for cure shrinkage. (14)

TABLE VIII. Most important tape and film adhesives. (14)

Type	Backbone polymer	Crosslinking resin	Catalyst	High-pressure cure
Nylon-epoxy	Soluble nylon	Liquid epoxy	DICY-type	No
Elastomer-epoxy	Nitrile rubber	Liquid epoxy	DICY-type	No
Nitrile-phenolic	Nitrile rubber	Phenolic novolac	Hexa, sulfur	Yes
Vinyl-phenolic	PVB or PVF	Kesol phenolic	Acid	Yes
Epoxy-phenolic	Solid epoxy	Resol phenolic	Acid	Yes

## MIL-HDBK-691B

Table IX summarizes the bond strengths of these tape and film adhesives.

TABLE IX. Range of bond strengths of tape and film adhesives at room temperature. (14)

Adhesive Type	Tensile Shear Strength		T-Peel Strength	
	(psi)	(MPa)	(lb/in)	(N/m)
Nylon-epoxy	5500-7200	39-49	80-130	14,000-22,750
Elastomer-epoxy	3700-6000	26-41	22-90	3,850-15,750
Nitrile-phenolic	3000-4500	21-31	15-60	2,625-10,500
Vinyl-phenolic	3000-4500	21-31	15-35	2,625- 6,065
Epoxy-phenolic	2000-3200	14-22	6-12	1,050- 2,100

Following is a brief discussion of the major film and tape adhesives. More detailed information, particularly on their chemistry, will be found in 4.3.1.12 (on PI and PEI) and 4.3.3.3.

**4.2.5.1 Vinyl-phenolics.** The "vinyl" in vinyl-phenolic adhesives is a somewhat misleading term referring either to a polyvinyl formal (PVF) or polyvinyl butyral (PVB) (see 4.2.1.3.5). Vinyl-phenolics have generally excellent durability, both in water and in other adverse environments. Cures are at 350°F (177°C). Despite their generally excellent performance properties, however, the modern trend is to move away from vinyl-phenolic adhesives toward one of the newer types which have been developed to provide cures at lower temperatures and pressures and with higher hot strength, higher peel strength and other performance advantages. (14)

**4.2.5.2 Epoxy-phenolics.** Although epoxy-phenolic adhesives account for only a small fraction of the present usage of structural adhesives, they continue to be important in the largely military market for adhesives designed for service between 300 and 500°F (149 and 260°C). Despite the fact that these adhesives were first developed almost 25 years ago by Forest Products Laboratory and despite the enormous effort which has gone into the development of new polymeric systems designed for high-temperature use, epoxy-phenolics are still considered to be among the best adhesives for long-term use in the range from 300 to 500°F (149 to 260°C), but epoxy-phenolics have less resistance to 350°F (177°C) exposure than nitrile-phenolics. Cure is usually at 300°F (149°C). Cures at 350°F (177°C) tend to cause out-gassing and foaming. Cures as low as 200°F (93°C) for 24 hours will minimize this condition. (14)(15)

**4.2.5.3 Nitrile-phenolics.** Nitrile-phenolic adhesives are made by blending a nitrile rubber with a phenolic novalac resin, plus many other compounding ingredients. These adhesives account for the largest poundage volumes of any type of tape, film or solution adhesive type. Their major uses are in the automotive industry, in bonding brake shoes and clutch disks. They are also used in aircraft assembly and in many other smaller applications because of their low cost, high bond strengths at temperatures up to 250°F (121°C) and exceptional bond durability on steel and aluminum. Nitrile-phenolics are known to have exceptional durability after extended salt-spray, water-immersion and other corrosive environments. They are particularly good at preventing undercutting by means of corrosion of metal substrates.

## MIL-HDBK-691B

Nitrile-phenolic tape adhesives will probably occupy their "workhorse" position for a long time to come. The major disadvantages of the nitrile-phenolic adhesives are the need for high-pressure cure (up to 200 psi or 1.38 MPa) when the trend is toward cure at lower pressures and the need for high-temperature (300°F - 149°C), long-term cures when the trend is toward adhesives which cure rapidly at or below 250°F (121°C). None of these objectives are serious enough to threaten the use of this adhesive type for brake shoes, clutch disks or most of its other traditional uses.

By the late 1950's, it was determined that nitrile-phenolics had gone about as far as they could from the point of view of improvement of strength properties. Soon other elastomer-modified adhesive types began to bid for the military and commercial airframe markets. The newer nylon-epoxy and rubber-epoxy adhesives, crosslinked with epoxy rather than with phenolic resins, were developed in the early 1960's. They were more expensive but offered advantages in cure rate, low-cure pressure and high peel values - all of which are important in the airframe adhesives industry.<sup>(14)</sup>

**4.2.5.4 Nylon-epoxies.** These adhesives, which first became prominent in the early 1960's, were welcomed when developed because of their excellent advantages. Where adhesives technologists had attempted for many years to provide more than about 50 lb/in in climbing-drum peel strength (6,750 N/m), these nylon-epoxy adhesives provided a quantum jump in toughness, yielding peel strengths above 150 lb/in (26,250 N/m), tensile-shear strengths above 7000 psi (48 MPa) and exceptional fatigue and impact properties. (Note: Peel-strength values in Table IX are T-peel, which is not the same as climbing-drum peel; but T-peel values in Table IX are also very high.) Although their desirable properties have won for the nylon-epoxies some important applications, notably in the lamination and assembly of helicopter rotor blades, the fact is that this class has never overcome several serious drawbacks which have limited its use to date. These problems are:

- o loss in peel strength at low temperatures (see Table V);
- o poor creep resistance;
- o extreme sensitivity to moisture.

Nylon-epoxy films not only have the unfortunate tendency to pick up substantial amounts of water before cure, but also tend to lose bond strengths rapidly after cure upon exposure to water or moist air. It has been shown that, after 18 months exposure to 95% relative humidity, a conventional nitrile-phenolic adhesive loses only a fraction of its initial strength, going from 3000 to 2500 psi (21 to 18 MPa) tensile shear<sup>(15)</sup>. In contrast, one of the best nylon-epoxy adhesives degrades from about 5000 to 1000 psi (34 to 6.8 MPa) in just two months under the same test conditions. It has also been shown<sup>(16)</sup> that nylon-epoxy tapes which show initial strengths above 6000 psi (42 MPa) will fracture within a few days when exposed to humid air at loadings only a small fraction of the initial dry failure load. Considerable effort has been made to solve this moisture problem. Many of these efforts involve primers, often resol-phenolic-resin based, applied to the metal surfaces before laying up with the nylon-epoxy film. The results are not all that might be hoped for, however; and nitrile-rubber epoxy or acetal-toughened epoxy film adhesives are still superior from the point of view of bond durability.<sup>(14)</sup>



## NIL-HDBK-691B

**4.2.5.5 Elastomer-epoxies.** The modern trend in aircraft adhesives is toward epoxy-based tape or film adhesives where the epoxy is toughened with an elastomer, usually a nitrile rubber, and where the epoxy is cured with catalysts which permit cure at low pressures in the shortest possible time and at the lowest-possible cure temperature. The use of adhesives to assemble progressively larger wing, tail and fuselage sections has placed an increasing premium on cure temperatures in the 180 to 250°F (82 to 121°C) range (permitting the use of lower steam pressure and thinner-walled autoclaves) and on shorter cure cycles, permitting more units to be assembled per autoclave per day. As indicated in Table IX, the maximum bond strengths for elastomer-epoxies are generally still below the maxima attainable with the nylon-epoxies at room temperature. A major advantage of the nitrile-epoxy adhesives, however, is that the peel strength does not decrease as abruptly at subzero temperatures as do the peel values of the nylon-epoxies. The bond durability of these new high-peel elastomer-epoxies is satisfactory, as measured by most long-term moisture tests, but it does not match the durability of the older vinyl-phenolic or nitrile-phenolic types.<sup>(14)</sup> Nitrile-epoxies should not be used for exposure to marine environments or under continuous immersion in water.<sup>(15)</sup>

**4.2.5.6 Aromatic polymers.** Aromatic polymers, such as polyimide (PI) and polybenzimidazole (PBI), are available in film and tape adhesives recommended for some high-temperature applications. These adhesive types, discussed briefly above in 4.2.1.3.1, show better bond strengths above 500°F (260°C) in air than epoxy-phenolic, although the latter gives better strength retention after exposure to water or other polar liquids at lower temperatures. The major disadvantage of these aromatic polymers, which have limited their use as adhesive systems to date, are their high cost (generally 10 or more times that of epoxy-based adhesives), the difficulties in handling or curing, and the problems involved in the elimination of volatiles during cure in order to obtain a void-free bond. A long and careful series of cure and post-cure steps at progressively increasing temperatures up to the 600-700°F (316-371°C) level, coupled with intermittent application and release of high clamping pressures, is required to obtain optimum results with these adhesives. These facts, together with the recent de-emphasis by military and commercial aircraft designers on adhesives which operate at temperatures higher than those which can be provided by the best epoxy-based adhesives, have reduced the estimates of the future potential for the heterocyclic aromatic adhesives. Of all the many aromatic polymers once considered as candidates for the high-temperature adhesives of the future, only the polyimides now remain in serious contention for the 500-800°F (260-427°C) service-temperature market.<sup>(14)</sup>

**4.2.6 Pressure-sensitive adhesives (PSA's).** A pressure-sensitive adhesive is a substance capable of holding things together when the surfaces are brought into contact under briefly applied pressure at room temperature. Generally, pressure-sensitive adhesives are composed of a rubbery type polymer which is modified with several additives such as plasticizers, tackifiers, fillers, solvents and stabilizers. In order of decreasing volume and, generally, increasing price, the following are used as basic polymeric raw materials: natural rubber, styrene-butadiene rubber, reclaimed rubber, butyl rubber and butadiene-acrylonitrile rubber, polyacrylates and polyvinyl alkyl ethers. The rubbers as a whole are used in pressure-sensitive adhesives



## NIL-HDBK-691B

because of their good flexibility, ease of tackification and probably most important, economics. A major disadvantage of the rubber is poor aging, which results in a loss of elasticity and tack and a yellowing of the adhesive layer. The acrylates and polyvinyl alkyl ethers are more expensive but exhibit better aging characteristics. Thus, when rigid, high-performance standards are required for a pressure-sensitive adhesive, polyvinyl alkyl ethers or polyacrylates become the polymers of choice.(1)

Paper, cellophane, plastic films such as polyethylene, polyester, polyvinyl chloride, cloth and metal foils may be used as backing for such tapes. Generally, the adhesive coat is applied by calendaring or solvent spreading. Tapes are made both with adhesive on one face and with adhesive on both sides (double-faced). The one-face tape is used for sealing, masking, holding and reinforcing operations. The double-faced tapes are used primarily for joining operations where there is a need to control the amount of adhesive and where pressure sensitivity is needed.(1)

**4.3 Classification by Rayner.** This section is based on a discussion of synthetic organic adhesives and is included here because it provides a rather useful insight into the chemistry of a number of the adhesives of interest to the users of this handbook. Unfortunately, some of the discussion will overlap that given in 4.2 above.(17)

**4.3.1 Thermosetting resin adhesives.** A thermosetting synthetic resin is one that, on curing, undergoes an irreversible chemical and physical change to become substantially infusible and insoluble. The term thermosetting is applied to the resin both before and after curing. Some thermosetting adhesives are condensation polymers and some are addition polymers. The important examples are urea -, melamine -, phenol - and resorcinol-formaldehyde adhesives and epoxy, polyisocyanate and polyester adhesives. They will be considered in that order.

**4.3.1.1 Urea-formaldehyde adhesives.** A urea-formaldehyde resin or glue, commonly called a urea glue, is the condensation product of unsubstituted urea and formaldehyde. These materials are usually supplied as two-part systems, including resin and hardening agent. Extenders and fillers are used in the formulations. Curing is accomplished under pressure without heat. The most common application is in plywood. Urea glues are not as durable as other types but are suitable for a fair range of service applications. They are generally low-cost and are easy to apply and cure. Their pot life is limited to 1 to 24 hours.(17)(16)

**4.3.1.2 Melamine-formaldehyde adhesives.** A melamine-formaldehyde adhesive, also called a melamine glue, is a condensation product of unsubstituted melamine and formaldehyde. These adhesives have much in common with urea-formaldehyde resins, but they are much newer and have not attained great importance as adhesives. They are, however, widely used as textile finishes and in the manufacture of decorative laminates and plastic moldings, as well as on plywood. Melamine adhesives are supplied as powders to be mixed with hardening agents. A minimum temperature of about 149°F (65°C) is required for curing, along with pressure. Melamine-formaldehyde glues are equivalent in durability and water resistance to phenolics and resorcinols. They are often combined with ureas to lower costs. Service temperatures are higher than for ureas.(17)(18)

## MIL-HDBK-691B

**4.3.1.3 Phenol-formaldehyde adhesives.** In the adhesives field, a phenol-formaldehyde resin, commonly called a phenolic glue, means a condensation product of formaldehyde and monohydric phenol. (See also 4.2.1.1.2 above.)(17)

**4.3.1.4 Resorcinol-formaldehyde adhesives.** These adhesives cure on addition of formaldehyde, compared to phenolics, which cure on addition of strong acids. They are usually supplied in alcohol-water solutions to which formaldehyde must be added. Curing is at room temperature or higher, with moderate pressure. These adhesives are suitable for exterior use and are unaffected by boiling water, mold, fungus, grease, oil and most solvents. They are used primarily on wood and plywood, plastics, paper and fiberboard. (See also 4.2.1.1.3 above.)(18)

**4.3.1.5 Epoxy-resin adhesives.** In the unhardened state, the chemical structure of an epoxy resin is characterized by the epoxide group. There are two broad methods of adding such a group. The first and most important method, from the point of view of adhesives, involves reacting a substance already containing an epoxide group, such as epichlorohydrin, with a substance having replaceable hydrogen atoms. The resultant product is a glycidyl compound which, in the most important cases, is a glycidyl ether, amine or ester. The glycidyl ethers include the bisphenol A epoxy resins, the type usually referred to in the general meaning of epoxy resins. In the second method of forming epoxy resins, peracetic acid or any other appropriate oxygen-donating compound, is used to effect epoxidation of an olefinic compound.(17)

Epoxy adhesives comprise a liquid or a fusible solid containing epoxide groups and a curing agent containing functional groups with which the epoxide groups combine to form a crosslinked polymer. When the reaction between resin and hardener is capable of taking place at room temperature, the two components are mixed immediately before use; but, if the mixture is relatively inactive under ordinary storage conditions, the components may be mixed together and marketed as a single-package adhesive. The "B-stage" adhesive systems also comprise a single component; but, in this case, the resin and hardener have been reacted to an intermediate but still fusible stage. The curing that takes place when the resin and hardener are brought into intimate contact, for example, by melting the solid under appropriate conditions, is an irreversible reaction that results in a thermoset resin. This reaction does not involve condensation polymerization, and therefore, no low-molecular-weight substance, such as water, is split off. For this reason, the shrinkage that takes place during cure is slight, and this is one of the properties that makes epoxy resins especially valuable as adhesives. Furthermore, a wide range of end products having a correspondingly wide range of properties can be obtained by use of different resin/hardener adhesive systems. Epoxy adhesives are the most versatile adhesives available. They have excellent tensile-shear strength, poor peel strength and excellent resistance to moisture and solvents. Epoxy adhesives are used on metals, plastics, glass, wood, rubber and ceramics.

## NIL-HDBK-691B

Types of hardeners used in curing bisphenol A epoxy resins include the following: (17)

- o Aliphatic polyamine hardeners. Used in adhesive systems capable of curing at normal or slightly elevated temperatures. Most important are diethylenetriamine (DETA), triethylenetetramine (TETA) and diethylaminopropylamine (DEAPA).
  - o Fatty polyamides. (Versamides<sup>1</sup>) Condensation products of polyamines and unsaturated fatty acids. These are high-melting linear polyamides of the nylon type, containing carboxyl and amino end groups and amide groups along the chain. The amount required for curing is large and the proportion not very critical. They are used to impart flexibility as well as for curing and are probably the most widely-used epoxy curing agents.
- <sup>1</sup>Reg. trade name of Henkel Corp.
- o Aromatic polyamine hardeners. Mostly solid. Include metaphenylenediamine (MPD), diaminodiphenylmethane (DDA) and diaminodiphenyl sulphone (DDS). In general, these hardeners provide poorer bond strengths at high temperatures and are more sensitive to temperature cycling than the aliphatic amines. Shrinkage is also high.
  - o Anhydride hardeners. Organic polycarboxylic anhydrides. Most require severe curing cycles. Provide improved thermal stability over the amines. Anhydride-cured epoxies are often brittle and require a flexibilizer, which will result in reducing the heat and chemical resistance.
  - o Boron trifluoride hardeners. Boron trifluoride monoethylamine (BF<sub>3</sub>-MEA) melts at 95°C and is used in one-package adhesives.
  - o Phenolic resins as hardeners. The phenolic may be either a novolak or a resite and may be used with or without some other curing agent or catalyst. In epoxy-phenolic alloys (see 4.2, 5.2 and 4.3.3), the phenolic is in considerable excess of the epoxy and functions only in part as a hardener.
  - o Miscellaneous curing agents. Most important is dicyandiamide (DICY), used much in metal bonding. It melts at about 200°C (392°F) and is nonreactive at room temperature, so it is convenient for use in a one-package adhesive in the form of a powder or rod.

For additional discussion of epoxy adhesives, see 4.2.1.1.1 above.

4.3.1.6 Polyisocyanate (polyurethane) adhesives. The term polyisocyanate as used here is intended to mean an aliphatic or aromatic isocyanate containing two or more isocyanate groups. Resins derived from polyisocyanates have a chemical similarity to epoxy resins in that both form addition polymers with compounds containing active hydrogen groups. Their importance as adhesives, however, is much less than that of epoxy adhesives. Adhesives

## MIL-HDBK-691B

interest has been mainly in aromatic polyisocyanates. The most commonly used isocyanates in adhesives are tolylene diisocyanate (TDI), used primarily in gluing metal, wood and certain plastics, and triphenylmethane-p,p',p'-triisocyanate, used mostly where one adherend is rubber. HDI is also used to some extent.(17) (See also 4.2.1.1.6.)

**4.3.1.7 Polyester resin adhesives.** In the field of adhesives, polyester resins have not so far found wide application, unless the laminating use of the unsaturated polyesters as adhesive bonding is included. For a previous discussion, see 4.2.1.1.3 above.

**4.3.1.6 Silicone Adhesives.** Certain silicone adhesives are thermosetting. They are used mainly for bonding of silicone rubber, an application in which crosslinking must be infrequent if the adhesive is to have a rubbery nature after curing. The silicone is usually dimethyl polysiloxane, which is normally cured by heating with a silicic acid ester and a catalyst.

Certain forms of the adhesive are capable of being cured at room temperature and of giving good resistance to heat. Although the bond strength of organo-silicon resins is normally not high, it can be improved by incorporating an epoxide, polyester or phenolic resin, additions which can reduce hot strength and thermal stability.(17) (See also 4.2.1.1.7 above.)

**4.3.1.9 Furane adhesives.** These materials contain the chemical group known as the furane ring. They include the condensation polymers of furfuraldehyde (furfural) and furfuryl alcohol. These furane compounds polymerize on addition of an acid, passing through a liquid resinous state and have adhesive properties. Furan resin adhesives are claimed to effectively bond thermoplastic materials and rubbers and also phenolic laminates where adhesion to smooth surfaces is better than to sanded surfaces.(17)

**4.3.1.10 Acrylic adhesives.** (The discussion here is on thermosetting acrylic adhesives. For other types, including cyanoacrylates, see 4.3.2.3.) Within the past few years, various acrylic adhesives called "reactive adhesives," "modified acrylics," "second-generation acrylics" or "reactive-fluid adhesives" have become available. These are formulations of monomeric materials that polymerize in the glue line to become an integral part of an adhesive assembly. The term "first-generation acrylic adhesives" refers to adhesives in existence for over twenty-five years. This older technology utilizes solutions of polymers, usually rubber, in methacrylate monomers and involves polymerization of these monomers in the presence of reinforcing resin. Currently several companies are marketing the newer "second-generation acrylic adhesives." These adhesives are based on a combination of different modifying polymers for acrylics and a surface activator. The modifying polymer reinforces and toughens the bond and provides a reactive chemical site which acts as a catalyst in the presence of special activators. Adhesion takes place when the monomers and activator graft-polymerize in the modifying polymer in the joint line.

In commercial form, the "second-generation" acrylic adhesive system consists of two components, each being a 100%-solids composition in fluid form and each reacting to form the adhesive film. The "second-generation" acrylic adhesives resemble the epoxy and polyurethane adhesives functionally; but the new

## NIL-HDBK-691B

acrylics cure by a free-radical reaction, rather than by ionic polymerization. Because of this free-radical reaction, second-generation acrylics do not require careful metering and accurate mixing for full performance. Other advantages of the new modified acrylics include:

- o Tolerance for oily and otherwise poorly prepared surfaces;
- o Rapid bonding at room temperature, which can be speeded further with mild heat or the use of accelerators;
- o Low shrinkage during curing;
- o High peel and impact strength, combined with excellent shear strength;
- o Good environmental resistance and elevated-temperature properties.

Excellent bonds can be obtained with a wide variety of substrates. Aluminum, brass, copper, stainless steel and carbon steel are easily bonded to similar or dissimilar metals. Most plastics, including glass-reinforced grades, can also be bonded, along with wood, glass, cement-asbestos board and hardboard. Some types will bond cured elastomers. In a typical application, a thin layer (0.0001 inch or 0.002 mm) of the activator is applied to one of the adherends, and a layer of the adhesive anywhere from 0.001 to 0.01 inch (0.025 to 0.25 mm) is placed on the other adherend. The two substrates are then pressed together and secured until adequate handling strength develops. Most second-generation acrylic adhesives cure to the point of handling strength in 2 to 20 minutes, but some cure in as little as 10 seconds. In all cases, full cure is obtained in 24 hours or less. The second-generation acrylic adhesives give excellent shear, peel and impact strengths at temperatures from -107 to 250°F (-107 to 121°C). Short exposures up to 350°F (177°C) are possible. Peel and impact strengths are considerably higher than for all other rapid-setting adhesives, as shown in Table X.

Bonds made with the second-generation acrylics hold up well under a wide range of environments, including temperatures up to 350°F (177°C). Properly-cured bonds will resist immersion in such chemicals as isooctane, motor oil, aircraft hydraulic fluid, 10% sodium chloride solution, distilled water, ethyl alcohol, dilute mineral acids and alkalies. However, the adhesives are not resistant to concentrated acids, alkalies and acetones. Resistance to weathering, including salt-spray environments, is also excellent.

The second-generation acrylic adhesives will probably see increasing use in applications where epoxy and contact adhesives can be used to replace spot welding in certain applications where immediate handling of joined metal parts is required. Another broad area of anticipated application is in the bonding of dissimilar substrates, including metals and other materials with different coefficients of expansion. (19)(20)

4.3.1.11 Soluble nylon adhesives. Adhesives utilizing alcohol-soluble nylons are referred to in several sections of this handbook. Certain soluble nylons, such as *N*-methyl methoxy-nylon, can be made substantially infusible and insoluble by heating in the presence of an acid catalyst and are reported to give high adhesion to wood, even in boiling water. A valuable feature of the soluble nylons is that they are incompatible with many other resins, permitting the formulation of adhesive mixtures, such as nylon-epoxy. (17)



## MIL-HDBK-691B

TABLE X. Comparison of properties of acrylic and other adhesive types (room-temperature curing). (20)

Type	First-Generation Acrylic	Second-Generation Acrylic	Epoxy	Urethane	Cyanoacrylate	Anaerobic
<b>Lap-Shear Strength</b>						
Oily, nonblasted steel	2500-2800 psi (15.0-19.3 MPa)	2400-2600 psi (16.5-17.9 MPa)	750-1000 psi (5.17-6.89 MPa)	0	NA	600-800 psi (4.13-5.52 MPa)
Oily, nonblasted steel 300°F (177°C) 30' heat cycle	650-900 psi (4.48-6.20 MPa)	2400-3000 psi (19.3-20.6 MPa)	1000-1200 psi (6.89-8.27 MPa)	700-1000 psi (4.82-6.89 MPa)	NA	NA
Solvent-cleaned nonblasted steel	1750-2200 psi (12.1-15.2 MPa)	2400-3000 psi (16.5-20.6 MPa)	1800-2100 psi (12.4-14.5 MPa)	550-650 psi (3.79-4.48 MPa)	200 psi (1.38 MPa)	NA
Solvent-cleaned sandblasted steel	3000-3700 psi (20.6-25.5 MPa)	3300-3500 psi (22.7-24.1 MPa)	1800-2100 psi (12.4-14.5 MPa)	650-1050 psi (4.48-7.24 MPa)	4000 psi (27.6 MPa)	2150-2550 psi (14.8-17.6 MPa)
Etched aluminum	3700-4000 psi (25.5-27.5 MPa)	3400-3600 psi (23.4-24.8 MPa)	2000-2400 psi (13.8-16.5 MPa)	1750-2050 psi (12.1-14.1 MPa)	3000 psi (20.0 MPa)	NA
Solvent-cleaned aluminum	900-1800 psi (6.21-12.4 MPa)	2000-2200 psi (13.8-15.2 MPa)	1600-1800 psi (11.0-12.4 MPa)	375-400 psi (2.58-2.76 MPa)	1000 psi (6.89 MPa)	950-1550 psi (6.55-10.7 MPa)
<b>Impact Strength</b>						
Room temperature	10-20 ft-lb/in <sup>2</sup> (21010-42040 J/m <sup>2</sup> )	14-16 ft-lb/in <sup>2</sup> (29430-33630 J/m <sup>2</sup> )	10-12 ft-lb/in <sup>2</sup> (21010-25220 J/m <sup>2</sup> )	5-11 ft-lb/in <sup>2</sup> (10510-23120 J/m <sup>2</sup> )	3-5 ft-lb/in <sup>2</sup> (6306-11000 J/m <sup>2</sup> )	3-5 ft-lb/in <sup>2</sup> (6306-11000 J/m <sup>2</sup> )
-20°F (-29°C)	3.5-4.5 ft-lb/in <sup>2</sup> (7357-9459 J/m <sup>2</sup> )	10-14 ft-lb/in <sup>2</sup> (21020-29430 J/m <sup>2</sup> )	3-5 ft-lb/in <sup>2</sup> (6306-10510 J/m <sup>2</sup> )	2.5-5.3 ft-lb/in <sup>2</sup> (5255-11140 J/m <sup>2</sup> )	NA	NA
0°F (-18°C)	5-8 ft-lb/in <sup>2</sup> (10510-16016 J/m <sup>2</sup> )	11-14 ft-lb/in <sup>2</sup> (2300-29428 J/m <sup>2</sup> )	5-6 ft-lb/in <sup>2</sup> (10510-12612 J/m <sup>2</sup> )	2.5-3.5 ft-lb/in <sup>2</sup> (5255-7357 J/m <sup>2</sup> )	NA	NA
180°F (82°C)	10-20 ft-lb/in <sup>2</sup> (21000-42000 J/m <sup>2</sup> )	11-13 ft-lb/in <sup>2</sup> (23000-27000 J/m <sup>2</sup> )	5-6 ft-lb/in <sup>2</sup> (11000-13000 J/m <sup>2</sup> )	4-5.5 ft-lb/in <sup>2</sup> (8400-12000 J/m <sup>2</sup> )	NA	NA
<b>T-Peel Strength (room temperature)</b>						
Solvent-cleaned steel	24-26 pli: (4200-4550 N/m)	25-30 pli: (4375-5250 N/m)	5-10 pli: (875-1750 N/m)	29-30 pli: (5075-5250 N/m)	NA	1-5 pli: (262 N/m)
Etched aluminum	0-6 pli: (1400-2000 N/m)	25-30 pli: (4375-5250 N/m)	15-20 pli: (2620-3510 N/m)	36-38 pli: (6300-6650 N/m)	NA	1-2 pli: (175-350 N/m)
Set Time	120 minutes	2-4 minutes	120-180 minutes	15 minutes	0.5 minutes	1 minute

## NIL-HDBK-691B

**4.3.1.12 Polyaromatic adhesives.** These adhesives, polyimide and polybenzimidazole, are frequently grouped with the thermosets, because of their high melting points. They are strictly thermoplastics, however, and are discussed under 4.2.1.3.1.

**4.3.2 Thermoplastic-resin adhesives.** A thermoplastic-resin adhesive is one which melts or softens on heating and rehardens on cooling without (within certain temperature limits) undergoing any chemical change. At temperatures above the melting point an irreversible chemical change such as depolymerization or oxidative degradation may take place. When used as adhesives, thermoplastic resins are used in the form of solutions, dispersions in water or solids. They are usually "set" by purely physical means. When applied as solutions or dispersions, adhesion follows evaporation or absorption of the liquid phase (as in "solvent activation"). When applied by melting and cooling the solid, the terms "hot-melt" or "melt-freeze" are used to describe the method of use. (See 4.2.3.)

Although the terms "setting" and "curing" are generally used synonymously in connection with both thermoplastic and thermosetting adhesives, the term "setting" is more common with thermoplastic adhesives, unless a chemical process such as polymerization is involved, when the term "curing" is more appropriate. Thermoplastic adhesives fall into many different chemical classes, but they all comprise predominantly linear macromolecules. Because of this common feature, their properties are, in many cases, similarly influenced by factors such as molecular weight and distribution, concentration of plasticizers and other additives and, in copolymers, the monomer ratio. Most thermoplastic adhesives are capable of bonding a wide variety of materials such as paper, wood and leather. A smaller number are capable also of bonding rubbers, metals and some plastics, the most notable exception being the silicone and fluorocarbon plastics (without special surface treatment). (17)

**4.3.2.1 Cellulose adhesives (cellulosics).** This group includes cellulose acetate, cellulose acetate butyrate and cellulose nitrate as cellulose esters, and cellulose ethers such as methyl, sodium-carboxyl-methyl, ethyl, hydroxyethyl and benzyl cellulose. The esters are used in solvent solutions. Cellulose acetate and cellulose acetate butyrate are water-clear and more heat-resistant but less water-resistant than cellulose nitrate. Cellulose acetate butyrate has better heat and water resistance than cellulose acetate and is compatible with a wide range of plasticizers. Cellulose nitrate is tough, develops strength rapidly, is water-resistant, bonds to many surfaces and discolors in sunlight. The dried adhesive (nitrocellulose) is flammable. As for the ethers, ethyl and benzyl cellulose can be used as hot-melt adhesives. Methyl cellulose is a tough material, completely nontoxic, tasteless and odorless, which makes it a valuable adhesive for food packages. It is capable of forming high-viscosity solutions at very low concentrations, so it is very useful as a thickening agent in water-soluble adhesives. Hydroxyethyl cellulose and sodium carboxymethyl cellulose can also be used as thickeners. The cellulose ethers have fair to good resistance to dry heat; water resistance varies from excellent for benzyl to poor for methyl cellulose. (17)(18)



## NIL-HDBK-691B

**4.3.2.2 Polyvinyl adhesives.** The vinyl group comprises the reactive part of a large number of compounds that produce thermoplastic polymers, most of which are extremely useful as adhesives. They include the following types.

**4.3.2.2.1 Polyvinyl ester adhesives.** The most important adhesive of this type is polyvinyl acetate (PVA). As an adhesive, it is used in solution, in aqueous dispersion and by hot-melt technique. In one form or another, it is probably the most widely-used thermoplastic adhesive. (See 4.2.2.1.4.) The well-known PVA emulsion glue, with a polymer content of about 50%, is a versatile industrial adhesive. After application to an adherend, water is eliminated from the emulsion through evaporation and absorption by an absorbent adherent, resulting in swollen particles coalescing to form a coherent adhesive film. Plasticizers are usually required, and these cause the most important shortcomings of PVA's, creep under stress at high temperatures. Bond strengths of up to several thousand psi are obtainable, but not under continuous loading.(10)

**4.3.2.2.2 Polyvinyl acetal adhesives.** Polyvinyl acetal is the generic name of a group of polymers that are products of reaction between polyvinyl alcohol and an aldehyde. In the preparation of these acetals, polyvinyl acetate is used, which is then partially hydrolyzed to the alcohol. (See 4.2.1.3.5.) As adhesives, the most important polyvinyl acetals are those from formaldehyde, namely the formal, and from butyraldehyde, the butyral. The properties of these polymers are largely dependent upon their molecular weights and on the degree of hydrolysis of the acetate. Considered as an adhesive by itself, that is to say not as one of the components of a two-polymer system, the butyral is much more important than the formal. This is because it is more readily soluble, has a lower melt-viscosity and is a softer and more flexible polymer, giving better peel strength and, therefore, higher apparent adhesion with thin adherends. In the two-polymer adhesive system (see 4.3.3.2.1), the formal is at least as important as the butyral.

The polyvinyl acetals give high strengths as hot-melt adhesives and, used in this way, can be considered as marginal structural adhesives, especially in adhering wood and metal. The most important hot-melt application of polyvinyl butyral is in making laminated safety glass. Although the polyvinyl acetals are normally considered to be thermoplastic polymers, they can be crosslinked by heat, especially in the presence of a trace of mineral acid, and thus made thermosetting. They can also be crosslinked chemically. Although small percentages of a number of chemical substances are sufficient to bring about crosslinking, the observed effect is small compared to that obtained with the much larger additions of thermosetting resins such as are used in the two-polymer systems, or by prolonged heating of the acetal.(17)

**4.3.2.2.3 Polyvinyl alcohol adhesives.** The polymer of polyvinyl alcohol is made commercially by acid hydrolysis of polyvinyl acetate. The monomer has not been isolated. According to the degree of polymerization and degree of hydrolysis, a wide range of polymers with molecular weights up to 200,000 may be prepared, having different solubilities in water. The solubility is dependent upon the percentage of acetate groups. Polyvinyl alcohols with higher acetate groups are less soluble in water. The limited resistance to water restricts the usefulness of polyvinyl alcohol as an adhesive. On the

## NHL-HDBK-691B

other hand, polymers with a low acetate content are resistant to nearly all organic liquids and, consequently, have an important place as adhesives in contact with greases and oils. It is possible to crosslink polyvinyl alcohol by heating with a small amount of a dicarboxylic acid. Such crosslinking results in increased water resistance. Polyvinyl alcohol is probably the most widely used water-soluble synthetic resin, and its chief use is in gluing porous materials such as leather, cloth and paper. Being nontoxic and odorless, it is especially useful in contact with food. It can also be used as a remoistenable adhesive. (17)

**4.3.2.2.4 Polyvinyl alkyl ether adhesives.** Polyvinyl alkyl ethers, some of which are elastomers, although not generally classified as synthetic rubbers, are vinyl polymers with valuable adhesive properties. The monomers are prepared from acetylene and an alcohol in the presence of an alkali alcoholate. Polyvinyl ethyl ether, polyvinyl n-butyl ether and polyvinyl isobutyl ether all range from extremely tacky semisolids to elastomeric solids; and, therefore, polymer blends can be made having properties appropriate to a wide range of adhesive applications. Polyvinyl methyl ether is a highly viscous liquid or semisolid. The largest use of the polyvinyl ethers is in pressure-sensitive adhesives. Polyvinyl stearyl ether is a waxy solid that is sometimes used as a modifier in adhesive compositions. The rubbery types of polymer are soluble in a wide range of organic solvents. In solution form they are used for sticking shoe soles and other high-tack applications. Copolymers of vinyl ethers have also been prepared, such as emulsion copolymers with acrylic esters or vinyl chloride and copolymers of lower alkyl vinyl ethers with acrylic esters. (17)

**4.3.2.2.5 Polystyrene adhesives.** Polystyrene is a vinyl monomer which polymerizes readily. Polystyrene as an adhesive is used in solution or as an aqueous dispersion. In both forms, it is necessary to limit applications to those where at least one of the adherends is porous, and one important example is the adhering of polystyrene tiles to a plaster wall. Polystyrene adheres very well to wood but not very well to metal nor to plastics, except polystyrene itself. For bonding the latter, a low-molecular-weight styrene polymer plus a peroxide catalyst is an excellent adhesive capable of polymerizing in the glue line. More valuable as an adhesive than polystyrene are the copolymers of styrene and butadiene, which result in adhesives much less brittle than polystyrene. These materials are commonly used in footwear for bonding leather and rubber soles. Styrene and -methyl styrene readily form copolymers with a large number of other monomers, including methyl vinyl ketone and methylene dimethacrylate. (17)

#### **4.3.2.3 Acrylic resin adhesives.**

##### **4.3.2.3.1 Acrylic esters.**

**4.3.2.3.1.1 Acrylate acid diesters.** An unusual type of chemically-blocked adhesive has become available in recent years and is used as an anaerobic sealant. This group of acrylate acid diesters is made up of essentially monomeric, thin liquids which polymerize to form tough plastic bonds when confined between closely-fitting metal parts. The self-hardening property of these adhesives which makes them unique is based on two factors: (1) contact with air keeps the monomeric adhesive liquid; and (2) metal surfaces accelerate the anaerobic polymerization out of contact with air. The acrylate

## MIL-HDBK-691B

acid diesters bond all common metals, glass, plastic parts and some plated-metal parts to themselves and to each other. Phenolic plastic parts and some plated-metal parts, such as cadmium and zinc, require a primer, which is essentially a heavy metal compound, such as ferric chloride. Polymerization or curing of the diesters is essentially a free-radical type addition polymerization. The most important use of anaerobic adhesives is as a liquid lock washer for screws and bolts. The cure can be accelerated by the use of activators or heat.(21) (See 4.4.5 for more detail.)

**4.3.2.3.1.2 Cyanoacrylate adhesives.** Cyanoacrylate adhesives are marginally thermosetting adhesives which form strong rapid-setting bonds between many materials without the need for heat or an added catalyst. The alkyl cyanoacrylate adhesives are now used to assemble electronic instruments, to bond gasket materials, apply strain gages, repair dentures, antiques and musical instruments, seal nuts and bolts, construct jigs, fixtures, displays and scale models. The simplest alkyl cyanoacrylate adhesive and the first to be offered commercially (in 1958) is based on a vinyl monomer identified as methyl 2-cyanoacrylate. This adhesive has been widely distributed in the United States and most other countries. In recent years, adhesives based on higher cyanoacrylic acid homologues, such as ethyl, propyl and butyl esters have been offered. Most of the cyanoacrylate adhesives are made by compounding the monomers with thickening agents, plasticizers and other additives. Moisture resistance of the methyl 2-cyanoacrylate is only fair. Some suppliers have claimed superior moisture resistance for the higher homologues of cyanoacrylate esters, but definitive data to substantiate this advantage is lacking. Ethyl cyanoacrylate has been shown to form stronger bonds than methyl cyanoacrylate between several different types of plastics substrates. The higher homologues, however, generally do not form bonds with as high strength as the methyl form. Most industrial uses for cyanoacrylate adhesives can be attributed to several bonding characteristics that set them apart from epoxies, cellulose and other adhesives. The outstanding features of the cyanoacrylates are:(22)

- o Very fast bond formation (down to 30 secs or less) can be achieved on a variety of metals, plastics, woods, elastomers and glass.
- o Very high bond strengths are possible (the thinner the bonding film, the stronger the bond). The bonds are also colorless.
- o No added catalyst or mixing is necessary; the one-component systems are simple to use.
- o Neither heat nor high pressures are needed, and no solvent must evaporate during bond formation. Contact pressure is usually sufficient, making clamps and weights unnecessary.
- o Very low shrinkage occurs in the bond, since neither heat nor solvent is used.
- o Cyanoacrylates are economical to use because of the low coverage needed. The volume price is high, but only a few milligrams (a very small drop) are needed for most bonds.

## NIL-HDBK-691B

When an alkyl cyanoacrylate is used as an adhesive, the formation of a bond takes place when the liquid monomer is converted to a solid polymer. Electronegatively disubstituted ethylenes, such as methyl 2-cyanoacrylate, polymerize by a base-catalyzed anionic mechanism. This polymerization is exothermic and can be initiated at low temperatures by very weak bases such as water and alcohols. Nearly all solid materials have sufficient traces of moisture adsorbed on their surfaces to trigger this polymerization. The key step in the successful application of a cyanoacrylate adhesive is the formation of a thin adhesive film between two well-mated surfaces. The thinner the film, the faster the rate of bond formation and the higher the bond strength. Table XI shows the bond strengths developed by methyl cyanoacrylate adhesive in a variety of substrates and combinations of substrates. The results, of course, depend on proper surface preparations. (22)

Generally, extensive testing of the cyanoacrylate bonds under varying conditions has demonstrated good bond aging properties. For example, rubber-to-rubber and rubber-to-metal bonds have weathered outdoors satisfactorily for more than seven years. Test bonds have also passed stringent water-immersion and salt-spray tests. Plastic-to-plastic and plastic-to-rubber bonds have aged satisfactorily for three to five years. Metal-to-metal bonds generally age rather poorly; but, under optimum bonding conditions where little of the glue line is exposed to moisture, the performance has been satisfactory. Generally, the cyanoacrylate adhesives have good resistance to various solvents. Immersion in alcohol, benzene, petroleum oils or gasoline for up to 30 days does not greatly affect the bond. Bonded rubber parts have good resistance to petroleum oils, gasolines, mineral-oil-type hydraulic fluids, diester-type lubricants and ethylene glycol-based fluids. Dilute alkaline solutions weaken the bond considerably; exposure to dilute acids weaken it to a lesser extent.

## MIL-HDBK-691D

TABLE XI. Shear strengths of various substrates bonded with methyl 2-cyanoacrylate adhesive.(22)

Substrate	Shear Strength	
	psi <sup>1</sup>	MPa <sup>1</sup>
Aluminum-aluminum (2024-S)	2700	18.6
Steel-steel (cold rolled)	3000 2	20.7 2
Aluminum-steel	1750 3	12.2 3
" "	80 4	0.55 4
Acrylic-acrylic	590 4	4.04 4
Rigid vinyl-rigid vinyl	900 4	6.21 4
Polyester glass-polyester glass	1100	7.59
Phenolic-phenolic	770 4	5.31 4
Nylon 6,6-nylon 6,6	650 4	4.52 4
Nylon 6,6-aluminum	500	3.44
Phenolic-aluminum	650	4.46
Butyl rubber-butyl rubber	70 4	0.48 4
SBK rubber-SBK rubber	90 4	0.62 4
Neoprene-neoprene	50 4	0.34 4
Natural rubber-natural rubber	50 4	0.34 4
Neoprene-phenolic	160 4	1.10 4
Butyl rubber-acrylic	170 4	1.16 4
Butyl rubber-polyester glass	100 4	0.69 4
SBK-polyester	110 4	0.759 4
Butyl rubber-steel	50 4	0.347 4
Butyl rubber-aluminum	70 4	0.486 4

- 1 Average lap-shear strength of 5 specimens aged for 24 hrs. at 73°F (23°C) following bond formation.
- 2 With surface activator; 10 min. cure.
- 3 Without surface activator; 10 min. cure.
- 4 Substrate failure.

Compared with other structural adhesives, the cyanoacrylates have relatively poor impact resistance. This is attributed principally to the thin, inflexible bond that is formed. It is especially noticeable when the adhesive is used between two rigid substrates, such as metals.

The methyl cyanoacrylate bond melts at approximately 330°F (165°C). Prolonged exposure of the bond to temperatures in this range results in gradual but permanent breakdown of the bond. Generally, the upper temperature for continuous bond exposure is about 170°F (77°C). At low-temperature extremes, bonds remain intact at least down to -65°F (-54°C). Grades of cyanoacrylates with specialized improved properties are now available. One has improved heat resistance (to 475°F or 246°C), high viscosity and very fast setting ability.(22)

## NIL-HDBK-691B

**4.3.2.3.2 Acrylic copolymer adhesives.** The most important acrylic copolymers are those from acrylonitrile. The acrylonitrile/butadiene copolymer has its widest use in the form of the latex and is used for adhering a variety of absorbent materials, including ceramic wall tiles. Another use is in making bonded (nonwoven) fabrics. Plasticized acrylonitrile/butadiene copolymer adhesives are used in pressure-sensitive tapes. This type of adhesive has rather low resistance to heat. Another acrylic copolymer of interest is that of butadiene and acrylic or methacrylic acid. This has been used as a rubber-steel adhesive.(17)

**4.3.2.4 Polyamide resin and nylon adhesives.** A polyamide is a polymer obtained by reacting a di- or poly-carboxylic acid with a di- or poly-amine. Two types of polyamide are of interest as adhesives: one is the Versamid type of polyamide resin, and the other is the nylon type of polyamide plastic.(17)

**4.3.2.4.1 Polyamide resin adhesives (Versamids).** These are relatively low-molecular-weight materials prepared by the condensation of dimerized vegetable fatty acids and polyamines. The resins vary from medium-viscosity liquids to hard thermoplastic solids. The liquids are well-known as hardeners for epoxy resins. The solid forms, containing few or no reactive amine groups, have adhesive properties by themselves. They have molecular weights from about 3000-9000 and melting points between 95° and 190°C (203 and 374°F). These materials are useful as hot-melt adhesives, either by themselves or in admixture with other components.(17)

**4.3.2.4.2 Nylon adhesives.** Used by themselves as hot-melt adhesives, the nylons are capable of giving fair adhesion to metal and a variety of other materials, including wood.(17)

**4.3.2.4.3 Nylon adhesives with traces of phenolics.** The adhesion of nylon, especially to metal, when used by the hot-melt technique, can be substantially improved by using a thermosetting phenol-formaldehyde resin in association with it. This combination of nylon and a phenolic resin is not included in the sections dealing with two-polymer adhesives (4.3.3.3), because very little phenolic resin is used (it may be as low as one percent), and the cohesive properties of the material are almost entirely those of the nylon. The quantity of phenolic resin is too small to modify the physical properties of the nylon, except at the adherend interface, where it increases adhesion by facilitating wetting. The most efficient way of using a nylon/phenolic adhesive system is to "prime" the face of each adherend with a thin coating of phenolic resin, evaporate the solvent and interpose a thin film of the nylon. The joint is then pressed under contact pressure at a temperature sufficient to melt the nylon and for a sufficient time to cure the phenolic resin.(17)

**4.3.2.5 Miscellaneous thermoplastic adhesives.** Most thermoplastic polymers can be used as hot-melt adhesives for bonding one material or another. (See 4.2.3 for additional more-detailed discussion.) The polycarbonates (which are really unconventional polyesters) and the formaldehyde linear polymers known as the polyacetals are examples of two that have been examined as adhesives, although better known as molding resins. The effect of priming the surfaces of the adherends with a phenolic resin follows the nylon pattern of behavior (see 4.3.2.4.3) in the case of the polycarbonates and brings about an increase



## LILL-HDEK-691B

in adhesive strength. With polyacetal, there is a considerable reduction in strength when the phenolic primer is used, indicating an extreme incompatibility. Polyethylene can be applied as a coating on cloth, cellophane or even certain metal foils and the polyethylene surfaces hot-welded. This naturally requires some degree of adhesion between the adherend and the polyethylene. The degree of adhesion shown by polyethylene to most adherends can be greatly increased by oxidizing the polyethylene, such as with a flame spray. (17) Polysulfides are sometimes considered as thermoplastic adhesives, supplied as Thiokols, but they are really rubbers and are considered briefly under Adhesive/Sealants (4.4.1.1.1) and Elastomeric Adhesives (4.4.7), especially Table XIII.

Other thermoplastic resins used as hot-melt adhesives include the following: ethyl cellulose, polyvinyl acetate and derivatives, ethylene-vinyl acetate copolymers (EVA), ethylene-ethyl acrylate copolymers (EEA), butyl methacrylates, polystyrene and copolymers, polyisobutylene, hydrocarbon resins, polypropylene, polyamides, polyesters, and phenoxies. The latter compounds are interesting in that, because of their high molecular weight (30,000), phenoxies cannot be maintained molten in a heated pot at reasonable temperatures for conventional hot-melt applications. A screw extruder which can apply both shear and heat to phenoxy resin is required to form a molten bead suitable for application. Phenoxy resins can be plasticized with diphenyl phthalate (DPP), tricresyl phosphate (TCP) or dicyclohexyl phthalate (DCHP) to give compositions suitable for formulation in hot-melt adhesives. Unplasticized phenoxy gives peel strengths of 15-20 lb/in. (3152-5253 N/m) in bonding Neolite to Neolite. Formulations with 60% DCHP raise the peel strength to 36-41 lb/in. (5076-5213 N/m). (21)(23)(24)

**4.3.3 Two-polymer adhesives (alloys).** The structural adhesives that have assumed increasing importance in recent years, chiefly in metal bonding, are the "two-polymer" adhesives that comprise a thermosetting and a thermoplastic polymer, including certain elastomers (see Table IX). Although each component has adhesive properties by itself, considered overall, the conjoint system forms a stronger and more versatile adhesive. The two-polymer systems have been particularly successful as film adhesives, which have been discussed in considerable detail in 4.2.5. The physical properties of each component polymer are modified by the addition of the other, and so the heat resistance of one may be increased, while that of the other is reduced. Similarly, the toughness of one may be increased by sacrificing the flexibility of the other. It is, therefore, possible to formulate a variety of adhesives with a wide range of characteristics by simply varying the ratio of one polymer to the other. By taking account of this ratio, some properties may be predicted. The first structural adhesives for metal to establish themselves technically and commercially were two-polymer adhesives. These were based on a polyvinyl acetal or a nitrile rubber, used in conjunction with a phenol-formaldehyde resin (vinyl-phenolic and nitrile rubber-phenolic). Their first important use was in adhering light alloys in aircraft construction. In the most widely-used two-polymer adhesive, the thermosetting component is a phenolic. Phenolic resins are generally compatible, although not easily miscible, with a number of thermoplastic polymers. Particularly good compatibility is shown between conventional alcohol-soluble phenolic resins and polyvinyl esters and acetals. Epoxies are of growing interest in two-polymer adhesive systems, and glycidyl ethers of bisphenol A and



## MIL-HDBK-691D

resorcinol are of special importance. The most important thermoplastic components are the polyvinyl acetals (polyvinyl formal and butyral) and synthetic rubber, in particular, nitrile rubber. Also of use as thermoplastic components and of increasing importance are the soluble nylons.(17)

Five of the most important two-polymer adhesives are discussed in detail above under 4.2.5.1 - 4.2.5.5. These adhesives, used in films and tapes, are (1) vinyl-phenolics, (2) epoxy-phenolics, (3) nitrile-phenolics, (4) nylon-epoxies and (5) elastomer-epoxies. This discussion will consider only alloys not mentioned previously. This includes neoprene-phenolic and epoxy-polysulfide. Neoprene-phenolic is available in solvent solutions and supported and unsupported film. Neoprene-phenolic adhesives are used to bond a variety of substrates. Curing is under heat and pressure. Normal service temperatures are from -70 to 200°F (-57 to 93°C). Because of their high resistance to creep and most service environments, neoprene-phenolic joints can withstand prolonged stress. Fatigue and impact strengths are excellent. Shear strength, however, is lower than that of other modified phenolic adhesives. Epoxy-polysulfides are available as two-part liquids or pastes that cure at room temperature or higher to rubbery solids that provide bonds with excellent flexibility and chemical resistance. These adhesives bond well to many different substrates. Shear strength and elevated-temperature properties are low, but resistance to peel forces and low temperatures is good. Of the five alloy-type adhesives discussed above, vinyl-phenolic is also available in solvent solutions and emulsions, liquid and coreacting powder; epoxy-phenolic is also available as a two-part paste; nitrile-phenolic and nylon-epoxy are also available in solvent solutions.(18)

**4.4 Additional classifications.** Some of the adhesive types discussed in this section have already been discussed above.

**4.4.1 Adhesives/sealants.** Sealants are materials used to exclude dirt, moisture and chemicals or to contain a liquid or gas. They are also used as surface coatings to protect against mechanical or chemical attack, to exclude noise, to improve appearance and to perform a joining function. Adhesives and sealants are often considered together because many formulations perform the same function. The distinction is that a "sealant" excludes and/or contains, while an adhesive is used for its adhesive or holding power. Modern sealants are formulated from synthetic elastomeric polymers, which, in uncured form, can be pourable or easily extrudable. Many of these modern sealants were commercially nonexistent in the early 1960's. Some of the polymers that have been used to formulate current sealants include butyl and polyisobutylene, chlorosulfonated polyethylene, chloroprene rubber, polyacrylate, silicone, polyurethane and polysulfide.(25)

**4.4.1.1 Types of sealants.** The large variety of formulations available make classification of sealant types difficult. For purposes of this discussion, they will be divided into (1) hardening type and (2) nonhardening types.(25)

**4.4.1.1.1 Hardening types.** These sealants can be divided into two classifications - rigid types, which cure or set up firm and have little or no resiliency, and flexible types, which remain flexible after cure. Common rigid sealants that are representative of this group are those based on compounds of epoxies, polyesters, acrylics, polyamides and polyvinyl acetates.

## MIL-HDBK-691B

Oleoresinous sealants have bases of linseed oil, tung oil, fish oil, etc., and fillers of clay and fiber. They can be formulated to dry "hard" or to remain pliable. Examples are calks and glazing compounds. Flexible sealants remain flexible after curing and generally are all elastomeric-based. Their range of flexibility varies considerably, as does their hardness - from 10A to 85D Shore durometer. Some of these sealants are true rubbers, many have good adhesive qualities, and all can be compounded to resist a variety of environmental conditions. The flexible sealants are either true elastomers - that is, they return to their original shape after being deflected - or are characterized by an ability to deform or stretch without tearing but do not return to their original shape. They may be either nonsolvent-release (two-part chemical reaction systems, catalyst-cured) or solvent-release. Typical nonsolvent-release systems include the following: (25)

- o polysulfide
- o polyurethane
- o silicone
- o modified epoxy
- o neoprene
- o acrylic (thermoplastic)

Typical solvent-release systems include the following thermoplastic elastomers:

- o polychloroprene (Neoprene)
- o chlorosulfonated polyethylene (Hypalon)
- o butyl

**4.4.1.1.2 Nonhardening types.** These soft-setting sealants stay "wet" after application, since plasticizers in them continuously come to the surface, and they never truly dry. They generally cannot be depended upon to perform a joining function, although some formulations are used as adhesives in very low-stress joints. These sealants are characterized by the "mastic" type of paste usually applied to seams with a trowel, spatula, brush or gun. Many consistencies are available. Some nonhardening sealants are formulated to such a consistency that they can be packaged in "tape" form. These are not adhesive-backed and can easily be thumbbed into place. Examples have butyl, acrylic, polybutene, asphalt and bituminous sealant bases. (25)

**4.4.1.2 Primers.** Primers are sometimes applied to metals before application of sealants to prevent corrosion (chromate primers are often used for this purpose) and to enhance adhesion, primarily through the use of polychloroprene. (26)

**4.4.2 Microencapsulated adhesives.** Microencapsulation is a method for separating a reactivating solvent or reactive catalyst from the adhesive base. The materials, whether liquids or solids, are packaged in very small "microscopic" capsules. When adhesion is desired, the encapsulated solvent is released by breaking the capsules through heat or pressure, and a tacky adhesive with instant grab is produced. Capsule solvent content varies with application, but, in most solvent-activated adhesives, 85-94% solvent by weight is contained within the capsule. The ratio of capsule to adhesive contained in a dry film is usually 1 to 3. In addition to solvents, small quantities of plasticizers or tackifiers may also be contained in the

## MIL-HDBK-691B

capsule. The solvents used are nonreactive to gelatin (the capsule material) and insoluble in water.

Heat-activated adhesives use a second principle to produce adhesion. A blowing agent is mixed with the solvent within each capsule. When heat is applied, the vaporization of the blowing agent ruptures the capsule, thus releasing either the entire adhesive or the solvent needed to make the adhesive tacky. A third major application of encapsulation in adhesives is the two-part system, such as in epoxy or polyurethane adhesives. The advantage of microencapsulation is the ability to store both the base resin and catalyst in the same container. The catalyst can be released by pressure or other means when it is desired to cure the adhesive. This system is best adapted to the thermosetting types of resins or elastomers. One problem has been the tendency of very active hardeners or catalysts to attack and dissolve or react with the capsule wall.(21)

This concept of microencapsulation of adhesives has not been used very much in recent years, according to a spokesman of the company developing it, because of problems associated with its use.(27) A report on this concept has been prepared under Picatinny Arsenal sponsorship and issued in 1971.(28)

**4.4.3 Electrically- and thermally-conductive adhesives.** Appropriate fillers have been used to produce adhesives with high thermal or electrical conductivity for specialized applications. Base resins include epoxies, urethanes, silicones and polysulfones. Epoxies are the most widely used, however.(29)

**4.4.3.1 Electrically-conductive adhesives.** Most adhesives of this type will have electrical conductivities (volume resistivities) in the range of 0.0005 - 0.01 ohm-cm. Some semiconductive adhesives have values of the order of 1 ohm-cm or higher. The reported values depend very much on the test method and type of test adherends used. Generally bulk resistivity techniques give much lower values than the methods involving thin gluelines, such as the ASTM technique (ASTM D-2739-72), where interfacial resistance plays an important role. Silver is preferable to gold as a filler because it is less costly and has lower resistivity. Under conditions of high humidity and DC potential, silver is reported to undergo electrolytic migration to the surface of the adhesive. Silver-coated copper microspheres do not migrate, nor does gold. The highest silver loading possible is somewhere in the vicinity of 85% by weight. Lower silver loadings cause conductivities to drop sharply, but may offer the advantage of higher adhesive strengths. Carbon (graphite) can also be used as a filler to give fairly low conductivities. Aside from silver and gold, other metallic fillers used in electrically conductive adhesives are nickel, aluminum and copper. Each of these metals presents particular compounding problems. Silver is often used in flake form; and it is, therefore, difficult to achieve particle-to-particle contact, as with spherical metal particles. Unfortunately, the stearate coating on silver flake tends to outgas at elevated temperatures and could contaminate critical parts, such as in microelectronic applications. Some silver products are uncoated and, therefore, will not evolve outgassed products. While silver has a tendency to migrate under certain conditions, copper and aluminum readily form oxide films which reduce electrical conductivity by hampering particle-to-particle contact.(29)

## HIL-HDEK-691B

**4.4.3.2 Thermally conductive adhesives.** A typical thermally conductive epoxy system used as an adhesive, as well as for other purposes, has a thermal conductivity of 7.55 BTU in/ft<sup>2</sup> hr °F (0.0026 cal/cm sec °C) and a volume resistivity of  $1.5 \times 10^{15}$  ohm-cm. Fillers used include alumina (aluminum oxide), beryllia (beryllium oxide), other unspecified inorganic oxides, boron nitride and silica. Theoretically, boron nitride should be an excellent thermally conductive filler, but weight loadings with this filler cannot go much over 40% in epoxy resins, and the products are always thixotropic pastes. Beryllia powder has an excellent conductivity by itself, but when mixed with a resin binder, its conductivity drops drastically. Beryllia is also high in cost and is toxic. Alumina is quite commonly used. (29)

**4.4.4 Premixed frozen adhesives.** In recent years reactive adhesives such as epoxies have been premixed, degassed and then quick-frozen in small squeeze tubes and syringes, ready to use, ranging in size upward from 1 cc. These adhesives are shipped packed in dry ice, along with a melting safety indicator. Storage upon receipt should be at -40°F (-40°C) or lower. This type of adhesive offers advantages in improved quality control and elimination of messy two-part mixing, with its resultant dermatitis possibility. (30)

**4.4.5 Anaerobic adhesives.** (31)(32)(33) An unusual type of chemically blocked adhesive has become available in recent years and has been promoted for use as a sealant. This group of adhesives is known as acrylate acid diesters (polyester-acrylic). These adhesives are essentially monomeric, thin liquids which polymerize to form a tough, plastic bond when confined between closely-fitting metal parts. The self-hardening property of the adhesives which make them unique is based on two factors: (1) contact with air before use keeps the monomeric adhesive liquid and (2) metal surfaces accelerate the anaerobic (meaning in the absence of air) polymerization out of contact with air. These materials bond all common metals, glass, ceramics and thermoset plastics to each other (see 4.3.2.3.1.1).

According to the Loctite patents, the preferred composition is tetraethylene glycol dimethacrylate monomer, cumene hydroperoxide as a catalyst (2%) and benzoic sulfimide (0.3%) as an accelerator. Because of the variability in the activity of the monomer and also to prevent premature gelling of the anaerobic monomer, benzoquinones may be added as stabilizers. Properly stabilized and containing the hydroperoxide catalyst and accelerator, the anaerobic adhesive will be stable for a year or longer in the presence of oxygen or air. This is generally accomplished by packaging in small polyethylene (oxygen-permeable) bottles, with an adequate air space. Polymerization or curing of the acrylate and diesters is essentially a free-radical-type addition polymerization. The presence of tetrafunctionality in the monomer can lead to crosslinking and a thermoset structure.

The first and probably still the most important use of the anaerobic adhesives is as a liquid lock washer for screws and bolts. Because of their excellent penetrating ability, they can be applied either before or after assembly. The prevailing torque for the strongest grades is many times greater than that of locknuts and lockscrews. The speed of cure of anaerobic adhesives is a relative property largely contingent upon the character of the parts being joined. Generally, the speed of cure of anaerobic products can be classified as fast (5 min - 2 hrs), medium (2 - 6 hrs) and slow (6 - 24 hrs),

## MIL-HDBK-691B

all at room temperature without primer use. Anaerobic adhesives can be speeded to faster cures with the application of heat. As a rule, the adhesive will cure outside the connection if temperatures exceed 200°F (93°C), despite the inhibiting effect of air. Heat cures up to 300°F (149°C) are practical. Anaerobic adhesives can be cured faster with accelerators or primers, especially on inactive surfaces. The recommended primers are degreasing solvents which, on evaporation, leave a light deposit of a catalyst which speeds curing.

These anaerobic adhesives fill all surface irregularities and tolerance gaps and effectively seal clearances up to 0.030 inches (0.76 mm). These compounds can be applied by high-speed applicators on moving production lines. The cured polyester film provides excellent chemical resistance to most liquids and gases within an operating-temperature range of -65° to 450°F (-55° to 232°C).

Anaerobic structural adhesives combining urethane-modified acrylic technology have been developed for more demanding applications. Such adhesives can be formulated to meet the requirements of MIL-A-132.

These adhesives are differentiated from the anaerobic sealants and thread-locking products in that the former products are designed to take normal (tensile) and shear loading, while the latter products find primary application in shear loading. In terms of adhesion theory, the anaerobic structural adhesive has both mechanical and chemical adhesives working for it, while the thread-locking and sealant-type products rely more heavily on mechanical adhesion. Table XII shows the improvement over the older resin systems. Because of brittleness, earlier anaerobic adhesives showed poor performance on gaps much larger than 0.020 inches (0.51 mm). While the greatest increases are in the areas of peel and impact, improvements are also apparent in the areas of elongation, tensile strength and fatigue resistance.

## MIL-HDBK-691B

TABLE XII. Properties of new and old anaerobic structural adhesives (modified after Murray). (31)

Property	Old	Improved
Tensile shear strength	1800-4000 psi (12.4-27.4 MPa)	2000-4500 psi (13.8-30.8 MPa)
Tensile strength	3000-8000 psi (20.7-55.2 MPa)	3000-10000 psi (20.7-69.0 MPa)
Impact strength	4-15 ft. lb/in <sup>2</sup> (8408-31530 J/m <sup>2</sup> )	8-25 ft. lb/in <sup>2</sup> (16816-52550 J/m <sup>2</sup> )
Fatigue strength	800-1200 psi (5.5-8.28 MPa)	800-1500 psi (5.5-10.3 MPa)
T-peel strength	3-15 pli (525-2627 N/m)	5-25 pli (876-4378 N/m)
Temperature range	-65°F to 400°F (-48°C to 204°C)	-80°F to 450°F (-62°C to 232°C)
Gap curing and bonding	to .020" (to 0.51 mm)	to .060" (to 1.5 mm)
Elongation	2%	50%

Previous anaerobic adhesives were limited to intermittent 400°F (204°C). Continuous aging at 450°F (232°C) is now possible. Tensile-lap-shear tests up to 3000 hours (4 months) with steel gave drop-offs from the original 3000 psi (20.7 MPa) down to 1900 psi (13.1 MPa), a reduction of only 37%. Further indications of environmental resistance are evidenced by salt-spray resistance tests. After 1500 hours over 50% of the original strength is still retained.

Military usage of anaerobic adhesive/sealants includes the following ordnance applications: (32)

- o Locking and sealing fuzes to ammunition rounds with automatic fuze assembly machine;
- o Wicking of sealant into assembled fuze parts to provide a lock between slip-fit parts;
- o Application to the base threads of the M-117 bomb. Adhesive acts as an anti-withdrawal device.
- o Automatic application to the windshields, fuze cap and cover and tracer port on the M-409 Sheridan round;
- o Automatic application to the fuze neck of the 40-mm, M-400 round;



## MIL-LDBK-691B

- o Use on the M-60 tank stud assembly;
- o Use with automatic indexing tables to simplify assembly of ammunition fuzes.

**4.4.6 Fast-setting adhesives.** These are the cyanocrylate adhesives, which set in periods ranging from a few seconds up. They are not high-strength structural adhesives and are used for specialized applications. (See 4.3.2.3.1.2 for detailed discussion.)

**4.4.7 Elastomeric adhesives.** Most of these are natural or synthetic rubber-based materials, usually with excellent peel strength but low shear strength. Their resiliency provides good fatigue and impact properties. Except for silicones temperature resistance is generally limited to 150 to 200°F (66 to 93°C), and creep under load occurs at room temperature. The basic types of elastomeric adhesives used for nonstructural applications are shown in Table XIII. These systems are generally supplied as solvent solutions, latex cements and pressure-sensitive tapes. Solvent solutions and latex cements require removal of the liquid vehicle from the adhesive before bonding can be carried out. This is accomplished by simple evaporation or forced heating. Some of the stronger and more environmentally resistant rubber-based adhesives require an elevated-temperature cure. Usually only slight pressure is needed with pressure-sensitive adhesives to achieve a suitable bond. Such adhesives are permanently tacky and flow under pressure to provide intimate contact with the adherend surface.

Pressure-sensitive tapes are made by placing these adhesives on a backing material, such as rubber, vinyl, canvas or cotton cloth. Upon application of pressure, the adhesive tightly grips the part being mounted as well as the surface to which it is affixed.

In addition to pressure-sensitive adhesives, elastomers are used in the construction industry for mastic compounds. Neoprene and reclaimed-rubber mastics are used to bond gypsum board and plywood flooring to wood framing members. These mastic systems cure by evaporation of solvent through the porous substrates.

Elastomer-adhesive formulation is more complex than that of other adhesives because of the need for antioxidant and tackifiers.(11)



MIL-HDBK-691B

TABLE XIII. Properties of elastomeric adhesives in nonstructural applications (modified after Patrie). (18)

Adhesive	Description	Curing Method	Usual Adherenda	Advantages	Limitations	Special Characteristics
Natural rubber (polyisoprene)	Solvent solutions, latexes and vulcanizing type	Solvent evaporation, vulcanizing type by heat or RT (two-part)	Natural rubber, masonite, wood, felt, fabric, paper, metal	Excellent resilience, moisture and water resistance	Becomes quite brittle with age; poor resistance to organic solvents; does not bond well to metals	Excellent tech, good strength, shear strength 30-160 psi (0.21-1.23 MPa); peel strength 0.56 pli (99.1 g/m). Surface can be tack-free to touch and yet bond to similarly coated surface
Reclaimed rubber	Solvent solutions, some water dispersible. Most are black; some gray and red	Evaporation of solvent	Rubber, sponge rubber, fabric, leather, wood, metal, painted metal, building materials.	Low cost, applied very easily with roller coating, spraying, dipping, or brushing; gains strength rapidly after joining, excellent moisture and water resistance	Becomes quite brittle with age; poor resistance to organic solvents	Low cost, widely used. Peel strength higher than natural rubber; failure occurs under relatively low constant loads
Butyl rubber	Solvent system, Latex	Solvent evaporation, chemical crosslinking with curing agents and heat	Rubber, metals.	Excellent aging characteristics; chemically crosslinked materials have good thermal properties	Metals should be treated with an appropriate primer before bonding. Attached by hydrocarbons	Low permeability to gases, good resistance to water and chemicals, poor resistance to oils, low strength
Polyisobutylene	Solvent solution	Evaporation of solvent	Plastic film, rubber metal foil, paper	Good aging characteristics	Attacked by hydrocarbons; poor thermal resistance	Sticky low-strength bonds; copolymers can be cured to improve adhesion, environmental resistance and elasticity; good aging; poor thermal resistance; attacked by solvents
Nitrile rubber	Latexes and solvent solutions compounded with resins, metallic oxides, fillers, etc.	Evaporation of solvent and/or heat and pressure of thermosetting	Rubber (particularly nitrile), metal, vinyl plastic	Most stable synthetic rubber adhesive, excellent oil resistance, easily modified by addition of resins	Does not bond well to natural rubber or butyl rubber	Most versatile rubber adhesive. Superior resistance to oil and hydrocarbon solvents. Inferior in tack range, but most dry tack-free, an advantage in pre-coated assemblies. Shear strength of 150-2000 psi (1.05-13.8 MPa), higher than neoprene, if cured

MIL-HDBK-691B

TABLE XIII. Properties of elastomeric adhesives in nonstructural applications (modified after Petrie)(1a) (Continued).

Adhesive	Description	Curing Method	Usual Adherenda	Advantages	Limitations	Special Characteristics
Styrene-butadiene rubber (SBR)	Solvent solutions and latexes. Because tack is low, rubber resin is compounded with tackifiers and plasticizing oils	Evaporation of solvent	Fabrics, foils, plastic film laminates, rubber and sponge rubber, wood	---	---	Usually better aging properties than natural or reclaimed. Low dead load strength, bond strength similar to reclaimed. Useful temperature range from -40°F (-40°C) to 160°F (71°C)
Polyurethane (see 4.3.1.6 and 4.2.1.1.6)	Two-part liquid or or paste	RT or higher	Plastics, metals, rubber	---	---	Excellent tensile shear strength from -40°F to 200°F (-24°C to 93°C) poor resistance to moisture before and after cure; good adhesion to plastics
Polysulfide (Thiokol)	Two-part liquid or paste	RT or higher	Metals, wood, plastic	---	---	Resistant to wide range of solvents, oils and greases; good gas impermeability; resistant to water, sunlight, ozone; retains flexibility over a wide temperature range; not suitable for permanent load-bearing applications
Silicone (see 4.3.1.6 and 4.2.1.1.7)	Solvent solution; heat or RT curing and pressure-sensitive; and RT vulcanizing solvents pastes	Solvent evaporation RT or elevated temperature	Metals, glass, paper, plastics and rubber, including silicone and butyl rubber and fluorocarbons	---	---	Of primary interest is pressure-sensitive type used for tape. High strength for other forms are reported from -100° to 500°F (-73° to 260°C); limited service to 700°F (371°C). Excellent dielectric properties
Neoprene (chloroprene)	Latexes and solvent solutions, often compounded with resins, metallic oxides, fillers, etc.	Evaporation of solvent	Metals, leather, fabric, plastics, rubber (particularly neoprene), wood, building materials	---	---	Superior to other rubber adhesives in most respects, strength, quick-setting, maximum temperature to 200°F (93°C), sometimes 350°F (177°C), aging, resistant to light, weather, mild acids and oils

## MIL-HDBK-691b

**4.4.8 Natural glues.** Natural glues include vegetable- and animal-based materials and are generally limited to use with paper, paperboard, wood and metal foil. While offering shear strengths ranging from 5-1000 psi (0.034-6.89 MPa), few of these adhesives retain their strength at temperatures over 212°F (100°C). Most natural glues possess poor resistance to moisture, vermin and fungus, but have good resistance to organic solvents. Typical adhesives within this group are discussed briefly below.

**4.4.8.1 Vegetable glues.** These adhesives are those which are soluble or dispersible in water and are produced or extracted from natural sources by relatively simple processes. Other adhesives, such as rubber cements, nitrocellulose and ethyl cellulose lacquer cements, are produced or extracted from plant sources, but are not water-soluble or water-dispersible and are not commonly considered as vegetable adhesives by the industry.(34)

**4.4.8.1.1 Starch.** Starch adhesives are derived primarily from the cassava plant, although corn, potatoes and other starches can be used. They are commonly prepared for use by dispersion in alkaline solutions, such as NaOH, with heating, and are then cooled to room temperature and applied as cold-press adhesives. They develop their strength by loss of water into the wood substrate. Tack is developed rapidly and normal wood processing is for 1-2 days at room temperature and 72-105 psi (0.5-0.7 MPa). Starch adhesives are also used for paper cartons and bottle labelling and stationery applications. Joint strengths are low compared to other vegetable-adhesive types, but are usually adequate for the normal applications. Starch adhesives have poor resistance to water and biodeterioration, but their resistance is improved by the addition of preservatives.(35)(36)

Military Specification MIL-A-17682E, "Adhesive, Starch", covers the requirements for an adhesive to be used for mounting paper targets to target cloth. The starch adhesives must be made from wheat, must be in fine-powder form, and must contain preservatives to prevent decomposition, weevil and mold growth in the package, and fermentation after mixing with water.

**4.4.8.1.2 Dextrins.** Dextrins are degradation products of starch produced by heating in the presence or absence of hydrolytic agents. Most commonly, acids or acid-producing substances are added to aid in decomposition. Other catalytic agents used include certain enzymes, alkali, and oxidizing agents. Dextrins can be used in formulations using many different substances and are used principally for adhesives, particularly for paper and paperboard. Laminating adhesives are usually made from highly soluble white dextrins and contain fillers such as clay, as well as alkalies or borax. Blends of white dextrins and gums are common. Where water resistance is desired, a urea-formaldehyde resin is added.(34)

Of particular interest for military applications is the Military Specification, MIL-A-13374D, "Adhesive, Dextrin, for Use in Ammunition Containers," which covers four classes of vegetable dextrin adhesives used in making spirally wound containers and chipboard spacers. The classes include:

- o a liquid adhesive in prepared form,
- o a cold-water-soluble type which must be mixed with water before use,

## MIL-HDBK-691B

- o a prepared dry adhesive which must be cooked with water before use,
- o a dextrin base in dry form to which additional optional ingredients may be added during preparation with water before use. The optional ingredients are alkaline chemicals, fillers, preservatives and defoamers.

4.4.8.1.3 Soyabean glue. Nitrogencus protein soyabean is the commonest and most representative of plant-protein adhesives derived from seeds and nuts, hemp and zein. This cheap glue is satisfactory for making semi-water-resistant plywood and for coating some types of paper. The protein from the soyabean is separated mechanically and used much like casein protein, with the addition of calcium salt to improve water resistance. Soyabean glues are used as room-temperature-setting glues to produce interior-type softwood plywood, where only limited moisture resistance is required. In recent years they have been largely replaced by protein-blend glues, such as combinations of soyabean and blood proteins, and by the newer versions of the phenolic-resin adhesive systems for such plywood. Cold-press bonding of plywood with the adhesive requires 4-12 hours at 102-145 psi (0.7001.0 MPa). Hot-press bonding requires 3-10 min at 212-284°F (100-140°C) and 145-218 psi (1.0-1.5 MPa) pressure. The water resistance of soyabean glues is limited, but like casein glues, they recover their strength on drying. Soyabean glues are susceptible to biodeterioration under humid conditions unless inhibitors are added. Heat resistance is poor. Their poor durability restricts their use to interior applications. They are sometimes extended with fillers for paper and paperboard laminating, cardboard-box fabrication, and particle binders. (35)(36)

4.4.8.1.4 Rosin. The most common form of rosin adhesive is colophony, a hard amorphous substance derived from the oleoresin of the pine. This material is used in solvent solution as a hot-melt mastic. It has poor resistance to water. Common rosin is subject to oxidation and has poor aging properties. It is brittle and is usually modified with plasticizers. Bond strengths are moderate and develop fairly rapidly. Applications are as a temporary adhesive in bonding paper and as a label varnish. Rosins are also used as components of pressure-sensitive adhesives based on styrene-butadiene copolymers and on hot-melt adhesives as tackifiers. Synthetic materials have replaced many of the rosin adhesives where the base material is scarce. (35)

A specialized form of rosin adhesive is Canada Balsam, covered by the recently cancelled Military Specification MIL-C-3469C, "Canada Balsam." This specification was for material prepared from oleoresin exuded from the Balsam fir tree, reasonably free from adulterants such as Oregon balsam, turpentine, colophony, spruce pitch, or similar substances and was designed for cementing optical elements. A common use is in permanently mounting glass cover slips to microscope slides. Canada Balsam is supplied in solid stick form and is dissolved in xylene in use. The specification for Canada Balsam has been superseded by a specification (MIL-A-3920C) calling for a thermosetting resin.

4.4.8.2 Glues of animal origin. These glues include glues derived directly and indirectly from animals, including insects and fish, and milk products. The general category should not be called "Animal Glues," since this term is a specialized form.

## HIL-HDBK-691B

**4.4.8.2.1 Casein glue.** Casein glues were developed about the time of World War I to meet the need for greater moisture resistance than could be obtained with the older animal and vegetable glues, although there are indications that this type of adhesive was used as early as 1365 BC. Casein is the protein of milk, from which it is obtained by precipitation. Dry-mix casein glues are the most common form, requiring only the addition of water. Casein glues are used at room temperature and set or harden by loss of water to the wood substrate and by a certain degree of chemical conversion of the protein to the more insoluble calcium derivative. In packaging, casein adhesives are used in applying paper labels to glass bottles. In woodworking, these glues are used primarily in laminating large structural timbers for protected interior applications, but are also used for general interior woodworking applications, including furniture. Casein glues are unsuitable for outdoor use, although they are more resistant to temperature changes and moisture than other water-based adhesives. Resistance to dry heat up to 158°F (70°C) is good, but under damp conditions the adhesives lose strength and are prone to biodeterioration (which can be inhibited by chlorinated phenols). Casein glues are often compounded with materials such as latex and dialdehyde starch to improve durability. Resistance to organic solvents is generally good. (35)(36)

**4.4.8.2.2 Blood albumen (blood glues).** The use of animal blood as an adhesive reaches backward into antiquity. Currently blood glues are used in a manner somewhat similar to casein glue. The proteins from animal blood obtained from slaughtering are precipitated out, dried, and made available as powders, which are then mixed with water, hydrated lime, or sodium hydroxide. The blood proteins undergo some heat coagulation so that they can be hardened by hot-pressing, as well as by loss of water. Typical processing conditions are 10-30 minutes at 150-248°F (70-120°C) and 72-102 psi (0.5-0.7 MPa) bonding pressure for plywood. These glues can also be used in cold-press applications. Blood glues were the first water-resistant plywood adhesives used during World War I. They were used in aircraft plywood before synthetic-resin adhesives became available. They are still used to a limited degree in making softwood plywood, sometimes in combination with casein or soybean proteins. Blood glues have also been used as extenders for phenolic-resin glues for interior-type softwood plywood. They are also used for porous materials such as cork, leather, textiles and paper and for such packaging applications as bonding cork to metal in bottle caps. (35)(36)

**4.4.8.2.3 Animal glues.** (Bone and hide glues). The term animal glue is normally confined to glues prepared from mammalian collagen, the principal constituents of skin, bone and sinew. Other types of glues obtained from animal sources are usually referred to according to the material they are derived from (casein, blood, fish, shellac). Bone glues are made from animal bones, while hide glues are made from tannery waste. These glues are available as liquid, jellies or solids in the form of flakes, cubes, granules, powder, cakes, slabs, etc., for reconstruction with water. They are used primarily for furniture woodworking, but are also used with leather, paper and textiles, and as adhesive binders for abrasive paper and wheels. Liquid hide glues are normally supplied with a gel depressant added to the molten glue mixture so that the dispersion remains liquid when cooled to room temperature for bottling. Such liquid glues harden only by loss of water to the adherend.

## NIL-HDBK-691B

Processing conditions of animal glues are dependent on the type glue. Animal glues set at temperatures in the range of 176-194°F (80-90°C), or at room temperature. Bonding pressures range from contact pressure to 145-203 psi (1-1.4 MPa) for hardwoods and 51-102 psi (0.35-0.70 MPa) for softwoods and are applied for periods from 5 minutes to several hours. Hide glues provide stronger joints than bone glues. Bond strengths usually exceed the strength of the wood and fibrous adherends. High-strength joints result where bonds are maintained under dry conditions, but structural applications are limited to interior service conditions. Gap-filling properties are useful where close-fit joints are not feasible, and in these situations filler powders are not required. (35)(37)

**4.4.8.2.4 Fish glues.** Fish glues are a byproduct of desalted fish skins, usually cod, and have properties similar to the animal skin and hide glues, which have largely replaced them in woodworking adhesives. Fish glues are available in cold-setting liquid form which does not gel at room temperature. Solvents such as ethanol, acetone or dimethylformamide may be added to assist the penetration of the glue into substrates which may already be coated or finished (e.g., certain paper, leather and fabrics). Fish glue tolerates repeated freezing and thawing without adverse effects in adhesion performance. Instant tack with good adhesion develops readily on remoistening dry glue films with cold water. Water resistance is conferred on dried glue films by exposure to formaldehyde vapors, which insolubilize the fish gelatin component. The main uses of fish glue are in the preparation of gummed tapes with animal/fish glue compositions and the bonding of stationery materials. Latex, animal glues, dextrans and polyvinyl acetate adhesives are sometimes modified with fish glues to improve wet-tack properties. High-purity fish glues are important photoengraving reagents. (35)

**4.4.8.2.5 Shellac.** Shellacs are thermoplastic resins, derived from insects, used in alcoholic solvent solution or as hot-melt mastics. They have good electrical insulating properties, but lack flexibility unless compounded with other materials. They are resistant to water, grease and oil. Bond strengths are moderate. Shellacs are used to bond porous materials, metals, ceramics, cork and mica. They are also used as adhesive primers for metal and mica, for insulating sealing waxes, and as components of hot-melt adhesives. Shellacs are the basic material in de Khotinsky cement. Their use has declined because of their high cost. (35)

**4.4.9 Inorganic glues.** Inorganic adhesives and cements have wide industrial application because they are durable, fire-resistant, and inexpensive when compared with organic materials. A distinction between adhesives and cements is not important. They are differentiated from enamels and ceramics by the presence of a clearly separated bonding agent, forming a thin film uniting surfaces nearly in contact. Inorganic cements may be thought of as rigid, nonstoichiometric, three-dimensional compositions forming a continuous skeleton between the adherends. These materials form strong resistant bonds for special applications and are still widely used. The characteristics of some of the more important commercial materials are summarized below. (38)



## NIL-HDBK-691B

**4.4.9.1 Soluble silicates.** The soluble silicates available commercially are the potassium and sodium silicates, particularly the latter. Sodium silicate is frequently called "water glass," and is ordinarily supplied as a colorless, viscous water solution. These adhesives display little tack, and positioning pressure must be applied to hold substrates together until the bond is sufficiently dry. The dry adhesive is brittle and water-sensitive, and until atmospheric carbon dioxide forms an insoluble material, the glue-line may be dissolved out by water. Water resistance can be improved by applying suitable aluminum salts to substrates such as paper prior to bonding. Sodium silicate is very resistant to high temperature (to 2012°F or 1100°C) and, being inorganic, is naturally resistant to mold growth and bacterial attack.

The main use of soluble silicate adhesives is for bonding paper and in the manufacture of corrugated boxboard, boxes and cartons. Where rapid absorption of water into the paper permits the use of high-speed machine operations, kaolin clay (8-10%) is frequently added to raise the viscosity and prevent excessive penetration of the adhesive into the cardboard. Other applications for silicates are:

- o Wood bonding (shear strengths up to 2900 psi or 20 MPa are possible) and manufacture of low-grade plywood.
- o Bonding metal sheets to various substrates (copper to walls, plywood to steel, aluminum foil to paper, aluminum to asbestos in oven doors, and metals to glass.
- o Bonding glass to glass, porcelain, leather, textiles, stoneware, etc.
- o Bonding glass-fiber assemblies; optical glass applications; manufacture of shatter-proof glass; binding solutions (potassium silicate) for phosphor coatings; pigments on glass substrates.
- o Bonding insulation materials based on wood, metals, ceramics, asbestos, fiberglass, mica, kieselguhr, etc. where fire-resistant properties of silicates are useful.
- o Refractory cements for tanks, boilers, ovens, furnaces; acid-proof cements.
- o Fabrication of foundry molds; briquettes and abrasive polishing wheel cements.

In addition to these applications, the soluble silicates may be reacted with silicofluorides or silica, to produce acid-resistant cements. These products have low shrinkage properties and a thermal expansion approaching that of steel. Compressive strengths approach 7252 psi (50 MPa), but the strength is lost at 752°F (400°C). The cements have poor resistance to strong alkaline solutions. (35)(38)

**4.4.9.2 Phosphate cements.** These cements are based on the reaction product of phosphoric acid with other materials, such as sodium silicate, metal oxides and hydroxides, and the salts of basic elements. Zinc phosphate is the most important metal phosphate cement, and is widely used as a dental cement. This

## LIL-HDBK-691B

material is also modified with silicates to produce the so-called "permanent materials" used for fillings. Compressive strengths up to 29,000 psi (200 MPa) are typical of these cements which are formulated to have good resistance to water (saliva). Copper phosphates are similarly employed, but have a shorter use-life and are used primarily as dental fillers for their antiseptic qualities. Other metal phosphates are aluminum, magnesium, chromium and zirconium. (35)

**4.4.9.3 Basic salts (Sorel cements).** A Sorel cement is a basic salt of a heavy metal, usually magnesite or magnesia cement or magnesium oxychloride cement. It is suitable for dry locations where 2-8 hours hardening will permit immediate use for bonding many refractory materials, ceramics and glass. The final strength will be in the range of 7000-10000 psi (48.3-68.9 MPa). Magnesium oxychloride is an inorganic adhesive notable for its heat and chemical resistance. It is usually supplied as a two-part product (magnesium oxide and magnesium chloride) which is mixed at the time of use. Copper is added to overcome the tendency to dissolve in water. These cements resist damage by cooking fats and greases, repel vermin, and prevent the growth of molds and bacteria. They conduct static electricity from flooring and similar materials. (35)(39)

**4.4.9.4 Litharge cements.** Mixtures of glycerine and litharge (PbO) are used as adhesives in the repair of tubs and sinks, pipe valves, glass, stoneware and ammonia gas conduits. A mixture of 1 part slightly diluted glycerine with 2-3 parts of lead oxide requires approximately 1 day to form what is considered a crystalline compound. This cement resists weak acid and nitric acid, but reacts with sulfuric acid. Litharge cements have also been used as ceramic seals in the potting of electronic equipment. (35)(39)

**4.4.9.5 Sulfur cements.** Liquid sulfur (melting point 230°F or 110°C) may be regarded as an inorganic adhesive of the hot-melt type. Service temperature should not exceed 199°F (93°C) because of a marked change in the expansion coefficient at 205°F (96°C) as a result of a phase change. Physical properties are improved by the addition of carbon black and polysulfides. Tensile strengths of about 580 psi (4.0 MPa), falling to 435 psi (3.0 MPa) have been reported after 2 years exposure in water at 158°F (70°C). The principal use of sulfur cements is for acid tank construction, where high resistance to oxidizing acids, such as nitric and hydrofluoric acid mixtures at 158°F (70°C) is required. Resistance to oleic acid, oxidizing agents and strong bases or lime is poor. Adhesion to metals, particularly copper, is good. (35)

**4.4.9.6 Hydraulic cements.** The principal types of cements which set by hydration are calcium silicate or Portland Cement, calcium aluminate cements, pozzuolanic cements, slag cements, natural limesilica cements, barium silicate and barium aluminate cements, ferrites and ferrates, and lime and gypsum cements. (Plaster of Paris and Keene's cement). The hydraulic cements are important building materials for buildings, roads, bridges and other outdoor construction work, rather than adhesives, as the term is conventionally understood. Plaster of Paris is used for both outdoor and indoor application. (35)(39)

## NIL-HDBK-691B

**4.5 Factors to be considered in adhesive selection.** There is no all-purpose adhesive. The best adhesive for a particular application will depend on the following:(18)

- o The materials to be bonded (adherends)
- o The service and assembly requirements
- o The economics of the bonding operation

By using these factors as criteria for selection, the large number of commercially available adhesives can be narrowed down to a few possible candidates. All the properties desired are often not available in a single adhesive system. In these cases, a compromise adhesive can usually be selected by deciding which properties are of primary importance.(18)

**4.5.1 Adhesive substrates (adherends).** The materials to be bonded are a prime factor in determining which adhesive is to be selected. Some adherends, such as stainless steel or wood, can be successfully bonded with a great many adhesive types; others, such as nylon, can be bonded with only a few. Typical adhesive-adherend combinations are listed in a number of tables published in various sources. These listings are intended only as guidelines to show common adhesives which have been successfully used in various applications. The selections are listed without regard to strength or service requirements. The lack of a suggested adhesive for a particular substrate does not necessarily signify that the resultant bond will be poor, only that information is not readily available on that particular combination.(16)

When these tables are used to show recommended adhesives for two different adherends, the adhesives selected may bond well, but the resultant joints may be inferior because of a mismatch in the thermal-expansion coefficients. In such cases, a resilient adhesive should be carefully chosen to compensate for the stress resulting from such a mismatch.(18)

**4.5.2 Service requirements.** Adhesives must also be selected with regard to the type of stress and environmental conditions to which they will be exposed. These factors will further limit the number of candidate adhesives to be considered. Information on the environmental resistance of various adhesive classifications will appear in Chapter 15. The chosen adhesive should have strength enough to resist the maximum stress during any time in service with reasonable safety factors. Overspecifying may result in certain adhesives being overlooked which can do the job at lower cost and with less demanding curing conditions.

**4.5.3 Assembly requirements.** Adhesives require time, pressure, and heat, singly or in combination, to achieve hardening. Curing conditions are often a severe restricting factor in the selection of an adhesive. Typical production factors involved in assembly are the equipment available, allowable cure time, pressure required, necessary bonding temperature, degree of substrate preparation required, and physical form of the adhesive. Table XIV lists the available forms and processing requirements of adhesives in general. See Chapters 5-7 for more details.

## HIL-HDBK-691B

**TABLE XIV. Available forms and processing requirements for adhesives.(18)**

**Common forms available**

- o Solid
- o Film
- o Paste
- o Liquid
- o Solvent solution
- o Emulsion

**Method of cure**

- o Solvent release
- o Fusion on heating
- o Pressure-sensitive
- o Chemical reaction

**Processing conditions**

- o Room temperature
- o Elevated temperature
- o Bonding pressure required
- o Bonding pressure not required

**4.5.4 Cost requirements.** Economic analysis of the bonding operation must consider not only the raw materials cost, but also the processing equipment necessary, time and labor required, and cost incurred by wasted adhesive and rejected parts. Raw materials cost for the adhesive should be based on the more realistic cost per bonded part, rather than price per weight or volume, because of variations in solids and density of adhesives.(18)

**4.5.5 Time-related requirements.** The following factors should also be considered in selecting an adhesive:

**4.5.5.1 Storage life (shelf life).** This is the period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use.(40)

**4.5.5.2 Working life (pot life).** This is the period of time during which an adhesive, after mixing with catalyst, solvent, or other compounding ingredients, remains suitable for use.(40)

**4.5.5.3 Tack range (open time) (open-tack time) (tack time) (tack-free time).** This is the period of time in which an adhesive will remain in the tacky-dry condition after application to an adherend, under specified conditions of temperature and humidity. In the tacky-dry condition, the volatile constituents have evaporated or have been absorbed sufficiently to leave the adhesive in a tacky state. Two films of adhesive will bond to each other during this period of time without the need for reactivation of the surfaces with either heat or solvent.(40)(41)

## NIL-HDBK-691B

**4.5.5.4 Assembly time.** This is the time interval between the spreading of the adhesive on the adherend and the application of pressure or heat, or both, to the assembly. For assemblies involving multiple layers or parts, the assembly time begins with the spreading of the adhesive on the first adherend. Open assembly time is the time interval between the spreading of the adhesive on the adherend and the completion of assembly of the parts for bonding. Closed assembly time is the time interval between completion of assembly of the parts for bonding and the application of pressure or heat, or both, to the assembly.(40)

**4.5.5.5 Curing time.** This is the period of time during which an assembly is subjected to heat or pressure, or both, to cure the adhesive. Further cure may take place after removal from the conditions of heat, or pressure, or both.(40)

**4.5.5.6 Drying time.** This is the period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat or pressure, or both.(40)

**4.5.5.7 Joint conditioning time (joint-aging time).** This is the time interval between the removal of the joint from the conditions of heat or pressure, or both, used to accomplish bonding, and the attainment of approximately maximum bond strength.(40)

**4.5.5.8 Setting time.** This is the earliest time for which an adhesive joint may be handled without endangering the structural integrity of the joints. For a cured adhesive, cure is only partially complete at this point.(40)

**4.5.5.9 Earliest-handling time.** This is the earliest time for which an adhesive joint may be handled without clamps without endangering the structural integrity of the joint. For a cured adhesive, cure is only partially complete at this point.

**4.6. Adhesives for metals.** The chemical types of structural adhesives for metal bonding have been described earlier in this handbook. Since organic adhesives readily wet most metallic surfaces, the adhesive selection does not depend as much on the type of metal substrate as on other bonding requirements. Selecting a specific adhesive from a table of general properties is difficult because formulations within one class of adhesives may vary widely in physical properties. General physical data for structural metal adhesives are given in Table XV. This table may prove useful in making preliminary selections or eliminating obviously unsuitable adhesives. Once the candidate adhesives are limited to only a few types, the designer can search more efficiently for the best bonding system. Nonstructural adhesives for metals include elastomeric and thermoplastic resins. These are generally used as pressure-sensitive or hot-melt adhesives. They are noted for fast production, low cost, and low-to-medium strength. Typical adhesives for nonstructural-bonding applications have been described above. Most pressure-sensitive and hot-melt cements can be used on any clean metal surface and on many plastics and elastomers.(18) To achieve optimum joint strength, metals require surface treatment prior to bonding. Chapter 5 offers guidelines for such treatments. Recommended adhesive selections for plastics are listed in Chapter 8.

MIL-HDBK-691B

TABLE IV. Properties of structural adhesives used to bond metals (modified after Petrie). (18)

Adhesive	Service Temperature, °F	Min	Shear strength, psi	Min	MPa	Peel strength, lb/in	Impact strength, ft-lb/in	Creep resistance	Solvent resistance	Moisture resistance	Type of bond
Epoxy-amine	150°F(66°C)	-50°F(10°C)	3,000-5,000	20.7-34.5	Poor	Poor	Good	Good	Good	Good	Rigid
Epoxy-polyamide	150°F(66°C)	-60°F(15.6°C)	2,000-4,000	13.8-27.6	Medium	Good	Good	Good	Good	Medium	Tough & moderately flexible
Epoxy-anhydride	300°F(149°C)	-60°F(15.6°C)	3,000-5,000	20.7-34.5	Poor	Medium	Good	Good	Good	Good	Rigid
Epoxy-phenolic	350°F(177°C)	-423°F(-253°C)	3,200	22.1	Poor	Poor	Good	Good	Good	Good	Rigid
Epoxy-nylon	180°F(82°C)	-423°F(-253°C)	6,500	44.8	Very Good	Good	Medium	Good	Good	Poor	Tough
Epoxy-polyaniline	150°F(66°C)	-100°F(-73.3°C)	3,000	20.7	Good	Medium	Medium	Good	Good	Good	Flexible
Nitrile-phenolic	300°F(149°C)	-100°F(-73.3°C)	3,000	20.7	Good	Good	Good	Good	Good	Good	Tough & moderately flexible
Vinyl-phenolic	225°F(107°C)	-60°F(-51°C)	2,000-5,000	13.8-34.5	Very Good	Good	Medium	Medium	Medium	Good	Tough & moderately flexible
Neoprene-phenolic	200°F(93°C)	-70°F(-56.7°C)	3,000	20.7	Good	Good	Good	Good	Good	Good	Tough & moderately flexible
Polyimide	600°F(316°C)	-423°F(-253°C)	3,000	20.7	Poor	Poor	Good	Good	Good	Medium	Rigid
Polybenzimidazole	500°F(260°C)	-423°F(-253°C)	2,000-3,000	13.8-20.7	Poor	Poor	Good	Good	Good	Good	Rigid
Polyurethane	150°F(66°C)	-423°F(-253°C)	5,000	34.5	Good	Good	Good	Good	Medium	Poor	Flexible
Acrylate acid diester	200°F(93°C)	-60°F(-51°C)	2,000-4,000	13.8-27.6	Poor	Medium	Good	Good	Poor	Poor	Rigid
Cyanoacrylate	150°F(66°C)	-60°F(-51°C)	2,000	13.8	Poor	Poor	Good	Good	Poor	Poor	Rigid
Phenolic	180°F(82°C)	-70°F(-56.7°C)	2,500	17.2	Medium	Good	Good	Good	Poor	Good	Tough & moderately flexible
Thermosetting acrylic	250°F(121°C)	-60°F(-51°C)	3,000-4,000	20.7-27.6	Poor	Poor	Good	Good	Good	Good	Rigid



## MIL-HDBK-691B

**4.7 Adhesives for plastics.** Bonding of plastics is generally more difficult than metal bonding because of the lower surface energy of polymeric substrates. But most thermoplastics can be joined by solvent- or heat-welding, as well as with adhesives. Common assembly methods for plastics include: (18)

- o Mechanical fastening
- o Adhesive bonding
- o Induction bonding
- o Solvent cementing
- o Spin welding
- o Thermal welding
- o Ultrasonic welding

**4.7.1 Solvent cementing.** This technique, used primarily on relatively amorphous thermoplastic resins, will be discussed in detail in Chapter 7.

**4.7.2 Adhesive bonding.** Adhesive bonding is the easiest and usually the best method of fastening one type of plastic to another type, or to a different substrate when solvent cementing cannot ordinarily be used. Thermoplastic and rubber-based contact adhesives are often used to bond plastics when the application is nonstructural. These adhesives are generally less sensitive to heat and solvents than the parent plastic. Thermosetting adhesives such as epoxies or polyurethanes are commonly used for structural applications. When bonding plastics to almost any other type of material, the mismatch in thermal-expansion coefficients can impose great stress on the bond during thermal cycling. Thus, adhesives for plastics are generally resilient materials to allow distribution of stress at temperature extremes. To achieve optimum joint strength, plastics require surface treatments prior to bonding. Chapter 5 offers guidelines for such treatments. Recommended adhesive selections for plastics are listed in Chapter 6. (18)

**4.7.3 Thermal-welding techniques.** (42)(43) A limited amount of discussion will be given in this handbook to thermal-welding methods. In thermal welding, (or simply welding, as it is often called), there is always a molten-liquid phase of the plastic at some stage of the bonding process. Strictly speaking, this is not a form of adhesive bonding, unless one regards the molten plastic as a form of adhesive. The various techniques used will be outlined here briefly. Thermal-welding techniques may be roughly divided into those methods in which heat is applied directly to the plastic, and those in which some form of energy is applied which acts on the plastic in such a way as to cause heating at the interface or in the plastic as a whole. The required energy can be applied in many forms.

**4.7.3.1 Direct-heating methods.** Welding by direct application of heat provides an advantageous method of joining many thermoplastics that do not degrade rapidly at their melt temperatures. The methods used are as follows:

## MIL-HDBK-691E

**4.7.3.1.1 Hot-plate welding.** In this method the plastic to be bonded is heated by pressing the bonding surfaces into a flat hot plate, usually aluminum, with a non-stick coating of PTFE. The two molten surfaces are then pressed together and held under pressure until the bond has cooled. This method is normally used to join two parts of the same plastic, but it can be used to join different plastics, or even plastics to metal, by heating the surface when the molten plastic acts as a hot-melt adhesive on the other substrate. Careful control of temperature is necessary, and a list of some of the recommended temperatures is as follows:

For:	Use:	For:	Use:
ABS	450°F (232°C)	PPO, modified	525°F (277°C)
Acetal	500°F (260°C)	Polypropylene	400°F (204°C)
HD polyethylene	390°F (199°C)	Polystyrene	420°F (216°C)
LD polyethylene	360°F (182°C)	Nylon 6,6	475°F (246°C)
Phenoxyl	550°F (288°C)	PVC	450°F (232°C)
Polycarbonate	650°F (343°C)	SAN	450°F (232°C)
PPO	650°F (343°C)		

**4.7.3.1.2 Hot-gas welding.** This is a technique used mainly for joining plastic sheet (although other shapes can also be handled) using guns of about 400-600 watt input electricity (or burning butane or propane if gas heating is used). The electric guns are usually more portable and easier to use. For easily oxidized plastics such as polyethylene and polypropylene, either nitrogen or another inert gas must be used, but for PVC dry air is acceptable. A welding rod of the same material as the plastic to be bonded is used to produce a fillet, the design of which is of considerable importance. A large difference between melting and decomposition temperature is necessary if this technique is to be used. The most commonly used plastics are: low- and high-density polyethylene, polypropylene, and PVC. Acrylics and polyamide have also been joined by this method.

**4.7.3.1.3 Heated-tool welding.** This is essentially the same as hot-plate welding, except that it is broader in scope. Heat is applied to the surfaces of the plastics to be joined by bringing them into contact with a heated-metal plate or other tool and heating them until there is a build-up of molten material. The surfaces are then joined together, removed from the heat, and cooled. This method is used primarily with acrylics and plasticized PVC, although it is beginning to be used more and more with polyethylene and polypropylene. The method is widely used in welding pipe and large tubing.

**4.7.3.1.4 Radiant-heat welding.** In this method the components are passed one on each side of radiant heaters. This method can be applied to surfaces which are not flat, providing good mating surfaces are used. In some cases heat shields are used to protect areas which should not be heated.

## MIL-HDBK-691B

**4.7.3.1.5 Resistance-wire welding.** In this technique, a resistance wire is placed in the part, and while the faces are pressed together, a current is passed through which heats the wire and melts the plastic surfaces. Normally this method would be used where the plastic is joined to itself.

**4.7.3.1.6 Molten-polymer (extruded-bead) sealing.** In this technique, two sections of a thermoplastic are joined by extruding a bead of the same material between them. The extruded bead contains sufficient heat to cause the surfaces adjacent to the bead to fuse. A homogeneous structure results as the thermoplastic cools.

**4.7.3.2 Indirect-heating methods.** Indirect heating occurs when some form of energy is applied to the joint which acts on the plastic to cause heating at the interface or in the plastic as a whole. The methods used are as follows:

**4.7.3.2.1 Dielectric bonding (high-frequency bonding).** This technique is most widely used for bonding PVC to itself or to other compatible surfaces. However, any material with a sufficiently high dielectric-loss factor can be welded in this way. As the name implies, the thermoplastic to be sealed is placed in the position of a dielectric between the two electrodes. These transmit a high-frequency current to the thermoplastic and at the same time, exert the necessary pressure on it. When polar plastic materials are exposed to this high-frequency current, heat is generated throughout the material because of the friction between the molecules shifting back and forth in response to the electromagnetic field. With the combination of heat and pressure, a seal is effected.

**4.7.3.2.2 Induction heating (electromagnetic bonding).** In this method, an induction coil of the type used in metal heating is used in combination with iron or nickel, where heat is produced by eddy currents and hysteresis. The metal can be in the form of a grid or as a metal powder mixed into the plastic, which may be pre-molded into gasket form. This method is useful where small complex shapes are involved, but should not be used where strong corrosive agents could come into contact with the material.

**4.7.3.2.3 Ultrasonic welding.** In this method, a transducer, acting through a resonating horn, hammers the plastic surfaces together and this, combined with transverse slipping, causes very rapid heat build-up and diffusion of the surface. Ultrasonic welding is very fast and the surface need not be very clean. Rigid plastics with high moduli of elasticity are best. The horn should be placed perpendicular to the center of the part surfaces. Plastics can actually be welded through a vacuum-metallized layer. Metal inserts can be forced into place in this plastic by this technique. Except for this special technique, it can only be used for bonding plastics to plastics.

**4.7.3.2.4 Ultrasonic adhesive bonding.** This is a specialized technique usable on thermoplastics or thermosets, in which the ultrasonic action is in a thermoplastic or a thermosetting adhesive. (See 6.5.3.1.9)

**4.7.3.2.5 Spin or friction welding.** This technique utilizes the frictional heat produced when the surfaces of the same plastic are rotated together. One section is power-rotated against another part held stationery. Rubbing

## MIL-HDBK-691B

contact is maintained at a speed and pressure which generate frictional heat and melt the component surfaces. When sufficient melt is obtained, pressure is increased to squeeze out all bubbles. The stationary part is then released and the powered spindle stopped, halting the rubbing action and allowing the weld to cool under pressure. The frictional heat generated by spin-welding produces surface melting, while the temperature of the material immediately beneath the surface remains relatively unchanged. For many applications, no surface preparation is necessary. The average lineal velocity of the joint is normally about 20 ft/sec (6.1 m/sec) and the average pressure about 200 psi (1.38 MPa)

**4.8 Adhesives for elastomers.** The selection and use of adhesives for elastomeric materials can be guided by generalizations based on past experience. However, adhesive bonding of elastomers is, and probably will remain, an empirical art. This is due to the almost limitless scope of elastomers, adhesives, primers, substrates and intended usages available. Thus, the best rule to follow in the majority of adhesive applications is the actual testing of the strength of the bond obtained. This must be done or simulated, using the actual exact materials and processes of construction to be used in the resulting end item.(44)

**4.8.1 Vulcanized elastomers.** Bonding of vulcanized elastomers to themselves and to other materials is generally completed by using a pressure-sensitive adhesive derived from an elastomer similar to the one being bonded. Flexible thermosetting adhesives such as epoxy-polyamide or polyurethane also offer excellent adhesive strength to most elastomers. Surface treatments are discussed in 5.3.5.3. Elastomers vary greatly in formulation from one manufacturer to another. Fillers, plasticizers, antioxidants, etc., may affect the adhesive bond.(18) (See 8.3 for a general discussion of adhesive bonding of elastomers.)

**4.8.2 Unvulcanized elastomers.** Unvulcanized elastomers may be bonded to metals and other rigid adherends by priming the adherend with a suitable air- or heat-drying adhesive before the elastomer is molded against the adherend. The most common elastomers to be bonded in this way (also called vulcanized bonding) include nitrile, neoprene, urethane, natural rubber, SBR, and butyl rubber. Less common unvulcanized elastomers such as the silicones, fluoro-carbons, chlorosulfonated polyethylene, and polyacrylate are more difficult to bond. However, recently developed adhesive primers improve the bond of these elastomers to metal. Surface treatment of the adherend before priming should be according to good standards (usually by sandblasting, grit blasting, chemical cleaning, etc. of the substrate) to provide a clean surface free from oils, greases, oxides, release agents, etc. In this type of bonding, adhesion is obtained from a vulcanized bond accomplished simultaneously with the cure of the elastomer itself. This type of bond is generally superior to the type of adhesive bond described under 4.8.1.(18)(44)

**4.9 Adhesives for wood.** Until nearly the middle of the 20th century, glues based on naturally-occurring materials were the principal adhesive-bonding agents for wood. The basic ingredients for these were generally by-products of meat processing (for animal and blood glues), or casein, soybean and starch. In the early 1930's, synthetic resin adhesives began to appear on the

## MIL-HDBK-691B

woodworking scene, and because of their versatility and other advantages, they found widespread use in the woodworking industry. Some synthetic resin adhesives, when properly used, will produce joints that remain as strong as the wood, even in unprotected exposure to the weather. Most of them, and most of the "natural" glues, will produce adequate joints for normally dry interior use. Synthetic adhesives used for wood include: Phenolic resins (high-temperature-setting, intermediate-temperature-setting, resorcinols, and phenol-resorcinols), urea resins (urea-formaldehydes) as hot-press ureas, and room-temperature-setting ureas, melamine resins, melamine-urea resins, polyvinyl resins (as polyvinyl acetate), thermosetting polyvinyl emulsions, hot melts, epoxy resins, contact adhesives, and mastic adhesives. "Natural" adhesives used for wood include: Animal glue, casein glue, soybean glue and blood glue. (See 4.4.8 on Natural glues). See Chapters 5 and 8 for surface preparation and recommended adhesive discussion (more detailed than here.)(45)

**4.10 Adhesives for glass.** Glass adhesives are generally transparent resins that are water resistant to meet the requirements of outdoor applications. They include such materials as: polyvinyl butyral, phenolic-butyral, phenolic-nitrile, vinyl-nitrile, neoprene, polysulfide, rubber-base, silicone, vinyl acetate, epoxy, and cyanoacrylate (not particularly water-resistant). See Chapter 5 for discussion of surface preparation techniques.(18)

**4.11 Checklist for adhesive selection.** Adhesive manufacturers frequently provide checklists to potential users of adhesives so that they may be sure they have completely described their bonding requirements. An example of such a checklist is shown in Fig. 26. This particular list is shown so that those with bonding problems will have some idea of the type of information the adhesive supplier or adhesive technologist will need to know to be of assistance with the problem.(46)

(WP# ID-0706A/DISC-0033A. FOR MTL USE ONLY)

## MIL-HDBK-691B

## CHECKLIST FOR ADHESIVE SELECTION

<b>1. Use:</b>		<b>2. Application:</b>		
<input type="checkbox"/> Production		<input type="checkbox"/> Bonding		Approximate area to be joined _____
<input type="checkbox"/> Prototype		<input type="checkbox"/> Sealing		Approximate quantity of assemblies _____
<input type="checkbox"/> Development		<input type="checkbox"/> Joint mechanically reinforced?		
<input type="checkbox"/> Field repair				

<b>3. Surfaces:</b>		<b>4. Joint Type:</b>
_____ to _____		<input type="checkbox"/> Lap
Tradename (if any) _____		<input type="checkbox"/> Fillet
Finished metal: _____		<input type="checkbox"/> Edge
Base metal _____		(Attach sketch on separate sheet)
Finish _____		
Chemical description _____		

**5. Bonding Process Limitations:**

☐ Temperature. Max allowable \_\_\_\_\_ F.

☐ Pressure on glueline. Max allowable \_\_\_\_\_ psi.

☐ Organic vapors. \_\_\_\_\_ Moisture. \_\_\_\_\_ Corrosion.

☐ Other (describe) \_\_\_\_\_

Materials or components \_\_\_\_\_

**6. Service Conditions:**

Temperature: Max \_\_\_\_\_ F, Min \_\_\_\_\_ F.

Pressure: Max \_\_\_\_\_ psi, Min \_\_\_\_\_ psi.

Water: Fresh \_\_\_\_\_, Salt \_\_\_\_\_, Humidity \_\_\_\_\_, Condensation \_\_\_\_\_,

Spray \_\_\_\_\_, Immersion \_\_\_\_\_

Lubricating oil \_\_\_\_\_ Degreasing solvent \_\_\_\_\_

Hydraulic fluid \_\_\_\_\_

Design life \_\_\_\_\_

Outdoor: Sheltered \_\_\_\_\_, Direct exposure \_\_\_\_\_, Sunlight only \_\_\_\_\_

Indoor: Room condition \_\_\_\_\_, Controlled \_\_\_\_\_, Other \_\_\_\_\_

**7. Storage Conditions:**

Design life (if different from service design life) \_\_\_\_\_

Sealed \_\_\_\_\_, Sealed but opened for test \_\_\_\_\_

Outdoor: Sheltered \_\_\_\_\_, Direct exposure \_\_\_\_\_

Indoor: Warehouse \_\_\_\_\_, Room \_\_\_\_\_, Controlled atmosphere \_\_\_\_\_

<b>8. Mechanical Requirements:</b>		
<input type="checkbox"/> Temporary bond		Nature of load on glueline:
<input type="checkbox"/> Low strength		Peel _____ lb/in. of width.
<input type="checkbox"/> Moderate strength		Tension _____ psi.
<input type="checkbox"/> Structural		Shear _____ psi.
		Cleavage _____ lb/in. of width.

**9. Other Considerations:**

Color \_\_\_\_\_, Odor \_\_\_\_\_

Flammability \_\_\_\_\_, Other \_\_\_\_\_

FIGURE 26. Example of checklist for adhesive section.(46)



## MIL-HDBK-691B

## REFERENCES

- (4-1) Society of Manufacturing Engineers, Chapter 1, "Types of Adhesives," ADHESIVES IN MODERN MANUFACTURING, edited by E. J. Bruno, 1970.
- (4-2) C. C. Anderson, "Adhesives," Industrial and Engineering Chemistry, 59 (8): 91-96 (August 1967)
- (4-3) R. D. Paul and H. C. Winiarski, "Polyimide Adhesives for APSI Composites for Blades," Preprint Book, 22nd National SAMPE Symposium, Vol. 22, meeting held at San Diego, CA April 26-28, 1977 (pp. 195-201).
- (4-4) Bloomington Dept., American Cyanamid Co., "FM-34 Adhesive Film," Technical Bulletin, 25 January 1968.
- (4-5) J. A. Clark and J. M. Hawkins, "Characterization of a Urethane Modified Structural Epoxy Adhesive," Preprint, Division of Organic Coatings and Plastics Chemistry," Vol. 28, No. 1, American Chemical Society, 155th Meeting (April 1968), pp. 468-475.
- (4-6) D. R. Dreger, "Hot Melt Adhesives Put it All Together," Machine Design, 47 (1): 88-94 (Jan. 9, 1975).
- (4-7) R. B. Aronson, "Adhesives Cure Getting Stronger in Many Ways," Machine Design, 51 (3): 54-60 (Feb. 8, 1979).
- (4-8) Gulf Oil Chemical Co., Olefins and Derivatives Div., NUMEL<sup>R</sup> Engineering Adhesives, product brochure, 1982.
- (4-9) T. E. Baker, G. L. Fix, P. Gianas and J. S. Judge, "Characterization of a Hot Melt Adhesive System for Severe Environments," Proceedings, 10th National SAMPE Technical Conference, Vol. 10, "Materials Synergisms," Kiamesha Lake, N.Y., Oct. 17-19, 1978 (pp. 845-859).
- (4-10) J. J. Bell and W. J. Robertson, "Hot Melt Bonding with High Strength Thermoplastic Rubber Polymers," SAE Paper No. 740261, presented at Automotive Engineering Congress, Detroit, MI, Feb. 25 - March 1, 1974, 12 pp.
- (4-11) K. H. Miska, "Hot Melt Can Be Reactivated," Materials Engineering, 83 (4): 32 (April 1976).
- (4-12) 3M Company, Adhesives, Coatings and Sealers Division, Product Specification 4060, SCOTCH-WELD Thermoplastic Adhesive Film 4060, Sept. 15, 1971, Rev. Dec. 1, 1975.
- (4-13) F. T. Hughes, "Foamed Hot Melt Adhesives," Adhesives Age, 25 (9): 25-29 (Sept. 1982).
- (4-14) J. C. Bolger, Chapter 1, "Structural Adhesives for Metal Bonding," TREATISE ON ADHESION AND ADHESIVES, Vol. 3, edited by R. L. Patrick, Marcel Dekker, 1973.

## MIL-HDSK-691B

- (4-15) N. J. DeLollis, "Durability of Adhesive Bonds (A Review)," Proceedings, 22nd National SAMPE Symposium, VI, 22, "Diversity - Technology Explosion," San Diego, CA, April 26-28, 1977 (pp. 673-698).
- (4-16) J. D. Minford, "Durability of Adhesive-Bonded Joints," Chapter 2, TREATISE ON ADHESION AND ADHESIVES, Vol. 3., edited by R. L. Patrick, Marcel Dekker, 1973.
- (4-17) C. A. A. Rayner, "Synthetic Organic Adhesives," Chapter 4, ADHESION AND ADHESIVES, 2nd Edition, Vol. 1, Adhesives, edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1965.
- (4-18) E. M. Petrie, Chapter 10, "Plastics and Elastomers as Adhesives," in HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C. A. Harper, McGraw-Hill, New York, N.Y., 1975.
- (4-19) K. H. Miska, "Second Generation Acrylic Adhesives at Lower Cost," Materials Engineering, 84 (5): 40-42 (Nov. 1976.)
- (4-20) Anonymous, "Second-Generation Acrylic Adhesives," Adhesives Age, 19 (9): 21-24 (Sept. 1976).
- (4-21) S. B. Twiss, "Adhesives of the Future," Applied Polymer Symposia No. 3, "Structural Adhesive Bonding," presented at symposium sponsored by Picatinny Arsenal, held at Stevens Institute of Technology, Hoboken, N.J., Sept. 14-16, 1965, pp. 455-458 (1966). Wiley Interscience.
- (4-22) T. M. Brumit, "Cyanoacrylate Adhesives - When Should You Use Them?," Adhesives Age, 18 (2): 17-22 (Feb. 1975).
- (4-23) Union Carbide Corporation, technical literature (J-2421-A 106-3) on phenoxy adhesives (PRDA-8080), undated.
- (4-24) W. P. Mayer and R. M. Young, "Formulating Hot Melts with EEA Copolymers," Adhesives Age, 19 (5): 31-36 (August 1976.)
- (4-25) J. S. Amstock, Chapter 7, "Sealants," in HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, N.Y., 1973.
- (4-26) W. C. Wake, Chapter 6, "Rubbers," in ADHESION AND ADHESIVES, 2nd Edition, Vol. 1, Adhesives, edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1965.
- (4-27) Personal communication, Jim Scott, NCR Corporation, Dayton, OH, July 15, 1977.
- (4-28) G. H. Peters, C. K. Schaab, R. D. Hilbelink and T. R. Davis (NCR Co.), "Development of Multipurpose Capsular Adhesive Systems - Final Report, Picatinny Arsenal Technical Report 4215, May 1971.
- (4-29) A. H. Landrock, "Effects of Varying Processing Parameters on the Fabrication of Adhesive-Bonded Structures, Part VII, Electrically- and Thermally-Conductive Adhesives - Literature Search and Discussion," Picatinny Arsenal Technical Report 4179, March 1971.

## MIL-HDBK-691B

- (4-30) Ablestik Laboratories, Gardena, CA literature.
- (4-31) B. D. Murray, "Anaerobic Adhesive Technology," preprint booklet, symposium on Durability of Adhesive Bonded Structures, sponsored by U.S. Army Armament Research and Development Command, Oct. 27-29, 1976, pp. 599-610.
- (4-32) M. B. Pearce, "How to Use Anaerobics Successfully," Journal of Applied Polymer Science, Applied Polymer Symposia, No. 19, pp. 207-230, 1972.
- (4-33) C. L. Karnolt, "Anaerobic Adhesives for Sheet Metal Assembly", paper presented at Automotive Engineering Congress and Exposition, Detroit, MI, Feb. 24-28, 1975. SAE Paper No. 750140.
- (4-34) K. W. Kirby, Chapter 3, "Vegetable Adhesives," in ADHESION AND ADHESIVES, edited by R. Houwink and G. Salomon, Vol. 1, Adhesives, Elsevier Publishing Co., 1965.
- (4-35) J. Shields, ADHESIVES HANDBOOK, London, Newnes-Butterworth, 1976.
- (4-36) R. F. Blomquist, Chapter 17, "Adhesive Bonding of Wood," HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, N.Y., 1973,
- (4-37) A. M. Krogh and J. Wooton, Chapter 2, "Animal Glues and Related Protein Adhesives," in ADHESION AND ADHESIVES, 2nd Edition, Vol. 1, Adhesives, edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1965.
- (4-38) J. H. Wills, Chapter 8, "Inorganic Adhesives and Cements," in ADHESION AND ADHESIVES, 2nd Edition, Vol. 1, Adhesives, edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1965.
- (4-39) J. H. Wills, Chapter 6, "Inorganic Adhesives and Cements," in HANDBOOK OF ADHESIVES, 2nd Edition, edited by I. Skeist, Van Nostrand Reinhold, 1977.
- (4-40) ASTM D 907-82, "Standard Definitions of Terms Relating to Adhesives," published in Volume 15.06 Annual Book of ASTM Standards.
- (4-41) B. P. Barth, Chapter 23, "Phenolic Resin Adhesives," in HANDBOOK OF ADHESIVES, 2nd Edition, edited by I. Skeist, Van Nostrand Reinhold, 1977.
- (4-42) D. F. Gentle, "Bonding Systems for Plastics," pp. 142-170 in ASPECTS OF ADHESION, Vol. 5, Proceedings of the Conference held at The City University, London, England, 5-6 April 1967 and 9-10 April 1968. Edited by D. J. Alner, CRC Press, 1969.
- (4-43) A. H. Landrock, "Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures - Part XVIII. Adhesive Bonding and Related Joining Methods for Structural Plastics - Literature Survey," Picatinny Arsenal Technical Report 4424, November 1972.

MIL-HDBK-691B

- (4-44) J. E. Gaughan, Chapter 16, "Bonding Elastomeric Compounds," in **HANDBOOK OF ADHESIVE BONDING**, edited by C. V. Cagle, McGraw-Hill, N.Y., 1973.
- (4-45) M. L. Selbo, "Adhesive Bonding of Wood," USDA Forest Service, Forest Products Laboratory, Technical Bulletin No., 1512, Aug. 1975.
- (4-46) L. H. Sharpe, "The Materials, Processes and Design Methods for Assembling with Adhesives," Design Guide, Machine Design, 38 (19): 178-200 (August 18, 1966).

## MIL-HDBK-691B

## Chapter 5. ADHEREND SURFACE PREPARATION

**5.1 General discussion.** Adhesive bonding is a surface phenomenon. By definition, an adhesive is a substance capable of holding materials together by surface attachment. Thus, surface preparation prior to adhesive bonding is the keystone of successful bonding. The sole purpose of a surface preparation is to provide adherend surfaces receptive to the development of strong, durable adhesive joints. It is desirable, although not always practical, to have the basic adherend material exposed directly to the adhesive, with no intervening layer of oxide film, paint, chromate coating, phosphate coating, nor silicone release agent. Such layers are referred to as "weak boundary layers." Trying to bond such layers is similar to applying a pressure-sensitive tape to a powdered surface. Under such conditions, the adhesive never comes into contact with the adherend surface.

Quality control of all steps involved in surface preparation is important. Incoming production materials should be tested and determined to be suitable for use in the bonding process. Simple lap-shear tests (ASTM D 1002), peel tests (ASTM D 903, D 1781 and D 1876), or other tests established as appropriate, should be used to determine the quality of surface preparation. Results of quality-control tests should be recorded in official logs in order to provide traceable evidence of quality. Histograms - plots of frequency (occurrence of a value) vs. sample joint strength - are useful in establishing knowledgeable process control. The bonding-process specification should require this data.

Selecting a surface preparation for adhesive bonding requires a systems approach. Many factors, both obvious and less apparent, influence their selection. The size of component parts and the availability of equipment and facilities are in the obvious category. The rapid depletion of active chemicals in a bath, or the accumulation of foreign materials in the bath which give rise to weak boundary layers, resulting in poor adhesive joint strength, are examples of the less obvious factors.

Rigid process control is essential to avoid the production of scrap. The best surface preparation for metals for initial joint strength, durability and uniformity of quality is generally a chemical-immersion or spray process. Choosing such a process is desirable only if the production scheme or the entire system will tolerate it. Cost is another factor that must be considered and must be balanced against the need for reliability, maintainability and criticality of joint. In the entire system, from manufacture of individual parts to inspection of the final assembly, many compromises must be made. It is only by preparing a complete process specification, including detailed surface preparation requirements, that good process control can be obtained.<sup>1</sup>

**5.2 Primers (for metals).** Primers for pretreatment of adherends are growing in importance. The function of a primer in a bonding system can be one or more of the following:

- o Protecting the adherend surface (after cleaning)
- o Adjusting the free surface energy of the adherend
- o Adjusting the rheological properties of the interface
- o Improving surface interaction (solubility) between adhesive and adherend
- o Promoting chemical reaction between adhesive and adherend

## HIL-HDBK-691B

In certain applications, the use of a primer as a protectant may be just a convenience which, however, increases production costs. In other cases, however, correct priming will be crucial in producing a necessary chemical reaction.(2)

An adhesive primer is usually a dilute solution of an adhesive in an organic solvent that is applied to a dried film thickness of 0.00006 to 0.002 inch (0.0015 to 0.051 mm). With many structural adhesives, primers are used to increase peel strength and help prevent corrosion. However, a primary use is in preventing the prepared metal surface from decreasing in activity by oxidation on exposure to air. The primer extends the time that may elapse between surface preparation and adhesive application (See 5.3.4). With aluminum, for example, the maximum safe time interval between surface preparation and bonding is 12 hours. By utilizing an adhesive primer, the lapse time may be extended to 30 days or even 6 months, depending on the particular primer/adhesive system used. This process allows a shop to prepare the surface of a large number of parts, prime them, and store them for relatively long periods prior to bonding. Planning and scheduling are not as dependent on the surface preparation operation. There is another significant advantage to this process. In the fabrication sequence of a bonded assembly it is not always possible to integrate the bonding operation at a point in time that allows complete immersion of the bonding surfaces in the preparation solutions. At the scheduled time for bonding, the subassembly to be bonded may have progressed in its fabrication to a stage that it cannot be immersed in a chemical solution without damage to one of its components. In such instances, the surface should be prepared and primed prior to the installation of the limiting component.(3)

Utilizing an adhesive primer to permit optimum surface preparation and extended storage and handling of prepared details is an established sound practice used throughout the bonding industry. Adhesive primers are usually not fully cured during their initial application. They are dried at room temperature and some are force-dried for 30 to 60 minutes at 150°F (66°C). This provides a dry nontacky surface which can be protected from contamination and physical damage by wrapping with clean paper, sealed in polyethylene bags, or covering with a nontransferring adhesive-backed paper.(3)

Suggestions for specific primers to be used for particular adhesive systems can usually be found in the adhesive manufacturer's literature. The forced drying of the primer is often called "flashing". A recommended flash period for a particular primer (HYSOL Adhesive DA 952 Primer) is 60 minutes at 75°F (23°C) or 15 minutes at 75°F (24°C) followed by 15 minutes at 150°F (66°C).(3)

"Primers" are also advertised for some plastics and rubbers. In some cases these are not really primers, but etching agents.

### 5.3 Surface preparation.

5.3.1 Importance of surface preparation. Surface preparation of adherends prior to bonding is one of the most important factors in the adhesive-bonding process. The strength of the initial bond and its permanence are very much dependent on the type of surface that is in contact with the adhesive. The degree to which adherends must be prepared is related to the service environment and the ultimate joint strength required. Surface preparations of metals can range from simple solvent wiping to a combination of mechanical



## MIL-HDBK-691B

abrading, chemical cleaning, and acid etching. In many low-strength to medium-strength applications, extensive surface preparation may be unnecessary. But, where maximum bond strength, permanence, and reliability are called for, carefully controlled surface-preparation processes are necessary. The following factors should be considered in the selection of a surface preparation:

- o The ultimate initial bond strength required
- o The degree of permanence necessary and the service environment
- o The amount and kind of contamination initially on the adherend
- o The type of adherend

The strength of an adhesive joint is considerably increased when loose deposits such as rust, scale, flaking paint, and organic contaminants are removed from the surface so that the adhesive can more easily wet the substrate. Table XVI shows the effect of metallic-surface preparations on adhesive-bond strength for a number of metals.(4)

TABLE XVI. Effect of metal substrate surface treatment on adhesive-bonded joints.(4)

Adherend	Treatment	Adhesive	Shear Strength	
			psi	MPa
Aluminum	As received	Epoxy	444	3.06
	Vapor degreased		837	5.77
	Grit blast		1751	12.1
	Acid etch		2756	19.0
Aluminum	As received	Vinyl-phenolic	2442	16.8
	Degreased		2741	18.9
	Acid etch		5173	35.7
Stainless Steel	As received	Vinyl-phenolic	5215	36.0
	Degreased		6306	43.5
	Acid etch		7056	48.7
Cold-rolled Steel	As received	Epoxy	2900	20.0
	Vapor degreased		2910	19.9
	Grit blast		4260	29.6
	Acid etch		4470	30.8
Copper	Vapor degreased	Epoxy	1790	12.3
	Acid etch		2330	16.1
Titanium	As received	Vinyl-phenolic	1356	9.35
	Degreased		3180	21.9
	Acid etch		6743	46.5
Titanium	Acid etch	Epoxy	3183	21.8
	Liquid pickle		3317	22.9
	Liquid hone		3900	26.9
	Hydrofluorosilicic acid etch		4005	27.6

## MIL-HDBK-691B

Surface preparations enhance the quality of a bonded joint by performing one or more of the following functions:(4)

- o Remove contaminants
- o Control adsorbed water
- o Control oxide formation
- o Poison surface atoms which catalyze polymer breakdown
- o Protect the adhesive and the adherend from each other
- o Match the adherend crystal structure to the adhesive molecular structure
- o Control surface roughness

Plastics and elastomers are even more dependent than metals on surface preparation to provide good bonds. Most of these materials are contaminated with mold-release agents or are waxed to improve appearances. Such contaminants must be removed before bonding. Polytetrafluoroethylene, polyethylene, and certain other polymeric materials are completely unsuitable for adhesive bonding in their natural state. The surfaces of these materials must be chemically altered prior to bonding.(4)

**5.3.2 General cleaning methods.** The methods following are listed in approximate order of increasing effectiveness. The method ultimately chosen will be the one which provides the necessary strength and permanence with the least time and labor.(4)

**5.3.2.1 Solvent wiping.** Where loosely held dirt, grease, and oil are the only contaminants, simple solvent wiping will provide surfaces that will prove satisfactory for weak-to medium-strength bonds. This technique, although widely used, is the least-effective treatment. With plastics and rubbers, consideration must be given to chemical compatibility with the adherend. Volatile solvents such as toluene, acetone, methyl ethyl ketone (MEK), and trichloro ethylene (TCE) are acceptable. TCE is often favored because of its nonflammability. A clean cloth saturated with the solvent should be wiped across the area to be bonded until no signs of residue are evident on the cloth or the substrate. Special precautions should be taken to prevent the solvent from becoming contaminated. For example, the wiping cloth should never touch the solvent container, and new wiping cloths must be used when needed. After cleaning, the parts should be air-dried in a clean, dry environment before being bonded.(4)

**5.3.2.2 Vapor degreasing.** This is a form of solvent cleaning that is particularly desirable when a number of parts must be prepared. It is more reproducible than solvent wiping. The method consists of suspending the adherends in a container of chlorinated solvent vapor such as trichloroethylene (B. Pt. 250°F, 121°C). When the hot vapors come in contact with the relatively cool substrate, solvent condensation occurs, dissolving the organic contaminants from the surface. Vapor degreasing is superior to solvent wiping in that the adherend surfaces are continuously being washed in distilled uncontaminated solvent. When the boiling point of the solvent is lowered significantly by dissolved contaminants, the vapor degreaser should be cleaned and the solvent replaced. Plastics and elastomers may be adversely affected by the hot solvent, so this process should not be used. For these materials, carefully selected solvents or detergent solutions are acceptable cleaning liquids.(4)

## MIL-HDBK-691B

**5.3.2.3 Abrasive cleaning.** Sandblasting, wire brushing, abrasion with sandpaper, emery cloth, and metal wool are mechanical methods effective for removing heavy, loose particles such as dirt, scale, tarnish, and oxide layers. Degreasing should be carried out before abrasive treatment to prevent contaminants from being rubbed into the surface. Blasting with clean, dry air or solvent wiping will remove solid particles left on the surfaces after abrading, or wet-abrasive blasting, followed by a spray rinse, may be used.<sup>(4)</sup>

Each metal and alloy has an optimum range of abrasive sizes. Joint strength generally increases with the degree of surface roughness. Excessively rough surfaces, however, are more likely to result in voids being left at the adhesive/adherend interface, causing stress risers which may be detrimental to the adhesive joint. Recommended abrasive sizes for several metals are as follows:<sup>(4)</sup>

Steel	Dry-blast	80-100 grit
Stainless steel	Wet-blast	140-325 grit
Aluminum	Wet-blast	140-325 grit
Brass	Dry-blast	80-100 grit
Brass	Wet-blast	140-325 grit

Hand-sanding, wire-brushing, and other methods that are highly related to the operator's skill and patience are less reproducible and should be used only when no other method is possible.<sup>(4)</sup>

Fiberglass-reinforced plastics can be cleaned by grit-blasting, or they can be cleaned with a solvent (trichloroethylene) followed by sanding with 80-20 grit, again followed by solvent-cleaning with trichloroethylene. Non-reinforced plastics are generally solvent-cleaned, followed by sanding with 180-320 grit sandpaper, depending on the gage of the adherend. A "soft" plastic will be more susceptible to damage or erosion of material by coarse abrasives, so a finer grit, such as No. 320, should be used. Again, solvent-wiping should follow the abrasive process.<sup>(5)</sup>

For a more detailed discussion of the abrasive process, see the discussion in Reference 5.

**5.3.2.4 Chemical cleaning (alkaline cleaning).** Strong detergent solutions, usually heated, are used to emulsify surface contaminants on both metallic and nonmetallic substrates. Parts for cleaning are immersed in a well-agitated solution maintained at 150-210°F (66-99°C) for approximately 10 minutes. The surfaces are then rinsed immediately with deionized water and dried. Chemical cleaning is generally used in combination with other surface treatments. Chemical cleaning will not, by itself, remove heavy or strongly attached contaminants such as rust or scale. Alkaline detergents recommended for cleaning are combinations of alkaline salts such as sodium metasilicate and tetrasodium pyrophosphate, with surfactants included. Many commercial detergents are available. Typical ones are OAKITE and SPREX.<sup>(4)</sup>

**5.3.2.4.1 Water purity.** The common factor in all chemical processing methods is water, and the purity of the water used may determine the success or failure of the process. There are very few areas of the country where tap water can be used for the overall treatment of metals for adhesive bonding. Table XVII indicates the general requirements for acceptable water.<sup>(6)</sup>

## NIL-HDBK-691B

TABLE XVII. General requirements for water used in cleaning solutions and rinsing.(6)

Property	Value Required
Specific resistance	50,000 ohm/cm <sup>2</sup> at 30°C
Total alkalinity	10 ppm max. as CaCO <sub>3</sub>
Phenolphthalein alkalinity	1 ppm max. as CaCO <sub>3</sub>
Chloride content	15 ppm max.
pH	7.5 max.

5.3.2.5 Other cleaning methods. Vapor-honing and ultrasonic cleaning are efficient treating methods for small, delicate parts. Vapor-honing is similar to grit-blasting, except that very fine abrasive particles are suspended in a high-velocity water or steam spray. Ultrasonic cleaning employs a bath of cleaning liquid or solvent that is ultrasonically activated by a high-frequency transducer. The part to be cleaned is immersed in the liquid, which carries the sonic waves to the surface of the part. High-frequency vibrations then dislodge the contaminants. Commercial ultrasonic-cleaning units are available from a number of manufacturers.(4)

5.3.2.6 Chemical etch. Chemical treatment of substrate surfaces is the most effective method of surface preparation. This type of treatment changes the physical and chemical properties of the surface to produce greater wettability and a stronger surface. Specific chemical treatments are required for each substrate material and will be discussed in 5.3.5. The part or area to be bonded is usually immersed in an acid solution, such as the FPL etch, for a matter of minutes. The parts are then immediately rinsed with deionized water and dried. Chemical solutions must be changed regularly to prevent contamination and assure repeatable concentration. Tank temperature and agitation must also be controlled. Personnel using acid-etch solutions should be trained in the handling, use and disposal of such solutions and must wear suitable clothing. Paste-type etching products are available that simultaneously clean and chemically treat surfaces. They react at room temperature and need only be applied to the specific area to be bonded. However, these paste etchants generally require much longer treatment time than acid-bath processes.(4)

5.3.2.7 Combined cleaning methods. More than one cleaning method is usually required for optimum adhesive properties. A three-step process that is recommended for most substrates consists of (1) degreasing, (2) mechanical abrasion, and (3) chemical treatment. Table XVIII shows the effect of various combinations of aluminum-surface preparations on lap-shear strength. Optimum bond strength on aluminum occurs when a treatment consisting of vapor degreasing, abrading, alkaline cleaning, and acid etching is used.(4)

MIL-HDBL-691B

TABLE XVIII. Surface preparation of aluminum vs lap-shear strength. (7)

Group Treatment	Lap Shear Strength				Coeff of Variation (CV), %
	Avg value (X)		Std deviation(s)		
	psi	MPa	psi	MPa	
1. Vapor degrease, grit-blast 90-mesh grit	3091	21.3	105	0.724	3.5
Alkaline clean, Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -H <sub>2</sub> SO <sub>4</sub> , distilled water.					
2. Vapor degrease, grit-blast 90-mesh grit, alkaline clean Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -H <sub>2</sub> SO <sub>4</sub> , in tap water.	2929	20.2	215	1.48	7.3
3. Vapor degrease, alkaline clean, Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -H <sub>2</sub> SO <sub>4</sub> , distilled water.	2800	19.3	307	2.12	11.0
4. Vapor degrease, alkaline clean, Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -H <sub>2</sub> SO <sub>4</sub> , tap water.	2026	19.5	115	0.793	4.1
5. Vapor degrease, alkaline clean, chromic-H <sub>2</sub> SO <sub>4</sub> , deionized water.	2874	19.8	163	1.12	5.6
6. Vapor degrease, Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> -H <sub>2</sub> SO <sub>4</sub> , tap water.	2756	19.0	363	2.50	1.3
7. Unsealed anodized.	1935	13.3	209	1.44	10.8
8. Vapor degrease, grit-blast 90-mesh grit.	1751	12.1	138	0.951	7.9
9. Vapor degrease, wet and dry sand, 100+240 mesh grit, N <sub>2</sub> blown.	1758	12.2	160	1.10	9.1
10. Vapor degrease, wet and dry sand, wipe off with sandpaper.	1726	11.9	60	0.414	3.4
11. Solvent wipe, wet and dry sand, wipe off with sandpaper (done rapidly).	1540	10.62	68	0.470	4
12. Solvent wipe, sand (not wet and dry) 120 grit.	1329	9.17	135	0.931	1.0
13. Solvent wipe, wet and dry sand, 240 grit only.	1345	9.28	205	1.41	15.2
14. Vapor degrease, aluminum wool.	1478	10.2	---	---	---
15. Vapor degrease, 15% NaOH.	1671	11.5	---	---	---
16. Vapor degrease.	837	5.77	72	0.497	8.5
17. Solvent wipe (benzene).	353	2.43	---	---	52.2
18. As received.	444	3.06	232	1.60	---

Resin employed: EA 934 supplied by Hysol Division, the Dexter Corp. Resin cured 16 hrs at 750°F. (24°C.) plus 1 hr at 180°F. (82°C). Fillet on overlap left intact, adhesive on sides of specimens removed.

## MIL-HDBK-691B

The reader will do well to analyze the data in Table XVIII carefully. The workers who prepared this table have discussed the results briefly, but the conclusions are reasonably obvious. Again, the reader should be reminded that these figures refer to a particular set of conditions. Tap water from other sources might give different results, for example. Also many of the methods used involve subjective treatments (hand sanding etc). Different workers might obtain different results. The general pattern of results, however, is apparent.

**5.3.2.8 Activated-gas surface treatment of polymer.** Recently it has been shown that the treatment of certain polymeric surfaces with excited inert gases greatly improved the bond strength of adhesive joints prepared from these materials. With this technique called "plasma treatment", a low-pressure inert gas is activated by an electrodeless radio-frequency discharge or microwave excitation to produce metastable excited species which react with the polymer surface. The type of plasma gas ( $O_2$ , He,  $H_2$ ) can be selected to initiate a wide assortment of chemical reactions. Atoms are expelled from the polymer surface to produce a strong, wettable crosslinked skin. Commercial instruments are currently available to treat polymer materials in this manner. Branson International Plasma Corporation, 31172 Huntwood St., P.O. Box 4136, Hayward, CA 94544 is the only source known at present. Table XIX shows the bond strengths of various plastic-aluminum composites pretreated with activated gas and bonded with an epoxy adhesive.



TABLE XIX. Typical adhesive-strength improvement for aluminum-plastic lap shear sandwich specimens bonded with EPON-VERSALID 140 (7/30) epoxy adhesive. (u)

Plastic Material	Control		Lap Shear Strength				After various plasma treatments*			
	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa
High-density polyethylene	315 ± 38	2.17 ± 0.26	1160 ± 136	8.0 ± 0.93	to	3500 ± 68	24.3 ± 0.47			
Low-density polyethylene	372 ± 52	2.57 ± 0.36	1250 ± 33	8.62 ± 0.22	to	1466 ± 106	10.11 ± 0.73			
Nylon 6	846 ± 166	5.83 ± 1.15	1220 ± 120	8.41 ± 0.83	to	3956 ± 195	27.3 ± 1.34			
Polystyrene	566 ± 17	3.90 ± 0.12	3118 ± 278	21.50 ± 1.92	to	4015 ± 85	27.7 ± 0.59			
MYLAR A (PET film)	530 ± 51	3.66 ± 0.35	1215 ± 29	8.38 ± 0.20	to	1660 ± 40	11.45 ± 0.28			
MYLAR D (PET film)	618 ± 25	4.26 ± 0.17	1185 ± 83	8.17 ± 0.57	to	1216 ± 522	8.39 ± 3.60			
TEDLAR polyvinyl fluoride	278 ± 2	1.92 ± 0.014	1200 ± 80	8.28 ± 0.55	to	1370 ± 80	9.45 ± 0.55			
LEXAN polycarbonate	410 ± 10	2.83 ± 0.69	660 ± 27	4.58 ± 0.19	to	928 ± 66	6.40 ± 0.46			
Polypropylene	370	2.55	200	1.38	to	3080 ± 180	21.2 ± 1.25			
Cellulose acetate butyrate	1090 ± 27	7.52 ± 0.19	455 ± 95	3.14 ± 1.34	to	2516 ± 22	17.4 ± 0.15			
CELCON acetal copolymer	118 ± 4	0.81 ± 0.007	186 ± 58	1.28 ± 0.40	to	258 ± 16	1.78 ± 0.11			

MIL-HDBK-691B

\* O<sub>2</sub>, He, N<sub>2</sub> for various periods (30 sec to 60 min)

## MIL-HDBK-691B

Plasma-treated polymers generally form adhesive bonds that are 2 to 10 times stronger than the bonds formed after traditional chemical or mechanical preparation. Table XX shows the results of tests recently carried out to show the relative advantages of plasma treatment compared to other methods of surface preparation.

TABLE XX. Results of lap shear tests in various polymers showing the advantage of plasma processing (samples prepared and bonded by the International Plasma Corporation.\* Tests performed by Hales Testing Laboratories, Oakland, CA. (9))

Polymer	Relative Bond Strength**				
	Control	Plasma	Abrasion	Corona	Chemical
High-density polyethylene	1.0	12.1	---	4.5	5.1
Polypropylene	1.0	221	---	81	649
Polyester (GE Valox 310)	1.0	18.9	2.9	---	1.0
Silicone rubber	1.0	>20	4.7	---	---

\*Now Branson International Plasma Corporation

\*\*Results normalized to the controls for each polymer

5.3.3 Evaluation of cleaned parts before and after bonding. There are several methods available for determining the thoroughness of surface preparation. Before bonding, the subjective "water-break" test can be used, or else the quantitative and objective contact-angle test may be carried out. After bonding it is possible to evaluate the effectiveness of surface preparation by determining the mode of failure of the adhesive joint.

5.3.3.1 Water-break test. The water-break test depends on the observation that a clean surface (one that is chemically active or polar) will hold a continuous film of water. This is known as a water-break-free condition. A break in the water film indicates a soiled or contaminated area. Since water (distilled) may temporarily bridge slightly soiled areas, a drainage time of about 30 seconds should be allowed. The possibility also exists that a continuous film of water will form as residual cleaning solution remains on the surface. Care must be taken to ensure that the surface is thoroughly rinsed before testing. If a water-break-free condition is not observed in the treated surface, it should not be used for bonding or adhesion. Such surfaces should be reprocessed through the cleaning cycle. If repeated failures to pass the water-break test occur, the treating process should be thoroughly analyzed to determine the cause of the problem<sup>(3)</sup>.

5.3.3.2 Contact-angle test. Wettability can be determined by measuring the contact angle between the polymer surface and a drop of a reference liquid. A small contact angle indicates that the liquid is wetting the polymer effectively. Large angles show that wetting is poor. Every surface exhibits a critical surface tension,  $\gamma_c$  of wetting. Liquids with surface-free energies

## MIL-HDBK-691B

below will have zero contact angles, and will wet the surface completely, while liquids with surface-free energies above will have finite contact angles. Some examples are shown in Table XXI, showing the effect of various surface-preparation techniques in altering the contact angle between different polymers and distilled water.

**TABLE XXI. Wettability of various plastics after different surface-preparation techniques, based on distilled water contact angle.(9)**

Polymer	Control	Plasma	Flame	Corona	Chemical
Polypropylene	87°	22°	87°	35°	60°
Polyester	71°	18°	--	--	75°
PVC	90°	35°	--	--	79°
Polycarbonate	75°	33°	--	--	76°
Silicone rubber	93°	17°	--	--	--
High-density polyethylene	87°	42°	38°	42°	54°

**5.3.3.3 Mode of failure of adhesive joint.** The objective of treating an adherend prior to bonding is to obtain a joint where the weakest link is the adhesive layer and not the interface. Thus, destructively tested joints should be examined for mode of failure. (See 1.6 Mechanisms of Bond Failure, for discussion of the significance of mode failure). If failure is cohesive within the adhesive layer or adherend, the surface treatment is optimum for that particular combination of adherend, adhesive and testing condition. But it must be realized that specimens may exhibit cohesive failure initially and interfacial (adhesive) failure after aging. Both adhesive and surface preparations must be tested with respect to the intended service environment.(4)

**5.3.4 Surface exposure time.** Surface exposure time (SET) is the time expired between the surface preparation and actual bonding. After the parts to be bonded are cleaned they must be protected from contamination during transportation and storage. Under no condition should the clean surface be touched with bare hands or soiled gloves. If the line is to be continuous, the parts will ideally go from the last stage of the cleaning line, generally a drying oven, to the priming booth (if a primer is to be used), or by the shortest possible route, or directly to the lay-up room.

If, however, the parts are to be routed to the priming booth, but more than a few hours are required between cleaning and priming, it is generally recommended that they be covered, or, for still longer periods, wrapped in clean kraft paper until the priming can be carried out. The primed parts should be dried in accordance with the manufacturer's instructions as soon as possible. The dried primed surfaces, if they are not to be bonded immediately, should again be protected from airborne contaminants and unauthorized handling by wrapping in kraft paper. If the parts are to be bonded without the use of

## MIL-NDBK-691B

a primer, they must, of course, also be protected in the above manner. The period of time for which the parts can be safely stored will vary, depending on the nature of the adherends, the adhesive, and the ultimate bond strengths required.

With a polyamide epoxy adhesive, the time allowable depends on the adherend and the type of treatment. Many aircraft companies specify time limitations between cleaning and bonding. One, for example, requires that when aluminum has been treated with the sulfuric-sodium dichromate etch, the part should be bonded within 6 days for all adhesives, except modified epoxies, for which up to 14 days are allowed. If the cleaning method has been a wet abrasive blast, the parts must be bonded within 4 days, and even this method may be used only for nonstructural applications.

Picatinny Arsenal (now U.S. Army ARDEC) has published a large number of reports and papers in this area for a number of adherend types. Both shear tests and peel tests have been used in this evaluation. There is occasionally a question as to which test is more sensitive to the quality of surface preparation or other changes connected with the bonding process. The peel tests, in particular, the roller peel test, has been found to be more sensitive to variation in surface preparation than shear tests. From the peel tests it is apparent that, in general, increasing SET does tend to reduce the critical joint strength. In general, it has been found that up to 30 days may elapse between completion of surface preparation and actual bonding when the faying surfaces are protected from physically becoming dirty and the relative humidity is kept at about 50%, without serious loss in joining strength. Temperatures above normal room temperatures and/or high humidities will cause deterioration in shorter periods of time.(10)(11) See also SAMPE Journal for a number of articles based on Picatinny Arsenal Technical Reports, issued over a number of years.

### 5.3.5 Specific surface treatments.

#### 5.3.5.1 Metals.

5.3.5.1.1 General discussion. The following sections list commonly recommended surface-preparation procedures, usually only one or two, for specific metallic adherends. The general methods previously described in 5.3 are all applicable, but the processes listed below have been specifically found to provide reproducible structural bonds and fit easily into the bonding operation.(1)(3)(12)

5.3.5.1.2 Aluminum and alloys. Chemical treatments have been found to be most effective in preparation of aluminum surfaces for adhesion, particularly where long-term environmental exposure is required. The sulfuric acid-dichromate etch process developed by Eickner at the Forest Products Laboratory (commonly referred to as the FPL etch) has been proven over the years to be an effective, controllable and reliable surface preparation method for aluminum prior to structural adhesive bonding. The airframe and aerospace industries use this process almost exclusively. Chromate conversion coating and anodizing, which are methods designed for organic coatings, are also used prior to bonding. Corrosion protection is a major consideration in the selection of aluminum surface treatments for adhesion, especially when

## HIL-HDBK-691B

application requires severe environmental exposures such as high humidity. The presence of corrosion at the adhesive-metal interface of bonded aluminum lap-shear specimens has been observed when such specimens fail or develop low bond strength during humidity exposures. Corrosion-resistant adhesive primers, as well as anodic and chromate conversion coatings, help to prevent corrosive failure of adhesion. Solvent cleaning, alkaline cleaning and mechanical treatments such as blasting, sanding or scouring are suitable for the development of high initial adhesion, but due to their lack of corrosion protection, are of no value where environmental resistance is needed.(3)

Blasting provides an excellent surface for at least high initial adhesion, but, under certain conditions, there may be a danger of surface oxidation between blasting and processing. For bonding silicone rubbers, fluoro-elastomers and other high-temperature-resistant polymers to aluminum, blasting should be accomplished with sand or aluminum oxide. Steel grit-blasting is believed to leave a ferrous deposit in the aluminum which may act as a starting point for corrosion, and will not withstand high-temperature service(18).

FPL Immersion Etch. The most successful and accepted method of preparing aluminum alloys for laboratory or production bonding where corrosion resistance is not required is the FPL etch. This method has recently been improved (see below).

The original method is given here, for comparison. Much of the data reported in the literature is based on this method.

- a. Wash with acetone to remove gross contaminants
- b. Degrease with perchloroethylene vapor
- c. Immerse for 10 minutes at 140-150°F (60-66°C) in the following solution:

Deionizer water	30 pbw*
Sulfuric acid (sp. gr. 1.84)	10 pbw
Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ )	1 pbw

\*parts by weight

In making up the solution, add the acid to 60% of the water, stir in the dichromate, and then add the rest of the water. NEVER add the water to the concentrated acid!

- d. Rinse 1-2 min. in running tap water at 104°F (40°C)
- e. Rinse with deionized water at room temperature
- f. Dry in an air-circulating oven at 104°F (60°C)
- g. Cover or wrap parts in kraft paper to protect them from dust or dirt. Store at 73°F (23°C) for the desired SET. Ordinarily parts are bonded within 48 hours.

## MIL-HDBK-691B

ASTM D2651-79, Method A.(13) (PPL Immersion Etch - Improved Method). This method is currently the most successful method of preparing aluminum alloys for laboratory or production use. The procedure is as follows:

- a. Degrease, solvent wipe, or both
- b. Immerse for 10 minutes at 155°F (68°C) in the following solution:

Water	30 pbw*
Sulfuric acid (sp.gr. 1.84)	10 pbw
Sodium dichromate	1 pbw

\*parts by weight

- c. Rinse with water not over 150°F (65.5°C)
- d. Air-dry, dry in an oven, or use infrared lamps at not more than 150°F (65.5°C)

ASTM D2651-79, Method B.(13) In this method a mild acid surfactant solution may be used instead of the strong sulfuric acid-sodium dichromate solution described for Method A.

- a. Immerse the parts for 15 minutes at 115°F (46°C) in the following solution:

Water	92.9 pbw*
Sulfuric acid (sp.gr. 1.84)	1.0 pbw
Sodium dichromate	6.0 pbw
Pluronic F 68 (or equivalent)	1.0 pbw

\*parts by weight

The time of immersion may be increased, depending on the limits allowable for the amount of metal removed.

- b. Rinse with water not over 150°F (65.5°C)
- c. Air-dry, dry in an oven, or use infrared lamps at not more than 150°F (65.5°C)

ASTM D2651-79, Method C.(13) Some modifications of Method A have been used successfully. It is known that improved bonds are obtained with certain adhesives by increasing the concentration of the sodium dichromate-sulfuric acid solution to as high as the following formulation by weight: 17 parts water, 7 parts sulfuric acid (sp. gr. 1.84) to 2 parts sodium dichromate. Alkaline degreasing solutions may also be used instead of, or in addition to vapor degreasing and prior to the sodium dichromate-sulfuric acid solution treatment. Some commercially available proprietary solutions may be used. Otherwise a common process for this part of the surface preparation is to immerse for 10 minutes at 60-180°F (70-80°C) in the following solution by weight: 3.0 parts sodium metasilicate, 1.5 parts trisodium pyrophosphate, 1.5 parts sodium hydroxide, 0.5 part NACCONOL HR or equivalent and 133.0 parts water.

ASTM D2651-79, Method E.(13) This method covers proprietary, commercially available metal surface preparations.



## MIL-HDBK-691B

ASTM D2651-79, Method F.(13) (PPL Paste Etch). This technique is used for secondary bonding of parts that contain previously bonded areas, for repair of a bonded assembly, or when the size of a part makes it impractical to immerse. The parts should be bonded in the temperature range of 70-90°F (21-32°C). A paste is made up using the sulfuric acid-sodium dichromate solution, Methods A and C above, in finely divided silica or Fuller's earth, and applied to the surface (Cabot Chemical Company's CAB-O-SIL N5 fused silica is often used). The paste should not be allowed to dry after application by brush (polypropylene). The paste should remain in place for 20-25 minutes. Additional coats may be applied to prevent the paste from drying out or turning green. All traces of the paste should then be removed with a clean cheesecloth. Water may be sprayed on if desired. Dry at a maximum of 150°F (66°C). Bond strengths obtained from this type of surface preparation are somewhat lower than those obtained by immersion.

ASTM D2651-79, Method G.(13) A successful and widely used method of surface preparation for structural adhesive bonding of 2024, 7075 and 6061 aluminum alloys is as follows:

a. Vapor-degrease, emulsion-degrease, or solvent-wipe, as required by the condition of the metal. This step may be omitted when the metal is not obviously oily or ink-marked.

b. Immerse in a nonsilicated, nonetching, free-rinsing alkaline cleaner in accordance with the cleaner manufacturer's recommendations. Spray or immersion-rinse thoroughly without delay with demineralized water (minimum 70°F (21°C)). The cleaner must not be allowed to dry on the surface prior to rinsing. The parts should exhibit a water break-free surface.

c. Immerse in sodium dichromate (sulfuric acid etch solution for 12-15 minutes at 150-160°F (66-71°C)). The parts should not be allowed to dry between etch and rinse cycles. The solution is made up as follows:

Sulfuric acid, 55Be°	38.5-41.5 oz/gal (287.9-310.0 g/L)
Sodium dichromate	4.1-9.0 oz/gal (28-67.3 g/L)
Aluminum alloy -2024 bare (for seeding)	0.2 oz/gal (1.5 g/L min)
Temperature	150-160°F (66-71°C)

d. Rinse thoroughly in demineralized water at 70-130°F (21-54°C).

e. Allow parts to dry thoroughly at temperatures up to 140°C (60°C).

f. Handle all detail parts that have been processed for adhesive bonding with clean white cotton gloves only.

NOTE: ASTM D2674-72 (1979)e2(14) is recommended for controlling the effectiveness of the sulfochromate etchant solutions described above. There are three methods in this standard, A, B, and C, each with a different objective.

Chromate-Free Etch Process. (P2 Etch)(14a)(14b)(14c)(14d)

The use of carcinogenic and polluting acid chromate etchant can be avoided by employing a P2-etch process developed and patented by Picatinny Arsenal workers. This relatively new process yields bonds as strong as, and more durable than chromic acid etch.

Degreasing, solvent cleaning, or alkaline cleaning should be carried out prior to using the P2 etch, which has the following composition:

Sulfuric Acid, conc (sp. gr. 1.84)	370 g
Ferric Sulfate, 75%	150 g
Dilute with deionized water to make 1 liter	

After immersion in the P2 etch solution at a temperature of 150°F + 50°F (66 + 2.80°C) for 12 minutes the aluminum is rinsed in deionized water for 2 minutes, then dried for 35 minutes at 140°F (60°C).

The P2 etch yields bonds at least equal to those made with the sulfuric acid - dichromate (FPL) etch and has also proven to be an acceptable deoxidizer prior to phosphoric acid anodizing (PAA) described below.

Anodization is sometimes used for bare aluminum (nonclad machined or chem-milled parts which must be corrosion-protected. Anodic coatings used include chromic acid, sulfuric acid, and phosphoric acid types. Anodizing is the common commercial term used to designate the electrolytic treatment of metals where stable films or coatings are formed on the surface. Anodic coatings can be formed on aluminum alloys in a wide variety of electrolytes, utilizing either alternating or direct current, or combinations of both. Both sulfuric acid and chromic acid are used in anodic oxidation. Anodization on aluminum is rather complex, and some aspects of the process are still unknown. In general, the anodic coating is considered to be essentially aluminum oxide, and it is formed by reaction of the aluminum with the oxygen or hydroxyl ion of the water in the electrolyte when the aluminum is made the anode.

Phosphoric Acid Anodizing (PAA). This method is currently considered one of the better methods for assuring long-term durability under adverse conditions. The procedure is given in ASTM D 3933, which was published in the fall of 1980.(15)

Sealed chromic-acid anodize.(16)

- a. Degrease. Wash in three successive baths of acetone to remove grease, oil, markings, and solvent-removable soils.
- b. Alkaline clean. Immerse 5 minutes in a deionized water solution containing 1.5 oz/gal. (11.2 g/liter) at 140°F (60°C).
- c. Rinse. Rinse in running tap water for 2 minutes.

## MIL-HDBK-691B

d. Etch or deoxidize. Immerse parts 2-3 minutes in bath at 140°F (60°C) consisting of:

Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ )	1 pbw	=	1 pbw
Sulfuric acid (sp.gr. 1.84)	10 pbw		10 pbw
Deionized water	30 pbw		30 pbw

e. Rinse. Rinse 2 minutes in running tap water at room temperature.

f. Anodize. Make the parts the anode and the stainless steel tank the cathode. To make up the anodizing solution use 10% by wt of chromic acid flake in deionized water. Maintain this solution at 92-98°F (33-36°C). Apply DC voltage in increments of 5-10 volts, as shown graphically in Figure 27. Observe a 2 to 2-1/2 minutes delay between the initial voltage and the second increase. Make each additional increase at approximately 1 minute intervals until a voltage of  $40 \pm 2$  volts is obtained. Not less than 5 minutes nor more than 10 minutes should be required to reach  $40 \pm 2$  volts. Process the parts at the  $40 \pm 2$  volts reading for 30-35 minutes. Do not allow the parts to remain in anodize solution for more than 5 minutes after the current is turned off.

g. Rinse. Rinse 2 minutes in running tap water at room temperature.

h. Seal. Immerse for 9 minutes in a bath at 180°F (82°C) consisting of 100 ppm chromic acid in deionized water.

i. Dry. Dry in an air-circulating oven at 140°F (60°C) for 30 minutes.

Chemical conversion coatings. These are chemical films formed non-electrolytically on aluminum (and other metals) by chemical reaction between the coating solution and the aluminum. They form adherent corrosion-resistant surface layers of low-solubility oxide, phosphate or chromate compounds. The majority of conversion coatings now in use are proprietary formulations. They may be applied, depending on the formulation, by spraying, dipping or brushing. Three of the coatings utilized in the preparation of aluminum surface for adhesive bonding are ALODINE, Parker and IRIDITE. The process cure for applying conversion coatings varies slightly, depending on the particular formulation being used. However, generally, the procedure involves the following steps:

Solvent degrease  
Alkaline clean  
Rinse  
Deoxidize  
Rinse  
Conversion Coat  
Rinse  
Dry

5.3.5.1.3 Beryllium.(1)(3) Beryllium and its alloys constitute a health hazard when handling or processing. It produces dust, chips, scale, slivers, mists or fumes. In general, there should be no problem in surface preparation or bonding if its characteristics are recognized. Beryllium is a strong, lightweight metal receiving attention as a material of construction in specialized fields. An impediment to its use is the tendency of the metal to

MIL-HDBK-691B

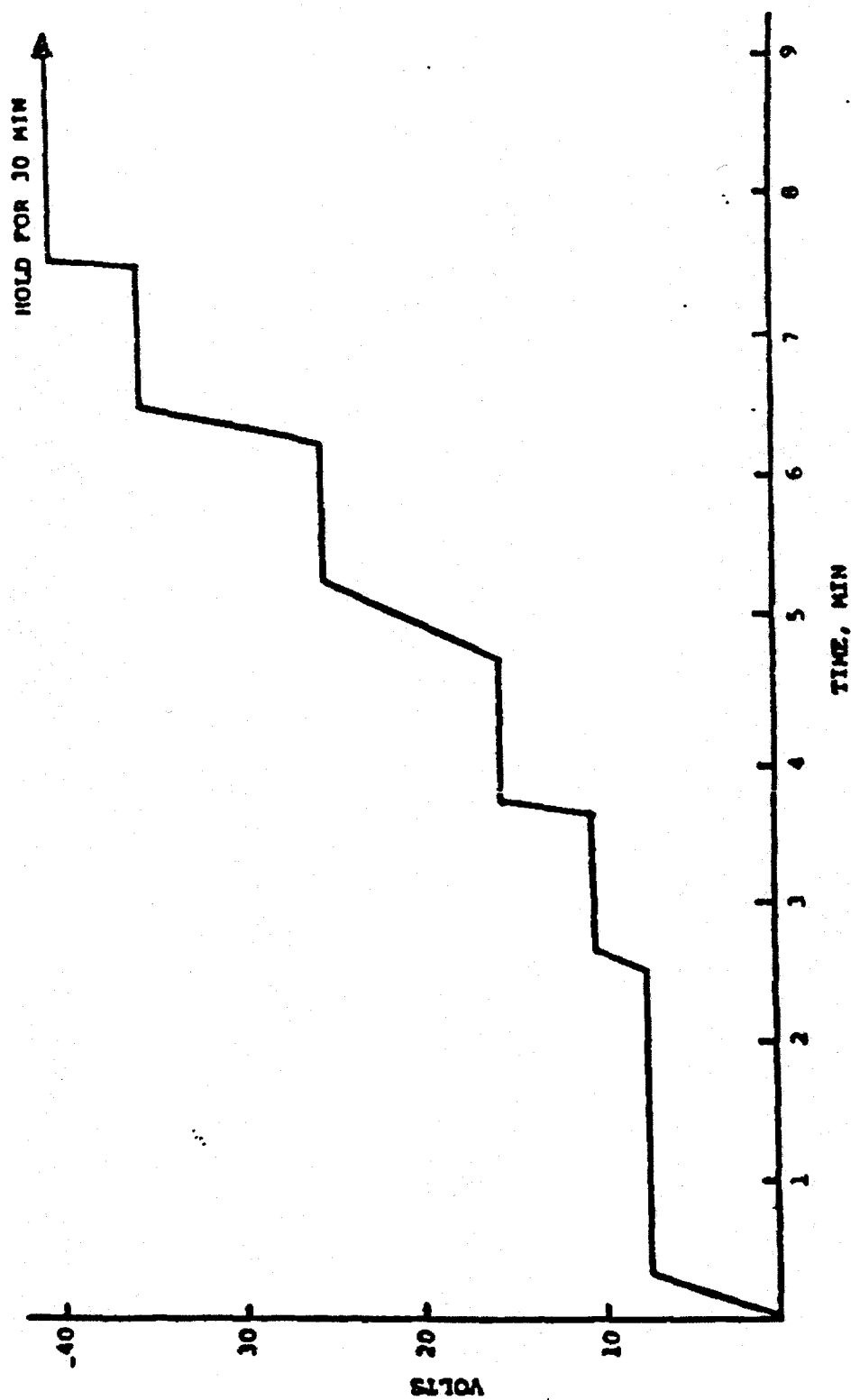


FIGURE 27. Voltage increases for aluminum anodizing. (16)

## MIL-HDBK-691B

corrode or become pitted when subjected to a moist atmosphere for long periods of time. Corrosion appears on the surface as irregular spots or snow-white hydrolysis product. By treating beryllium metal with a chromium-containing solution, a thin, transparent coating less than 100 Angstrom units thick is formed which effectively retards oxidation or erosion of the metal. The following procedure has been recommended.

BERYLCOAT "D" Process Procedure.

## A. SCOPE:

A recommended procedure is described for surface treating beryllium parts to provide a corrosion-resistant barrier using BERYLCOAT "D", a proprietary solution available from Brush Wellman, Inc., 17876 St. Clair Avenue, Cleveland, OH 44110

## B. MATERIALS:

B.1 Materials required:

B.1.1 Recommended Solvents are Freon TP, Genesolv "D" or 1,1,1, - Trichlorethane (Chlorothene NU, etc.)

B.1.2 Deionized or distilled water

B.1.3 10% Oxalic Acid Solution

B.1.4 BERYLCOAT "D" Concentrate

## C. NOTES:

C.1 Use of BERYLCOAT "D" Concentrate

C.1.1 Make up BERYLCOAT "D" passivation solution by mixing BERYLCOAT "D" Concentrate with an equal volume of distilled or deionized water. Thoroughly agitate the concentrate prior to mixing. Undiluted BERYLCOAT "D" Concentrate should NOT be used for surface treating beryllium parts.

C.1.2 Once opened, BERYLCOAT "D" concentrate has an approximate shelf life of 120 days.

C.1.3 BERYLCOAT "D" passivation solution has an approximate shelf life of 90 days. To insure the application of an adequate corrosion barrier, the BERYLCOAT "D" Passivation solution should be replaced after 70-90 days.

C.1.4 The action of BERYLCOAT "D" passivation solution will deteriorate with use and the solution should be discarded after processing approximately 1600 square inches (1 square meter) of surface area of parts per gallon (0.004 cubic meter) of solution.

C.1.5 BERYLCOAT "D" passivation solution should be thoroughly agitated immediately prior to the immersion of parts.

## MIL-HDBK-691B

**C.2 OXALIC ACID SOLUTION.**

C.2.1 A 10% oxalic solution is made up by dissolving 10 grams (0.01 kg) of oxalic acid crystals in 100 ml (0.0001 cubic meter) of distilled or deionized water.

C.2.2 The oxalic acid solution should not be stored, but made fresh for each batch of parts.

C.2.3 The action of the solution will deteriorate with use and the solution should be discarded after processing approximately 200 square inches (1/8 square meter) of surface area of parts per liter (0.00001 cubic meter) of solution.

**D. GENERAL PROCESSING RECOMMENDATIONS:**

D.1 Do NOT use tap water.

D.2 Parts should NOT be handled with bare hands while carrying out any part of the procedure. The use of clean white lint-free gloves, clean polyethylene or rubber gloves as well as non-metallic or plastic-coated cleaning fixtures, racks, containers or tongs is recommended. Avoid the use of uncoated metallic processing equipment, especially those made of aluminum.

D.3 Agitation of the parts or solution is required during all immersion operations.

D.4 All solutions should be maintained at room temperature. Parts MUST be at room temperature prior to immersion in any of the working solutions.

**E. PROCESS PROCEDURE:****E.1 Cleaning**

E.1.1 Parts heavily contaminated with cutting fluids, oil, grease, dirt, etc. should be vapor-degreased prior to proceeding with the following cleaning procedure.

E.1.2 Immerse lightly soiled or vapor-degreased parts in clean solvent for 15 minutes with agitation of the part or the solvent. If available, ultrasonic cleaning is preferred. Remove parts from the solvent and allow to drain for several minutes.

E.1.3 Immerse parts in fresh, clean solvent with agitation for 5 minutes.

E.1.4 Dry parts with a flow of clean dry air or nitrogen. Drying may also be accomplished by placing the parts in an air-circulating oven operated at a temperature between 200° and 250°F (90° and 120°C).

NOTE: Care must be exercised to insure adequate cleaning and drying of recessed areas and holes.

E.1.5 Wash parts thoroughly in deionized or distilled water using agitation or flooding. Check for "water-break-free" surface. If contamination is still evident, gently scrub the affected areas with soft, lint-free cloth or tissue saturated with solvent, and repeat steps E.1.2 to E.1.5.



## MIL-HDBK-691B

**E.2 Surface Activation Treatment**

E.2.1 Immerse parts in a 10% oxalic acid solution for 20 minutes with periodic agitation. Parts and solutions MUST be at room temperature.

E.2.2 Wash parts thoroughly in clean deionized or distilled water using agitation or flooding. PASSIVATE IMMEDIATELY.

**E.3 Passivation**

E.3.1 Immerse parts in BERYLCOAT "D" passivation solution prepared as above for 30 minutes. The BERYLCOAT "D" passivation solution must be thoroughly agitated immediately prior to immersion of parts. Gently agitate parts or solution periodically during the passivation treatment in order to expose the surface to fresh solution and to dislodge any bubbles that may form on the parts.

E.3.2 Wash parts thoroughly in deionized or distilled water, using agitation or flooding for 3 minutes.

E.3.3 Immerse parts in at least three separate baths of fresh deionized or distilled water for 10 minutes at a time to remove all traces of BERYLCOAT "D" passivation solution.

E.3.4 Dry parts in a flow of clean dry air or nitrogen. Drying may also be accomplished by placing the parts in an air-circulating oven operated at a temperature between 200° and 250°F (90° and 120°C).

Bonding should be carried out within 24 hours after passivating. For Jet Propulsion Laboratory (JPL) reports, specifications and procedures using this basic procedure see Refs. 8, 9, 10 in Ref. 1.

5.3.5.1.4 Brass. Brass is an alloy of copper containing zinc. Sand-blasting or other mechanical methods may be used, or the following procedure, which combines mechanical and chemical treatment:

a. Abrasive blasting. Use either dry or wet methods. The abrasive particle size is not particularly critical.

b. Rinse with deionized water.

c. Treat with a 5% solution of sodium dichromate in deionized water.

d. Rinse in deionized water.

e. Dry.

This procedure causes some staining of the surface, but the stains do not materially affect the bond quality.<sup>(6)</sup>

5.3.5.1.5 Bronze. Bronze is an alloy of copper containing tin. Treat as with brass.

5.3.5.1.6 Cadmium (Cadmium plate). This metal, ordinarily used as a plating on steel, can normally be made bondable to a maximum extent by electroplating with silver or nickel. Another procedure is as follows<sup>(17)</sup>:

## MIL-HDBK-691B

- a. Degrease or solvent-clean with trichloroethane.
- b. Scour with commercial, nonchlorinated abrasive cleanser such as BABO or AJAX.
- c. Rinse with distilled water.
- d. Dry with clean, filtered air at room temperature.

**5.3.5.1.7 Copper and alloys.** Copper is used in three basic forms: pure, alloyed with zinc (Brass), and alloyed with tin (Bronze). See 5.3.5.1.4 for Brass and 5.3.5.1.5 for Bronze. The difficulty in bonding copper is not due to the continuous oxide layer present, as with the steels, but to its tendency to form brittle amine compounds with curing agents from some adhesive systems. The most successful surface treatments, for a wide variety of adhesives, are those that form a barrier that adheres well to the copper and is receptive to good adhesion with the adhesive material. Such treatments are black-oxide or Ebonol-C, given below, and chromate conversion coatings, which are particularly suitable when the adhesive to be used is slightly corrosive to copper. Other etch treatments, such as ferric sulfate, followed by a dichromate rinse, may also produce barrier films. This method is also described below.(3)

One major adhesive manufacturer suggests that good bonds to copper are more dependent on the adhesive system used than on the method of surface-preparation, provided that clean surfaces are used. This company states that an adhesive that bonds well to copper will do so if any good surface-preparation method is used, while an adhesive that does not bond to copper cannot be made to do so by changing the surface preparation method. Mechanical preparation methods are generally suggested as being preferable to chemical methods.(18)

Two of the chemical methods frequently recommended for copper are listed as follows:

**Black Oxide Coating.** This method is listed as Method E in ASTM D2651-79. (13) It is intended for copper alloys with over 95% copper (not brasses or bronzes). It should be used when thermally bonding with polyethylene and when the adhesive to be used contains chlorides.

- a. Degrease
- b. Immerse for 30 seconds at room temperature in the following solution:
 

Nitric Acid (70% technical)	10 pbv
Water	90 pbv
- c. Rinse in running water and transfer to the next solution. Do not allow to dry.
- d. Immerse for 1-2 minutes at 90°C (208°F) in the following solution:

EBONOL C or equivalent - 24 oz. to make 3.6 liters or one gallon of aqueous solution.

NOTE - Do not boil the above solution.

## MIL-HDBK-691B

- e. Rinse in running cold tap water.
- f. Air-dry.
- g. Bond as soon as possible within the working day.

The thickness of the oxide produced by this treatment is 3500 Å in 3 minutes and increases to 11,000 Å in 20 minutes, such thickness varying with different alloys of copper. Because of the high surface area and porous structure of the surface layer, fairly high joint strengths are obtained under peel stress, but not under shear stress, particularly with structural adhesives. Other limitations of this method are that it should not be used for treating thin films of copper because of high relative dimensional change due to etching, and it should not be used on low-copper alloys (i.e., brass and bronze), because it is not as effective with these alloys.

Sodium Dichromate-Sulfuric Acid Process. This method is listed as Method C in ASTM D2651. (13) In studies carried out by Picatinny Arsenal it proved superior to the Ferric Chloride Method.

- a. Wash with acetone.
- b. Immerse for 10 minutes at 150°F (66°C) in a solution containing:

Ferric sulfate (commercial)	1 pbw (1 lb.) (45.4 g)
Sulfuric acid (95%)	0.75 pbw (0.75 lb.) (340 g)
Deionized water	8 pbw (1 gallon) (3.784 liters)

- c. Rinse in deionized water at room temperature.
- d. Immerse in a solution containing:

Sodium dichromate	1 pbw
Sulfuric acid (95%)	2 pbw
Deionized water	17 pbw

until a bright clean surface is obtained.

- e. Rinse with deionized water.

Optional steps:

- f. Dip in concentrated ammonium hydroxide (sp. gr. 0.88).
- g. Wash in tap water.
- h. Rinse in deionized water.
- i. Air-dry at room temperature (Max 104°F) (40°C).

Oxidation with Alkaline Permanganate. In this immersion method, which is claimed to be superior to existing methods, surface oxides are removed by 1/2 min. immersion in water solution of concentrated phosphoric and nitric acids at room temperature. In the case of low-copper alloys (such as brass and bronze), the adherend is then immersed in hot sodium hydroxide to selectively etch out zinc. The adherend is fully immersed in hot alkaline potassium

## MIL-HDBK-691B

permanganate and then rinsed. The treatment does not corrode copper to any appreciable extent, and generates a thin, continuous, mechanically strong film of oxides 500 - 1000 Å thick. The treatment is as follows<sup>(19)</sup>:

- a. Vapor-degrease if grossly oily.

Etch 1/2 min. in:

Phosphoric acid, conc	75 pbv
Nitric acid, conc	10 pbv
Water	15 pbv

- c. Rinse with water.

- d. Immerse in 20% NaOH at 200°F (93°C) for 5 min. (in case of low-copper alloys such as brass or bronze).

- e. Rinse with water.

- f. Immerse in the following solution at 200°F (93°C) for 5 min.:

Potassium permanganate	1 pbw
Sodium hydroxide	1 pbw
Water	98 pbw

- g. Rinse in water.

5.3.5.1.8 Magnesium and alloys. The preparation of magnesium surfaces for adhesion involves consideration for corrosion resistance, particularly where long-term environmental exposure is concerned. Magnesium, because of its high position in the EMF series, is more susceptible than other common metals to galvanic corrosion. The greatest enemy of magnesium in causing corrosion is the chloride ion in an aqueous solution. Other electrolytes, such as the strong and weak acids, are also to be avoided, with two exceptions, chromic acid and hydrofluoric acid, which essentially do not attack magnesium. Accordingly, these two acids are used in preparing surfaces for adhesive bonding. Magnesium is quite resistant to alkaline conditions, and this resistance is used, under controlled conditions, in surface preparations for adhesive bonding. Minor constituents used in magnesium alloys play a significant part in adhesive bonding. There appears to be an interplay or compatibility criterion between adhesive selection, the surface-preparation method, and the specific alloy in influencing bond strength.<sup>(1)(3)</sup> With an adhesive system using an exceptionally good metal adherend, original adhesion may be excellent whether the metal is degreased only, roughened, or chemically treated. With less efficient metal adhesives, chemical treatment will probably be required for optimum results. In any case, maximum environmental resistance is obtained by a good chemical method.<sup>(10)</sup>

Suggested methods are as follows:

Chromic Acid (Hot). This method is very similar to Method A/B (Combination of A and B) described in ASTM D 2651-79.<sup>(13)</sup> It generally gives excellent results over a wide range of alloys, resulting in negligible metal removal.

- a. Solvent-degrease, using acetone or other suitable solvent. Exercise caution during vapor degreasing of magnesium alloys. Contaminants, such as metal particles, oils, etc., may result in a fire or explosion hazard.

## MIL-HDBK-691B

b. Immerse for 10 minutes at 160-190°F (71-78°C) in the following alkaline pretreatment solution:

Sodium metasilicate	3.0 oz/gal. (22.4 g/liter)
Tetrasodium pyrophosphate	1.5 oz/gal. (11.2 g/liter)
Sodium hydroxide	1.5 oz/gal. (11.2 g/liter)
Detergent (or NACCONAL NR,) (a sodium alkylaryl sulfonate)	0.5 oz/gal (3.73 g/liter)
Water, demineralized	1 gal. (3.785 liters)

- c. Rinse in demineralized water at room temperature.
- d. Immerse for 10 minutes at 150-160°F (66-71°C) in an aqueous solution of 20 wt % chromium trioxide (CrO<sub>3</sub>).
- e. Rinse in demineralized water at room temperature.
- f. Air-dry at temperatures not over 140°F (60°C).

Chromic Acid (Room Temperature). Identical to the Hot method above except for d, e and f, as follows:

- d. Immerse for 2 minutes at RT in the following solution:

Chromium trioxide	24 oz/gal. (179.2 g/liter)
Water, demineralized	1 gal. (3.785 liters)

- e. Rinse in demineralized water at RT.
- f. Air-dry at temperatures not over 140°F (60°C).

Caustic (Alkaline) Treatment. This procedure is the same as Chromic Acid (Room Temperature), but followed by immersion in a sodium hydroxide solution. To avoid confusion, all steps are given here:

a. Solvent-degrease, using acetone or other suitable solvent. Exercise caution during vapor degreasing of magnesium alloys. Contaminants such as metal particles, oils, etc., may result in a fire or explosive hazard.

b. Immerse for 10 minutes at 180-190°F (71-88°C) in the following alkaline pretreatment solution:

Sodium metasilicate	3.0 oz/gal (22.4 g/liter)
Tetrasodium pyrophosphate	1.5 oz/gal (11.2 g/liter)
Sodium hydroxide	1.5 oz/gal (11.2 g/liter)
Detergent (as NACCONAL NR,) (a sodium alkylaryl sulfonate)	0.5 oz/gal (3.73 g/liter)
Water, demineralized	1 gal. (3.785 liters)

- c. Rinse in demineralized water at room temperature.
- d. Immerse for 10 minutes at room temperature in the following solution:

Chromium trioxide	24 oz/gal. (179.2 g/liter)
Water, demineralized	1 gal. (3.785 liters)

## MIL-HDBK-691B

- e. Rinse in demineralized water at room temperature.
- f. Immerse in the following solution for 1-3 minutes at 180°F (80°C):

Sodium hydroxide	12-16 oz/gal. (89.6-119.5 g/liter)
Water, demineralized	1 gal. (3.785 liters)

- g. Rinse in demineralized water at room temperature.
- h. Air-dry at temperatures not over 140°F (60°C).

5.3.5.1.9 Nickel and alloys. Nickel is frequently used as a plating metal (see 5.3.5.1.16). Thin nickel-plated parts should not be etched or sanded. A recommended practice is light scouring with a non-chlorinated commercial cleanser (AJAX, BABO, etc.), rinsing with distilled water, drying under 120°F (49°C), and then priming as soon as possible. Recommended methods for nickel and alloys are(1):

Nitric Acid Process

- a. Vapor-degrease in trichlorethane
- b. Etch for 4-6 seconds at room temperature ( 68°F, 20°C) in conc nitric acid (sp. gr. 1.41).
- c. Wash in cold and hot water, followed by a distilled water rinse.
- d. Air-dry at 104°F (40°C).

Chromic Acid - Hydrochloric Acid Process

- a. Vapor-degrease or solvent-clean
- b. Immerse in the following solution at room temperature for 60-80 seconds:
 

Chromic acid (CrO <sub>3</sub> )	15 pbw
Hydrochloric acid	20 pbw
- c. Spray-rinse with deionized water.
- d. Oven-dry at 130°F (54°C) until dry.

NOTE: If immersion is impossible, the above solution may be applied with a cheesecloth (after solvent cleaning). Allow to remain on the part for approximately one minute. Apply to approximately one square foot (0.093 square meter) at a time.

5.3.5.1.10 Steel (mild, carbon), iron. Relatively little research has been carried out in the area of surface treatments of steel preparatory to adhesive bonding, compared to aluminum. This is due primarily to the fact that the aircraft-related industries have provided the impetus for much of the structural bonding research accomplished to date, and aluminum, because of its favorable strength-to-weight ratio, is a preferred construction material for aircraft. For Army munitions applications, however, steel alloys are at least as important as aluminum alloys, and steel assemblies are increasingly being joined by adhesive bonding.(20)



## HIL-HDBK-691B

Many problems exist in bonding steels. The steel alloys are normally used where high "in-service" temperatures and other rigid requirements are expected, and this poses problem areas, i.e., corrosion, rust, thermal degradation of adhesives and primers, and loss of adhesion at faying interfaces due to moisture. Surface preparation is even more critical in bonding steel than in many other metals. Initial adhesion to steel is usually good, but the bond deteriorates rapidly under rigid environmental conditions. For this reason, primers are usually recommended. Many steel alloys will form surface oxides in a very short period of time, and drying cycles after cleaning will be critical. Alcohol rinses after water rinses tend to accelerate drying and reduce undesirable surface layers. Mild steel may require no more extensive treatment than degreasing and abrasion to give excellent results in adhesive bonding. Tests should be carried out with the adhesive to be used to determine whether a chemical etch or other treatment is necessary.(1)(21)

Mechanical methods. ASTM D2651-79, Method A for Carbon Steel.(13)  
Mechanical methods, such as wire brushing, rubbing with metal wool, hand-sanding, dry-sand blast, grit-blast, or vapor honing, may be used on degreased surfaces of the metal. All abrasive materials should be free from contamination that may be spread or rubbed onto the steel. Dry-grit or sandblasting tends to warp thin sheet metals. These methods are suitable only for thick-section parts. Vapor-blasting by water or steam and an abrasive is the most effective method and does not warp parts if done carefully. Hand sanding, rubbing with metal wool, and wire brushing, are the least effective methods. Care should be exercised in using any mechanical method to prevent deep gouges or rough surfaces which are not conducive to good bonding. Surfaces should be washed, vapor-degreased, brushed or air-blasted with oil-free air to remove all traces of the abrasions. The adhesive should be applied immediately after the treatment.

Solvent wiping should be used only as a last resort. Solvents such as methyl ethyl ketone (MEK), acetone and isopropyl alcohol usually contain sufficient water to cause steel to rust. Xylene or toluene are preferable solvents. When volatile solvents evaporate from a metal surface they may chill the surface. In a humid environment this may result in condensation of water, which nullifies the cleaning effort.(1)

Acid Treatment. This treatment is for use when abrasive equipment is not available.(1)

a. Prepare a solution of:

Orthophosphoric acid, conc (sp. gr. 1.73)	1 pbw
Ethyl alcohol, denatured	1 or 2 pbw
or	
Hydrochloric acid, conc	1 pbw
Distilled water	1 pbw

(NOTE: Add the acid to the water)

b. Degrease in a vapor bath of trichloroethane

c. Immerse 10 minutes in the phosphoric acid solution at 140°F (60°C).

OR

## NIL-MDBK-691B

Immerse 5-10 minutes at 68°F (20°C) in the hydrochloric acid solution.

- d. Remove the black residue on the metal with a clean, stiff brush while holding the metal under cold, running, distilled or deionized water.
- e. Dry the metal by heating at 250°F (120°C) for one hour. Freshly-etched or sandblasted steel rusts quickly when the relative humidity is more than 30%. If the steel cannot be stored immediately in areas of low humidity, then the adhesive should be applied shortly after the surface has been cleaned.

Iodophosphate Treatment. This is a relatively new surface treatment based on an oxidation of the steel to provide a continuous film of epsilon- $(Fe_2O_3)$ . It is reported to give strong and durable adhesive joints and to improve the salt spray and humidity resistance of polymer-coated steel. The steps are as follows:(22)

- a. Vapor-degrease.
- b. Alkaline-clean in a solution of 3% sodium phosphate and 3% sodium carbonate for 5 min. at 180°F (82°C).
- c. Rinse in deionized water.
- d. Immerse in a solution of 50 g. potassium iodide (KI) per liter of 1:1:: conc. phosphoric acid:water for 2-10 min. at 200 ± 20°F (93 ± 11°C).
- e. Rinse in deionized water and dry at 60-160°F (16-71°C). This method can be adapted to spraying techniques for commercial operation. Note that no corrosive chloride ion is used.

A very recent Army Study(20) determined the relative durability in a harsh, warm, moist environment, of bonds made to high-strength carbon steel after surface treatments by four different methods. The two best methods were found to be the phosphoric acid/alcohol method and the iodophosphate method, both described above. For a summary of results on these two methods, using a second-generation acrylic adhesive and an epoxy adhesive, see Table XXXIV below.(20)

5.3.5.1.11 Steel, stainless. Stainless or corrosion-resistant (CRES) steels are characterized by a high chromium content (11% or higher) as the prime alloying element. There have been a great many surface preparation methods reported in the literature. In addition to mechanical methods, strong acids and strong alkalis are used. A wet-abrasive blast with a 200-grit abrasive, followed by thorough rinsing to remove the residue, is an acceptable process for some uses, but does not produce extremely high bond strengths. Strong acid treatments are usually used for general bonding, producing strong bonds with most adhesives. Passivation in nitric acid solution and concentrated sulfuric acid-saturated sodium dichromate solution both produce high-strength bonds, but with low or marginal peel strengths. Joints prepared by the passivation process may fail under vibration stress, particularly when a thin stainless steel sheet is bonded with low-peel-strength adhesives.

Types 301 and 302 stainless steels can be treated by the acid-etch process outlined below. This process results in a heavy black smut formation on the

## MIL-HDBK-691B

surface that must be removed for maximum adhesion. The acid-etch process is claimed to produce bonds with high peel and shear strengths.

The 400 series of straight-chromium stainless steels should be handled in the same manner as the plain carbon steels. The precipitation-hardening (PH) stainless steels each present an individual problem and processes must be adopted or developed for each.(3)(6)

Mechanical Methods - as in 5.3.5.1.10 for carbon steel.

Acid Etch - (for Types 301 and 302 Stainless Steel)(23).

- a. Degrease. Wash with acetone to remove grease, oils, markings and solvent-removable soils. (Vapor degreasing can follow with a suitable safety solvent).
- b. H<sub>2</sub>SO<sub>4</sub> Etch. Immerse the parts for 4 minutes at 140°F (60°C) in a solution of 25-35% by volume of sulfuric acid (sp. gr. 1.48) in deionized water. Timing should not start until gassing is evident. A piece of 1020 steel may be rubbed across the parts to start the etching process.
- c. Rinse. Rinse in running tap water at service-water temperature for 2 minutes.
- d. Smut removal. Immerse parts for 5 minutes at 150°F (66°C) in a solution of 22-28 parts by weight sulfuric acid (sp. gr. 1.84) and 2-3 parts by weight sodium dichromate in deionized water.
- e. Rinse. Rinse in running tap water at service-water temperature for 2 minutes.
- f. Dry the parts at 140°F (60°C) for 30 minutes in a preheated air-circulating oven.
- g. Packaging. Wrap the parts in clean kraft paper until ready to bond. This surface-preparation procedure has been used successfully with both 3M Co. AF-126-2 film adhesive and 3M Co SCOTCHWELD EC 2414R paste adhesive. The film adhesive was cured at 50 psi (345 kPa) and 250°F (121°C) for 1 hour and for paste adhesive was cured at 8 psi (55 kPa) and 250°F (121°C) for 40 minutes. Stressed durability studies (ASTM D 2919) gave excellent results for exposures at 140°F (60°C) and 95% RH.

Bromophosphate Treatment. This treatment is a modification of the Iodophosphate Treatment given above under carbon steel. KBr is used instead of KI, and 1-5% by volume of conc H<sub>2</sub>SO<sub>4</sub> is suggested to be added to the treating solution in the case of difficult-to-etch CRES steels to ensure the removal of the existing surface layers(22).

- a. Vapor-degrease.
- b. Alkaline-clean in a solution of 3% sodium phosphate and 3% sodium carbonate for 5 min. at 180°F (82°C).
- c. Rinse in deionized water.

## MIL-HDBK-691B

- d. Immerse in a solution of 50g potassium bromide (KBr) per liter of 1:9:10 conc  $H_2SO_4$ :: conc phosphoric acid:  $H_2O$  for 2-10 min at  $200 \pm 20^\circ F$  ( $93 \pm 11^\circ C$ )
- e. Rinse in deionized water and dry at  $60-160^\circ F$  ( $16-71^\circ C$ ), spray rinsing may be used.

Note that no chloride ion is used in this method.

5.3.5.1.12 Tin. This is one of the few metals for which abrasive cleaning may be used without being followed by an acid etch of some type. The oxide coating must be removed, but after the abrasive operation, the faying surface should be scrubbed thoroughly. (17)

- a. Solvent-clean with trichloroethane.
- b. Use abrasive cleaning only to remove foreign matter that the solvent does not remove. Scraping, fine sanding, or scouring are suitable methods.
- c. Solvent-clean to remove abrasive particles(3).

5.3.5.1.13 Titanium and alloys. Since titanium is intended for application at temperatures up to  $600^\circ F$  ( $316^\circ C$ ) the surface preparation methods are directed towards durability at the higher temperatures. The preparation of titanium surfaces is primarily directed towards the development of a strong adherent surface film. The development of surface-preparation techniques for titanium has been based primarily on empirical use of established processes that were found successful in stainless steel and aluminum, rather than custom-tailored processes based on analyses of the requirements. Chemical treatments such as the nitric-hydrofluoric acid pickle, followed by the phosphate-fluoride conversion coating, have found widespread use, as well as proprietary acid etchants and strong alkaline etchants. One of the problems requiring close control with titanium processing is hydrogen embrittlement. Extreme caution must be exercised when treating titanium with acid etchants that evolve hydrogen. Immersion times must be closely controlled and optimized. (24)

Stabilized Phosphate-Fluoride Method (Picatinny Arsenal Etch)(1). This method, developed by Wegman at Picatinny Arsenal, is an improvement over the basic phosphate-fluoride treatment described in MIL-A-9067. The improvement is obtained by the addition of the sodium sulfate in the pickle. The method is reported to give good initial bond strength and excellent durability under adverse conditions, including high temperature/high humidity  $140^\circ F$  ( $60^\circ C$ ) - 95% RH under load. The proper crystalline structure is established by the phosphate-fluoride process, which is then stabilized with incorporation of sodium within the crystalline structure.

- a. Vapor-degrease or clean with acetone.
- b. Alkaline-clean: Immerse parts in non-silicated alkaline cleaner for 5 minutes at  $150^\circ F$  ( $66^\circ C$ ). A suitable formulation is 1.5 oz/gal (11.2 g/liter) OAKITE HD 246 in deionized water.
- c. Rinse in running tap water at  $105^\circ F$  ( $40^\circ C$ ) for 2 min.

## MIL-HDBK-691B

- d. **Modified HF Pickle:** Immerse for 2 minutes at room temperature in a solution containing:

Hydrofluoric acid, 70%	2-3 fl oz/gal (16-23 ml liter)
Sodium sulfate, anhydrous	3 oz/gal (23 g/liter)
Nitric acid, 70%	40-50 fl oz/gal (312-391 ml/liter)
Water, deionized	to make 1 gal (3.785 liters)

- e. Rinse in running tap water at service temperature for 2 minutes.
- f. **Phosphate-fluoride etch:** Soak parts for 2 minutes at room temperature in a solution containing:
- |                        |                                    |
|------------------------|------------------------------------|
| Trisodium phosphate    | 6.5-7.0 oz/gal (48.7-52.4 g/liter) |
| Potassium fluoride     | 2.3-3.0 oz/gal (18.7-22.5 g/liter) |
| Hydrofluoric acid, 70% | 2.2-2.5 oz/gal (16.5-18.7 g/liter) |
| Water, deionized       | to make 1 gal (3.785 liters)       |
- g. Rinse in running tap water at service temperature for 2 minutes.
- h. **Hot-water Soak:** Immerse in deionized water at 150°F (66°C) for 15 minutes.
- i. **Final Rinse:** Rinse in water at room temperature to 160°F (71°C) for 15 minutes.
- j. Dry at 140°F (60°C) for 30 minutes in a preheated air-circulating oven.
- k. Wrap the parts in clean kraft paper until ready to bond. This method has been shown to give excellent durability for both 6,4 titanium and chemically-pure (CP) titanium. The 6,4 titanium, however, shows a loss of lap-shear strength after 5-years outdoor exposure, while the CP material does not.

Alkaline Cleaning.(23) Use steps a, b, c, j, and k only under above procedure for Stabilized Phosphate-Fluoride Method. The results give poorer durability than the Stabilized-Phosphate Fluoride Method.

Alkaline Etch.(3)

- a. Vapor-degrease or clean with acetone.
- b. Alkaline Clean: Immerse parts in non-silicated alkaline cleaner for 5 minutes at 150°F (66°C). A suitable formulation is 1.5 oz/gal (11.2 g/liter) OAKITE HD 246 in deionized water.
- c. Rinse in running tap water at 105°F (40°C) for 2 min.
- d. Rinse in running deionized water for 1 minute at service temperature.
- e. Alkaline Etch: Immerse for 5-10 minutes at 180-200°F (82-93°C) in a solution of 4 lbs/gal (479 g/liter) TURCO 5578.

## MIL-HDBK-691B

- f. Rinse under tap water at service temperature for 2 minutes.
- g. Rinse under deionized water at service temperature for 1 minute.
- h. Dry at 140°F (60°C) for 30 minutes in preheated air-circulating oven.
- i. Wrap the parts in clean kraft paper until ready to bond.

VAST (Vought Abrasive Surface Treatment) The VAST treatment given under 5.3.5.1.17.2 may also be used.

5.3.5.1.14 Tungsten and alloys (including tungsten carbide).

Hydrofluoric-Nitric-Sulfuric Acid Method.(25)(26)

- a. Degrease in a vapor bath of trichloroethane
- b. Abrade the surface using medium-grit emery paper.
- c. Degrease again in trichloroethane.
- d. Using equipment constructed of fluorocarbon resin, polyethylene or polypropylene, prepare the following solution:

Hydrofluoric acid, 60%, sp. gr. 1.18	5 pbw
Nitric acid, conc, sp. gr. 1.41	30 pbw
Sulfuric acid, conc, sp. gr. 1.84	50 pbw
Water, distilled	15 pbw

Blend the hydrofluoric acid and the nitric acid with water and then slowly add the sulfuric acid, stirring constantly with a TEFLON or polyethylene rod. Add a few drops of 20% hydrogen peroxide.

- e. Immerse for 1-5 minutes in the above solution at room temperature.
- f. Rinse under tap water.
- g. Finish rinsing in distilled water.
- h. Dry in an oven at 160-180°F (71-82°C) for 10-15 minutes.

5.3.5.1.15 Zinc and alloys. The most common use of zinc is in galvanized metals. Zinc surfaces are almost always prepared mechanically.(1)

Abrasion (for general-purpose bonding)

- a. Grit- or vapor-blast with 100-grit emery cloth.
- b. Vapor-degrease in trichloroethane.
- c. Dry at least 2 hours at room temperature, or 15 minutes at 200°F (93°C) to remove all traces of trichloroethane.



## MIL-HDBK-691B

Sulfuric Acid/Dichromate Etch (suitable for freshly galvanized metal).(1)

a. Vapor-degrease in trichloroethane.

b. Etch for 3-6 minutes at 100°F (38°C) in:

Sulfuric acid, conc, sp. gr. 1.84	2 pbw
Sodium dichromate, crystalline	1 pbw
Water, distilled	8 pbw

c. Rinse in running tap water.

d. Rinse in distilled water.

e. Dry in air at 104°F (40°C).

5.3.5.1.16 Plated metals (includes cadmium, chromium, gold, nickel, solder, platinum, rhodium, and zinc). Metals are usually plated as a corrosion-preventive measure, or to retain surface conductivity for metals, such as aluminum, which otherwise develops a dielectric film of aluminum oxide. Cleaning procedures involving acid-etch or abrasion must be used with care, since they tend to remove the plating. If the surfaces are protected from contamination after the plating and cleaning process, they are usually clean enough for bonding. One method of obtaining improved bondability is to vapor-hone or sandblast the surface before plating. This provides an increase in surface area as well as some mechanical benefits in increased shear strength.(27)

In many cases, the freshly plated surfaces may not require any additional preparation because the plating process itself produces a clean, bondable surface. The conditions under which the plating process is carried out have a marked effect in the surface condition of the plated metal. Plating conditions determine the adhesion, porosity and surface stress of the metal deposit. Current density, composition and temperature of the plating bath, for example, all have an effect on the bondability of the plated surface. Where mechanical treatment is indicated, care must be taken to abrade the surface lightly. Fine grains of sand, abrasive paper, or steel wool will have minimum penetrating effect. Chemical treatments for plated metals are of specialized utility, depending on the metal deposited in the plating process. Degreasing and solvent wiping are often satisfactory for plated-metal preparation. If the plating does not adhere tightly to the base metal, the plating process itself should be investigated.(18)

Wet-Abrasive Scour(29).

a. Vapor-degrease or solvent-clean.

b. Scour surfaces with tap water and scouring powder.

Scouring may be facilitated with clean cloths or non-metallic brushes. Surfaces should be thoroughly rinsed in clean running tap water, followed by a final rinse with distilled water. They should be water-break-free (see 5.3.3.1) and thoroughly dried at temperatures up to 150°F (66°C).

## MIL-HDBK-691B

Dry-Abrasive Treatment(29).

- a. Wipe, spray or immerse in 1,1,1 trichloroethane, or FREON TMC or N-17, acetone, MEK or toluene.
- b. Lightly and uniformly abrade surface with 180-230 grit abrasive paper.
- c. Solvent-clean as in (a).

5.3.5.1.17 Weldbonding (see also Chapter 12). The chemical etching of metal surfaces for welding and adhesive bonding is necessary to assure high-strength joints. There are differences in the surface requirements after cleaning for welding and bonding. To produce Class A resistance welds it is necessary to have a chemically active surface which may have a high surface resistance. Final selection of the cleaning process should be based on the end use of the hardware and consideration of the relative importance of weld quality and adhesive joint strength.(29)

Minford et al. of ALCOA have shown that, for certain aluminum and steel alloys used for non-critical automotive applications, no cleaning or special surface preparation was necessary. Procedures for aluminum and titanium are given as follows:

5.3.5.1.17.1 Aluminum.

Low-Voltage Phosphoric Acid/Sodium Dichromate Anodize (for alloys 2024-73 and 7075-T6 bare)(30)(31). This method was developed by the Northrop Corporation for the Air Force Materials Laboratory. It has been found to be superior to the previously recommended method (PPL Etch + 60-Minute Dichromate Seal).

- a. Vapor-degrease in trichloroethane vapor for 60 seconds, followed by spray-rinse of condensed trichloroethane fluid for an additional 60 seconds. All parts must be free of water prior to vapor degreasing.
- b. Alkaline-clean 10-15 minutes at  $155 \pm 10^\circ\text{F}$  ( $68.5 \pm 5.5^\circ\text{C}$ ) in TURCO 4215-S solution (6-8 oz/gal or  $44.9\text{-}59.9 \text{ kg/m}^3$  or g/l).
- c. Immediately spray-rinse with cold deionized water for at least 5 minutes and inspect for water-break-free condition (see 5.3.3.1). Should water breaks occur, repeat above steps.
- d. Immerse alkaline-cleaned parts in a deoxidizer solution consisting of 8-16% by volume nitric acid and 2.7-3.3 oz per gallon Amchem 7 ( $20.2\text{-}24.7 \text{ kg/m}^3$  or g/L) for 7-10 minutes at room temperature. (NOTE: When chemical addition is required to maintain solution strength, Amchem 17 should be used instead of Amchem 7).
- e. Immediately spray-rinse in cold deionized water for at least 5 minutes.
- f. Anodize at  $1.5 \pm 0.2$  volts for 20-25 minutes in a solution of  $1.35 \pm 0.15$  oz of phosphoric acid and  $1.35 \pm 0.15$  oz of sodium dichromate per gallon of solution (each  $10.1 \pm 1.12 \text{ g/L}$ ). Anodizing should be conducted in a room-temperature solution using a "ripple-free" DC power supply.

## NIL-HDBK-691B

- g. Immediately spray-rinse in cold deionized water for at least 5 minutes.
- h. Oven-dry 30-60 minutes at 140-150°F (60-66°C).
- i. Cleaned parts must be handled only with clean white cotton gloves and may be stored for periods up to 21 days prior to weldbonding by wrapping in chemically neutral paper.

5.3.5.1.17.2 Titanium. Grumman Aerospace Corporation has developed two surface treatments for titanium weldbonding under an Air Force Materials Laboratory contract. They are as follows (32):

Vapor Honing/Pasa Jell 107M Procedure.

- a. Remove organic contaminants by MEK solvent rinse.
- b. Remove inorganic contaminants by immersion in non-etch alkali (hot OAKITE 164) at 140°F (60°C).
- c. Rinse in tap water.
- d. Vapor-hone, using aluminum oxide slurry.
- e. Rinse in tap water.
- f. Immerse in PASA JELL 107M solution\* at ambient temperature for 10 minutes.
- g. Rinse in tap water.
- h. Air-dry.
- i. Use adherends within 8 hours after pretreatment.

Modified VAST (Vought Abrasive Surface Treatment) System. VAST is a combination mechanical-chemical surface treatment that is essentially a wet-hone operation. The surface to be treated is impinged with a slurry of abrasive grit in an acid solution in the original process. In the modification by Grumman the panels are first vapor-honed in the aluminum oxide slurry, then etched in a spray application of 2%  $H_2SiF_6$ . The original process is as follows:

- a. Wipe surfaces with MEK.
- b. Alkaline-clean with TURCO 5578 - 5 oz/gal (37.3 g/liter).
- c. Rinse with deionized water at room temperature.

\*A proprietary solution containing  $HNO_3$ ,  $Na_2Cr_2O_7$ ,  $H_2SiF_6$  and proprietary surfactants.

## NIL-HDBK-691B

- d. Use VAST process of surface impingement in suitable chamber. The slurry consists of 2000 ml of 2% hydrofluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) and 500 ml of 240-grit purified aluminum oxide ( $\text{Al}_2\text{O}_3$ ), such as white aluminum oxide.
- e. Rinse with tap-water spray at room temperature.
- f. Immerse 1 minute in 5% nitric acid solution (optional, depending on titanium alloy).
- g. Rinse in deionized water at room temperature.
- h. Air-dry.
- i. Bond within 4 days after treatment to be sure, although experiments have shown no changes up to 9 days (33).

5.3.5.2 Plastics.

5.3.5.2.1 General discussion. The following sections list commonly recommended surface-preparation procedures, usually only one or two, for specific plastic adherends. The discussion in 5.3 above should also be studied, but the procedures listed below have been specifically found to provide reproducible structural bonds and fit easily into the bonding operation.

5.3.5.2.2 Thermoplastics. As opposed to thermosetting plastics, thermoplastic surfaces must usually be physically or chemically modified to achieve acceptable bonding. This is particularly true of the crystalline thermoplastics, such as the polyolefins, linear polyesters and fluorocarbons. Methods used to improve the bonding characteristics of these surfaces include:

- o Oxidation via chemical or flame treatment.
- o Electrical discharge to leave a more reactive surface.
- o Ionized inert gas, which strengthens the surface by crosslinking and leaves it more reactive (See 5.3.2.8).
- o Metal-ion treatment.

The treatments outlined below are recommended for use when thermoplastics are to be joined with adhesives. Solvent cements and thermal welding are other methods for fastening thermoplastics which do not require chemical alteration of the surface. (See chapter 7 for discussion of solvent cementing and 4.7.3 for discussion of thermal welding. As with metallic substrates, the effects of plastic surface treatments decrease with time. It is essential to prime or bond soon after the surfaces are treated.<sup>(4)</sup>)

5.3.5.2.2.1 Acetal copolymer (CELCON).<sup>(34)</sup>

- a. Wipe parts with acetone.
- b. Air-dry.

## MIL-HDBK-691B

- c. Etch faying surfaces for 10-15 seconds in a solution containing:

Sulfuric acid	400 pbw
Potassium dichromate	11 pbw
Water, deionized	44 pbw

- d. Immediately flush parts with tap water.
- e. Rinse with deionized water.
- f. Oven-dry at 140°F (60°C).

Activated gas plasma has also been used successfully in preparing CELCON surfaces.

5.3.5.2.2.2 Acetal-homopolymer (DELRIIN).

- a. Wipe with acetone or MEK
- b. Immerse in the following chromic acid solution for 10-20 seconds at room temperature 68-86°F (20-30°C):

Potassium dichromate ( $K_2Cr_2O_7$ )	75 g or 15 pbw
Sulfuric acid, conc	1500 g or 300 pbw
Tap water	120 g or 24 pbw

Dissolve the potassium dichromate in the clear tap water, then add the sulfuric acid in increments of about 200 g, stirring after each addition.

- c. Rinse in running tap water for at least 3 min.
- d. Rinse in distilled or deionized water.
- e. Dry in an air-circulating oven at 100°F (38°C) for about 1 hour.

"Satinizing". (U.S. Pat. 3,325,426) is described by du Pont for preparing DELRIIN for painting, metallizing and adhesive bonding. In the process, a mildly acidic solution produces uniformly-distributed anchor points in the adherend surface. Adhesives bond mechanically to these anchor points, resulting in strong adhesives.

- a. Prepare the following formulation:

Kieselguhr (pyrogenic silica)	0.5% by wt
1,4-dioxane	3.0% by wt
Para-toluene sulfonic acid (p-TSA)	0.3% by wt
Perchloroethylene	96.2% by wt

No preferential treatment is required for mixing the ingredients. The first three components above may be worked into a premix, to which the perchloroethylene may be added whenever a batch is needed for "satinizing". Since 1,4-dioxane is flammable, it should be used only in areas suitable for work with combustible products. The ingredients contained in the "satinizing"

## MIL-HDBK-691B

solution are known to be hazardous by reason of the flammability of 1,4-dioxane and the toxicity of vapors of 1,4-dioxane, perchloroethylene, and formaldehyde. Careful attention should be given to the design of ventilation equipment for use in this process. Both perchloroethylene and 1,4-dioxane vapors will be evolved from the dip bath. Also, formaldehyde will be liberated from the surface of the part as a result of the etching process. Ventilation should be incorporated at the dip bath to remove those vapors in such a way that they will not be drawn across the breathing zone of an operator. Steps 1-3 below should be carried out in explosion-proof equipment, as 1,4-dioxane is flammable. Excessive air velocity is to be avoided, as unnecessarily high losses of etching solution will result.

The liberation of formaldehyde fumes from the part surface, as well as the continued evaporation of liquids (perchloroethylene and 1,4-dioxane), will continue through Steps 2 and 3. Accordingly, these steps will require ventilation to remove hazardous vapors as well. Exhaust equipment should be designed in such a way as to prevent any condensation of water which would subsequently find its way back to the equipment used in Steps 1 and 2.

b. Convey the parts through the following four-step operation:

1. Dip. Immerse the DELRIN article in bath for 10-30 seconds at 175-250°F (79.5-121°C). The part is cleaned simultaneously by the degreasing action of the perchloroethylene. Parts should not touch each other or other objects. The bath area should be ventilated to remove formaldehyde fumes. An efficient stirrer should be used to keep the kieselguhr solid assistant in suspension and to insure homogeneity.

2. Chemical Action. Transfer the DELRIN parts to an air oven adjusted to 100-250°F (38-121°C). In this step the solvents from the previous step are evaporated and rapid etching is induced. The depth of the etch is controlled concurrently by the temperature and time of exposure in the oven. At 250°F (121°C) adequate etching should take no longer than one minute. Lower oven temperatures require longer exposure times. The oven area should be ventilated to remove formaldehyde fumes.

3. Water Rinse. Remove the DELRIN parts from the oven and then spray hot water at 160-175°F (71-79.5°C). This stops the etching action.

4. Air dry. Dry in an oven with air, with the rate of drying adjusted in keeping with production and floor space requirements. A short high-temperature 250°F (121°C) drying step for several minutes will reduce the tendency of the part to continue to release formaldehyde vapors. The part is now ready for bonding.

#### 5.3.5.2.2.3 Acrylonitrile-butadiene-styrene (ABS). (35)

##### Abrasive treatment.

- a. Sand with a medium-grit sandpaper.
- b. Wipe free of dust.
- c. Dry in an oven at 160°F (71°C) for 2 hours.
- d. Prime with Dow Corning A-4094 or General Electric SS-4101.



## MIL-HDBK-691B

Warm Chromic-Acid Etch(1).

- a. Degrease in acetone.
- b. Etch in the following solution for 20 minutes at 140°F (60°C).

Sulfuric acid, conc	26 pbw
Potassium dichromate	3 pbw
Water	11 pbw

- c. Rinse in tap water.
- d. Rinse in distilled water.
- e. Dry in warm air.

5.3.5.2.2.4 Cellulosics (Cellulose acetate, cellulose acetate butyrate (CAB), cellulose nitrate, cellulose propionate, ethyl cellulose). Cellulosics are usually solvent-cemented. Treatment for surface preparation prior to conventional adhesive bonding is given here, particularly for applications where the cellulosic is to be bonded to a dissimilar adherend.

Abrasion and Cleaning(1).

- a. Solvent-degrease in methyl or isopropyl alcohol.
- b. Grit- or vapor-blast, or use 220-grit emery cloth.
- c. Solvent-degrease again.
- d. Heat 1 hour at 200°F (93°C) and apply adhesive while still hot.

Plasma-arc treatment has also been used successfully on CAB.

5.3.5.2.2.5 Ethylene-tetrafluoroethylene copolymer (ETFE). This higher temperature-resistant thermoplastic, supplied by du Pont as TEFZEL, became available in 1976. It is readily processed by conventional methods, including extrusion and injection molding. Recommended assembly techniques include screw assemblies, snap-fit, press-fit, cold or hot heading, spin-welding and heat-bonding. No information has been found in the literature on adhesive bonding. A new type CE high-performance film type is made cementable with a transparent treatment for bonding. Du Pont claims that the material is receptive to many adhesives.

5.3.5.2.2.6 Ethylene-vinyl acetate (EVA). This is really an elastoplastic, with properties intermediate between that of a true plastic and an elastomer. (12)

- a. Degrease in methanol.
- b. Prime with epoxy adhesive.
- c. Fuse into the surface by heating for 30 min at 212°F (100°C).

## MIL-HDBK-691B

5.3.5.2.2.7 Fluorinated ethylene propylene (FEP). This resin is supplied by du Pont as TEFLON FEP. FEP is prepared by the same methods as are used for PTFE (5.3.5.2.2.25) and PCTFE (5.3.5.2.2.15).

ASTM Procedure (ASTM D2093).

- a. Wipe with acetone
- b. Treat with sodium-naphthalene complex for 15 minutes at room temperature. Sodium naphthalene solutions are commercially available.

Sodium-naphthalene complex solutions should be kept in tightly-stoppered glass containers to exclude air and moisture. Extreme care should be taken in handling the solutions, since they are hazardous, due to the explosive property of the sodium. Directions are given in the literature for making up sodium-naphthalene complex solutions, which contain sodium metal, naphthalene and tetrahydrofuran in varying proportions.

- c. Remove from solution with metal tongs.
- d. Wash with acetone to remove excess organic material.
- e. Wash with distilled or deionized water to remove the last traces of metallic salts from the treated surface.
- f. Dry in an air-circulating oven at  $99 \pm 5^\circ\text{F}$  ( $37 \pm 3^\circ\text{C}$ ) for about 1 hour.

Other methods used include flame oxidation, corona discharge (activated gases), and exposure to electric discharge from a spark coil.

5.3.5.2.2.8 Ionomers(12). This is a class of polymers in which ionized carboxyl groups create ionic links in the intermolecular structure. Du Pont supplies ionomers as SURLYN resin. Properties are similar to crosslinked thermosets, although these resins are processed at conventional temperatures, like other thermoplastic resins. Ionomers are somewhat similar to polyethylene in that adhesive bonds do not develop high strength.

- a. Solvent-degrease in acetone or MEK.
- b. Grit- or vapor-blast, or use 100-grit emery cloth. 180-grit alumina may be used.
- c. Solvent-degrease again.

5.3.5.2.2.9 Nylon (Polyamide)(1). Both solvent cementing and adhesive bonding are used with nylon, but the solvents are quite different from those used for cellulose and polystyrene. Nylon molding resins are not usually cemented by conventional solvent-type cements because of their lack of solubility in ordinary non-toxic solvents. Nylon is often bonded to metals, introducing problems not found in the nylon-to-nylon bonds. In this case, conventional adhesives are used. Nylons are relatively crystalline thermoplastics that are not considered solvent-sensitive. For this reason solvent cleaning preparatory to adhesive bonding is carried out with relatively strong solvents.

## MIL-HDBK-691B

- a. Wash with acetone.
- b. Dry.
- c. Hand-sand with 120-grit abrasive cloth until the gloss is removed.
- d. Remove sanding dust with a short-haired stiff brush.

In nylon-to-metal bonding, reasonably strong bonds may sometimes be obtained without abrading the nylon. The actual surface, however, must be abraded with grit paper or steel wool and then washed with a solvent.

5.3.5.2.2.10 Perfluoroalkoxy resin (PFA). This is a relatively new class of melt-processable fluoroplastics introduced by du Pont in 1972. These materials combine high-temperature performance with thermoplastic processing. Surface preparation is as given for PEP (See 5.3.5.2.2.7).

5.3.5.2.2.11 Phenylene oxide-based resins (NORYL). This family of engineering resins is characterized by outstanding dimensional stability at high temperatures, broad temperature use range and other desirable properties. Solvent cementing is the usual method for joining. NORYL is the General Electric designation for polystyrene-modified polyphenylene oxide.

Acid etch\*

a. Solvent-clean with isopropanol or aqueous solutions of most commercial detergents.

b. Sand or chromic-acid etch

c. If chromic-acid etch is used, etch 1 minute at 176°F (80°C) in the following solution:

Sulfuric acid, conc	375 g
Potassium dichromate	18.5 g
Water	30 g

d. Rinse in distilled water

e. Dry

\* A Boeing-Vertol report prepared for Picatinny Arsenal showed that a chromic acid cleaning solution at essentially the same strength as given above and used for 3 minutes at 150°F (66°C) became ineffective after its first use (when used with AP-30 nitrile-phenolic adhesive and modified T-peel tests). The study was made with unmodified polyphenylene oxide, however. Boeing-Vertol recommended preparing the unmodified polyphenylene oxide by vacuum-blasting, followed by an acetone wipe.

5.3.5.2.2.12 Polyaryl ether (ARYLON). This is an engineering thermoplastic, (Uniroyal Chemical Co.) combining outstanding heat distortion and high impact strength with ease of processibility. It is normally joined by solvent cementing.

## MIL-HDBK-691B

5.3.5.2.2.13 Polyaryl sulfone. This new engineering thermoplastic, supplied as ASTREL 360 Plastic by the 3M Co., retains structurally useful properties up to 500°F (260°C). The manufacturer's literature mentions welding by thermal, ultrasonic or solvent techniques. Air Force-sponsored studies described the following three procedures. The solvent-wash method was recommended.(1)

Sandblast (resulted in 1470 psi or 10.14 MPa tensile-shear strength with Hysol epoxy film adhesive EA 9614 steel-plastic-steel).

- a. Ultrasonic-clean with an alkaline-etching solution.
- b. Cold-water rinse.
- c. Alcohol-wash.
- d. Sandblast with 150-mesh silica sand.
- e. Alcohol-wash.
- f. Dry with nitrogen.

Acid Etch (resulted in 1380 psi (9.52 MPa) tensile-shear strength with EA 9614-steel-plastic-steel).

- a. Ultrasonic-clean in an alkaline cleansing solution.
- b. Cold-water rinse.
- c. Bathe 15 minutes at 150-160°F (66-71°C) in acid-etch solution containing:

Sodium dichromate	3.4% by wt.
Sulfuric acid, conc.	96.6% by wt.

- d. Cold-water wash.
- e. Dry at 150°F (66°C) in an air-circulating oven.

Solvent-wash (recommended method). Resulted in 2023 psi (13.95 MPa) tensile shear strength with EA 9164-steel-plastic-steel. EA 2290 was also used successfully with solvent wash.

a. Triple-wash (3 successive washes) in a 65/35 mixture by volume of FREON PCA and reagent-grade isopropyl alcohol. This mixture is also available from the du Pont Co. as FREON TP-35, except that FREON TF solvent is used instead of FREON PCA. The latter is an ultrapure version of TF and essentially becomes TF as soon as it is opened.

- b. Dry at 150°F (66°C) in an air-circulating oven..

## MIL-HDBK-691B

5.3.5.2.2.14 Polycarbonate (supplied as LEXAN-General Electric Co., MERLON-Mobay Chemical Co., and TUPPAK-Rohm & Haas Co.). Solvent-cementing is the recommended method for bonding polycarbonate to itself, or to certain plastics soluble in the same solvents (i.e., cellulose acetate butyrate, acrylics, or polyurethane). However, adhesive bonding must be used in bonding to metals, wood, rubber and most other plastics. Polycarbonate, like nylon, will readily absorb moisture from the surrounding atmosphere. For this reason, it is desirable to keep the humidity low before bonding. One of the methods described below actually uses an oven drying just before bonding.

In surface preparation of polycarbonate for adhesive bonding, the most common solvents recommended for cleaning are methyl alcohol, ethyl alcohol, isopropyl alcohol, petroleum ether, heptane and VM&P naphtha. Ketones, toluol, trichloroethylene, and benzol should not be used, since polycarbonate is not compatible with these solvents, which cause crazing or cracking. A number of other cleaning solvents, including paint thinners, are similar to ketones in that they cause crazing or cracking, so care should be taken in the solvents selected for cleaning. This problem is so serious that one helicopter manufacturer is now specifying a coating material to prevent cracking of polycarbonate ducts. Light solutions of detergents, such as ALKANOX or JOY, are also suggested(1).

Flame treatment.

- a. Wipe with ethanol to remove dirt and grease.
- b. Pass the part through the oxidizing portions of the flame of the Bernzomatic propane torch.
- c. Treatment is complete when both sides are polished to a high gloss, free of scratches and visible flaws. The process usually requires 5-6 passes on both sides.
- d. Allow the part to cool for 5-10 minutes before bonding.

Oven drying.

- a. Place the part in an air-circulating oven at 160°F (71°C) for 1 hour.
- b. Five to 10 minutes after removal from oven, parts are cool enough to bond.

Abrasion.

- a. Wipe with ethanol, methanol, or other solvent, or cleaner mentioned above.
- b. Air-dry.
- c. Sand with fine-grit (120-grit) (400-grit maximum) abrasive cloth or sandpaper.
- d. Remove sanding dust with a clean dry cloth or a short-haired stiff brush.

## MIL-HDBK-691B

e. Repeat solvent wipe.

Plasma treatment has also been used successfully with polycarbonate.

5.3.5.2.2.15 Polychlorotrifluoroethylene (PCTFE). This fluorocarbon resin has excellent chemical resistance and offers problems in surface preparation because of its high surface tension and non-polar surface. Surface preparation is as given for FEP (see 5.3.5.2.2.7).

5.3.5.2.2.16 Polyester (thermoplastic). Thermoplastic polyesters are the condensation products of a saturated glycol and an aromatic dicarboxylic acid or its ether derivatives. Polyethylene terephthalate (PET) is a thermoplastic polyester that has been used for years in the form of films and fibers (MYLAR, DACKON, CELANAR, etc.). More recently polybutylene terephthalate (PBT), a condensation product of 1,4-butanediol and terephthalic acid, has been developed. PBT resins are high-temperature resistant crystalline thermoplastics with melting points around 400°F (227°C). Three commercially available PBT resins are:

VALOX (General Electric Company)  
 CELANEX (Celanese Plastics Company)  
 GAFITE (GAF Corporation)

Glass-filled grades of these resins are also available. Thermoplastic polyesters are generally resistant to solvents and chemicals, including alcohol, ethers and aliphatic hydrocarbons, most chlorinated hydrocarbons, aqueous salt solutions and aqueous acid and basic solutions under specified conditions. Specific surface preparation in the above thermoplastic polyesters are given as follows:

VALOX Thermoplastic Polyester.

A. Abrasion method.

1. Sand lightly with 240-grit sandpaper.
2. Degrease with toluol or trichloroethane. Toluol is recommended for the unreinforced VALOX.

B. Plasma treatment. Activated gas plasma, using oxygen, argon, or water vapor plasma, has been reported by GE to give good adhesive bonds 3-4 times stronger than those obtained with the above method. (See 5.3.2.8).

CELANEX Thermoplastic Polyester.

- a. Sandpaper.
- b. Degrease by wiping with a solvent such as acetone.

5.3.5.2.2.17 Polyethylene<sup>(1)</sup>. Polyethylene has a non-polar, non-porous, inert surface and, for this reason, adhesives cannot link chemically or mechanically to an untreated polyethylene surface. Solvent-cementing is not suitable for bonding the polyolefins, either to themselves or to other materials. Therefore, to obtain a suitable bond between the polyethylene and



## MIL-HDBK-691B

other materials, the surface must be pretreated. There are a number of surface-treatment methods in use, including chemical, electronic, flame and primer treatments.

Oxidation treatments are the most successful in preparation of the surfaces of polyethylene. These include immersion in a chromic acid solution, exposure to corona discharge, flame-oxidation, immersion in an aqueous solution of chlorine, or exposure to chlorine gas in the presence of ultraviolet light. The chromic acid oxidation method is probably the most convenient for use with molded plastic parts of diverse contour.

#### Chromic Acid Etch.

- a. Wipe with acetone, MEK or xylene.
- b. Immerse in the following chromic acid solution for 60-90 minutes at room temperature, or 30-60 seconds at 160°F (71°C).

Potassium dichromate ( $K_2Cr_2O_7$ )	75 g	15 pbw
Tap water	120 g	24 pbw
Sulfuric acid, conc	1500 g	300 pbw

Dissolve the potassium dichromate in the clean tap water, then add the sulfuric acid in increments of about 200 g., stirring after each addition.

- c. Rinse in running tap water for at least 3 min.
- d. Rinse in distilled or deionized water.
- e. Dry in air-circulating oven at 100°F (38°C) for about 1 hour.

#### Oxidizing-Flame Method.

Polyethylene may also be prepared for bonding by the oxidizing-flame method, which utilizes an oxyacetylene burner passed over the faying surface until it appears glossy. To insure that too much oxide is not on the surface, a light scouring with soap and water should be carried out. Wash with distilled water and dry at room temperature. Flame treatment is fast and provides bond strengths greater than the chromic acid treatment, but it requires very careful control. Otherwise, heat warpage of the polyethylene will result. The method is simplest to use in pieces of thick cross-section, where the danger of heat warpage is minimal.

Gas-plasma treatment has also been used and is particularly recommended for complex geometric surfaces which cannot be sanded or flame-treated adequately (See 5.3.2.8).

Table XXII shows the results of studies carried out by Picatinny Arsenal workers using the different surface treatments for each of these different adhesives: epoxy, polyester, and nitrile-phenolic. The effectiveness of the surface treatments tested, in descending order, are as follows:

1. Flame treatment or activated gas plasma treatment

## MIL-HDBK-691B

2. Acid treated\*, water rinsed, acetone dried.
3. Acid treated\*, water rinsed, wiped and air dried at 73°F (23°C)
4. Acid treated\*, water rinsed, oven dried at 160°F (71°C)
5. Acid treated\*, water rinsed, oven dried at 194°F (90°C)
6. Sanded (400-A aluminum oxide paper)

\*in solution containing:

potassium dichromate	75 pbw
sulfuric acid, conc	1500 pbw
potable tap water	120 pbw
for 5 minutes at 60°C	

Flame treating, acid treating and activated gas plasma treating surface preparations of the epoxy bonded specimens produced bonds so strong that failure always occurred in the polyethylene, rather than in the bond, upon application of load. Only the sanded epoxy specimens and the control failed adhesively. The sanded specimens failed at approximately 3 1/2 times the failing load of control. Upon inspection of the results for the polyester adhesive, differences in surface treatment become evident. Flame treatment resulted in all specimens failing in the adherend at a value of 434 psi (2.99 MPa) calculated on the basis of a 0.5 sq in (3.23 sq cm) area. The actual strength of the adhesive bond is, of course, greater than this, since it was the substrate that failed, leaving the bond intact. Some adherend failures were also noted in the following specimens:

Acid treated, acetone dried

Acid treated, wiped and air dried

30 min helium plasma

30 min oxygen plasma

The-nitrile phenolic proved to be a considerably poorer adhesive for polyethylene than the epoxy or polyester systems, but still pointed up the effectiveness of flame treatment and activated plasma treatment. The solvent-type, nitrile-phenolic thermoplastic adhesive used in this study has the usual disadvantage of solvent-type adhesives in bonding nonporous materials. The solvent, which must be evaporated to effect a "cure", is trapped and can only migrate out slowly through the edges. Heating only expands the solvent as a gas, which creates large unbonded areas.

Regardless of the adhesive used, it is evident that the untreated control gave bond strengths below each of the surface-treated specimens, and well below all but the sanded nitrile-phenolic specimens.

## MIL-HDBK-691B

**5.3.5.2.2.18 Poly(ethylene-chlorotrifluoroethylene) (E-CTFE copolymer) (HALAR).** This copolymer, supplied by Allied Corporation, has been shown to form fairly good bonds with epoxy adhesives after sodium etching or flame-treating (see sodium etch directions under 5.3.5.2.2.7). The specific sodium etch evaluated by Allied Corporation is TETRA-ETCH. Etching time was 1-2 minutes. The flame treatment involves a brush for 15-30 sec with a propane torch. The tip of the flame should just touch the surface and should be moved just rapidly enough to avoid charring and/or warping. Recent Army studies gave far superior results with sodium etch than with flame treatment (995 psi or 6.87 MPa vs. 250 psi or 2.43 MPa), using EC 2214 Hi-Temp room-temperature-curing Versamid-epoxy adhesive.

**5.3.5.2.2.19 Polymethylmethacrylate (PMMA) (PLEXIGLAS) (LUCITE).** Usually in bonding PMMA to itself, straight solvent cementing would be used. Treatment for surface preparation prior to using conventional adhesives is given here, particularly for applications where the PMMA is bonded to a dissimilar material.(1)

- a. Wipe with methanol, acetone, MEK, trichlorethane, isopropanol, or use detergent.
- b. Abrade with fine-grit (180-400 grit) sandpaper or emery paper, or use abrasive scouring with small amounts of water, dry-grit blasting, or wet-abrasive blasting.
- c. Wipe with a clean, dry cloth to remove particles.
- d. Repeat solvent wipe.

**5.3.5.2.2.20 Polymethylpentene (TPX).** This material, formerly made by ICI Ltd., is now supplied by Mitsui Petrochemical Industries Ltd. It is a copolymer of 4-methylpentene-1 and is useful up to 400°F (204°C). Chemical behavior is similar to other polyolefins.(1)

**Degreasing-Abrasion (for general-purpose bonding).**

- a. Solvent-clean in acetone.
- b. Grit-or vapor-blast, or use 100-grit emery cloth.
- c. Solvent-clean again in acetone.

MIL-HDBK-691B

TABLE XIII. Effects of various surface treatments on lap-shear strength of adhesive-bonded HD polyethylene\* (36)(77)(38)

Control	Flame-Treated	Sanded	Acid-treated Oven-dried at 90°C (194°P)	Acid-treated Oven-dried at 71°C (160°P)	Acid-treated Wiped, Air-Dried 22°C (72°P)	Acid-treated Acetone-Dried (30 sec)	Helium (30 min)	Activated-Gas Plasma Treatment Oxygen (30 min)
46 psi 0.32 MPa	480 psi 3.31 MPa	195 psi 1.34 MPa	475 psi 3.28 MPa	457 psi 3.15 MPa	499 psi 3.44 MPa	497 psi 3.43 MPa	464 psi 3.20 MPa	466 psi 3.21 MPa
								455 psi 3.07 MPa
<u>Epoxy (EPON 828/aramid 140 polyamide-modified epoxy)</u>								
85 psi 0.59 MPa	434 psi 2.99 MPa	175 psi 1.21 MPa	277 psi 1.91 MPa	297 psi 2.05 MPa	357 psi 2.46 MPa	394 psi 2.72 MPa	190 psi 1.31 MPa	346 psi 2.39 MPa
								263 psi 1.81 MPa
								2.96 MPa
<u>Polyester Laminac 4116/4134 styrene-unsaturated polyester resin</u>								
44 psi 0.30 MPa	138 psi 0.95 MPa	56 psi 0.39 MPa	96 psi 0.66 MPa	108 psi 0.75 MPa	110 psi 0.76 MPa	112 psi 0.77 MPa	--	178 psi 1.23 MPa
							--	--
								176 psi 1.21 MPa

\*Pigment, high-density, Marlex 5002

Notes: Test specimens were single-lap shear specimens prepared from 4 x 1 x 1 inch (101.6 x 25.4 x 25.4 mm) polyethylene coupons. Overlaps of 1/2 inch (2.7 mm) were used. After bonding, all specimens were cured for 72 hours at RT (23°C) (73°P), then postcured 4 hours at 40°C (104°P), and finally conditioned at 23°C (73°P) -50% RH for at least 24 hours before testing.

## MIL-HDBK-691B

Chromic-acid etch.

- a. Solvent clean in acetone.
- b. Immerse for 1 hour at 140°F (60°C) in:

Sulfuric acid, conc	26 pbw
Potassium dichromate	3 pbw
Water	11 pbw

- c. Rinse in tap water.
- d. Rinse in distilled water.
- e. Dry in warm air.

Acid-permanganate etch.

- a. Solvent-clean in acetone.
- b. Immerse for 5-10 min at 194°F (90°C) in a saturated solution of potassium permanganate acidified with sulfuric acid.
- c. Rinse in tap water.
- d. Rinse in distilled water.
- e. Dry in warm air.

Lacquered prime coat. Prime surface with a lacquer based on urea-formaldehyde resin diluted with carbon tetrachloride.

Note: U-F lacquers are normally baked at 300°F (149°C) to cure them. Since the plastic substrate (TPX) will withstand 400°F (204°C), drying at up to 300°F (149°C) is feasible. No further pretreatment is necessary.

**5.3.5.2.2.21 Polyphenylene sulfide, (RYTON).** This is a crystalline polymer with a high melting point 550°F (288°C), outstanding chemical resistance, thermal stability and nonflammability. There are no known solvents below 375-400°F (190-204°C). Surface preparation is as follows:

- a. Solvent-degrease in acetone.
- b. Sandblast.
- c. Solvent-degrease again in acetone.

A Picatinny Arsenal study recommended wiping the faying surfaces with ethanol-soaked lintless paper, sanding with 120-grit sandpaper, and cleaning off the dust with a stiff, bristled brush.(39)

**5.3.5.2.2.22 Polypropylene.** Treatment is, in general, similar to that for polyethylene, except that thermal treatment somewhat more vigorous than that for polyethylene is usually recommended. Thus, while the treatment

## MIL-HDBK-691B

recommended for polyethylene is 60-90 min at RT, or 30-60 sec at 160°F (71°C), polypropylene should be treated for 1-2 min at 160°F (71°C).<sup>(1)</sup>

Chromic-acid etch.

- a. Wipe with acetone, MEK, or xylene.
- b. Immerse in the following chromic acid solution for 1-2 min at 160°F (71°C):

Potassium dichromate ( $K_2Cr_2O_7$ )	75g	15 pbw
Tap water	120g	24 pbw
Sulfuric acid, conc	1500g	300 pbw

Dissolve the potassium dichromate in the clean tap water, then add the sulfuric acid in increments of about 200 g., stirring after each addition.

- c. Rinse in running tap water for at least 3 min.
- d. Rinse in distilled or deionized water.
- e. Dry in air-circulating oven at 100°F (38°C) for about 1 hour.

Oxidizing-Flame Method.

As in Polyethylene.

Gas-Plasma Method.

As in Polyethylene.

**5.3.5.2.2.23 Polystyrene.** Polystyrene is usually bonded to itself by solvent cementing, although conventional adhesive bonding, thermal welding, and electromagnetic bonding have been used. Conventional adhesive bonding may be necessary for bonding polystyrene to a dissimilar polymeric material, and will be required for bonding to metals. Surface-preparation methods suggested for conventional adhesive bonding are as follows<sup>(1)</sup>:

Abrading or Sanding.

- a. Degrease with methyl or isopropyl alcohol.
- b. Abrade with 200-grit sandpaper and remove dust particles.

Sodium Dichromate-Sulfuric Acid Process.

- a. Degrease with isopropyl or methyl alcohol.
- b. Immerse for 3-4 min in the following solution maintained at 210-220°F (99-104°C).

Sulfuric acid, conc.	90 pbw
Sodium dichromate	10 pbw



## MIL-HDBK-691B

- c. Rinse thoroughly with distilled water.
- d. Dry below 120°F (49°C).

(Comment: This is a somewhat radical modification of the chromic-acid-etching process. Note that no water is used to dilute the acid, thus permitting a much higher immersion temperature without boiling off the water. The usual high-temperature immersion in the conventional chromic-acid solution is 160°F (71°C).

Nonimmersion Process. If polystyrene parts are to be used in high-frequency electrical applications, it may be desirable that only the faying surfaces be treated, and the following treatment is then recommended:

- a. Degrease with methyl or isopropyl alcohol.
- b. Apply to the faying surfaces the following thixotropic paste:

Sulfuric acid, conc.	3 pbw
Powdered potassium	1 pbw

Add CAB-O-SIL fused silica earth as required to obtain a thixotropic paste.

- c. Heat parts to 180°F (82°C) and hold for 3-4 minutes (with paste on surface).
- d. Rinse thoroughly with distilled water.
- e. Dry below 150°F (66°C).

5.3.5.2.2.24 Polysulfone (UDEL). Polysulfone is a thermoplastic with a very high strength and one of the highest service temperatures (340°F or 171°C) of any melt-processible thermoplastic. While highly resistant to mineral acids, alkalies, salts, detergent solutions, oils and alcohol, polysulfone is attacked by polar solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons. This material stress cracks easily and is considered notch-sensitive. Polysulfone can be solvent-cemented or conventionally adhesive-bonded. Ultrasonic welding is also used. Air Force-sponsored studies described the following three procedures. Acid Etch was found to give the best results.(1)

Acid Etch (resulted in 2483 psi (17.2 MPa) tensile-shear strength with Hysol epoxy film adhesive EA 9614-steel-plastic-steel)

- a. Ultrasonic-clean in alkaline etching solution
- b. Cold-water rinse.

## MIL-HDBK-691B

- c. Bathe 15 min at 150-160°F (66-71°C) in an acid-etch solution containing:

Sodium dichromate	3.4% by wt
Sulfuric acid, conc	96.6% by wt

- d. Cold-water wash.

- e. Dry at 150°F (66°C) in an air-circulating oven.

Solvent Wash (resulted in 2223 psi (15.3 MPa) tensile-shear strength with EA 9614-steel-plastic-steel. EA 2290 was also used successfully with solvent wash).

a. Triple-wash (3 successive washes) on a 65/35 mixture by volume of FREON PCA and reagent-grade isopropyl alcohol. This mixture is also available from the du Pont Co. as FREON TP-35, except that FREON TF solvent is used instead of FREON PCA. The latter is an ultrapure version of TP and essentially becomes TF as soon as it is opened.

- b. Dry at 150°F (66°C) in an air-circulating oven.

General Electric Method. (This method was published as part of Air Force-sponsored study).<sup>(40)</sup> Polysulfone parts were prepared for bonding to niobium with 3M Company SCOTCH-WELD epoxy-nylon Film Adhesive 42 (AF-42). The polysulfone surface was prepared as follows:

- a. Degrease in alcohol.
- b. Grit-blast with 27-50 micron  $Al_2O_3$  a.
- c. Clean in ultrasonic cleaner, according to GE Direct Energy Conversion Operation Specification No. P50GN417S1. The essential steps are as follows:
  1. Immerse parts in Neutra-clean 7b (12+ 1 oz/gal (89.6 ± 7.5 g/l) distilled water) for 7-10 min at 145-155°F (63-69°C).
  2. Rinse with tap water.
  3. Rinse with distilled water.
  4. Rinse with isopropyl alcohol for 30 sec. minimum.
  5. Flush with nitrogen.
  6. Dry with warm air at 150°F (66°C)

(Note: Procedure differs somewhat between tubular and non-tubular parts.)

- a. Use S.S. White Airbrasive Equipment or equivalent.

## MIL-HDBK-691B

b. Shipley Company, Inc., Wellesley, MA.

Other methods include:

Vapor degreasing in methanol

Sanding or vapor blasing

Alcohol-wipe and/or light sanding, + vinyl, urethane or silicone primer.

5.3.5.2.2.25 Polytetrafluoroethylene. (PTFE) (TEFLON TFE), (HALON TFE) (FLUON). This widely-known homopolymer does not melt like a true thermoplastic, and has a very high melt-viscosity. As with other fluoroplastics, it is relatively inert chemically. PTFE is prepared by the same methods as are used for FEP (5.3.5.2.2.7) and PCTFE (5.3.5.2.2.15).

5.3.5.2.2.26 Polyvinyl chloride (PVC). The only resins to be considered in this discussion are the straight homopolymer rigid compounds. Even these contain up to 5% plasticizer, making it difficult to effect bonds with epoxy and other non-rubber types of adhesives. The homopolymer is not readily soluble, and is therefore difficult to bond by solvent-cementing techniques, although a number of solvents have been used with varying degrees of success. Thermal bonding, especially hot-gas welding, is quite commonly used in joining rigid PVC. A number of different procedures have been recommended for surface preparation of rigid PVC. In general, a solvent is always used to remove plasticizer, grease, dirt, etc. Abrasion of the surface may or may not be used. It may be achieved with sandpaper (various grits), vapor-blasting, steel wool, or scouring powder(1).

- a. Wipe with solvent such as methanol, low-boiling petroleum ether, MEK, toluene, or TCE.
- b. Abrade with medium-grit (200-grit) sandpaper.
- c. Blow off the dust.
- d. Repeat solvent-wipe.
- e. Dry.
- f. For maximum strength, prime with nitrile-phenolic adhesive, or bond immediately.

5.3.5.2.2.27 Polyvinyl fluoride (PVF). (TEDLAR). According to the du Pont Company, there are two types of TEDLAR film, type B, with both sides already treated for bonding, and type S, which is untreated and is used as a release film. The type B is ordinarily used in laminating to metals, wood and other materials, and should require no further surface preparation for adhesive bonding, according to the manufacturer(1).

## MIL-HDBK-691B

Alkaline Etch.

- a. Degrease with isopropyl alcohol.
- b. Immerse 2-5 min in Prebond 700 alkaline compound, 8 oz/gal (59.7g/l), maintained at 160-170°F (71-77°C).
- c. Rinse.
- d. Dry below 120°F (49°C)

Activated Gas Plasma treatment has been successfully applied by Picatinny Arsenal workers on 2-mil PVF film. For details on the general process, see 5.3.2.8.

Sodium-Naphthalene Etch - This treatment, described under 5.3.5.2.2.7 for FEP, may also be used.

5.3.5.2.2.28 Polyvinylidene fluoride (PVDF). (KYNAR). Polyvinylidene fluoride is a high-performance, high-molecular-weight homopolymer introduced in 1961. It is resistant to most acids and bases, aliphatics, aromatics, alcohols and chlorinated solvents. Strongly polar solvents such as ketones and esters cause partial solvation, particularly at elevated temperatures. KYNAR is serviceable over the range -80° to +300°F (-62° to +149°C).  
(1)

Solvent Clean - Abrasion

- a. Solvent-clean with isopropyl alcohol.
- b. Abrade with any of the following methods:
  1. Sanding, hand or machine. Use 180-320 grit aluminum oxide paper.
  2. Abrasive scouring. Use tap water and a fine, non-chlorinated scouring powder. Rinse with tap water, then distilled water.
  3. Grit-blast, dry. Use nonmetallic grit such as flintstone, silica, silicon carbide or aluminum oxide.
  4. Abrasive-blast, wet. Use 3:1 slurry water and 220-325 grit aluminum oxide. Rinse in distilled water.
- c. Solvent-clean again as in (a.)(3).

Activated Gas Plasma. This technique, discussed above in 5.3.2.8, has been used successfully with polyvinylidene fluoride.

## MIL-HDBK-691B

5.3.5.2.2.29 Styrene-acrylonitrile (SAN). (LUSTRAN) (TYRIL). This copolymer is usually solvent-cemented with solvents similar to those used by polystyrene, although the solvents usable are more restricted. On applications where solvent cements cannot be used, as for example, in bonding to metals, the procedure outlined under 5.3.5.2.2.23 for polystyrene may be used. British workers suggest simply solvent degreasing with trichloroethane. Gasoline can also be used to clean the surface.(1)

5.3.5.2.3 Thermosets. Most thermoset plastics are not particularly difficult to bond. Obviously, solvent cementing is not suitable for bonding thermosets to themselves, since they are not soluble. In some cases, solvent solutions can be used to join thermoplastics to thermosets. In general, conventional adhesive bonding is the only practical non-mechanical method of joining a thermoset to a thermoset or to non-plastic materials. Ultrasonic bonding can be used only with ultrasonic adhesives. Thermoset resins are usually molded and the mold-release agent must be removed. This is usually carried out by detergent-wash, solvent-wash, or solvent-wipe, followed by light sanding to break the smooth surface glaze. A final solvent-wipe with clean solvent and clean lint-free cloth or paper tissue is usually used. The solvents used include acetone, methyl ethyl ketone (MEK), toluene, low-boiling petroleum ether, trichloroethane, and isopropyl alcohol. Fine abrasive paper (sand, carborundum or aluminum oxide), abrasive grit (metal, sand or oxide) or metal wool (steel, aluminum or brass) or steel shot, are usually used for abrasion of the surface.(41)

5.3.5.2.3.1 Diallylphthalate (DAP). This resin has exceptional electrical insulating properties, high-temperature stability and good resistance to most chemicals and moisture. Surfaces are hard and tough and pick up very little moisture. Parts are usually molded or glass laminates and do pose adhesive bonding problems. At present, sanding or buffing appear to be the best surface treatments. Fillers are present in all forms, and include minerals, Orlon, glass and asbestos.(1)

- a. Wipe with acetone or other suitable solvent (see list above under 5.3.5.2.3).
- b. Sand-, grit-, or vapor-blast, or use steel wool.
- c. Wipe with a clean, dry cloth to remove grit and particles.
- d. Repeat solvent-wipe.

5.3.5.2.3.2. Epoxies. Epoxy resins offer a wide range of properties. They show good dimensional stability and good electrical properties and mechanical strength. They have good creep resistance and will operate over a wide temperature range ( $-100^{\circ}$  to  $+800^{\circ}\text{F}$ ) ( $-73^{\circ}$  to  $+427^{\circ}\text{C}$ ). Epoxies are easily adhesive-bonded, requiring only a clean dry surface, usually solvent-cleaned and sanded. Both filled and unfilled grades are available. Fillers include minerals, glass, silica glass and glass microballons. Epoxy laminates should be treated as covered under 5.3.5.2.4.1 Reinforced Thermosets (Laminates).(2)

## MIL-HDBK-691B

- a. Wipe with acetone or other suitable solvent (see list above) or vapor degrease.
- b. Abrade by scouring or other treatment listed above under 5.3.5.2.3.
- c. Wipe with a clean, dry cloth to remove grit.
- d. Repeat solvent treatment.
- e. Apply a silane-type primer, such as Hughson Chemical Company's CHEMLOK 607, diluted with 5-10 volumes of methanol or ethanol (optional).

**5.3.5.2.3.3 Melamine-formaldehyde (Melamines).** The amino resins, like urea-formaldehyde, are hard, rigid, and abrasion-resistant. They have excellent dimensional stability and good creep resistance. They are self-extinguishing, have superior electrical properties and are noted for their high impact strength and resistance to water and solvents. Only filled resins are available. Fillers include cellulose, rag, and glass.(1)

- a. Scrub with an abrasive household detergent.
- b. Rinse with tap, then deionized water.
- c. Dry.
- d. Sand.
- e. Wipe with isopropyl alcohol.
- f. Dry.
- g. Prime or bond.

The procedure given for Epoxies may also be used.

**5.3.5.2.3.4 Phenol-formaldehyde (Phenolics).** Phenolics have an excellent combination of high physical strength and high-temperature resistance, good electrical properties, and good dimensional stability. Phenolics are widely bonded, not only on molded parts, but also as laminates and castings. Both filled and unfilled phenolics are available. Fillers are asbestos, cellulose, wood, flour and glass. The method of surface preparation given under 5.3.5.2.3.2 for epoxies is suggested.(1)

**5.3.5.2.3.5 Polyester.** These unsaturated, non-linear resins are similar to epoxies and phenolics in their surface-preparation requirements, basically requiring only sanding for good results. The method of surface preparation given under 5.3.5.2.3.2 Epoxies is suggested.(1)



## MIL-HDBK-691B

5.3.5.2.3.6 Polyimide (\*Polymer SP-du Pont Co.) (Polyimide 2080 - The Upjohn Co.) (TORLON - Amoco Chemicals Corp.) (KINEL - Rhone Poulenc, Inc.) Polyimides are a class of polymeric materials distinguished by exceptional thermal stability. They are available commercially in several forms, including fabricated parts and shapes, molding resins, films and coatings for wire and film. Some polyimides, condensation polymers, are essentially linear, with structures similar to those of thermoplastics. Others, addition polymers used as engineering resins in parts (moldings and laminates), are thermosetting. Du Pont's VESPEL precision parts are available in graphite-PTFE-and  $\text{MoS}_2$ -filled bearing compositions, as well as unfilled. Such parts will withstand temperatures to 900°F (482°C) for short periods.

Du Pont Company Recommendations (for VESPEL Parts). (42)

a. Remove surface contamination, such as dirt, and oil, with solvents. Clean by refluxing in perchloroethylene or trichloroethane, or clean ultrasonically in FREON TF (trichlorotrifluoroethane).

b. Mechanically abrade with a wet or dry abrasive blast. A light abrading (approx. surface roughness of 50-100 microinches) is preferable to maintain a uniform adhesive thickness. Such abrading can be obtained with an air- or air-liquid abrasive blast.

c. Remove residual particles with the solvent in (a.).

d. Dry.

\*du Pont markets precision parts made from this resin under the tradename VESPEL. The resin itself is not available commercially.

Sodium-Hydroxide Etch.

a. Degrease in acetone.

b. Etch for 1 min at 60-90°C (140-194°F) in:

Sodium hydroxide	5 pbw
Water	95 pbw

c. Rinse in cold water

d. Dry in hot air.

5.3.5.2.3.7 Polyurethane. This resin, which is sometimes thermoplastic, is formed from the reaction of a polyisocyanate with compounds containing a reactive hydrogen. The plastic may be flexible or rigid and can be obtained in various densities and forms, i.e., sheets, molding and a casting resin, etc. Polyurethanes are unexcelled as cryogenic materials and have excellent

## MIL-HDBK-691a

adhesion and skid resistance, good chemical resistance, and superior impact resistance, but are limited at elevated temperatures (250°F or 121°C). They also have good electrical properties. Cleaning usually involves light sanding and a dry bonding surface. A primer will usually improve adhesion.(1)

- a. Wipe with acetone or MEK.
- b. Abrade with 100-grit emery cloth, sandpaper, or steel wool.
- c. Wipe with a clean dry cloth to remove grit and particles.
- d. Wipe again with solvent in (a).
- e. Dry.
- f. Use urethane or silicone primer to improve adhesion.

**5.3.5.2.3.8 Silicone resins.** Silicone resins are provided in several forms. They are used as thermally stable electrical insulation resins, paint vehicles, molding compounds, laminates, impregnating varnishes, encapsulating materials, and as baked-on release agents. Recommended surface preparation is as follows:(1)

- a. Wipe with acetone or other suitable solvent (see list above under 5.3.5.2.3).
- b. Sand-, grit-, or vapor-blast, or use steel wool.
- c. Wipe with a clean, dry cloth to remove grit and particles.
- d. Repeat solvent wipe.

Silicone laminates should be treated as covered under 5.3.5.2.4.1 Reinforced Thermosets (Laminates).

**5.3.5.2.3.9 Urea-formaldehyde.** These amino resins, like melamine-formaldehyde, are hard, rigid, abrasion-resistant materials. They have excellent dimensional stability and good solvent and creep resistance. They are self-extinguishing and have superior electrical properties. They are noted for high impact strength and resistance to water and solvents.(1)

- a. Scrub with an abrasive household detergent.
- b. Rinse with tap, then deionized water.
- c. Dry.

## MIL-HDBK-691B

- d. Sand.
- e. Wipe with isopropyl alcohol.
- f. Dry.
- g. Prime or bond.

The procedure given for epoxies may also be used.

#### 5.3.5.2.4 Reinforced plastics/composites.

5.3.5.2.4.1 Reinforced thermosets (Laminates). The reinforced thermosets of greatest utility and interest are glass-reinforced. The methods used in preparing glass-reinforced plastic (GRP) surfaces for adhesive bonding are governed by: 1. the configuration of the part, 2. the facilities available in the bonding shop, and 3. the user's experience and preference. The methods commonly accepted for preparing GRP laminates for bonding all involve removal of the original resin surface area, and yielding a roughened faying surface for bonding. Removal of surface gloss is usually sufficient to dispose of surface soils, exuded resin impurities, absorbed gases or vapors, and release agents used during the manufacture of the GRP. The methods of surface preparation in general use for laminated plastics are as follows:(1)

A. Tear-ply (peel-ply) method. During the manufacture of the GRP laminate, either one or both outer surfaces of the laminate are made of a layer of an adhesive material, the outer layer of which can later be stripped or peeled off without much effort. Nylon and DACRON are frequently used for this purpose. This ply is cured as an integral part of the laminate. The resin used in the construction of the GRP adheres poorly to the nylon or DACRON cloth incorporated in the outer layer or layers, permitting the nylon or DACRON cloth to be peeled uniformly in one piece. The texture of the nylon or DACRON layer is reproduced in the outer layer of the laminate. When the adhesive-bonding operation is to be performed, slide a thin knife blade under a ply, peel the desired distance and trim. Remove loose particles by brushing or blowing the surface with clean, filtered air. There is very little chance of surface contamination with tear ply. Figure 28 shows how tear ply is used. Note that it is applied only to the areas that are to be adhesive-bonded. The tear-ply technique is preferred over machine-or hand-sanding because of the reduced danger of surface contamination.

B. Sanding or sandblasting. The surface of laminated plastics may be sanded lightly with medium-grit (80 to 120 grit) emery paper or other abrasive paper capable of roughening the surface without substantially damaging the reinforcing fibers. It is generally best for the direction of bonding to be parallel to the surface fiber orientation so that the damage to these fibers

## MIL-HDBK-691B

will be minimized. This technique works most satisfactorily on large laying surfaces where the edges, rounded as a result of sanding, can be trimmed, or where the edge effects are negligible. Sanding dust may be removed with a short-haired stiff brush. If water-break-free surfaces are not obtained, the procedure should be repeated.(1)

Grit-blasting or sandblasting may be used if available. A specially trained operator is needed to produce uniformity within pieces by sandblasting. A clean, uniform-size grit is essential for proper surface preparation with sandblasting. This may be a problem when treating GRP surfaces, and for this reason this technique is not often used.(1)

After sanding or sandblasting, the surface is sometimes wiped with solvent such as MEK, acetone, toluene, trichloroethane, FREON TF, FREON TMC or M-17, depending on the known mold lubricants. In some cases, solvent is used before and after abrading the surface. If water-break-free surfaces are not obtained, the procedure should be repeated.(1)

Picatinny Arsenal workers have found that hand-sanded and machine-sanded glass-reinforced plastic laminates, after treatment prior to bonding, can be stored up to 30 days at 73°F (23°C) and 50% RH, with no adverse effect on the bond strength. Machine sanding gave slightly better results than hand sanding and provided a more uniform and faster method. Tear-ply and sanding gave about the same results, but the tear-ply technique provides less danger of surface contamination. Variations in bond strength are more likely to occur as a result of changes in the sanding technique than because of the difference in methods. One year of outdoor exposure of the bonds to hot, arid environments (Yuma, Arizona) hot, humid environments, (Panama), and seasonal environments (Dover, N.J.) had little or no adverse effect on the bond strength.(43)

The Picatinny workers found that surface exposure time (SET) for GRP laminates varied with the adhesive used. In general, bond quality diminished with increased SET. The best overall adhesive evaluated was epoxy film adhesive, which was found to be the least sensitive to surface preparation. In general, it was found that the best results were obtained when GRP laminates were bonded within four hours after sanding. If absolutely necessary, bonding can be carried out after periods of time up to 14 days SET, with only moderate strength loss.(43)

Jackson, using a double-step joint, evaluated a number of different abrasive techniques for preparing the surfaces of fiber glass-reinforced epoxy laminates with a room-temperature-curing epoxy adhesive. The study showed that abrasive techniques that remove a thin layer of the material (grit-blasting and wet-blasting) are superior to solvent-cleaning and treatments that deform or make coarse changes in the surface geometry without removing material (knurling and grooving). Although Jackson did not include hand- and machine-sanding in this study, it is highly probable that these methods would compare favorably to the dry- and wet-blasting.(44)

MIL-HDBK-691B

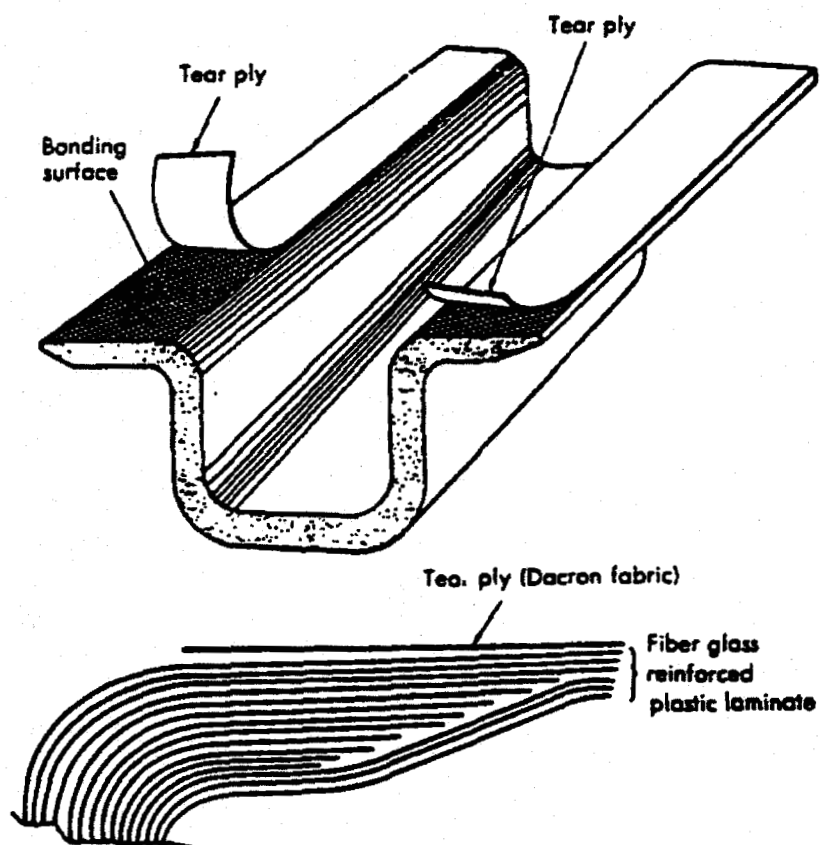


FIGURE 28. Structural reinforced plastic laminate with a tear ply.(3)

## MIL-HDBK-691B

C. Manual Scouring. The faying surface is scrubbed with tap water and an abrasive household-type cleaner to remove contaminants and release agents. Clean cloths or non-metallic bristle brushes will facilitate the scouring. The surface is then rinsed with clean running tap water, followed by a rinse in distilled water, and then dried at 130-150°F (54-66°C).

The parts should exhibit a water-break-free surface. If they do not, the above procedure should be repeated.(45)

D. Solvent-Soak and Abrading. If water-break-free surfaces cannot be obtained by tear-ply, sandblasting or sanding, or manual scouring, the plastic laminates should be treated as follows:

- a. Soak for 48 hours in reagent-grade acetone.
- b. Dry for 3-4 hrs at 190-200°F (88-104°C).
- c. Sand lightly with 200-grit sandpaper.
- d. Remove particles by air-blast or vacuum.
- e. Check for water-break-free condition. If achieved, parts may be bonded. If not, resoak the laminates in acetone for an additional 24 hours minimum and repeat the rest of the procedure. Parts that do not pass the water-break-free test should be rejected.(45)

5.3.5.2.4.2 Reinforced thermoplastics (glass-reinforced). Although it might be assumed that glass-reinforced thermoplastics should be handled in a manner similar to that prescribed for the base unreinforced resin, this is not necessarily so. In general, there is a severe drop (up to 50%) in the expected adhesive bond strength with glass reinforcement. Whether this phenomenon is the result of finishes used on the glass, or other causes, is not fully known.

Theberge and coworkers at LNP studied solvent bonding of glass-reinforced nylon 6 and polystyrene. Aqueous phenol was used to solvent-cement the former and methylene chloride the latter. The drop in strength of the glass-reinforced nylon 6 was about 50%, and of the glass-reinforced polystyrene about 10%. The magnitude of the difference in bond strength was found to be inversely proportional to the holding force applied during solvent cure, and could be practically eliminated with holding pressures of 200 psi (1.38 MPa) or greater. The LNP workers suggested that reinforced resins have solvent bond strengths lower than those of the unreinforced resins for the following reasons:(46)

1. Glass-reinforced resins have rougher surface finishes than the neat resins.
2. Glass fibers are difficult to disperse across the bonded area. As was expected, the amorphous polymer (polystyrene) yielded higher bond strengths than the crystalline polymer (nylon 6).

## MIL-HDBK-691B

**5.3.5.2.5 Plastic foams.** Plastic foams are generally treated by the same surface-preparation techniques as prescribed for the base polymer system. This is particularly true for the "structural foams", which are thermoplastics. In some cases these thermoplastic foams may be solvent cemented. The thermosetting foam most commonly encountered is polyurethane, which is available in rigid, semi-rigid and flexible form. The rigid foams are obtainable in a wide range of densities. Obviously the denser grades, with their increased surface area of actual material exposed, will be easier to prepare by the usual technique of sanding lightly and then removing the resultant dust by vacuum or blowing-off. The cellular structure of plastic foams offers an advantage in surface preparation in that a physical interlocking of the two faying surfaces is possible in a foam-to-foam bond.

With rigid polyurethane foams, a conventional adhesive bond may not be necessary, since foam "poured-in-place" or "foamed-in-place" will adhere tenaciously to most substrates while it is curing.(1)

### 5.3.5.3 Rubbers.

**5.3.5.3.1 General discussion.** Up until recently, the superiority of vulcanized bonded rubber over adhesively-bonded rubber has been generally acknowledged. Nearly all commercially available types of elastomers can be strongly bonded to a large variety of substrates by vulcanization. The strength of similar bonds formed by adhesive bonding, or post-vulcanization (PV) bonding, as it is also called, was originally thought to be much weaker and less resistant to environmental exposure. Recent published work has shown this to be untrue, with some exceptions. The benefits of PV bonding may be summarized as follows:(47)

- o A variety of vulcanized elastomers can be bonded.
- o Common elastomer surface treatments can be used.
- o Bonded systems possess good environmental resistance.
- o Bonds are comparable to vulcanization bonding.
- o Applicable to rubber-to-metal parts as well as to rubber-to-rubber assemblies.
- o Large sizes or complicated shapes may be PV bonded, which would not be economically feasible by "bond-in-the-press" technique.
- o Vulcanization bonding is impractical for field repair where the required equipment is usually unavailable.

Table XXIII shows bond values obtained with seven elastomers, comparing the bond values obtained with both vulcanized bonding and post-vulcanization (adhesive) bonding with a 300°F (149°C) cure. In most cases, the results are comparable. EPDM was the only elastomer where a significant decrease in bond strength was obtained by post-vulcanization bonding.



## MIL-HDBK-691B

TABLE XXIII. Comparison of vulcanization and post-vulcanization bonding\*. (47)

	Vulcanization		Post Vulcanization	
	(pli)	(N/m)	(pli)	(N/m)
Natural Rubber (A)	45	7880	43	7529
Natural Rubber (B)	75	1313	56	9806
SBK	189	33094	100	17513
Neoprene	93	16284	116	20312
Butyl Rubber	101	17685	66	11623
Nitrile Rubber	95	16635	136	23814
EPDM	130	22763	28*	4903**

\*Adhesive used was Hughson Chemical CHEMLOK 234B

\*\*Failure occurred at rubber-cement interface. All other value were for rubber-tearing bonds.

Many military rubber end-items which require bonding can benefit from the advantages of post-vulcanization bonding. The following list of elastomers includes all those used by the Army, with the addition of thermoplastic elastomers. Vulcanized rubber parts are often contaminated with mold-release agents, talc, dirt, grease, plasticizers, extender oils, or other compounding ingredients that can migrate to the surface and interfere with adhesive bonding. Solvent washing and abrading are common surface treatments for most elastomers, but chemical treatment is often recommended for maximum strength and other properties. Many synthetic and natural rubbers require "cyclizing" with concentrated sulfuric acid until hairline cracks appear on the surface. Some rubbers require primers for optimum bonding.

Mechanical abrasion is usually accomplished by sanding or buffing the surface with 80-240 grit sandpaper or a buffing wheel. The dust from the buffing process or other contamination is usually removed by a clean cloth dipped in a suitable solvent. The solvent must be reasonably compatible with the chemical type of rubber being cleaned. If the solvent is very strongly incompatible with the rubber involved, or if too much is used, the rubber will swell excessively, may curl unacceptably, or may be degraded. Particular care must then be taken not to trap solvent in a system that is totally closed, or else the rubber may be damaged. On the other hand, a mild wipe of a somewhat aggressive solvent may help tackify the rubber surface. Methyl ethyl ketone (MEK) and toluene are solvents commonly used for cleaning elastomers. MEK is a strong solvent for the fluorocarbon elastomers, and excessive curling has been experienced in using MEK in any quantity in this type of elastomer. If this occurs, a more compatible solvent, such as toluene, may be substituted. Chlorinated solvents, such as perchloroethane and 1,1,1-trichloroethane, are also used. Cyclization, mentioned above, and chlorination are other commonly used surface preparation methods, and will be described below under 5.3.5.3.2 Neoprene.

## MIL-HDBK-691B

Recent work has shown that the bondability of elastomers is a function of polarity. The less polar EPDM and butyl elastomers are more difficult to bond than the more polar nitrile, neoprene, SBR, and natural rubber. In this study, using butt joints of rubber to steel, six different surface-preparation techniques for each of three different rubbers were studied. Two different high-temperature-curing adhesives were evaluated and a metal primer was used over the steel. The results for post-vulcanization bonding at elevated temperatures to 300°F (149°C) show little correlation between surface treatment and what is essentially flatwise-tensile strength. The results, shown in Table XXIV, for natural rubber indicate that adhesion can be achieved nearly independent of surface treatment, although slightly higher values are obtained when the surface is mechanically abraded. When testing SBR, adhesion with CHEMLOK 236 is nearly independent of surface preparation, but surface treatment does improve the bondability with the CHEMLOK 234B adhesive. Adhesion to neoprene is essentially independent of surface treatment with either adhesive. It should be noted that these results were obtained with butt joints. It is possible that peel tests could give different results.(47)

MIL-HDBK-691B

TABLE XXIV. Effect of surface treatment of rubbers on rubber-to-metal adhesive-bonded butt joints. (47)

Adhesive	TCE Wipe	TREATMENT				Abrasion	Chlorination	Cyclization
		Ultrasonic Degreasing	Hot Alkaline					
			Rinse					
			Natural Rubber					
Chemlok 236	1219 psi* (8.40 MPa)	1050 psi (7.24 MPa)	1052 psi (7.25 MPa)	1230 psi (8.48 MPa)	904 psi (6.23 MPa)	885 psi (6.10 MPa)		
Chemlok 234B	650 psi (4.48 MPa)	789 psi (5.44 MPa)	941 psi (6.49 MPa)	1362 psi (9.39 MPa)	808 psi (5.57 MPa)	1014 psi (6.99 MPa)		
SBR Rubber								
Chemlok 236	1016 psi (7.00 MPa)	1032 psi (7.12 MPa)	940 psi (6.48 MPa)	1128 psi (7.78 MPa)	775 psi (5.34 MPa)	625 psi (4.31 MPa)		
Chemlok 234B	260 psi (1.79 MPa)	878 psi (6.05 MPa)	902 psi (6.22 MPa)	1141 psi (7.89 MPa)	1000 psi (6.89 MPa)	650 psi (4.48 MPa)		
Neoprene Rubber								
Chemlok 236	816 psi (5.63 MPa)	801 psi (5.52 MPa)	880 psi (6.07 MPa)	937 psi (6.46 MPa)	898 psi (6.19 MPa)	1037 psi (7.15 MPa)		
Chemlok 234B	747 psi (5.15 MPa)	717 psi (4.94 MPa)	965 psi (6.65 MPa)	985 psi (6.79 MPa)	1006 psi (6.94 MPa)	1010 psi (6.96 MPa)		

Chemlok 205 metal primer was used on the steel surface.

One coat of either of the two adhesives was used in the rubber and one coat of the same adhesive was applied over the metal primer.

Cure was 45 minutes at 300°F (149°C).

\*Data given are "adhesion values" obtained by measuring bond strength in tension using butt specimens pulled by the method described in ASTM D 429, Method A, using cylindrical rubber specimens 1/2" (12.7 mm) thick and 1.13" (28.7 mm) diameter, bonded to equal diameter low-carbon steel plates 3/8" (9.52 mm) thick, as described in ASTM D 395, Para. 5.3

## MIL-HDBK-691B

5.3.5.3.2 Neoprene (polychloroprene)(CR). Neoprene is the generic name for polymers of chloroprene (2-chloro-1,3 butadiene) manufactured since 1931 by du Pont. Presently there are 22 types of solid neoprene and 13 types of neoprene latex.

Abrasive treatment(1)(3)

- a. Scrape surface with a sharp blade to remove gross layers of wax, sulfur and other compounding ingredients which may have floated to the surface.
- b. Solvent-wipe with ethyl, isopropyl, or methyl alcohol, MEK, or toluene.
- c. Uniformly abrade surfaces with 80-120 grit abrasive paper. Machine sanding with a "jitterbug" oscillating sander is preferred over hand sanding because the machine sanding produces a more uniform surface with less effort. A buffing wheel may also be used.

- d. Solvent-wipe again as in (b.) to remove particles.

Cyclization(3)(48) This process is often applied preparatory to bonding with flexibilized epoxy adhesives. It has been used successfully in many rubbers, in addition to neoprene. A commonly used cyclization procedure is as follows:

- a. Scrape surface with a sharp blade to remove gross layers of wax, sulfur and other compounding ingredients which may have floated to the surface.
- b. Solvent-wipe with ethyl, isopropyl, or methyl alcohol, MEK or toluene.
- c. Immerse rubber surface in conc. sulfuric acid (sp. gr. 1.84) for 30 seconds to optimize bond strength. Determine optimum time for each rubber composition.
- d. Rinse thoroughly with tap water. Hot water is preferable.
- e. Rinse thoroughly with distilled water.
- f. Neutralize by immersing 5-10 min in a 10-20% solution of ammonium hydroxide (sodium hydroxide is also used).
- g. Rinse thoroughly with tap water.
- h. Rinse thoroughly with distilled water.
- j. Dry at temperatures up to 150°F (66°C).
- k. Flex the resultant brittle surface of the rubber with clean rubber or plastic gloves so that a finely cracked appearance is produced. (Cyclizing hardens and slightly oxidizes the surface, permitting the necessary wetting of the adhesive bond). The finely cracked surface indicates that the rubber is ready for bonding. Light lacy lines on the surface indicate insufficient immersion time. Deep, coarse cracks and a thick crusty surface indicate excessive immersion. If immersion is not feasible, the acid may be made up into a thick paste by the addition of barium sulfate (barytes) or CAB-O-SIL (G.L. Cabot Corp.), or use 100 pbw conc. sulfuric acid:5 pbw SANTOCEL C (Monsanto Co.) or equivalent. A stainless steel or other acid-resistant spatula should be used to apply the paste. After the paste is applied, the rest of the treatment steps d. through j. should be carried out.

## MIL-HDBK-691B

A modified cyclization procedure used by Boeing-Vertol in a Picatinny Arsenal-sponsored study is as follows:

- a. Clean in toluene.
- b. Force-dry 1 hour at 140°F (60°C)
- c. Immerse 2 min in conc. sulfuric acid.
- d. Rinse in tap water.

Results obtained with this procedure are shown in Table XXV.

TABLE XXV. Effects of modified cyclization on neoprene\*/aluminum\*\* bonds.(49).

	Adhesive		
	AF-30 (nitrile-phenolic film)	FM-1000 (nylon-epoxy film)	FM-37 (modified epoxy foam)
<u>T-peel strength</u>			
1b/3" width	105	149	18
N/m	6130	8699	1051
<u>Bell-peel strength</u>			
1b/3" width	98	106	--
N/m	17,160	18,561	---
<u>Flatwise-tensile strength</u>			
psi	473	666	322
MPa	3.26	4.59	2.22

\*MIL-S-6855, Class 2, Grade 40-50 Shore "A" Durometer, 0.035" (0.9 mm) thick  
 \*\*0.016" (0.41 mm) 2024-T3 clad aluminum

Chlorination(3)

- a. Scrub neoprene in 120-140°F (49-60°C) nonionic detergent solution (2-3% by wt).
- b. Rinse thoroughly in tap water.
- c. Rinse thoroughly in distilled water.
- d. Air-dry.

## MIL-HDBK-691B

e. Immerse 1-1/2 to 3 min. in the following solution at room temperature (prepare solution just prior to use, adding ingredients in the order listed):

Distilled water	97.0 pbw
Sodium hypochlorite (as Clorox or Purex)	3.0 pbw
Hydrochloric acid (sp. gr. 1.20)	0.3 pbw

f. Rinse thoroughly with distilled water and dry at temperatures up to 150°F (66°C).

Activated Gas-Plasma. This method, described generally above under 5.3.2.8, has been used successfully with neoprene. The best results were obtained by Picatinny Arsenal studies with ammonia, air and nitrogen plasmas at 30 min. (50)

NOTE: See Table XXIV and comments for comparison of methods for neoprene.

5.3.5.3.3 Ethylene-propylene-diene terpolymer (EPDM). This rubber, along with the copolymer of ethylene or propylene (EPH), forms a classification called ethylene-propylene rubbers. However, since EPDM, the terpolymer, is in much greater use than EPH, the former is frequently called ethylene-propylene rubber. Its outstanding property is very high resistance to ozone and weathering. Commercial production was begun in the U.S. in 1963, and this is now considered the fastest-growing elastomer. Being less polar, EPDM is relatively difficult to bond. (41)

Abrasive treatment. (As in Neoprene; acetone or MEK are recommended as solvents).

Cyclization. (As in Neoprene).

5.3.5.3.4 Silicone rubber (polydimethylsiloxane). These rubbers are completely synthetic materials finding wide application for many uses. They comprise two types, heat-vulcanizing and room-temperature vulcanizing (RTV). Both types have unique properties unobtainable with organic rubbers, particularly where superior endurance and extended life expectancy are required. Silicone elastomers maintain their usefulness from -150 to 500°F (-100 to 316°C). Resistance to oxidation, oils and chemicals is high and their stability against weathering is very good.

Solvent cleaning.

- Sand with a medium-grit sandpaper
- Solvent-wipe surfaces with acetone, MEK, ethyl, methyl or isopropyl alcohol, or toluene.

Soap-and-water wash. A simple washing with a mild (IVORY) soap and water, followed by thorough rinsing, was found to give satisfactory results in a Picatinny Arsenal study. (51)

Primers. Priming the silicone rubber with Hughson's CHENLOK 607 adhesive in methanol solvent has been found to give good results. The primer should be dried at < 395°F (200°C) for 10-15 min. Other satisfactory primers

## MIL-MDBK-691B

include Hughson's CHEMLOK AP-133, a silanol-type primer supplied in denatured alcohol at 5% solids. This primer should be air-dried 15-40 min at room temperature.(12)

Activated-Gas Plasma. This method, described generally above under 5.3.2.8, has been used unsuccessfully with silicone rubbers, as shown in Table XX above. Sandia Laboratory workers have also demonstrated the advantage of activated-gas plasma in bonding silicone rubber (RTV 630 - General Electric Co.) to aluminum with a mineral-filled standard epoxy coating resin. Activated argon was used for 10 min. at 250 watts/Torr. Tensile strength of rubber disks bonded between aluminum plugs was increased from 10 psi (0.0005 MPa) for the untreated to 384 psi (2.65 MPa) for the treated immediately after treatment, but the strength was gradually reduced to 102 psi (0.70 MPa) after 7 days, and after 30 days the specimen fell apart on handling. The authors feel that the failure level decrease reflects a change in the polymer, rather than in the interface.(52)

5.3.5.3.5 Butyl rubber (IIR). Butyl rubber has been commercially produced since 1942 and is a well-established specialty elastomer with a wide range of applications. It is a copolymer of isobutylene and isoprene. Its special properties are: low gas permeability, thermal stability, ozone and weathering resistance, vibration damping and higher coefficient of friction and chemical and moisture resistance.(41) Being less polar, butyl rubber is relatively difficult to bond.

Abrasive treatment. (As in Neoprene; toluene is recommended as a solvent).

Cyclization. (As in Neoprene).

Chlorination. (As in Neoprene).

Primers. Prime with butyl rubber adhesive in an aliphatic solvent(25) or use such silicone primers as Union Carbide's AP-133, Y-4310, or Y-5042.

Activated-Gas Plasma. This method, described generally above under 5.3.2.8, has been used successfully with butyl rubber. Very good results were obtained in Picatinny Arsenal studies using air and nitrogen plasmas at 30 min.(50)

5.3.5.3.6 Chlorobutyl rubber (CIIR). This modified butyl rubber was introduced in 1960. It contains about 1.2 wt % of chlorine and has greater vulcanization flexibility and enhanced cure compatibility than other general-purpose elastomers.(41)

Abrasive treatment. ((As in Neoprene).

Cyclization. (As in Neoprene).

Chlorination. (As in Neoprene).

Other methods. See Table XXVI for a comparison of results obtained by a number of different surface-preparation methods.



## MIL-HDBK-691B

TABLE XXVI. Peel strength of epoxy-polyamide resin adhesive to chlorobutyl rubber pretreated by various methods.(3)

<u>Surface Treatment</u>	<u>Peel Strength</u>	
	lbs/in width	N/m
Cyclization	18.0	3152
Solvent-clean and chlorinate	14.0	2452
Solvent-clean, abrade, chlorinate	16.0	2802
Detergent-clean and chlorinate	30.0*	5254
Ethanol-wipe	7.0	1226
Abrade and ethanol-wipe	7.0	1226
MEK-wipe	6.0	1051
Abrade and MEK-wipe	6.5	1138
*broke rubber		

5.3.5.3.7 Chlorosulfonated polyethylene (CSM). (HYPALON - du Pont Co.) This synthetic rubber, also known as chlorosulfonyl polyethylene, introduced in 1952, is characterized by ozone resistance, light stability, heat resistance, weathering, resistance to deterioration by corrosive chemicals and good oil resistance. Presently available types contain from 25-43% chlorine and 1.0-1.4% sulfur.(41)

Abrasive treatments. (As in Neoprene; acetone or MEK are recommended as solvents).

Primers.

- Wipe with toluene.
- Force-dry 1 hour at 140°F (60°C).
- Prime with an adhesive primer such as 3M Co. SCOTCHCAST XR-5001 or Bloomingdale BR-1009-8 (polyamide epoxy in solvent blend).

See Table XXVII for results of a Picatinny Arsenal-sponsored study using primers.

TABLE XXVII. Effect of surface preparation on T-peel strength of Hypalon rubber.(49)

<u>Surface Preparation</u>	<u>Adhesive</u>	
	AP-30 (nitrile-phenolic film)	FM-1000 (nylon-epoxy film)
Toluene wipe + 3M Co. SCOTCHCAST XR-5001 primer	---	66 lbs/3" width (3853 N/m)
Toluene wipe + Bloomingdale BR-1009-8 primer	---	34.4 lbs/3" width (2008 N/m)
Sanded + Toluene wipe + 3M Co. SCOTCHCAST XR-5001 primer	31 lbs/3" width (1810 N/m)	---
*0.33" (8.4 mm) thickness 78 Shore "A" Durometer, bonded to 0.016" (0.41 mm) 2024-T3 clad aluminum		

## MIL-HDBK-691B

5.3.5.3.8 Nitrile rubber (Butadiene-acrylonitrile) (NBR). Nitrile rubbers are copolymers of butadiene and acrylonitrile and are frequently referred to as BUNA N. The properties vary with the acrylonitrile content. Nitrile rubbers exhibit a high degree of resistance to attack by oils at both normal and elevated temperatures. The Army has found that carboxylated, butadiene-acrylonitrile (XNBR) is of particular interest, exhibiting much higher tensile strength and modulus, lower elongation, higher hardness, much improved hot-tear and tensile, better low-temperature brittleness, improved ozone resistance, and better retention of physical properties.(41)

Abrasive treatment. (As in Neoprene; methanol is recommended as a solvent).

Cyclization. (As in Neoprene, except that the exposure should be for 10-15 min.).

Chlorination. (As for Neoprene).

Primers. Primers have been used successfully with BUNA N rubber. Primers that have been particularly recommended for this type of rubber include the following:

Hughson CHEMLOK AP-131 Primer for bonding to steel  
 Hughson CHEMLOK 205 (Adhesive) for bonding to aluminum  
 Hughson CHEMLOK 220 (Adhesive) for bonding to aluminum  
 3M Company's SCOTCHCAST XR-5001 for bonding to aluminum  
 3M Company's HX-740 reactive imine (for bonding with carboxy-terminated polybutadiene liquid adhesive used with CHEMLOK 220). (The HX-740 apparently dissolves the plasticizer in the rubber).

Procedure.

- a. Wipe with toluene.
- b. Force-dry at 140°F (60°C).
- c. Prime with an adhesive primer (such as those listed above).

See Table XXVIII for results of a Picatinny Arsenal-sponsored study using primers.

MIL-HDBK-691B

TABLE XXVIII. Effects of surface preparation on T-peel strength of adhesive-bonded BUNA N rubber joints. (49)

Surface Preparation	Adhesive		
	AP-30 (nitrite phenolic film)	PM-1000 (nylon epoxy film)	PM-37 (modified epoxy foam)
Toluene wipe + 3M Co. SCOTCHCAST XR-5001 primer	110 lbs/3" width (6422 N/m)	125 lbs/3" width (7209 N/m)	21 lbs/3" width (1226 N/m)
Sanded + toluene wipe + 3M Co. SCOTCHCAST XR-5001 primer	131 lbs/3" width (7648 N/m)	110 lbs/3" width (6422 N/m)	---
Toluene wipe	90 lbs/3" width (5254 N/m)	5 lbs/3" width (292 N/m)	31 lbs/3" width (1810 N/m)
Sanded - toluene wipe	140 lbs/3" width (8173 N/m)	15 lbs/3" width (876 N/m)	---
*0.132" (3.3 mm) thickness 65 Shore "A" Durometer, bonded to 0.016" (0.41 mm) 2024-T3 clad aluminum.			

## NIL-HDBK-691B

Bell-peel strengths. (0.132" or 3.3 mm) BUNA N to 0.064" (1.6 mm) (2024-T3 Clad aluminum) for toluene-wiped and then XR-5001-primed specimens for AF-30 and FH-1000 were 39 and 38 lbs/1" width respectively (6829 and 6654 N/m). Flatwise-tensile strengths for the same surface treatment for AF-30, FH 1000, FH-37, were 234, 252 and 185 psi, respectively (1.6., 1.73 and 1.28 MPa).(49)

Activated-gas plasma. This method, described generally above under 5.3.2.8, has been used successfully with BUNA N rubber. The best results were obtained by Picatinny Arsenal studies using ammonia, air and nitrogen plasmas at 30 min.(50)

5.3.5.3.9 Polyurethane elastomers. In this category we normally consider thermosetting materials derived from the reaction of an isocyanate with a hydroxy compound. Their unique elastomeric properties are: exceptionally high abrasion resistance at moderate temperatures, excellent oil and solvent resistance, very high tear and tensile strength and high hardness with good mechanical strength. Both polyester (AU) or polyether (EU) types are available, as are thermoplastic polyester urethane rubbers. They are usually completely soluble in strong polar solvents such as tetrahydrofuran and dimethyl formamide, and at high temperatures, they can be molded, calendered or extruded.(41)

Abrasion treatment. (As in Neoprene; methanol is recommended as a solvent).

Primers. A number of primers can be used, including Hughson's CHEMLOK primers AP-134, 4-5224 and AP-131, and Union Carbide's All00 (an aminosilane).

5.3.5.3.10 Synthetic natural rubber (Polyisoprene) (IR). This rubber approximates the chemical composition of natural rubber (NR). Its predominant structure is cis-1,4-polyisoprene, the same as that of natural rubber. In general, the synthetic polyisoprenes are lower in modulus and higher in elongation than the natural product. Synthetic polyisoprene was first introduced commercially in 1960.(41)

Abrasion treatment. (As in Neoprene; methanol or isopropane are suggested as solvents).

Cyclization. (As in Neoprene, except that exposure should be for only 5-10 min., since this is not an acid-resistant rubber. Some workers suggest much shorter exposure (10-45 secs.).

Chlorination. (As in Neoprene).

NOTE: See Table XXIV and comments for comparison of methods for natural rubber.

5.3.5.3.11 Styrene-butadiene rubber (SBR) (BUNA S). This rubber type, once called GR-S, is the most important synthetic rubber and the most widely used in the world. It is a copolymer of styrene and butadiene.(41)

Abrasion treatment. (As in Neoprene; toluene is recommended as a solvent; excessive toluene results in swollen rubber. A 20-minute drying time will restore the part to its original dimensions).

Cyclization. (As in Neoprene, except that the exposure time should be for 10-15 min.)

## MIL-HDBK-691B

Chlorination. (As in Neoprene).

Primers. Primers used successfully include butadiene-styrene adhesive in aliphatic solvent and Hughson Chemical Company's CHEMLOCK 205 adhesive in methyl isobutyl ketone (MIBK) diluent.

Activated-gas plasma. This method, described generally above under 5.3.2.8, has been used with some success with BUNA S rubber. The best results were obtained by Picatinny Arsenal studies using helium, air and nitrogen plasmas.(50)

NOTE: See Table XXIV and comments for comparison of methods for SBR.

5.3.5.3.12 Polybutadiene (Butadiene rubber) (BR). Although this type of rubber was introduced in Europe in the early 1930's, it was almost unknown in the US until 1960. Presently it is second to SBR in usage.(41)

Abrasion treatment. (As in Neoprene; methanol is recommended as a solvent).

Cyclization. (As in Neoprene, except that the exposure time should be 10-15 min, since this is a non-acid resistant rubber).

Chlorination. (As in Neoprene).

Solvent wipe. A sample solvent wipe with methanol may be used.

5.3.5.3.13 Fluorosilicone elastomers. The fluorine-containing silicone rubbers have been developed into the second largest volume of the fluoro-elastomer types. The fluoroelastomers not containing silicones are discussed below under 5.3.5.3.17. Fluorosilicone rubbers retain most of the useful qualities of the regular silicone rubbers and improved resistance to many fluids, except for ketones and phosphate esters. They are most useful when low-temperature resistance is required, in addition to fluid resistance.(41)

Solvent clean. Solvent wipe with methyl, ethyl or isopropyl alcohol or toluene.

5.3.5.3.14 Epichlorohydrin rubber. (HYDRIN - B.F. Goodrich) (HERCLOR - Hercules Inc.) This elastomer homopolymer (CO) and the copolymer (ECO) combine exceptional resistance to aliphatic hydrocarbons with high resistance to aromatic and halogenated hydrocarbons, ozone, weathering, gas permeability, compression set, impact and tear. They have good tensile strength, resilience, and resistance to abrasion, water, acids and alkalis. They also have good low-temperature and heat resistance. Epichlorohydrin elastomers of both types require a simple cleaning with solvents such as acetone (not MEK), alcohols, or aromatics, such as toluene. No abrasion is necessary.(41)

5.3.5.3.15 Polysulfide rubber. The first introduction of a polysulfide rubber for commercial application was in 1930 when Thiokol Chemical Company developed THIOKOL Type A. Since then a number of other types have been developed. The types commonly used now are types PA and ST. THIOKOLS are highly-impermeable to gases, and have excellent resistance to ozone, oxidation, weathering and aliphatic and aromatic hydrocarbons.(41)

Abrasion treatment. (As in Neoprene; methanol is recommended as a solvent).

## NIL-HDBK-691B

Chlorination.

- a. Degrease in methanol.
- b. Immerse overnight in strong chlorine water.
- c. Wash.
- d. Dry.

Primers. Silicone primers recommended by Hughson Chemicals for use with polysulfides sealants include Hughson's CHEMLOK AP-131, Y-4310 and Y-5254.

5.3.5.3.16 Polypropylene oxide. (propylene oxide rubber) (PO) (PAREL 58 - Hercules Inc.) This elastomer is a sulfur-vulcanizable copolymer of propylene oxide and allyl glycidyl ether. Its vulcanizates are particularly attractive for dynamic uses where high resilience, excellent flex life, and flexibility at extremely low temperatures are required. It performs similarly to natural rubber in these applications, but in addition has the added advantages of (1) good resistance to aging at high temperatures, (2) good ozone resistance and (3) moderate resistance to loss of properties in contact with fuels, and/or some solvents.(53)

The surfaces of this elastomer should be prepared by solvent wiping with TCE, xylene, toluene, or other appropriate solvent.(54)

5.3.5.3.17 Fluorocarbon elastomers. These materials, also called fluoroelastomers, include KEL-F elastomers and Fluorel (both 3M Company). VITON and FLUOREL are both copolymers of vinylidene fluoride and hexafluoropropylene (FPM). KEL-F is a copolymer of chlorotrifluoroethylene and vinylidene fluoride and is called polychlorotrifluoroethylene (CFM). It was first developed in 1954. VITON and FLUOREL are the most important members of this group today. These elastomers have excellent resistance to ozone, oxidation, weathering, heat, aliphatic and aromatic hydrocarbons, and alcohols. They are also highly impermeable to gases, have good strength, electrical resistivity, and resistance to abrasion, water, acids, and halogenated hydrocarbons. This type usually includes the fluorosilicone elastomers, but these have been treated separately under 5.3.5.3.13.(41)

Sodium etch. For optimum bond strength use this procedure, described above under 5.3.5.2.2.7.

Dry abrasion. For relatively low adhesion, with low environmental resistance.

- a. Wipe or spray with, or immerse in 1,1,1-trichloroethane, FREON THC or M-17, acetone, MEK, toluene, ethyl or isopropyl alcohol.
- b. Abrade lightly and uniformly with 180-320 grit abrasive paper.
- c. Repeat (a).

5.3.5.3.18 Polyacrylate (polyacrylic rubber) (AHC) (ANH). Polyacrylate elastomers are noted primarily for their high resistance to heat, ozone, oxidation, weathering, aliphatic hydrocarbons, and sulfur-bearing oils. They

## MIL-HDBK-691B

also have good resilience and gas impermeability and moderate strength. Abrasion resistance is not as good as with nitrile rubber or SBR. At present there are four major suppliers.(41)

Dry abrasion. (As in fluorocarbon elastomers; methanol has also been used as a solvent).

5.3.5.3.19 Thermoplastic rubber. (thermoplastic elastomer) This is a new class of polymers in which the end-use properties of vulcanized elastomers are combined with the processing advantages of thermoplastic. Because of their unique molecular configuration they may be processed with the same techniques utilized with thermoplastics, but the mechanical properties of the final articles are essentially undistinguishable from those of similar articles fabricated from conventional vulcanized elastomers.(1)

There are several types, including polyester (HYTREL - du Pont Co.), polystyrene-butadiene-polystyrene block polymers and polystyrene-isoprene-polystyrene block copolymers (both types KRATON - Shell Development Co.) polyolefin (TPR thermoplastic rubber - Uniroyal, Inc.), (SOMEL Thermoplastic elastomer - du Pont Co.) and urethane, mentioned briefly above under 5.3.5.3.9 Polyurethane elastomers.(41)

Since these materials are thermoplastic and therefore may be soluble in a wide range of organic solvents, it is quite possible that solvent cementing would be the most appropriate method of bonding the thermoplastic rubbers to themselves or to mutually compatible plastics. Solvent cementing might work with KRATON, but not with TPR and HYTREL, however. In some cases a thermal-fusion (welding) method will prove the best method, as in HYTREL, which does not have reactive bonding sites. In cases where the thermoplastic rubber must be bonded to metals or other non-plastic or non-rubber materials, neither solvent cementing nor fusion techniques can be considered. In such cases conventional adhesives must be used, and surface preparation for such adhesive bonding must be considered. In the case of HYTREL polyester elastomer, du Pont recommends cleaning with MEK and then using commercial primers. Abrading is not recommended. Polyurethane rubber, on the other hand, has reactive sites and would be cementable with solvents.

#### 5.3.5.4 Miscellaneous materials.

##### 5.3.5.4.1 Asbestos (rigid).(12)

- a. Degrease in acetone.
- b. Abrade with 100-grit emery cloth.
- c. Remove dust.
- d. Degrease in acetone.
- e. Dry in air to allow solvent to evaporate.
- f. Prime with diluted adhesive or low-viscosity rosin ester.



## MIL-HDBK-691B

5.3.5.4.2 Brick and fired non-glazed building materials.(4)

- a. Degrease with MEK
- b. Abrade surface with a wire brush.
- c. Remove all dust and contaminants.

5.3.5.4.3 Carbon and graphite.

- a. Abrade with 320-grit emery cloth.
- b. Remove dust.
- c. Solvent-degrease with acetone.

5.3.5.4.4 Glass (non-optical).(4)(12)Abrasive treatment (for general-purpose bonding).

- a. Grit-blast with aluminum oxide or carborundum and water slurry (one part by volume 220-325 grit slurry of aluminum oxide in carborundum to 3 parts by volume distilled water).
- b. Degrease in acetone or detergent.
- c. Dry 30 min at 100°C (380°F).
- d. Apply the adhesive before the glass cools to room temperature.

Acid etch (for maximum strength).

- a. Clean in acetone or detergent.
- b. Immerse for 10-15 min at 20°C (52°F) in:

Sodium dichromate	7 pbw
Sulfuric acid, conc	400 pbw
Water	7 pbw

- c. Rinse in tap, then distilled water.
- d. Dry thoroughly.

Primers. Adhesion to clean glass may be promoted by the use of silicone primers. The selection of primers depends on the particular adhesive system used. The addition of silane additives to the adhesive system also improves adhesion to glass.

5.3.5.4.5 Glass (optical).(4)

- a. Clean in an ultrasonically agitated detergent batch; or use trichlorotrifluoroethane with FREON T-WD 602 water-in-oil-type emulsion cleaning agent.
- b. Rinse.

## MIL-HDBK-691B

b. Rinse.

c. Dry below 100°C (380°F).

5.3.5.4.6 Ceramics (unglazed).(3)(12) For unglazed ceramics, such as aluminum, silica, etc.:

a. Grit-blast with aluminum oxide or carborundum and water slurry (one part by volume 220-325 grit slurry of aluminum oxide or carborundum to 3 parts by volume distilled water).

b. Degrease in acetone or detergent.

5.3.5.4.7 Ceramics (glazed).(12) For glazed ceramics such as porcelain:

a. Solvent-degrease in acetone or in warm aqueous detergent.

b. Rinse.

c. Dry.

5.3.5.4.8 Concrete.

5.3.5.4.8.1 Portland-cement type.(3)

a. If the concrete is contaminated with oil or grease, scrub with a detergent solution (approximately 2% in water) and thoroughly rinse, or clean with any appropriate solvent.

b. If the concrete is contaminated with old paint, plant growth, soot or other soil, it should be dry-grit-blasted with a non-metallic grit, such as flintstone, silica, silicone carbide, or aluminum oxide. For old concrete, the surface should be blasted or cut down until good solid material is exposed (1/16") (1.6 mm) or more. If there is a heavy layer of loose material it is advisable to first remove the bulk of it by vacuuming or sweeping. Dust and loose particles should be cleaned off by blowing with clean filtered air.

c. If grit-blasting is not used, the cement should be acid etched with a solution of 15% by wt of conc. hydrochloric acid in water. One gallon of this solution will treat 5 sq yds (4.2 sq. met).

5.3.5.4.8.2 Bituminous type.(4)

a. Scrub with a 2% by wt solution of detergent.

b. Rinse with a high-pressure hose until the surface no longer feels slippery.

c. In cases where limestone, dolomite or other carbonate aggregate is present in the bituminous concrete, improved adhesion will be obtained by using the acid-etch solution outlined under 5.3.5.4.8.1 for Portland cement.

d. In areas where an excessively heavy cake of oil and grime is present, use a combination of a detergent wash and mechanical cleaning.

## MIL-HDBK-691B

5.3.5.4.9 Wood, plywood.(55) Careful machining is essential in preparing wood for glueing. To obtain the strongest joints, the wood surfaces should be machined smooth and true with sharp tools, and be essentially free from machine marks, chipped or loosened wood grain, and other surface irregularities. To provide uniform distribution of glueing pressure, each lamination or ply should be of uniform thickness. When possible, machining should be accomplished just before glueing, so the surfaces are kept clean and are not distorted by moisture changes. Where the four sides of a piece are to be glued, it is preferable to glue in two operations and machine just before each operation.

Surfaces made by saws are usually rougher than those made by planers, jointers and other machines operated with cutter heads. Modern saws freshly sharpened, well-aligned, and skillfully operated are capable of producing surfaces adequate for glueing many products without further preparation, and thereby provide a savings in time and labor. Except where the saws are usually well-maintained, however, glue joints between sawed surfaces are weaker and more conspicuous than those between well-planed or jointed surfaces. Consequently, if inconspicuous glue joints of maximum strength are required, planed or jointed surfaces are generally more reliable. Machine marks caused by feeding the stock through a planer too fast for the speed of the knife prevent complete contact of the joint faces when glued. Machine marks in cores of thinly-veneered panels are likely to show through the finished surface. Unequal thickness or width, which cause uneven distribution or glueing pressure and usually result in weak joints, may be due to the grinding, setting or wearing of machine knives. Knives that are dull or improperly set or ground may produce a burnished surface that interferes with glueing or formation of the strongest glue bonds.

Wood surfaces are sometimes intentionally roughened by tooth planing, scratching, or sanding with course sandpaper, in the belief that rough surfaces are better in glueing. However, comparative strength tests at the U.S.D.A. Forest Products Laboratory failed to show the advantage of roughening wood surfaces. Also, studies of the penetration of glue into wood have shown the theoretical benefit of the roughened surface to be improbable. Light sanding has proved an advantage in preparing for glueing such surfaces as resin-impregnated wood, laminated paper/plastic, plywood that has been pressed at high temperatures and pressures, or wood that has been glazed from dull tools or by being pressed excessively against smooth, hard surfaces.

Within recent years, significant developments in sanding equipment have been reported. Advantages of so-called abrasive planning in preparing wood for glueing are reported to be deeper cuts in a single pass, close tolerances and improved surface quality for glueing.

5.3.5.4.10 Painted surfaces. For strong bonds it is not possible to attain good results without removing the paint surface, for even if the bond between the adhesive and the two surfaces, paint and other adherend is good, the strength of the joint will be no better than the strength of the bond between the surface that has been painted and the paint. For temporary or other bonds that do not require maximum strength, clean the painted surface with a detergent solution, abrade with a medium-grit emery cloth, and wash again with detergent.(4)

MIL-HDBK-691B

REFERENCES

- (5-1) A.H. Landrock, "Processing Handbook on Surface Preparation for Adhesive Bonding", Picatinny Arsenal Technical Report 4883, December 1975.
- (5-2) G. Salomon, Introduction, ADHESION AND ADHESIVES, Vol. 2 - Applications, 2nd Edition, edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1967.
- (5-3) R.C. Snogren, HANDBOOK OF SURFACE PREPARATION, Palmerton Publishing Co., N.Y., 1974.
- (5-4) E.H. Petrie, Chapter 10, "Plastics and Elastomers as Adhesives", HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A. Harper, McGraw-Hill, N.Y., 1975.
- (5-5) Society of Manufacturing Engineers, Chapter 4, "Surface Preparation for Bonding", ADHESIVES IN MODERN MANUFACTURING, edited by E.J. Bruno, 1970.
- (5-6) H.L. Rogers, "Surface Preparation of Metals for Adhesive Bonding", pp. 327-340, APPLIED POLYMER SYMPOSIA No. 3, Structural Adhesive Bonding, edited by H.J. Bodnar, Wiley-Interscience, 1966.
- (5-7) H. Chessin and V. Curran, "Preparation of Aluminum Surfaces for Bonding", pp. 319-325, APPLIED POLYMER SYMPOSIA No. 3, Structural Adhesive Bonding, edited by M.J. Bodnar, Wiley-Interscience, 1966.
- (5-8) J.R. Hall et al., "Activated Gas Plasma Surface Treatment of Polymers for Adhesive Bonding", Journal of Applied Polymer Science, 13: 2085-2096, 1969.
- (5-9) International Plasma Corporation (IPC), Product Bulletin 2402.
- (5-10) R.F. Wegman et al., "Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures - Part 2, Important Considerations for the Bonding Process", Picatinny Arsenal Technical Report 3999, July 1970.
- (5-11) W.C. Tanner, "Manufacturing Processes with Adhesive Bonding", pp. 1-21, APPLIED POLYMER SYMPOSIA No. 19, Processing for Adhesives Bonded Structures, Wiley-Interscience, 1972.
- (5-12) J. Shields, ADHESIVES HANDBOOK, 2nd Edition, Newnes-Butterfield, London, 1976.
- (5-13) American Society for Testing and Materials (ASTM), ASTM D 2651-79 (1984), Standard Recommended Practice for PREPARATION OF METAL SURFACES FOR ADHESIVE BONDING, Vol. 15.06, Annual Book of ASTM Standards.
- (5-14) American Society for Testing and Materials (ASTM), ASTM D 2674-72 (1984), Standard Methods of ANALYSIS OF SULFOCHROMATE ETCH SOLUTION USED IN SURFACE PREPARATION OF ALUMINUM, Vol. 15.06, Annual Book of ASTM Standards.

## MIL-HDBK-691B

- (5-14a) W.J. Russell, "Chromate-Free Process for Preparing Aluminum for Adhesive Bonding," pp 105-117, APPLIED POLYMER SYMPOSIA NO. 32, Durability of Adhesive Bonded Structures, edited by M. M. Bodnar, Wiley-Interscience, 1977.
- (5-14b) W.J. Russell and E.A. Garnis, "Chromate-Free Method of Preparing Aluminum Surfaces for Adhesive Bonding: An Etchant Composition of Low Toxicity", U.S. Army ARRADCOM, Large Caliber Weapon Systems Laboratory, Technical Report ARLCD-TR-78001, May 1978.
- (5-14c) N.L. Rogers and W. Russell, "Evaluation of Nonchromated Etch for Aluminum Alloys (P2-Etch)," U.S. Army ARRADCOM, Large Caliber Weapon Systems Laboratory, Contractor Report (Bell Helicopter Textron) ARLCD-CR-80008, April 1980.
- (5-14d) R.F. Wegman et al., "The Function of the P2 Etch in Treating Aluminum Alloys for Adhesive Bonding." Preprint Book, pp 273-281, 29th National SAMPE Symposium, Vol. 29, Reno, Nevada, April 3-5, 1984.
- (5-15) American Society for Testing and Materials (ASTM), ASTM D 3933-80, Standard Practice for PREPARATION OF ALUMINUM SURFACES FOR STRUCTURAL ADHESIVES BONDING, (PHOSPHORIC ACID ANODIZING), Vol. 15.06, Annual Book of ASTM Standards.
- (5-16) R.F. Wegman et al., "Evaluation of the Adhesive Bonding Processes Used in Helicopter Manufacture, Part 1 - Durability of Adhesive Bonds Obtained as a Result of Processes Used in the UH-1 Helicopter", Picatinny Arsenal Technical Report 4186, September 1971.
- (5-17) C.V. Cagle, "Surface Preparation for Bonding Beryllium and Other Adherends", Chapter 21 in HANDBOOK OF ADHESIVE BONDING, edited by C.V. Cagle, McGraw-Hill, N.Y., 1973.
- (5-18) Hughson Chemical Co., Technical Bulletin 7101C, June 1977, "Preparation of Substrates for Bonding".
- (5-19) H.N. Vazirani, "Surface Preparation of Copper and its Alloys for Adhesive Bonding and Organic Coatings", Journal of Adhesion, 1: 208-221 (1969)
- (5-20) A.T. Devine, "Adhesive Bonded Steel: Bond Durability as Related to Selected Surface Treatments", U.S. Army ARRADCOM Technical Report ARLCD-TR-77027, December 1977.
- (5-21) C.V. Cagle, "Bonding Steels", Chapter 14, HANDBOOK OF ADHESIVE BONDING, edited by C.V. Cagle, McGraw-Hill, N.Y., N.Y., 1973.
- (5-22) H.N. Vazirani, "Surface Preparation of Steel for Adhesive Bonding and Organic Coatings", Journal of Adhesion, 1: 222-232 (1969).
- (5-23) S.A. Slots and R.F. Wegman, "Durability of Adhesive Bonds to Various Adherends", Picatinny Arsenal Technical Report 4917, June 1976.
- (5-24) R.F. Merschel, Chapter 10 - Titanium, HANDBOOK OF SURFACE PREPARATION, R.C. Snogren, Palmerton Publishing Co., N.Y., N.Y., 1974.

## MIL-HDBK-691B

- (5-25) W.H. Guttman, **CONCISE GUIDE TO STRUCTURAL ADHESIVES**, Reinhold, N.Y., 1961.
- (5-26) Hysol Division, The Dexter Corporation, Olean, N.Y., "Preparing the Surface for Adhesive Bonding", Bulletin G-1-600 (undated).
- (5-27) H.J. DeLollis, **ADHESIVES FOR METALS**, Industrial Press, N.Y., N.Y., 1970.
- (5-28) R.C. Snogren, "Selection of Surface Preparation Processes", Parts 1 and 2, Adhesives Age, 12: (7, 8) (July, August 1969).
- (5-29) R.D. Beemer, "Introduction to Weld Bonding", SAMPE Quarterly, 5: 37-41 (October 1973).
- (5-30) B.B. Bowen et al., "Improved Surface Treatments for Weldbonding Aluminum", AFML-TR-159, October 1976.
- (5-31) K.C. Wu and B.B. Bowen, "Advanced Aluminum Weldbonding Manufacturing Methods", Preprint Book, pp 536-554, 22nd National SAMPE Symposium, Vol. 22, San Diego, CA, April 26-28, 1977.
- (5-32) J. Mahon et al., "Manufacturing Methods for Resistance Spotweld - Adhesive Bond Joining of Titanium", AFML-TR-76-21, March 1976.
- (5-33) G.W. Lively and A.E. Hohman, "Development of a Mechanical-Chemical Surface Treatment for Titanium Alloys for Adhesive Bonding". Proceedings, 5th National SAMPE Technical Conference, Oct. 9-11, 1973, Kiamesha Lake, N.Y., pp. 145-155.
- (5-34) H.C. Ross et al., "Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures - Part A, Adhesive Bonding Structural Plastics", Picatinny Arsenal Technical Report 4318, July 1972.
- (5-35) R.F. Wegman, "Adhesive Bonding of Silicone Rubber to KRALASTIC for the LAW Launcher", Picatinny Arsenal Technical Memorandum 1865, March 1969.
- (5-36) A.T. Devine and H.J. Bodnar, "Effects of Various Surface Treatments with Adhesive Bonding of Polyethylene", Adhesives Age, 12 (5): 35-37 (May 1969).
- (5-37) A. Devine et al., "Effects of Surface Treatments on Bonding to Polyethylene with Various Type Adhesives", Picatinny Arsenal Memorandum 1797, October 1967.
- (5-38) J.R. Hall et al., "Surface Treatment of Polymers with Activated Gas Plasma for Adhesive Bonding", Picatinny Arsenal Technical Report 3788, January 1968.
- (5-39) H.C. Ross, "A Preliminary Study of Adhesive Bonding of Newer Structural Plastics", Picatinny Arsenal Technical Memorandum 2204, April, 1976.
- (5-40) J.F. Austin et al., "Oxygen Concentration Bonding Program", Summary Report, April-August 1969, ASD-TR-7-42, Dec. 1970. Contract F33657-66-C-1076 with ASD, WPAPB, Ohio.

## MIL-HDBK-691B

- (5-41) A.H. Landrock, "Effects of Varying Processing Parameters in Fabrication of Adhesive-Bonded Structures - Part XVIII. Adhesive Bonding and Related Joining Methods for Structural Plastics - Literature Survey", Picatinny Arsenal Technical Report 4424, November 1972.
- (5-42) E.I. Du Pont de Nemours & Co., Inc., Plastics Dept., Experiment Station, Wilmington, DE, "Adhesive Procedure for VESPEL Precision Parts", unnumbered release, 6 pp., rev. Dec. 1973.
- (5-43) A.T. Devine et al., "Effect of Surface Exposure Time on Bonding of Glass Reinforced Plastic", SAMPE Journal, 7 (3): 16-1 (February 1961).
- (5-44) L.C. Jackson, "Preparing Plastics Surfaces for Adhesive Bonding", Adhesives Age, 4 (2): 30-32 (February 1961).
- (5-45) C.V. Cagle, ADHESIVE BONDING: TECHNIQUES AND APPLICATIONS, McGraw-Hill, N.Y., N.Y., 1968.
- (5-46) J. Theberge et al., "Low-cost Glass Fortified Thermoplastic Resins for Automotive Applications", Proceedings, 27th Annual SPI Conference, Reinforced Plastic/Composites Institute, Washington, D.C., Feb. 8-10, 1972. Paper 14-C, 12 pp.
- (5-47) B.P. Spearman and J.D. Hutchison, "Post Vulcanization Bonding Techniques", Adhesives Age, 17 (4): 30-33 (April 1974).
- (5-48) L.H. Sharpe, Chapter 26, "Adhesive Bonding", Fastening and Joining Reference Issue, Machine Design, 41 (21): 119-128 (Sept. 11, 1969).
- (5-49) R.T. McIntyre et al., "Effects of Varying Processing Parameters in the Fabrication of Adhesive Bonded Structures, Part VI, Production Methods", Picatinny Arsenal Technical Report 4162, February 1971.
- (5-50) C.A. Westerdahl et al., "Activated Gas Plasma Surface Treatment of Polymers for Adhesive Bonding - Part III", Picatinny Arsenal Technical Report 4279, Feb. 1972.
- (5-51) A.T. Devine et al., "Bonding LEXAN Polycarbonate to Silicone Rubber Gas Masks", Picatinny Arsenal Technical Report 3930, April 1970. AD 869 856L.
- (5-52) R.R. Sowell et al., "Effects of Activated Gas Plasma on Surface Characteristics and Bondability of RTV-Silicone and Polyethylene", Preprint Booklet, Vol. 31, No. 2, pp. 62-67, American Chemical Society, Div. of Organic Coatings and Plastics Chemistry, meeting held at Washington, D.C., September 1971.
- (5-53) Hercules Inc., Bulletin DRP-101A, "PAREL Elastomer".
- (5-54) Hughson Chemicals, Personal Communication, October 4, 1977.
- (5-55) M.L. Selbo, "Adhesive Bonding of Wood", U.S. Dept. of Agriculture Technical Bulletin 1512, 1975.



## MIL-HDBK-691B

## Chapter 6. THE CONVENTIONAL ADHESIVE BONDING PROCESS

**6.1 General discussion.** In assembling components by adhesive bonding, the availability of so many different methods of adhesive bonding can be used to advantage. But this multiplicity can also be a problem to the bonder. His choice of method of application can, for example, restrict the degree of freedom to be exercised in designing the end product. Also, the method of application can affect the selection of materials that can be used in manufacturing the product, and, very often, assembly cost. The following factors must be considered in selecting the bonding method:<sup>(1)</sup>

- o The size and shape of the parts to be bonded
- o The specific areas to which the adhesive is to be applied
- o The number of assemblies to be produced
- o The required production speed
- o The viscosity or other characteristics of the adhesive
- o The form of the adhesive (liquid, paste, powder, film, hot melt)

**6.2 Adhesive storage and preparation.**

**6.2.1 Adhesive storage.** Many adhesives must be stored in the dark or in opaque containers, while others should be stored at low temperatures to prolong shelf life. The manufacturer's directions, usually found in technical bulletins on the particular adhesive, frequently provide information on storage requirements. For example, the epoxy-phenolic film adhesive MT-424 (Bloomingdale) has the following storage schedule for newly prepared adhesive film which has been properly refrigerated during storage:

<u>Storage Temperature</u>		
<u>°F</u>	<u>°C</u>	<u>Useful Life, Days</u>
-10	-23	180
0	-18	150
30	-1	75
75	24	12
85	29	3
100	38	1

Basic resins and curing agents for thermosetting adhesives should be kept apart so that accidental container breakage will not lead to contamination problems. Containers for solvent-based adhesives should generally be sealed immediately after use to prevent solvent loss or the escape of toxic or flammable vapors.<sup>(2)(3)</sup>

**6.2.2 Adhesive preparation.** Adhesive preparation requires careful attention. After cold storage, the adhesive must be warmed to the correct temperature for application. Usually this is room temperature, but in some cases, such as in hot-melt adhesives, the application temperature may be considerably higher. Where component mixing is concerned, it may be important to measure the proportions correctly if optimum properties are required. This is especially true with catalytic reactions (e.g. amine curing agents for epoxy

## NIL-HDBK-691B

resins) where insufficient catalyst prevents complete polymerization of the binder resin, while too much catalyst can lead to brittleness in the cured material. Excess unreacted curing agents may cause corrosion of metallic adherends. Some two-component adhesives have less critical mixing ratios (See Fatty Polyamides under 4.3.1.5 on Epoxy resin adhesives), and component volumes may often be measured by eye without too adverse an effort on the ultimate bond strength properties.(2)

The weighed-out components of multiple-part adhesives must be mixed thoroughly. Mixing should be continued until no color streaks or density stratifications are noticeable. Caution should be taken to prevent air from being mixed into the adhesive through over-agitation. This can cause foaming of the adhesive during heat cure, resulting in porous bonds. If air does become mixed into the adhesive, vacuum degassing may be necessary before application. Only enough adhesive should be mixed to work with before the adhesive begins to cure. The working life of the adhesive (See 4.5.5) is decreased as the ambient temperature increases and the batch size becomes larger. One-part and some heat-curing, two-part adhesives have very long working lives at room temperature, and application and assembly speed or batch size are not critical.(4)

For a large-scale bonding operation, hand mixing is costly, messy and slow; repeatability is entirely dependent on the operator. Equipment is available that can meter, mix, and dispense multicomponent adhesive on a continuous or shot basis.(4)

**6.2.2.1 Small-portion mixer-dispensers.** There are a number of packaging systems currently available which store small amounts of liquid adhesive components (thermosetting), and provide means for convenient mixing and dispersing, all within the package. These may take the form of flexible plastic pouches with removable dividers (clamps) separating the components (for two- or three-part resin systems with mixing ratios from 1:1 to 1:100). These contain resin amounts varying from 2 grams up to as much as 100 grams. Other forms of container-dispensers are available in the form of two-barrel hypodermic syringes fused together. Polyethylene cartridge assemblies are also used. The hypodermic syringes and cartridge assemblies have an advantage over the pouches in that they make it easier to apply the adhesive to localized areas. The components in the pouches, which are frequently colored, are kneaded by hand until completely mixed, as evidenced by the resulting uniformity of color. A corner of the pouch is then snipped off and serves as a dispenser. A large number of adhesive systems are available in these units.

### **6.3 Methods of adhesive application.**

**6.3.1 General.** The selection of an application method depends on the form of the adhesive: liquid, paste, powder, film or hot melt. Other factors influencing the application method are the size and shape of parts to be bonded, the areas where the adhesive is to be applied, and production volume and rate.(4)

**6.3.2 Liquid adhesives.** Adhesives in liquid form may be applied by the following methods.

## MIL-HDBK-691B

6.3.2.1 Brushing. Brushing is commonly used for applying adhesives to adherends having complex shapes, or to selected areas of a surface without the use of masks. The control of adhesive film thickness is limited and films are often uneven and blobbed. Brushing requires very little equipment and results in a minimum of wastage. The technique is generally not suited to rapid assembly work. The brushes used should be stiff. Good brushes may be used repeatedly if they are properly cleaned immediately after each use.(2)

6.3.2.2 Flowing. Flowing is particularly useful for applying liquid adhesives to flat surfaces having irregular shapes. It is superior to brushing in that it provides a more uniform adhesive film thickness and a higher production rate. For this method the adhesive is fed under pressure through either a simple nozzle or a hollow brush. When a nozzle is used, the device is known as a "flow gun". With a brush it is called a "flow brush". The adhesive should be brushed on a single smooth sweep. A second sweep over the same area is not practical with most adhesive types.(2)

6.3.2.3 Spraying. Spraying is primarily used for covering large areas having nonuniform contours. It provides a higher production rate than flowing and also offers a more uniform film thickness. However, the solids content and consistency of the adhesive must be rigidly controlled to insure an even coating. The equipment used for spraying adhesives is quite similar to that used for spraying paint. The exact equipment design and operating conditions may be varied to permit the production of almost any desired type and thickness of coverage. The presence of a possible health hazard arising from solvent-spray mists should always be considered and adequate ventilation provided.(2)

6.3.2.4 Roll coating. This technique is based on the transfer of adhesive material from a trough, by means of a pick-up roller partially immersed in it, to a contacting transfer roller sheet. Material is continuously coated with adhesive when fed between the transfer roller and a pressure roller which is adjusted to determine the coat thickness. This method is most suitable for applying adhesives to flat sheets and films, and may be used for parts as large as 6 ft. (1.83 m) in width. Where it is feasible, it provides the highest-possible production rate and the most uniform possible coverage. On many occasions, when small stampings must be coated, it is economical to roll-coat large sheets, then cut the parts from the coated sheets. The wastage of coating on the unused portions is rarely as costly as the coating of small individual parts.(2)

When multiple coats of adhesive must be applied (by any process), the most uniform film thickness is achieved by applying the second coat perpendicular to the first. In addition, the time between successive coats must be carefully regulated. Too short a drying time may result in sagging, bubbling or blistering, while too long a time may lead to the lifting of earlier coats.(2)

6.3.2.5 Knife Coating. This method employs an adjustable knife blade, bar, or rod to control the deposition of adhesive flowing onto a sheet moving under the blade. The distance between the blade edge and the adherend surface determines the adhesive coating thickness.(2)

## NIL-HDBK-691B

**6.3.2.6 Silk screening.** This manual technique is used to insure that when selected areas or patterned spaces are adhesively coated, low-viscosity adhesives work well because they pass readily through the cloth onto the work. However, only relatively thin films can be applied by this method. By filling the pores in a cloth over areas to remain uncoated and leaving other portions of the cloth unfilled, effective masking is set up. Then the adhesive is poured on top of the cloth and a rubber squeegee is used to facilitate flow of the adhesive down through the cloth. The squeegee, by itself, is another manual method of applying adhesive. As a general rule, fast-drying or tacky adhesives cannot be satisfactorily silk-screened.(1)(2)

**6.3.2.7 Oil can and squeeze bottle.** The hand-pump oil can and the polyethylene squeeze bottle are often used for spot application of adhesive. Where it is necessary to apply adhesive inside a blind hole or some other point with limited access, the oil can with a stem of appropriate length can be a simple solution. Tips at the end of the stem can be devised to deliver multiple spots of adhesive. The squeeze bottle can sometimes be used for the same purpose, and also to apply a continuous bond. Some liquid adhesives are supplied in squeeze-bottle containers. When using polyethylene squeeze bottles, care should be taken that the adhesive will not affect the polyethylene itself.(1)

**6.3.2.8 Hand dipping.** The dipping process is capable of speeding up the coating of relatively large surfaces. Automatic versions are the most satisfactory, but hand dipping can be used to speed up the applications of adhesive. The devices used to facilitate immersion of parts into the adhesive bath or trough range from baskets to screens to perforated drums.(1)

**6.3.3 Pastes.** Bulk adhesives such as pastes or mastics are the simplest and most reproducible adhesives to apply. These systems can be troweled on or extruded through a caulking gun. Little operator skill is required. Since the thixotropic nature of the paste prevents it from flowing excessively, application is usually clean, and not much waste is generated.(3)

**6.3.3.1 Spatulas, knives, trowels.** A simple applying tool particularly effective for hard-to-spread adhesives is the spatula. Knives and trowels, both of which may have notches cut into their applying edges, are variations of the spatula. The depths of notches and the spacing between them help regulate the amount of adhesive applied. Holding the blade firmly and at a right angle to the surface is essential for proper adhesive application. The preferred shape for spatula notches is square. Triangular notches present sharp teeth which wear out much faster than the wide contact surfaces of the square notches. Shallow, rounded and closely spaced notches are often used with adhesives of higher liquid contents, because such notches permit the adhesive to flow together and form a continuous unbroken film(1)

**6.3.4 Powders.** Powder adhesives can be applied in three ways. They may be sifted into a preheated substrate. The powder which falls into the substrate melts and adheres. The assembly is then mated and cured according to recommended processes. A preheated substrate could also be dipped into the powder and then extracted with an attached coating of adhesive. This method helps to assure even powder distribution. Lastly, the powder can be melted

## MIL-HDBK-691B

into a paste or liquid and applied by conventional means. Powder adhesives are generally one-part epoxy-based systems that require heat and pressure to cure. They do not require metering, but often must be refrigerated for extended shelf life. Because coating uniformity is poor, large variations of joint strength may result with powder adhesives.(4)

**6.3.5 Films.** The use of dry adhesive films (See 4.2.5 Film and Tape Adhesives) is expanding more rapidly than other forms because of the following advantages:

- o High repeatability - no mixing or metering; constant thickness
- o Ease of handling - low equipment cost, relatively hazard-free; clean operating
- o Very little waste - preforms can be cut to size
- o Excellent physical properties - wide variety of adhesive types available

Film adhesives are limited to flat surfaces or simple curves. Application requires a relatively high degree of care to insure nonwrinkling and removal of separation sheets. Characteristics of available film adhesives vary widely, depending on the type of adhesives used. Film adhesives are supplied in both unsupported and supported types. The carrier for supported films is generally fibrous fabric or mat. Film adhesives are supplied as heat-activated, pressure-sensitive, or solvent-activated forms. Solvent-activated adhesives are made tacky and pressure-sensitive by wiping with solvent. This type of adhesive is not as strong as other types, but is well suited for contoured, curved, or irregularly shaped parts. Manual solvent-reactivation methods should be closely monitored so that excessive solvent is not used. Chemical formulations available in solvent-activated films include neoprene, nitrile, and butryal-phenolics. Decorative trim and nameplates are usually fastened onto a product with solvent-activated adhesives.(4)

**6.3.6 Hot-melts.** Although there are a number of variations in equipment, two basic types of systems are used to heat and apply hot-melt adhesives: melt-reservoir and progressive-feed systems. (See also 4.2.3 Hot-melt Adhesives)(5)(6)

**6.3.6.1 Melt-reservoir systems.** (tank-type applicators) This type consists of a melting pot or reservoir, a pump, feed hose, and an extrusion gun or applicator wheel to apply the melted adhesive to the product. Spray or jet guns are also used in packaging applications. Metering pumps provide the required amount in automated systems; extrusion guns are triggered manually for assembling products that do not lend themselves to automation. Hot-melt adhesive is loaded into the reservoir in granular, block or chip form, where it is heated and maintained at the desired delivery temperature. A typical reservoir system holds about 10 pounds (4.54 kg) and some systems accommodate two or more delivery guns - each equipped with separate heating controls.

One of the main advantages of reservoir-type systems is that they use adhesive materials in their least expensive form. Granular or pellet-form adhesives in bulk quantities cost only one-quarter to one-third as much as the same adhesive in cartridges or slug-form. Tank systems also have higher delivery rates than progressive-feed equipment - important for assembling



## MIL-HDBK-691B

products with several feet of bonded length - and they require less frequent loading. Adhesive output may vary from 10-20 lbs. (4.5-9.1 kg) per hour, depending on the adhesive used. Operation temperatures are under 400°F (204°C). These systems are excellent for handling low-performance, low-viscosity adhesives (1,000-50,000 cps) (1-50 Pa.s).

While the reservoir-type system has the advantage of holding a large amount of fluid adhesive in readiness, it also has some drawbacks. Maintaining a uniform temperature in this large volume of adhesive is sometimes difficult, since fresh solid adhesive must be added at periodic intervals. If the temperature of the fluid adhesive is too low at the nozzle the bond may be degraded, or carbonized deposits may form and plug the nozzle. The higher-performance hot melts are especially susceptible to these problems. These formulations have higher molecular weights and higher viscosities and they degrade more rapidly when heated in the presence of oxygen than the packaging hot melts. These materials require very close temperature controls and, for optimum results, elimination of oxygen from the dispersing system.

**6.3.6.2 Progressive-feed systems.** These systems heat only a small amount of adhesive at a time, thus eliminating some of the problems inherent in a reservoir system. Several versions of progressive-feed or "first-in, first-out" equipment are in use. In one type, granules or pellets of adhesive are loaded into a hopper. The adhesive melts on a heated grid, then flows to a gear pump and is immediately transferred under pressure, through an electrically-heated hose, to a heated gun. This equipment can feed hot melts at the rate of 20 pounds (9.1 kg) or more per hour, even though less than a pound of adhesive is maintained in the molten state.

Another type of progressive-feed system is a self-contained applicator gun (portable hot-melt gun). This system requires no insulated hose, because the adhesive is melted in the gun, from adhesive cartridges, pellets (slugs) or coiled cord. In cartridge or pellet adhesives, air pressure moves the fluid adhesive to the nozzle; in the coil-fed system, the coil is mechanically driven, which forces the adhesive through the gun into the workpiece.

Progressive-feed systems benefit from the first-in, first-out principle of application, which minimizes the possibility of adhesive degradation, and permits the use of higher-performance (usually more heat-sensitive) materials. Operating temperatures range from 350-600°F (176-315°C). Another advantage of self-contained applicators is their portability. These guns handle high-performance adhesives with viscosities up to 500,000 cps (5000 Pa.s) of the type that are used for structural applications. A disadvantage of these systems, for some adhesives, (principally polyamides), is that there is no holding period to allow time for moisture flash-off. Material cost is higher than for systems that use the granular form, as indicated under 6.3.6.1. The lower delivery rates (3-4 pounds) (1.4-1.8 kg) per hour of cartridge and coil-type progressive-feed systems may be a limitation, but only for applications requiring very long adhesive beads. These applicators cannot be used for tacky or low-durometer adhesives without special arrangements.

## MIL-HDBK-691B

Hand-held applicator guns of the type described above can be used for applications such as:<sup>(5)</sup>

- o Plastic to wood or metal
- o Metal parts assemblies
- o Fiberglass to wood laminates
- o Foam padding to metal and wood
- o Decorative panels and reliefs to wood or metal
- o Chipboard to wood or metal
- o Doweling and tongue-and-grooving
- o Welt and gimp attachment
- o Moldings to cabinets
- o Potting of electronic parts
- o Replacement for jigs and fixtures

6.4 Joint Assembly Methods. Many methods have been developed for assembling bonded joints; all have certain basic points in common:

- o The surface of the adhesive coating must become liquid at some point in the process to insure good contact.
- o Foreign materials, such as solvents and moisture, must be expelled from the joint to prevent the formation of voids.
- o Pressure must be applied to the joint until the adhesive sets sufficiently to hold the assembly together to prevent later accidental misalignment. While various specific methods of joint assembly may differ in detail, most may be classified as one of four basic methods described below: wet assembly, pressure-sensitive bonding, solvent activation, and heat activation.

6.4.1 Wet assembly. This is probably the commonest of the joint-assembly methods. With porous adherends, it may be used with any type of adhesive that will wet the adherend surface without being heated. With nonporous adherends, however, wet assembly is practicable only when the adhesive used contains no volatile solvents, since otherwise the sealed-in solvent would produce voids. The process consists essentially in aligning the parts, pressing them together while the adhesive coating is still wet from application, and maintaining the pressure until the bond is strong enough to hold the assembly together. To minimize the length of time that this pressure must be maintained, the adhesive coating is usually permitted to partially dry before assembly. The permissible predrying time is known as the "open assembly time" of the adhesive.

6.4.2 Pressure-sensitive and contact bonding. These methods are usable only when the adhesive retains some tack when dry. The joint assembly processes used for each are identical; the only difference is that with pressure-sensitive bonding only one of the adherends is coated, while with contact bonding, both are coated. For both processes, therefore, joint assembly consists of permitting the adhesive coating to dry completely, aligning the parts, and pressing them together to form the bond.



## MIL-HDBK-691B

**6.4.3 Solvent activation.** This is essentially a postponed wet assembly process and, as such, is usually unsuitable for nonporous adherends. In addition, it can be used only with adhesives that can be reactivated by solvents (unlike most two-part adhesives). Solvent activation is primarily desirable when it is convenient to precoat parts that are to be bonded at a later date, or when the adhesive used has an exceptionally low drying rate. Solvent activation consists of permitting the adhesive coating to dry completely, dampening the surface of the coating with a fast-drying solvent, such as methyl ethyl ketone, quickly aligning the parts, and promptly applying pressure until the adhesive sets sufficiently to hold the assembly together. Water is used as the solvent for "gummed" adhesives such as are used in gummed taped labels. Water-activated adhesives are usually made from animal glue or dextrin (see 4.4.8.2.3 and 4.4.8.1.2). Adhesives activated with organic solvents have not received wide acceptance because of the fire and health hazard involved and the inconvenience of activating with solvents. They are used in certain applications where a pressure-sensitive adhesive tape cannot supply the bond strength, solvent- or heat-resistance required.(7)

**6.4.4 Heat activation.** This method may be used only with adherends that can tolerate heat. Since no volatile solvents are employed, it is especially useful with nonporous adherends. However, it is suitable only for adhesives that can be reactivated by heating. Two-part adhesives are therefore excluded. Heat activation consists of permitting the adhesive coating to dry completely, aligning the parts, heating them, applying pressure so that the adhesive flows together, then allowing the adhesive to cool sufficiently to form the bond. Occasionally the parts are heated before their bonding surfaces are mated. Heat-activated adhesives are used on tapes which can be applied with heat and pressure. They can be made from a wide variety of thermoplastic solvents such as waxes, polyethylene, cellulose esters and ethers, nitrocellulose, polyvinyl acetate, polyvinyl chloride and many rubber-resin combinations. Typical tape applications are in fabric-mending tape and paperboard box manufacture (stay-tapes). Heat-activated adhesives provide a very high irreversible bond. No fire or health hazards are involved in their application. One disadvantage is the need for special high-temperature presses to apply this type of adhesive.(7)

## **6.5 Bonding equipment.**

**6.5.1 General.** After the adhesive is applied, the assembly must be mated as quickly as possible to prevent contamination of the adhesive surface. The substrates are held together under pressure and heated, if necessary, until cure is achieved. The equipment required to perform these functions must provide adequate heat and pressure, maintain constant pressure during the entire cure cycle, and distribute pressure uniformly over the bond area. For adhesives curing with simple contact pressure at room temperature, extensive bonding equipment is not necessary.(4)

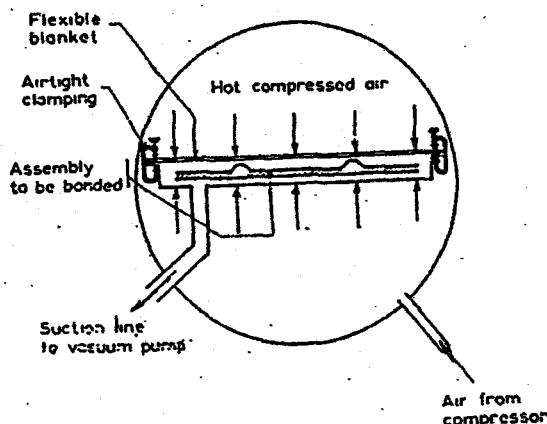
The exact conditions required for curing adhesive joints depend on the properties of the specific adhesive used. The manufacturer of the adhesive will invariably recommend the procedure best suited. In most instances curing is accomplished through the application of heat, or pressure, or both. Depending on the properties of the adhesive, curing pressure may range from contact pressure (1 to 5 psi) (6.9 to 34.5 kPa) to 500 psi (3447 kPa), while

## MIL-HDBK-691B

curing temperatures may range from room temperature up to 662°F (350°C), although the maximum temperature usually used is 350°F (177°C). With ceramic-based adhesives dependent upon a sintering action for adhesion, the processing temperatures can reach 982°F (528°C).<sup>(2)</sup>

**6.5.2 Pressure equipment.** Pressure devices may be designed to maintain constant pressure in the bond during the entire cure cycle. They must compensate for thickness reduction from adhesive flow-out or thermal expansion of assembly parts. Thus, screw-activated devices such as C-clamps and bolted fixtures are not acceptable when constant pressure is important. Spring pressure can often be used to supplement clamps and compensate for thickness variations. Dead-weight loading may be applied in many instances. This loading takes the form of bags of sand or shot, or similar materials. Dead loads may be used only in relatively flat adherends to provide relatively low pressures. The method is impractical for heat-cure conditions.<sup>(4)</sup>

Pneumatic and hydraulic pressures are excellent tools for applying constant pressure. Steam-heated or electrically-heated platen presses with hydraulic rams are often used for adhesive bonding. Some units have multiple platens, thereby permitting the bonding of several assemblies at one time. Large bonded areas, such as on aircraft parts, are usually cured in an autoclave. The parts are mated first, and covered with a rubber blanket to provide uniform pressure distribution. The assembly is then placed in an autoclave which can be pressurized and heated. This method requires heavy capital-equipment investment.<sup>(4)</sup> In autoclave bonding pressure in the assembly is applied as fluid pressure obtained principally from compressed air, and in older installations, from steam. The actual pressure on the parts is exerted by the pressure differential over the autoclave blanket or membrane, which is connected via an airtight seal with the bonding table. The differential can be produced by placing the assembly on a sealed table in a pressure vessel, while the assembly is connected with the atmosphere or a vacuum installation. The principle of adhesive bonding in an autoclave is shown in Figure 29.



**FIGURE 29.** Principle of adhesive bonding in an autoclave. The hot, compressed air supplies both curing temperature and pressure. The flexible blanket is forced against the assembly by the pressure resulting from the compressed air in the autoclave and the vacuum pressure under the blanket.<sup>(8)</sup>

## MIL-MDBK-691B

The autoclave itself can be either cylindrical or the clam-shell (watch-case) type. The latter is limited to relatively small panels. Heat and pressure can be applied by injection of live steam. Subsequent injection of cold air will allow for a relatively rapid cooling. The advantages of live steam are simple operation and short curing cycles. The disadvantages are appreciable in number. Independent variations of temperature and pressure are impossible. The high moisture content in the autoclave leads to several practical problems, of which the entry of moisture into the bonded joints, before the final cure, is an important one. The most commonly used way of pressurizing is application of compressed air from an accumulator next to the autoclave.(8)

Autoclaves can be heated with steam lines; however, high-pressure steam lines present a limiting factor because of the danger of live steam escaping if the pipes break down. For temperatures up to 400°F (204°C), circulating hot air is used to heat the autoclaves. To minimize the possibility of fire, inert gases such as carbon dioxide or nitrogen may be used. Most autoclaves are designed for a maximum pressure of 200 psi (1379 kPa). Cold air is circulated through the autoclave after the cure to drop the temperature as quickly as possible. With hot-air or inert-gas heating, temperature-rise times are about 20°C (36°F) per minute. However, with some adhesives such as nylon-epoxies this is too slow. In order to increase the heat-up rate to 5.4-10.8°F (3-6°C) per minute, electrically-heated platens are used in the autoclave to augment the hot-air heat.(9)

Autoclave bonding generally involves high pressures which can create assembly distortion problems not significant in other bonding equipment. For example, variations in glue-line pressure due to non-conformity of assembly parts is often a problem with autoclave bonding. The concentration of bonding pressure at adherend edges causes thinning of the glue-lines at the edge, which may lead to distortion of the structure.(2)

Vacuum bags are effective not only in applying pressures, but also in withdrawing any volatiles produced in curing. This type of assembly is usually carried out with flat panels, or panels of simple contours, where light pressures suffice to hold mating surfaces in contact. Such an assembly can be laid on a steam-heated or electrically heated, water-cooled table. A rubber blanket or plastic sheet, such as polyvinyl alcohol, is placed over the assembly and sealed to the table with a bead-type seal. The table is provided with a pipe or hose outlet to a vacuum pump. When the vacuum is applied, atmospheric pressure holds the assembly together. The table is then heated and the adhesive is cured. This type of equipment is considerably less cumbersome than a press, but is limited to assemblies that need no more than atmospheric pressure (14.7 psi or 101.3 kPa).(9) Greater pressures may be achieved by using "pressure bars" between the wall of the bag and the enclosed joint. For example, 60 psi (412 kPa) may be achieved on a 1-inch (2.54 cm) joint by using a T-bar with a 1-inch (2.54 cm) face over the joint and a 4-inch (10.16 cm) face against the wall of the bag.

**6.5.3 Heating equipment.** Many structural adhesives require heat as well as pressure. Most often the strongest bonds are achieved by an elevated-temperature cure. With many adhesives, trade-offs between cure time and temperature are permissible. But generally the manufacturer will recommend a certain curing schedule for optimum properties. If, for example, a cure of

## MIL-HDBK-691B

60 min at 300°F (149°C) is recommended, this does not mean that the assembly should be placed in a 300°F (149°C) oven for 20 min. It is the bond line that should be at 300°F (149°C) for 60 min. Total oven time would be 60 min plus whatever time is required to bring the adhesive up to 300°F (149°C). Large parts act as heat sinks and may require substantial time for an adhesive in the bondline to reach the necessary temperature. Bond-line temperatures are best measured by thermocouples placed very close to the adhesive. In some cases it may be desirable to place a thermocouple in the adhesive joint for the first few assemblies being cured.(4)

#### 6.5.3.1 Direct heat curing.

6.5.3.1.1 Oven heating is the most common source of heat for bonded parts, even though it requires long curing cycles because of the heat-sink action of large assemblies. Ovens may be heated with gas, oil, electricity, or infrared units. Good air circulation within the oven is mandatory to prevent nonuniform heating.(4) Recent oven models realize temperatures of  $450 \pm 10^\circ\text{C}$  ( $842 \pm 1.8^\circ\text{F}$ ). (2)

6.5.3.1.2 Liquid baths. Various liquids are used to provide rapid heat transfer by conduction. Water is commonly used, but for higher curing temperatures mineral or silicone oils are required. The silicone oils are useful inert and non-toxic heating media for temperatures up to 572°F (300°C). Direct contact between the bond and the heating medium should be avoided. The method depends on heat conduction through the adherend to cure the adhesive.(2)

6.5.3.1.3 Hot presses or platens. This equipment relies on electrical resistance heaters or steam to provide heat to the platens compressing the bonded assembly. The highest temperatures are obtained with electrical heating elements. These elements can be controlled by relay control, where the curing cycle involves various temperature-time stages. Steam heating is a faster process and it is often advantageous to circulate cooling water through the piping after curing. This technique is particularly effective in bonding assemblies that must be cooled under pressure.(2)

6.5.3.2 Radiation curing. This technique, involving infrared radiation heaters, produces an increase in the heat-transfer rate exceeding that of oven heaters. Infrared lamps provide a useful way of removing solvents from contact adhesives prior to bonding, and are useful in the rapid heating of localized areas of a substrate. The rate of heat transfer is dependent to some extent on the color of the workpiece; the darker the part, the more rapid the heating.(2)

6.5.3.3 Electric resistance heaters. In this method a conductive strip of metal is embedded in the adhesive to act as an internal resistance heater. The heating of the bond is achieved by the passage of electric current through a metallic adherend or conductor within or adjacent to the glue line for non-metallic adherends. Recently, graphite has been used as an internal electric resistance heater for curing structural adhesives. The graphite is available in various physical forms, such as felts, yarns, woven fabrics and tapes. It can be utilized as a heating element over a wide temperature range up to 680°F (360°C) in air and beyond 5072°F (2800°C) in an inert atmosphere. A negative coefficient of resistance with temperature prevents



## NIL-HDBK-691B

current surges during heating. Rapid heating and cooling of the cloth results from the low thermal mass and high emissivity of radiation per unit area of graphite fabric. This internal heat surface method with graphite resistance elements provides bond strength of joints which compare favorably with similar joints prepared by oven curing. Advantages of this method over conventional external heating methods are:(2)

- o Rapid attainment of curing temperature, since the adhesive is heated directly; provision is usually made for heat loss to adherends and the environment.
- o Easy application of heat to localized areas of an assembly.
- o Fabrication of assemblies with high-temperature-curing adhesives without the risk of distortion; uniform heating of fabric eliminates hot spots.
- o Closer control of glue-line temperatures with consequent realization of maximum adhesion performance. The fabric acts as a glue-line spacer and insures uniform thickness of the adhesive layer.
- o Restriction of heating to the glue-line, thereby avoiding unnecessary heating of adherends; reduced expenditure on large assemblies following a lower power consumption.
- o Simplicity of process, obviating the need for ovens or platens; ready on-site repair of damaged assemblies into transportable power equipment.
- o Realization of improvements in design and on-site modifications to structural units, in a room-temperature environment.

The graphite-fabric technique may be used to advantage with hot-melt adhesives to achieve easier processing. In conventional usage assemblies are heated up to the melting point of the hot melt (applied as a film or powder between the adherends) and then cooled. By impregnating graphite fabric with the hot melt and passing a current for a short period to liquify the adhesive, the need to heat up and cool down the entire assembly is eliminated and processing times thereby considerably reduced.(2)

Other methods for electrical heating of bonded assemblies utilize wrap-around electrical heating tapes or resistance elements within the jig supporting the jointed structure. It is generally difficult to attain uniform heating with these methods.(2)

**6.5.3.4 High-frequency dielectric (radio-frequency) heating.** The curing of glue-lines by heat conduction from hot platens is inefficient where thick non-conductive adherends are involved. High-frequency dielectric heating has been developed as a curing means for bonds based on organic polar materials or materials that behave as polar materials through the water they contain, which are poor conductors (unlike metals for which inductive heating is preferred) or insulators (e.g. polystyrene). This process is particularly effective with the thermosetting resins used for woodworking applications, and, to a lesser extent, animal and casein glues. The process is based on the absorption of energy by the adherend material (or dielectric) when it is

## MIL-HDBK-691B

placed in an alternating electric field. At high frequencies, from  $10-15 \times 10^6 \text{ Hz}$ , molecular vibration (resonance) occurs, which leads to heat generation within the material, provided the material has an appropriate loss factor at that frequency. High loss factors favor rapid heating. (NOTE: loss factor = dielectric constant (permittivity)  $\times$  power factor).(2)(10)

**6.5.3.5 Induction heating.** This is similar to dielectric heating. Electric power is used to generate heat in a conducting material. Hence the technique is applicable to metal adherends or to adhesive materials filled with metal powder. If one adherend is conductive and the other non-conductive, either dielectric or induction heating may be applied. The possibility of heat charring the adhesive, where rapid heat curing is involved, should be recognized and care taken to provide adequate control of heat input. Rapid heating, in general, should be avoided.(2)

**6.5.3.6 Low-voltage heating.** This method utilizes the principle of resistance heating in a simple and straightforward manner. The use of low voltage permits a cheap heating element to be used and allows relatively safe handling. For efficient operation the heating element should be in direct contact with the work being glued, so that heat transfer is by conduction. The only apparatus required is a step-down transformer with a capacity of giving low voltages (4, 6, or 12 V with currents of 500-1000 A) which are applied to a metal platen (galvanized or tinned mild steel or stainless steel in most cases). Low-voltage heating is used for a variety of wood-bonding applications (e.g., scarf joint manufacture, boat building hull work). This method is cheap in comparison with dielectric heating, but is not as efficient for gluing wood if the distance to the glue line (adherend thickness) is more than a few millimeters. The temperature of LVH elements may vary between  $167^\circ\text{F}$  ( $75^\circ\text{C}$ ) and  $392^\circ\text{F}$  ( $200^\circ\text{C}$ ).(2)(10)

**6.5.3.7 Ultrasonic activation.** This method of curing the adhesive is based on the transmission of mechanical vibrations from an ultrasonic transducer to the adhesive at the interface between the mating parts. It is used most efficiently where a bead or film adhesive can be incorporated. Energy concentrations of  $700 \text{ ft.lb/sec/m}^2$  ( $1.085 \times 10^6 \text{ W/m}^2/\text{s}$ ) are sufficient to melt, flow and cure many thermoplastic and thermosetting adhesives. The equipment used is the same as that made for ultrasonic welding of thermoplastics.

A wide variety of adhesives can be used with ultrasonic activation, but efficiency may vary with viscoelastic and curing characteristics. Thermoplastics of value include most hot-melt and heat-reactivated adhesives, particularly those with some elastomeric qualities. Thermoset adhesives may be used if a proper balance of activities and cure rate can be accomplished. Epoxy, nitrile and phenolic adhesives have been tested with some success. A fast-curing thermoset (B-stage) gives good results, since the resin can be quickly melted and flowed to the adherends. The curing reaction is initiated by the heat remaining in the adherends. With slow-curing thermosets flow can be accomplished, but continued ultrasonic activation causes a rapid temperature rise. This may initiate chemical or mechanical decomposition of the adhesive before the cross-linking reactions have been completed.

## MIL-HDBK-691B

The adhesive can be used in the form of a film, scrim or coating preapplied to one or both adherends, or a ribbon applied to one of the adherends. Liquid adhesives are generally unsatisfactory. Viscoelastic adhesives are particularly suitable. Ultrasonic activation usually increases the bond strength and reduces curing time where it can be employed as an alternative to conventional thermal or drying processes.(11)

**6.5.4 Adhesive thickness.** It is highly desirable to have a uniformly thin (2-10 mil or 0.05-0.25 mm) adhesive bond line. Starved adhesive joints (where some areas have no adhesive), however, will result in poor bonds. Three basic methods are used to control adhesive (bondline) thickness:(4)

- o Use mechanical shims or stops, which can be removed after the curing operation. Sometimes it is possible to design stops into the joint.
- o Employ a film adhesive that becomes highly viscous during the cure cycle, preventing excessive adhesive flow-out. With supported films, the adhesive carrier itself can act as the "shim". Generally, the cured bondline thickness will be determined by the original thickness of the adhesive film.
- o Use trial and error to determine the correct pressure-adhesive viscosity factors that will yield the desired bond thickness.



## MIL-HDBK-691B

## REFERENCES

- (6-1) Society of Manufacturing Engineers, Chapter 5, "Methods of Bonding", ADHESIVES IN MODERN MANUFACTURING, edited by E.J. Bruno, 1970.
- (6-2) J. Shields, ADHESIVES HANDBOOK, 2nd Edition, Newnes-Butterworth, London, 1976.
- (6-3) Bloomington Dept., American Cyanamid Co., Technical Literature.
- (6-4) E.H. Petri, Chapter 10, "Plastics and Elastomers as Adhesives", edited by C.A. Harper, McGraw-Hill, N.Y., 1975.
- (6-5) D.R. Dreyer, "Hot Melt Adhesives Put it All Together", Machine Design, 47 (1): 88-94 (January 9, 1975).
- (6-6) Nordson Corporation, Amherst, Ohio, Technical Bulletins.
- (6-7) C.W. Benmels, Chapter 47, "Pressure-Sensitive Tapes and Labels", HANDBOOK OF ADHESIVES, 2nd Edition, edited by I. Skeist, Van Nostrand Reinhold, N.Y., 1977.
- (6-8) R.J. Schliekelmann, Chapter 15, "Adhesive-Bonded Metal Structures", ADHESION AND ADHESIVES, 2nd Edition, Vol. 2 - Applications. Elsevier Publishing Co., 1967.
- (6-9) H.J. DeLollis, ADHESIVES, ADHERENDS, ADHESION, Robert E. Kreiger Publishing Co., Huntington, N.Y., 1980.
- (6-10) C.A.A. Rayner, Chapter 13, "Adhesive Bonding Process", ADHESION AND ADHESIVES, edited by R. Houwink and G. Salomon, 2nd edition - Applications. Elsevier Publishing Co., 1967.
- (6-11) R.L. Hauser, "Ultrasonic Bonding Techniques", APPLIED POLYMER SYMPOSIA No. 19, Processing for Adhesives Bonded Structures. Wiley Interscience, 1972.

(WP# ID-7181A/DISK-0544A FOR MFL USE ONLY.)

## MIL-HDBK-691B

## CHAPTER 7. SOLVENT CEMENTING OF PLASTICS (SOLVENT WELDING)

**7.1 Introduction.** Solvent cementing is a process in which thermoplastics are softened by the application of a suitable solvent, or mixture of solvents, and then pressed together to effect a bond. The resin itself, after evaporation of the solvent or solvents, acts as the adhesive. Many thermoplastic resins are more amenable to solvent cementing than to conventional adhesive bonding. This is particularly true of the relatively amorphous plastics such as cellulose, polycarbonate and polystyrene, although several other thermoplastics can also be solvent cemented with excellent results. Study of the individual treatments for each plastic covered will reveal that solvent cementing is a very complex art. In many cases, mixtures of solvent give better results than individual solvents. If evaporative rates are too fast, due to excessive volatility of the solvent, crazing or blushing often results. Often small amounts of the polymer of the substrate to be bonded are dissolved into the solvent to aid in gap filling and to accelerate curing. Solvents for cementing may be brushed, sprayed, dipped or applied with a syringe or equivalent. The parts should be held firmly in place during cure, and caution should be taken in applying the solvent, because excess may run into unwanted areas and result in damage to the appearance of the part.

Solvent cementing is the simplest and most economical method of joining noncrystalline thermoplastics. Solvent-cemented joints are less sensitive to thermal cycling than joints bonded with conventional adhesives, and the former are as resistant to degrading environments as the parent plastic. Bond strengths 85-100% of the parent plastic strength can be obtained. The major disadvantage of solvent cementing is the possibility of stress cracking. When two dissimilar plastics are to be joined, adhesive bonding is generally preferable because of solvent and polymer compatibility problems.(1)

Solvents used to cement plastics should be chosen with approximately the same solubility parameter ( $\delta$ ) as the plastic to be bonded. The solubility parameter is the square root of the cohesive energy density (CED) of the liquid solvent or polymer. CED's of organic chemicals are primarily derived from the heat of vaporization and molar volume of the molecules, and, until the advent of SI units, were expressed as calories per cubic centimeter. A non-polar molecule such as methane evaporates readily and is a gas at ordinary temperatures. It has a low CED, hence a low  $\delta$  ( $\sim 6$ ) ( $\sim 12.3$  in SI units). By contrast, a highly polar, associated (hydrogen-bonded) material of the same size, such as water, requires high heat input to evaporate it, and consequently has a very high  $\delta$  (23) (47 in SI units). Literature sources provide data on  $\delta$ 's of a number of plastics and resins.(2)(3)

The solubility parameters help explain why polystyrene ( $\delta = 9.1$ , or 18.6 in SI units) is soluble in butanone (9.3/19.0), but not acetone (10.0/20.5), while cellulose acetate (10.9/22.3) dissolves in ethyl acetate (9.1/18.6), but not butyl acetate (8.5/17.4). The concept of  $\delta$  also explains the fact that a plastic will sometime dissolve in a mixture of two liquids, neither one of which is itself a solvent. The classic example is the solubility of nitrocellulose (11/22.5) in the nonsolvents ethyl alcohol (12.7/25.9) and ether (7.4/15.1). The mixture of nonsolvents, one with too high a  $\delta$  and the other

## MIL-HDBK-691B

too low, has its  $\delta$  within the right range. Similarly, the solvent acetone (10.0/20.5), mixed with a small proportion of the non-solvent alcohol (12.7/26.0), is a better solvent for cellulose acetate (10.9/22.3) than acetone alone. Isopropyl alcohol (11.5/23.5) and toluene (8.9/18.2) combine to provide a superior solvent for ethyl cellulose (10.3/21.1). (2)(3)

Table XXIX lists the  $\delta$ 's for some of the more common solvents and shows to some extent how those  $\delta$ 's match up with the  $\delta$ 's of various thermoplastic resins. From a study of the exceptions, it appears that the more polar plastics require more polar solvents.

7.2 Types of plastics solvent-cemented. Table XXX lists some of the solvents or solvent mixtures used in solvent cementing plastics. Specific suggestions as to these plastics are as follows:

7.2.1 Cellulosics. These materials are most commonly bonded by solvent cementing. Adhesive bonding is used only to a minor extent. Spin welding or ultrasonic welding are also used on the harder flows of cellulosic plastics. Acetone is one of the most commonly used solvents for cementing cellulose ester plastics. However, it is not ordinarily considered good practice to use acetone or other low-boiling solvents alone because of their rapid evaporation, which is likely to cause moisture blush, a white, frosty appearance of the cemented joint. Low-boiling solvents may also evaporate before they have had time to soften the surfaces and affect adhesion. Blushing is avoided and evaporation loss reduced by adding to the low-boiling solvent one or more solvents of higher boiling point. Glycol ether esters are frequently supplied in proprietary formulations for this purpose. Naturally, addition of the higher-boiling solvent will increase the drying time of the cement. A large number of solvents and solvent mixtures, in addition to those listed in Table XXX, may be used. The manufacturers of the specific cellulosics have available technical bulletins listing these formulations. ASTM D 2560 is a specification for cellulose acetate butyrate in one of three recommended thinners. (5)

Before solvent cementing cellulose acetate articles to other plastics, the effect of plasticizer migration should be determined. The plasticizers present in cellulose acetate are active solvents for cellulose nitrate, many alkyd-type lacquers, and a number of other thermoplastic materials. With the softer flows of cellulose acetate, the plasticizer will, in some cases, migrate to the other material and cause it to craze or become soft and, in extreme cases, tacky. All plasticizers used in cellulose acetate have a strong tendency to cause crazing of polystyrene and polymethylmethacrylate.

Ethyl cellulose is usually bonded with ethyl acetate if only a single solvent is used. Suitable "dopes" for cellulosics may be prepared by adding 10-20% of the cellulosic plastic to the appropriate solvent mixture. Dope-type cements (also called bodied cements), by virtue of their containing plastic in solution, leave, upon drying, a film of plastic that forms the bond between the two surfaces to be joined. These cements, are generally used when an imperfect fit of the parts requires filling.

TABLE XXIX. Solubility parameters ( $\delta$ ) of solvents and resins.(3)

Solvent	Drying Rate	Solubility Parameter		RESIN			
		(Old Units) <sup>1</sup>	(SI Units) <sup>2</sup>	Polystyrene $\delta = 9.51$ ( $\delta = 19.4$ ) <sup>2</sup>	PMMA $\delta = 9.71$ ( $\delta = 19.8$ ) <sup>2</sup>	Vinyl Chloride Copolymers $\delta = 9.71$ ( $\delta = 19.8$ ) <sup>2</sup>	Cellulose Acetate $\delta = 10.91$ ( $\delta = 22.3$ ) <sup>2</sup>
Ether	Fast	7.4	15.1	-	-	-	-
Xylene	Medium	8.8	18.0	S	-	-	-
Toluene	Medium	8.9	18.2	S	-	-	-
Ethyl acetate	Fast	9.1	18.6	S	S	-	S
Methyl ethyl ketone	Fast	9.3	19.0	S	S	S	S
Trichloroethylene	Fast	9.3	19.0	S	S	-	-
Perchloroethylene	Medium	9.4	19.2	S	S	-	-
Methyl acetate	Fast	9.6	19.6	-	-	-	S
Methylene chloride	Fast	9.7	19.8	S	S	-	S
Ethylene chloride	Fast	9.8	20.0	-	S	-	-
Dioxane	Medium	9.8	20.0	-	-	S	-
Cyclohexanone	Medium	9.9	20.2	-	-	S	-
Acetone	Fast	10.0	20.5	-	-	-	-
Isopropyl alcohol	Medium	11.5	23.5	-	-	-	-
Nitromethane	Fast	12.7	26.0	-	-	-	S
Ethyl alcohol	Fast	12.7	26.0	-	-	-	-
Water	Medium	23.4	47.9	-	-	-	-

<sup>1</sup>Old units (hildebrands)-(cal/cc)<sup>1/2</sup>      <sup>2</sup>SI units-(MJ/m<sup>3</sup>)<sup>1/2</sup>      S = Soluble

## MIL-HDBK-691B

**7.2.2 Acrylonitrile-butadiene-styrene (ABS).** ABS is conventionally bonded with dope cement containing 15-25% ABS resin in a blend of ketone solvents, e.g., acetone, methyl ethyl ketone, and methylisobutyl ketone, or tetrahydrofuran or methylene chloride. ASTM D 2235(6), a specification for a solvent cement for ABS pipe fittings, calls for a solution of at least 15% ABS resin in acetone. The maximum permissible is 25% ABS. The minimum average lap shear strength is 800 psi (5.5 MPa). At room temperature it takes several days for the solvent to evaporate, although holding strength is reached in a few hours. Because of the rapid softening action of the solvent, pressure and the amount of solvent applied should be minimal<sup>(1)</sup>.

**7.2.3 Polyvinyl chloride.** PVC plastic pipe and fittings can be solvent cemented using solvent systems containing blends of tetrahydrofuran and cyclohexanone, or solvents such as those listed in Table XXX. ASTM D 2564, a specification for a solvent cement for polyvinyl chloride plastic pipe and fittings, calls for a mixture containing 10% minimum unplasticized PVC in an appropriate solvent system. Blends of tetrahydrofuran:cyclohexanone (80:20) have been found to give good results. Dimethylformamide is also used with these two solvents. The maximum amount of PVC added for bonding is usually 15%. The minimum average lap-shear strength under the specification is 250 psi (1.72 MPa) after a 2-hour curing time, 500 psi (3.45 MPa) after a 16-hour curing time, and 900 psi (6.21 MPa) after a 72-hour curing time.

The following formulation has worked satisfactorily to bond unsupported flexible PVC to itself<sup>(1)</sup>

PVC resin (medium molecular weight	100 pbw
Tetrahydrofuran	100 pbw
Methyl ethyl ketone	200 pbw
Methyl isobutyl ketone	25 pbw
Organic tin stabilizer	1.5 pbw
Diethylphthalate (a plasticizer)	20 pbw

This formulation is also reported to work well on rigid PVC. ASTM D 2564 is a specification calling for a minimum of 10% solids in an unspecified solvent.<sup>(7)</sup> ASTM D 2855 is a standard practice detailing a procedure for making solvent-cemented pipe joints with PVC.<sup>(8)</sup>

**7.2.3.1 PVC-ABS joints.** ASTM D 3138 is a specification for transition joints between PVC and ABS non-pressure piping components. The specification calls for a minimum of 10% unplasticized PVC in a solvent consisting of tetrahydrofuran in combination with cyclohexane or methyl ethyl ketone, or both. The minimum average lap-shear strength is 100 psi (0.7 MPa) after a 2-hour curing time, 400 psi (2.8 MPa) after a 16-hour curing time, or 600 psi (4.1 MPa) after a 72-hour curing time.<sup>(9)</sup>

**7.2.4 Polyamide (nylon).** The recommended adhesives for bonding nylon to nylon are generally solvents, such as aqueous phenol, solutions of resorcinol in alcohol, solutions of calcium chloride in alcohol, (sometimes bonded by the inclusion of small amounts of nylon), and solutions of nylon in formic acid or glacial acetic acid.

MIL-HDBK-691B

TABLE XXX. Representative solvents and solvent mixtures used in solvent cementing plastics (modified after Shields.)<sup>(4)</sup>

Plastics/adherenda	Solvents/solvent mixtures	
Acrylonitrile-butadiene-styrene (ABS)		Acetic acid (glacial)
Cellulose acetate (CA)		Acetone
Cellulose acetate butyrate (CAB)		Acetone: ethyl acetate: CAE (40:40:20)
Cellulose propionate (CP)		Acetone: ethyl lactate (70:10)
Cellulose nitrate (CN)		Acetone: methyl acetate (80:20)
Ethyl cellulose (EC)		Acetone: methyl acetate (70:30)
Polyamide (Nylon) (PA)		Butyl acetate: acetone: methyl acetate (50:30:20)
Polyacrylonitrile (PAN)		Butyl acetate: methyl methacrylate monomer (40:60)
Polycarbonate (PC)		Chloroform
Polystyrene (PS)		Chloroform: carbon tetrachloride (95:5)
Polyvinyl chloride (PVC) and copolymers (PVCA)		Cyclohexanone
Styrene-acrylonitrile (SAN)		Ethyl acetate
Styrene-butadiene (SB)		Ethyl acetate: ethyl alcohol (80:20)
Polyvinyl alcohol (PVA)		Ethylene dichloride
Polybutadiene oxide (PBO) and modified		Ethylene dichloride: methylene dichloride (50:50)
Polyphenylene oxide (PPO) and modified		Glycerine: water (15:85)
Acetal copolymer		Hexafluoroacetone sesquihydrate
Polyethyl ether		Hexafluoroisopropanol
Polyethylene terephthalate (PET)		Methyl acetate
Polyethylene terephthalate (PET)		Methylene chloride
Polyethylene terephthalate (PET)		Methylene chloride: methyl methacrylate monomer (60:40)
Polyethylene terephthalate (PET)		Methylene chloride: methyl methacrylate monomer (50:50)
Polyethylene terephthalate (PET)		Methylene chloride: trichloroethylene (85:15)
Polyethylene terephthalate (PET)		Methyl ethyl ketone (MEK)
Polyethylene terephthalate (PET)		Methyl isobutyl ketone (MIBK)
Polyethylene terephthalate (PET)		Methyl methacrylate monomer
Polyethylene terephthalate (PET)		Tetrachloroethane
Polyethylene terephthalate (PET)		Tetrachloroethylene (perchloroethylene)
Polyethylene terephthalate (PET)		Tetrahydrofuran: cyclohexanone (80:20)
Polyethylene terephthalate (PET)		Toluene
Polyethylene terephthalate (PET)		Toluene: ethyl alcohol (90:10)
Polyethylene terephthalate (PET)		Toluene: methyl ethyl ketone (50:50)
Polyethylene terephthalate (PET)		1,1,2 - Trichloroethane
Polyethylene terephthalate (PET)		Trichloroethylene
Polyethylene terephthalate (PET)		Xylene
Polyethylene terephthalate (PET)		Xylene: methyl isobutyl ketone (25:75)



## MIL-HDBK-691B

Aqueous phenol containing 10-20% (usually 12%) water is the most generally used cement for bonding nylon 6/6 to itself. The cement is prepared by melting phenol and stirring in the necessary water. The bond resulting is water-resistant, flexible, and has strength approaching that of the nylon. After cleaning the surface (acetone is often used), apply the cement with a brush or cotton swab to the mating surface. Wet the surfaces completely, using one or more coats as needed. If the fit is poor or loose at the interface, wait 2-3 minutes to soften the surface. Fasten the parts together with uniform pressure. If the phenol is exposed to moist air, the cement joint may turn white as it dries. Pre-cure 1 hour at 100°F (38°C) or overnight in a dry atmosphere at ambient temperatures to prevent this whitening. Next, immerse the joint in boiling water to remove the excess phenol. Immersion time is dependent on the area of the bonded section (5 min for 1/8 in or 3.2 mm wide surfaces) to as long as 1 hour for 1 inch or 2.54 cm wide surfaces. As a general rule, boil until the odor of phenol disappears.

Where boiling in water is impractical, the joint may be cured by prolonged air exposure at ambient temperatures or oven temperatures of 150°F (66°C). Adequate bond strengths for handling will be reached in 48 hours and maximum strength in 3-4 days. The curing time is dependent on the quantity of phenol used. Note that phenol is corrosive. Care should be exercised to prevent contact with the skin and eyes or inhalation of the vapor. Lap-shear strengths of 2400 psi (16.5 MPa) can be obtained with aqueous phenol.

Nylon 6,6 may also be bonded with a cement made by mixing equal parts by weight of resorcinol and ethanol. Stir in a shaker for 30 min. until all the resorcinol is in solution. Store the amber-colored solution in a brown bottle to avoid further darkening. Reasonably clean parts need no special preparation prior to cementing. Paint the solution generously onto both surfaces with an ordinary flat paint brush. Prevent run-off of the low-viscosity solution by working the brush over the surface 2-3 times. Allow 20-30 seconds for drying to permit the two mating surfaces to soften enough so that they cannot be wiped dry by a close fit. Longer waiting periods (up to 3 min.) will generally improve joint strength. After the softening period, press the mating surfaces together and clamp in place under light pressure for 10-15 min., after which the joint strength should be adequate for light handling. The bond reaches workable strength in about 90 minutes and approaches full strength in 24 hours. Curing can be accelerated by heating in a circulating-air oven at 150°C (66°C) for 30 min. Rubber gloves should be worn while preparing the resorcinol solution. Bond strengths are similar to those obtained with phenol.

A non-corrosive, non-toxic cement with no disagreeable odor may be used in applications involving foods and potable water supplies. The formulation is as follows:

Nylon 6,6	10 pbw
Calcium chloride	22.5 pbw
Ethanol (95% anhydrous)	67.50 pbw

Add the  $\text{CaCl}_2$  to the ethanol and shake for 2 hours, or until the  $\text{CaCl}_2$  is dissolved. Filter through a fritted glass funnel to clarify the cloudy solution. Add the nylon ground to pass a #10 screen to the solution and stir



## MIL-HDBK-691B

overnight, or until the nylon dissolves. The result is a clear, honey-like solvent cement that will last indefinitely. Using a brush or cotton swab, paint the cement onto the surfaces to be joined. After 30 seconds, assemble the parts and hold under contact pressure. After 30 minutes the joint can be handled lightly, but 24 hours are required to attain full strength.

**7.2.5 Polymethylmethacrylate.** Acrylics should be annealed before solvent cementing to minimize the formation of internal stresses that can cause crazing. Acrylic sheet can be annealed by heating in a forced-air oven at a temperature about 10°F (5°C) below the temperature which will cause the part to distort. Thin sections of acrylics are ordinarily heated for 2 hours at 140°F (60°C) for easy flow formulations, while hard flows will require temperatures of 170°F (77°C). Thicker sections will require much longer periods. Solvent cements recommended for acrylics include ethylene dichloride, and methylene chloride: diacetone alcohol (90:10) for medium joint strength, and a blend of methylene chloride:methylmethacrylate monomer (60:40) with 0.2 parts benzoyl peroxide catalyst and sufficient methylmethacrylate resin for body for high joint strength. The latter type of monomer-polymer cement gives the advantage of a fast initial set and machinability within 4 hours of assembly. Monomer-type cements made from methylmethacrylate monomer, acetic acid and ethylene dichloride are also used to give bonds of good weather resistance and generally greater bond strength than straight solvent cements. The monomer and monomer-polymer cements have the disadvantage of rather limited working (pot) lives because of the non-reversible polymerization reaction.

**7.2.6 Polycarbonate.** Solvent cementing is the most common method of bonding polycarbonate. It can be carried out with specific solvents, mixtures of solvents, and mixtures of polycarbonate and solvents. Methylene chloride, when used by itself, has an extremely fast evaporation rate. It is recommended for rapid assembly of two polycarbonate parts. This solvent is recommended for most temperature-climate zones and is especially useful for small areas. A solution of polycarbonate resin in methylene chloride in concentrations of 1-5% has a decreased evaporation rate. This type of bodied cement may be used in extreme cases where perfectly mated bonding areas are impossible to obtain. Ethylene dichloride by itself has a high boiling point and is only recommended for use in extremely hot climates. Mixtures of methylene chloride and ethylene dichloride with a maximum of 40 or 50% of the latter, are used where it is difficult to joint parts fast enough to prevent complete evaporation of the methylene chloride. Parts bonded with methylene chloride are usable at elevated temperatures after approximately 48 hours, depending on the bonding area, without having to resort to the drying schedule required to remove all the higher-boiling ethylene dichloride, or the solvent retained in a methylene chloride-polycarbonate mixture. Bond strengths of 9000-10000 psi (62-69 MPa) have been obtained in this way. It would take up to three weeks of drying to obtain comparable strengths with parts cemented with a 5% solution of polycarbonate in methylene chloride.

**7.2.7 Polystyrene.** Polystyrene may be bonded to itself by solvent cementing, conventional adhesive bonding, ultrasonic welding or electromagnetic bonding, but solvent cementing is the most effective method. In many applications, solvent cementing can be used to bond polystyrene to a variety

of dissimilar materials. A wide variety of solvent types are available, and the selections of the specific solvent to be used is determined by the time required for the joint to set, which in turn, is governed by the evaporation rate of the solvent. Fast evaporation rates result in a quick-setting joint, but usually result in crazing. Slower-drying solvents are often mixed with fast-drying cements for optimum results. A 50:50 mixture of ethyl acetate and toluene bodied with polystyrene is an excellent general-purpose adhesive. Perchloroethylene can be added to reduce flammability. Bond strengths up to 100% of the strength of the parent material are common<sup>(1)</sup>.

Table XXXI is a list of some of the solvents recommended for polystyrene, along with notations on crazing effects and joint strengths. As noted in this table, the fast-drying solvents tend to cause crazing in the relatively low-elongation polystyrene. The less soluble impact grades contain polybutadiene. Solvents attack this additive and cause subsequent stress cracking. Impact-grade polystyrene should be bonded with medium-to-slow-drying solvents. Quantities of polystyrene from 5-15% by weight are often added to provided gap filling properties. A polystyrene cement recommended for transparent joints consists of the following mixture:<sup>(12)</sup>

- 25% of solvent boiling under 100°C (212°F)
- 40% of solvent boiling between 100°C and 200°C (212-392°F)
- 30% of higher-boiling solvent (> 200°C) (> 392°F)
- 5% dissolved polystyrene (raised to 15% for air-tight or watertight seals)

Medium-boiling solvents provide an excellent compromise between the rate of drying and the occurrence of crazing. They cannot be used to bond parts requiring optical clarity for extended periods of time. High-boiling solvents can provide craze-free joints for periods of at least two years, and in many cases much longer, depending on the service conditions. When higher-boiling solvent cements are used, the addition of up to 70% methylene chloride in trichloroethylene speeds up drying without seriously contributing to the tendency to craze.<sup>(13)</sup>

**7.2.8 Acetal homopolymer.** Solvent cements are relatively ineffective with this highly crystalline material, although methylene chloride, methylene chloride mixed with ethylene dichloride, and acetal homopolymer in methylene chloride have been used.

**7.2.9 Acetal copolymer.** This crystalline material is somewhat more amenable to solvent cementing than the homopolymer. The solvent cement recommended is hexafluoroacetone sesquihydrate. This solvent is a severe skin and eye irritant and must be handled with care. Bond strengths for acetal copolymer to itself of 850 psi (5.86 MPa) in shear have been obtained on "as molded" surfaces. Excellent results have also been obtained in bonding the copolymer to nylon and ABS with this solvent, and it is believed likely that good results can be obtained with cellulose.

**7.2.10 Polysulfone.** Solvent cementing of polysulfone can be carried out with chlorinated hydrocarbons. A solution of 5% resin in methylene chloride can be used to bond polysulfone to itself. High pressures (500 psi or 3.5 MPa for 5 min) are required. A minimum amount of solvent should be applied to the

TABLE XXXI. Solvents recommended for cementing polystyrene (10)(11)

Solvent	Boiling Point		Crazing	Tensile Strength of Joint	
	(°F)	(°C)		(psi)	(MPa)
<u>Fast-Drying</u> (20 sec or less)					
Methylene chloride	104	40	Yes	1800	12.4
Ethyl acetate	171	77	Yes	1500	10.3
Methyl ethyl ketone	175	79	Yes	1600	11.0
Ethylene dichloride	182	83	Slight	1800	12.4
Trichloroethylene	187	86	Slight	1800	12.4
<u>Medium-Drying</u>					
Toluene (toluol)	232	111	Slight	1700	11.7
Perchloroethylene					
(Tetrachloroethylene)	249	121	Very slight	1700	11.7
Xylene (Xylol)	271-289	133-143	Very slight	1450	10.0
Diethyl benzene	365	185	Very slight	1400	9.7
<u>Slow-Drying</u>					
Mono-amyl benzene	396	202	Very slight	1300	9.0
Ethyl naphthalene	495	257	Very slight	1300	9.0

mating surfaces. The strength of a properly prepared joint will exceed the strength of the polysulfone parts. Polysulfone can be solvent-cemented to other plastics by using a solvent compatible with both plastics.

7.2.11 Polyphenylene oxide, polystyrene-modified. This material, currently available from General Electric as NORYL, may be solvent cemented to itself or to a dissimilar plastic using a number of commercially available solvents, solvent mixtures, and solvent solutions containing 1-7% of the resin. The addition of 5-20% of the resin will reduce the evaporation rate and fill minor imperfections in the surface of the bonded joints. Table XXXII lists recommended solvents for solvent cementing NORYL. Pressures of 110-600 psi (0.7-4.1 MPa) for 30-60 seconds are required.

When bonding NORYL resins to other plastics, certain solvents have been found to yield the best bond strengths. The recommended solvents for several plastics are listed below:

<u>Plastics</u>	<u>Solvent</u>
NORYL to ABS	Tetrahydrofuran
NORYL to acrylic	Tetrahydrofuran
NORYL to PVC	Tetrahydrofuran
NORYL to MYLAR polyester film	Ethylene dichloride
NORYL to LEXAN polycarbonate	Methylene dichloride
NORYL to polystyrene	Ethylene dichloride

## MIL-HDBK-691B

TABLE XXXII. Solvent cements recommended by GE for cementing NORYL modified polyphenylene oxide resins.<sup>(14)</sup>

Solvent	Remarks	Tensile Shear Strength		Evaporation Rate*
		(psi)	(MPa)	
Trichloroethylene	Very slow evaporation rate; generally used to control evaporation rate of other solvents.	2800	19.3	84
Ethylene dichloride	Slow evaporation rate; best suited for lengthy assembly times or use in high ambient temperature	3600	24.8	79
Chloroform	Fast evaporation rate; used for rapid assembly	2900	20.0	118
Methylene chloride	Very fast evaporation rate. Generally used in mixture with trichloroethylene	2800	19.3	147
Methylene chloride/ trichloroethylene (85%/15%)	Here the excellent bond strength of the methylene chloride prevails, but the rapid evaporation rate is slowed down by the TCE. Carbon tetrachloride is sometimes substituted for the TCE.	2500	17.2	133
Toluene	- - - - -	2950	20.3	Slowest

\* Carbon tetrachloride = 100

7.2.12 Structural foams (thermoplastic). Engineering structural foams may be solvent cemented to themselves or to other thermoplastics using a number of commercially available solvents. Solvent bonding is faster than adhesive bonding, and therefore may prove more economical in production. Solvent bonding is not recommended for thermoplastic polyester resins, such as du Pont's VALOX, since these resins have such excellent solvent resistance. Solvents recommended for NORYL modified polyphenylene oxide resin foams are ethylene dichloride, THF, and trichloroethylene. For polycarbonate, use acetone or methylene chloride. The mating ends of the parts should be dipped in a solvent tray to saturate the local joint area. Apply moderate pressure (10-60 psi) (0.07-0.4 MPa) for at least one minute after positioning. The strength of solvent-bonded joints is at least as strong in tensile stress as the foamed material.<sup>(15)</sup>

**7.3 Methods of application.** Before attempting to solvent cement plastics it is wise to carefully study the plastic manufacturer's technical bulletins, where detailed information is usually given on exactly how to achieve optimum joints. Space is not available in this handbook for more than a few comments. The solvent is usually applied by one of the following devices or techniques:

**7.3.1 Dip method.** In this method, one of the two parts to be joined is dipped into the cement just enough so that the solvent will act on the desired area for the maximum time. After dipping, the parts should be assembled immediately and held under light pressure for a short time. Bonding takes place by the formation of a "cushion" of solvent-swollen plastic surface. A period of about 15-30 seconds should be allowed before the pressure is increased, to avoid squeezing out this cushioned material from the dipped plastic surface before the solvent can act on the mating dry surface.

Specially-designed dipping fixtures, clamps and conveyors should be considered for each job. The area of attack of solvent on the piece can be controlled by laying a roll of glass rods in the cementing tray. The piece to be cemented is then rested on these rods. The level of the cement should be kept equal to the diameter of the rods. The areas of contact of solvent and cement can also be controlled by lining the bottom of the cement tray with a felt pad. Pieces to be cemented are then placed on the felt pad, which is kept thoroughly wet with the liquid solvent cement.(11)

**7.3.2 Capillary method.** For some applications where the surfaces to be cemented fit very closely, the cement can be introduced by brush, eye dropper, or hypodermic needle into the edge of the joint by capillary action. In other cases, it is possible to insert fine wire into the joint when the parts are assembled in the jig. The cement is then introduced into the joint. After the cement has reached all parts of the joint, the wires are removed. This procedure is useful in removing air bubbles and in filling voids in joints made in other ways.

Soak techniques are available in which pieces are immersed in the solvent, softened, removed and quickly brought together. Areas adjoining the joint area should be masked to prevent them from being etched. Cellophane tape is commonly used for this purpose. After the soak, parts should be assembled rapidly.

No matter which technique is selected, surfaces to be joined should be clean (use of a cleaning solvent, such as acetone, is often recommended), but not below 65°F (18°C), and fit together as flat surfaces. If the parts do not fit well, the time for a part to soften after application of cement must be increased to aid in obtaining satisfactory fit. Once the parts are mated, they must be fastened together by spring clamps, C-clamps, or toggle clamps so that uniform pressure is exerted on the bonded areas. Pressure should be low so that the part will not be flexed or stressed. Pressures of 100-200 psi (0.7-1.4 MPa) are often recommended. The pressure should be sufficient to squeeze out all air bubbles from the joint and to assure good contact of the mating surfaces. When the clamps are removed, an elevated-temperature cure is often called for, e.g. warm acrylic to 120°F (49°C), heat ABS to 130-150°F (54-66°C), and polycarbonate up to 175°F (79°C).(11)

## MIL-HDBK-691B

**7.3.3 Precautions.** Cementing trays should be made of materials that are inert to the cementing solvents. Care should be taken to avoid excessive contact of the hands or skin with cement solvents, since most of them will remove natural oils from the skin, and may cause chapping or even mild dermatitis after too frequent exposure. Where glacial acetic acid is used (as with nylon), contact should be carefully avoided because of its corrosive nature. Working areas must be well-ventilated. Breathing of concentrated vapors of ethylene dichloride, methylene chloride, glacial acetic acid, etc., may cause toxic effects. Cement tanks, trays, and storage containers should be equipped with light covers to reduce evaporation when not in use.

Since solvent vapors as well as solvents themselves can cause crazing, assemblies within closed spaces should be adequately ventilated. An air line can be inserted to sweep its vapors out, or vacuum can be used, along with a tube to bleed fresh air to the side opposite the vacuum takeoff. Where it is impossible to remove solvent vapors from the joint itself, after the bond has been made, the joint should be designed so that solvent vapors can be excluded from the adjacent area.(11)

ASTM F402 is a recommended practice suggesting precautions to take in handling solvent cements used for joining thermoplastic pipe and fittings.(16)



## MIL-HDBK-691B

## REFERENCES

- (7-1) E.H. Petrie, Chapter 10, "Plastics and Elastomers as Adhesives", HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A Harper, McGraw-Hill, N.Y., N.Y., 1975.
- (7-2) J. Miron and I. Skeist, Chapter 41, "Bonding Plastics", HANDBOOK OF ADHESIVES, 2nd Edition, edited by I. Skeist, Van Nostrand-Reinhold, N.Y., 1977.
- (7-3) I. Skeist, "Choosing Adhesives for Plastics", Modern Plastics, 34 (5): 121-130, 236 (May 1956).
- (7-4) J. Shields, ADHESIVES HANDBOOK, 2nd Edition, Newnes-Butterworth, London, 1976.
- (7-5) American Society for Testing and Materials (ASTM), ASTM D 2560-80, Standard Specification for SOLVENT CEMENTS FOR CELLULOSE ACETATE BUTYRATE (CAB) PLASTIC PIPE, TUBING, AND FITTINGS, Vol. 08.04, Annual Book of ASTM Standards.
- (7-6) American Society for Testing and Materials (ASTM), ASTM D 2235-81, Standard Specification SOLVENT CEMENTING for ACRYLONITRILE-BUTADIENE-STYRENE (ABS) PLASTIC PIPE AND FITTINGS, Vol. 08.04, Annual Book of ASTM Standards.
- (7-7) American Society for Testing and Materials (ASTM), ASTM D 3564-80, Standard Specification for SOLVENT CEMENTS FOR POLY(VINYL CHLORIDE) (PVC) PLASTIC PIPE AND FITTINGS, Vol. 08.04, 1983 Annual Book of ASTM Standards.
- (7-8) American Society for Testing and Materials (ASTM), ASTM D 2855-81, Standard Recommended Practice for MAKING SOLVENT CEMENTED JOINTS WITH POLY(VINYL CHLORIDE) (PVC) PIPE AND FITTINGS, Vol. 08.04, Annual Book of ASTM Standards.
- (7-9) American Society for Testing and Materials (ASTM), ASTM D 3138-83, Standard Specification for SOLVENT CEMENTS FOR TRANSITION JOINTS BETWEEN ACRYLONITRILE-BUTADIENE-STYRENE (ABS) AND POLY(VINYL CHLORIDE) (PVC) NON-PRESSURE PIPING COMPONENTS, Vol. 08.04, Annual Book of ASTM Standards.
- (7-10) Monsanto Company, St. Louis, MO, "Cementing Monsanto LUSTREX Styrene", Product Information Bulletin No. 1001A, January 2, 1968.
- (7-11) Chapter 27, "Joining and Assembling Plastics", PLASTICS ENGINEERING HANDBOOK OF THE SPI, 4th Edition, edited by J. Frados, Van Nostrand Reinhold, N.Y., N.Y., 1976.
- (7-12) J.L. Been, "Bonding", article, pp. 503-538 "Adhesion and Bonding", ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY, Vol. 1, Wiley-Interscience, 1964.
- (7-13) H.W. Riley, "Joining and Fastening Plastics", Materials in Design Engineering, 47 (1):129-144 (January 1958) (Manual No. 145).



MIL-HDBK-691B

- (7-14) General Electric Company, NORYL Design Guide CDX-83.
- (7-15) General Electric Company, Pittsfield, MA, "The Handbook of Engineering Structural Foam", SFR - 3B (6/81) and "Engineering Structural Foams - Design Guide", SFR - 28 (1983).
- (7-16) American Society for Testing and Materials (ASTM), Standard Recommended Practice for SAFE HANDLING OF SOLVENT CEMENTS USED FOR JOINING THERMOPLASTIC PIPE AND FITTINGS, Vol. 08.04, Annual Book of ASTM Standards.

## MIL-HDBK-691B

## CHAPTER 8. RECOMMENDED ADHESIVES FOR SPECIFIC ADHERENDS

**8.1 General Discussion.** Section 5.3.5 above outlines recommended surface preparations for all types of adherends, and Section 7.2 provides specific recommendations for solvent cementing of plastics. In this chapter consideration is given to the type of adhesive recommended. Tables are frequently published listing large numbers of adhesive types recommended for specific adherends. Such tables can often lead to less than optimum results in providing information needed to assure durable bonds because the user tends to forget that some combinations of adhesives and adherends are superior to others. The emphasis in the following sections is on giving information on a few of the adhesive types known to give strong lasting bonds for particular adherends.

**8.2 Metals.**

**8.2.1 Aluminum and alloys (1), (2), (3).** The best adhesives for aluminum are modified epoxies and phenolics. Vinyl plastisols have been used recently in automotive applications in bonding the outer panels of car hoods. These adhesives, the so-called "Hershey Drop" or anti-flutter adhesives, are used because of their sound-insulating properties. Extruded onto the underside of the hood in a predetermined pattern, the plastisol will undergo fusion and hardening at the elevated temperature of the paint bake cycle. These adhesives are used because of their ability to absorb and strike through light films of oil to form a firm bond with the metal. Commercially available epoxies are also capable of providing durable joints on oil-contaminated surfaces. Vinyl plastisols give initial shear strengths in the range of 600-800 psi (4.1-5.5 MPa), compared to an elastomeric anti-flutter adhesive which gives about 350 psi (2.4 MPa). Flexible epoxies are now beginning to be used to replace the vinyl plastisols for these applications.

TABLE XXXIII lists adhesive types found to give satisfactory results for a number of adherend types and conditions. This table is from a booklet prepared by the Reynolds Metal Company. The original source provides actual commercial adhesives and their manufacturers. Shear values for the adhesives in this table range from about 400-7200 psi (2.8-5.0 MPa), compared to 7000-4500 psi (48-310 MPa) for aluminum itself. It is only at the low end of the aluminum and the high end of the adhesive range that the shear values are comparable.

**8.2.2 Beryllium.** Adhesives used with beryllium include the following:

- Epoxy-phenolic (350°F or 177°C cure - 50 psi or 345 kPa)
- Nitrile-phenolic (350°F or 177°C cure - 50 psi or 345 kPa)
- Epoxy (RT cure, contact pressure)
- Epoxy-nylon
- Polyimide (PI)
- Polybenzamidazole (PBI)
- Epoxy-nitrile

## NIL-HDBK-691B

TABLE XXXIII. Selection Guide for General Aluminum Bonding Applications  
(modified after Ref. 1).

Material	Type and Form	Service Temperature	
		(°F)	(°C)
Aluminum to itself (Cryogenic or very low temp. appl.)	Glass-Supported modif. phenolic	-423 to +500	-253 to +260
	Modified epoxy supported film	-423 to +500	-253 to +260
	Epoxy-phenolic glass cloth	-423 to +700	-253 to +371
Aluminum to itself (low-temp. appl. below 70°F or 21°C)	2-part epoxy paste	-60 to +200	-51 to 93
Aluminum to itself (Electrical conductive appl.)	2-part epoxy silver paste	-50 to +150	-46 to +66
	1-part modif. epoxy paste	to +350	to +177
	1-part epoxy silver paste	to +250	to +121
Aluminum to itself (general-purpose)	2-part epoxy paste	-67 to +200	-55 to 93
	1-part epoxy paste	-40 to +250	-40 to 121
Aluminum to itself (high-temp. appl.)	2-part epoxy system	to +600	to +316
	Part A paste		
	Part B powder		
	epoxy-phenolic glass cloth	to +700	to +371
	2-part epoxy system		
	Part A liquid	long-time service	
	Part B powder	to +600 °F	to +316
	1-part epoxy paste	to +450	to +232
Aluminum to itself (fast cure)	2-part epoxy	-67 to +150	-55 to +66
	2-part epoxy syrup	to +120	to +49
	2-part epoxy liquid	to +120	to +49
Aluminum to itself (moisture present on Al)	2-part epoxy paste	-50 to +180	-46 to +82
Aluminum to itself (oily surface)	2-part epoxy	-50 to +200	-46 to +93
Aluminum to concrete	2-part epoxy paste	-20 to +180	-20 to +82
Aluminum to flexible fiberglass	1-part neoprene phenolic	-30 to +300	-34 to +149
Aluminum to rigid fiberglass	2-part modified epoxy paste	-67 to +180	-55 to +82
	1-part Al-filled modified epoxy paste	-40 to +250	-40 to +121
Aluminum to foams (polystyrene, urethane, etc.)	2-part epoxy light paste	-40 to +200	-40 to +93
	1-part reclaimed rubber (water-dispersed) paste	-35 to +300	-37 to +149

## MIL-HDBK-691B

TABLE XXXIII. Selection Guide for General Aluminum Bonding Applications (Continued).

Material	Type and Form	Service Temperature	
		(°F)	(°C)
Aluminum to glass	2-part epoxy thin syrup	-67 to +200	-55 to 93
	silicone rubber paste	-80 to +350	-62 to 177
	2-part modified epoxy/- amine acid paste	-67 to +200	-55 to +93
Aluminum to nickel steel	2-part epoxy paste	to +180	to +82
Aluminum to MYLAR (polyester film)	1-part synthetic rubber resin	-50 to + 250	-46 to +121
Aluminum to nylon	2-part epoxy paste	to +180	to +82
	cyanoacrylate 1-part liquid	-65 to +175	-54
Aluminum to PVC	1-part synthetic rubber resin	-50 to +250	-58 to +121
	2-part epoxy paste	-67 to +200	-55 to +93
Aluminum to TEFLON	1 & 2-part epoxy pastes	to +500	to +260
Aluminum to rubber (general)	epoxies (for high strength)		
	cyanoacrylate 1-part liquid	65 to +175	-54 to +79
Aluminum to rubber (BUNA N-nitrile), HYPALON, natural, filled gum stock, GR-S, KEL-F, neoprene, red sheet, sponge, pure gum.)	1-part synthetic rubber liquid	-30 to +230	-34 to +110
Aluminum to silicone rubber	1-part silicone rubber paste	-85 to +450	-65 to +232
Aluminum to wood	2-part epoxy paste	-67 to +180	-55 to 82
	1-part epoxy paste	-67 to +350	-55 to +.77

## MIL-HDBK-691B

Since beryllium retains significant strength at temperatures up to 1000°F (538°C) the high-temperature application area is important for this somewhat exotic metal. As indicated above in 4.2.1.3.1, the polybenzamidazoles are relatively stable in air at temperatures up to 550°F (288°C) for short periods of time. Polyimides can be used at somewhat lower temperatures for longer periods. The more conventional adhesives listed above are much more temperature-sensitive than PBI and PI and offer considerably higher strengths at room temperatures, and equivalent, or even slightly higher strengths at 250°F (121°C) (4) (5).

8.2.3 Brass. Adhesives used with copper and copper alloys (see 8.2.6) can be used with brass. As indicated above, the surface preparations of brass and copper may or may not be different.

8.2.4 Bronze. Adhesives used with copper and copper alloys (see 8.2.6) can be used with bronze.

8.2.5 Cadmium. No particular adhesive types have been recommended for cadmium, which is usually found as a plating (see 8.2.15).

8.2.6 Copper and alloys. Copper, because of its unusual oxide characteristics, is normally a difficult metal to bond. A project, sponsored by the International Copper Research Association, (INCRA), (1971), showed the unique ability of properly formulated dicy-cured epoxy coatings and adhesives to provide bond-strength retention to copper after extended exposure to moisture and stress. Long-term boiling water, peel and thermal-shock tests were run by the investigators on steel, aluminum and copper samples, using a variety of successful commercial coatings and adhesives, as well as formulations with and without special additives. Most of the compounds studied showed no failure in tests up to six months duration on aluminum or steel, but failed rapidly, frequently in a few days, on copper. Amine- and anhydride-cured liquid epoxy adhesives, as well as several vinyl phenolic film adhesives, were among the many formulations showing most rapid deterioration on copper (6).

The INCRA report (6) showed that only those heat-cured epoxies which contained dicyandiamide (DICY) or melamine provided long-term bond durability, performing about as well on copper as on aluminum or steel. DICY was shown to be beneficial, either when used as the sole curing agent with epoxy resins, or when mixed with other curing agents, or when used to pretreat the copper surface before binding. Even when simply added to coatings, (e.g., phenolic-cured epoxies which cure by a different mechanism), DICY and a melamine compound both increased time to adhesive failure significantly on either bare or alkaline permanganate-treated copper.

Surface treating the copper, using either the Black Oxide Coating Process or the Alkaline Permanganate Process (see 5.3.5.1.7 for both), was found to extend the useful lifetime with several adhesives and coatings relative to bare, acid-etched copper. Only the DICY or melamine systems, however, showed useful bond retention to acid-etched copper (7) (8).

## MIL-HDBK-691B

Besides epoxies, other adhesive types used successfully with copper include polyurethane, silicone, nylon-epoxy, nitrile-phenolic, neoprene-phenolic, acrylic, cyanoacrylate, anaerobics, and partially-hydrogenated polybutadiene (for bonding copper to polyethylene).

**8.2.7 Magnesium and Alloys.** In order to obtain optimum bond strength with magnesium alloys, equal consideration must be given to the specific alloy, the method of surface preparation, and to the adhesive. Ordinarily, epoxy adhesives are used for bonding magnesium alloys, but other adhesive types used include epoxy/phenolics, polyurethanes, silicones, and cyanoacrylates.

A problem with epoxy adhesives is that the chemical nature of the epoxy formulation appears to have a sensitivity to the surface chemistry condition of a magnesium alloy after a surface preparation has been used on the alloy. Jackson (9) has carried out a comprehensive study showing the interaction between alloys (AZ31B-M24, ZK60A-T5, ZK60A-T6, HM21A-T8, HK31A-M24, and LA141A-O), adhesives (epoxy, rubber-based, polyamide-epoxy, phenolic-epoxy, and novalac-epoxy), and surface preparation method (solvent degrease, RT-chromic acid, hot chromic acid, alkaline, Dow 17, and Ebonol C). The results, reported as shear strength, are variable and it is difficult to draw any general conclusions. The Jackson paper should be consulted before any decisions are made as to which combination of adhesive, surface preparation and alloy should be used.

**8.2.8 Nickel and Alloys.** Nickel is a metal usually used in alloy form. Relatively little work has been carried out on adhesive bonding of nickel-base alloys because most of these alloys are used at temperatures above the present maximum service temperatures of organic adhesives, or under corrosive conditions. Inorganic adhesives of sufficient ductility and low-enough maturing temperatures have not been developed to compete effectively with brazing and welding for joining high-temperature structures. (10)

Epoxy adhesives are ordinarily used to bond nickel and its alloys. In all likelihood PBI and PI adhesives can also be used for high-temperature applications involving nickel (10). Other adhesives used include epoxy-nylons, polyamides, phenolic-nitriles, phenolic-polyvinyl butyrals, phenolic-polyvinyl formals, polyisocyanates, melamines, and neoprenes. (11)

**8.2.9 Steel (Mild) (Carbon) (Iron).** As indicated in Chapter 5, steel alloys are important adherends in Army bonding applications. Adhesive types used successfully include the following:

- Nitrile-phenolic - high moderate-temperature strength, but drops off rapidly at higher temperatures
- Polybenzimidazole (PBI) - high strength over a wide temperature range
- Epoxy-phenolic
- Polyimide
- Acrylic (two-part RT-curing)
- Epoxies (tape, 250°F (121°C) cure, 1 hr at 50 psi pressure)
- (paste, 250°F (121°C) cure, 1 hr at contact pressure)
- (two-part bisphenol-A system/polyamide curing agent, RT-cure at contact pressure)



## MIL-HDBK-691B

The above types are recommended for high-strength bonds. Other adhesive types for less stringent requirements include thermoplastics and rubber-base materials. (12)

A recent Army study (13) evaluated four surface-preparation methods for 4340 steel, an ultra-high-strength steel commonly used for munitions, using two different adhesives, a one-part 250°F (120°C) curing epoxy paste (EC-2214) and a two-part room-temperature-curing acrylic (TAME 200). Results for the best two surface-preparation methods are given in Table XXXIV. It was found that there was little difference (6%) in the strengths of the joints made with EC 2214, regardless of surface preparation. Results with the acrylic, TAME 200, indicated very large differences (up to 45%) in strength among bonds made. Both adhesive types showed excellent elevated-temperature properties. The EC 2214 was essentially unchanged at 140°F (60°C) but the TAME 200 was considerably stronger at the higher temperature than it was at room temperature. Nevertheless, the epoxy still had a higher strength at 140°F (60°C) than the acrylic.

**8.2.10 Steel, stainless.** In general, the adhesives used for mild steel can be used for bonding stainless steel.

**8.2.11 Tin.** No particular adhesive type is recommended for tin, although epoxies are probably the most useful.

**8.2.12 Titanium and alloys (14) (15).** Adhesive systems used for titanium should normally be capable of withstanding high-temperatures, since titanium is used primarily because of its high-temperature resistance. Adhesives used include: epoxy, nitrile-epoxy, nitrile-phenolic, polyimide, and epoxy-phenolic. Polyimide adhesives provide strengths of 1600-1800 psi (11.0-12.4 MPa) at 600°F (316°C). Epoxy-phenolics (novolacs) and nitrile epoxies are normally tested at 350°F (177°C).

High-peel-strength adhesives such as nitrile-phenolics should be considered for use in metal-to-metal bonds at the sacrifice of lap-shear strength at temperatures above 350°F (177°C), provided the design will permit a reduction in shear strength.

Nitrile-epoxies are recommended for skin-to-core applications because less volatiles are released during cure than with epoxy-phenolics. The volatiles released during cure create internal pressure, which can result in core-node bond and skin-to-core bond failures.

Polyimide adhesives are not used for skin-to-core bonds because the temperature environment is not high enough to make them attractive and because of the inherent problems caused by high volatile release during cure.

**8.2.13 Tungsten and alloys.** Little information has been found on recommended adhesives for tungsten, although nitrile rubber and epoxies have been used (11).

**8.2.14 Zinc and alloys.** Adhesives used include epoxies, silicones, cyanoacrylates, nitrile-phenolic, and rubber-based adhesives (see 8.2.15).

**8.2.15 Plated metals.** A Boeing-Vertol paper (16) reports an extensive study on cadmium- and zinc-plated steel surfaces, using nitrile-phenolic adhesives (16).

NIL-HDBK-691B

TABLE XXIV. Lap Shear Strength and Durability of Acrylic and Epoxy Adhesives Bonded to 4340 Steel, Using Two Different Surface Preparations. (1)

Surface Preparation	Control Shear Strength 740P (230C) 140P (60C)	Strength after hot-water soak @ 1400P (60C) <sup>b</sup> (100 hrs)	Strength after hot-water soak @ 1400P (60C) <sup>b</sup> (500 hrs)	Time to Failure @ 1400P (60C)/95% RH and 4.8 MPa Stress
	(psi) (MPa)	(psi) (MPa)	(psi) (MPa)	(hours)
	TABLE 2004 Two-Part Room-Temperature-Curing Acrylic Adhesive			
Phosphoric Acid/Alcohol	2570 17.72 3552 23.11 3098 21.36 32.4 2005 13.82 59.8 2118 16.39 70.9			2448
Diphosphate	1802 12.43 2030 14.00 2400 16.55 116.2 1613 11.12 79.4 1690 11.65 83.2			2198
	EC 2214 <sup>d</sup> One-Part 25C0P (120C) - Curing Epoxy Paste Adhesive			
Phosphoric Acid/Alcohol	5348 36.87 5338 36.80 4038 27.84 75.7 4005 24.17 65.7 3048 19.74 53.6			217
Diphosphate	5338 37.63 5525 38.09 3173 27.04 71.0 3970 27.37 71.9 3148 19.70 51.7			148

<sup>a</sup> B. F. Goodrich Company, Akron, Ohio  
<sup>b</sup> After oven drying at 1400P (60C) for 8 hrs., then conditioning at 740P (230C)/50% RH for 3 weeks; tested at 740P (230C).  
<sup>c</sup> Retention of 1400P (60C) control strength  
<sup>d</sup> 3M Company, St. Paul, MN.

## MIL-HDBK-691B

**8.3 Plastics.****8.3.1 Thermoplastics.**

**8.3.1.1 Acetal copolymer (CELCOM) (17).** Thermal welding is ordinarily used for bonding to obtain optimum bond strengths, but adhesives may have to be used under certain conditions. Three types of adhesives are used in bonding acetal copolymer: solvent, structural and non-structural. Hexafluoroacetone sesquihydrate is used in solvent cementing (see 7.2.9). Most structural adhesives are based on thermoset resins and require the addition of a catalyst and/or heat to cure. This type adhesive is normally used in applications which require maximum bond strength and minimum creep of the adhesive joint under sustained loading. Many structural adhesives can be used continuously at temperatures up to 350°F (177°C), which is higher than the recommended continuous-use temperature of 220°F (104°C) of the copolymer.

Structural adhesive types recommended are:

Epoxy (to 160°F or 71°C)

Polyester with isocyanate curing agent (to 200°F or 93°C)

Polyvinyl butyral (modified with a thermosetting phenolic)(to 250°F or 121°C)

Cyanoacrylate (to 181°F or 82°C)

Structural adhesives for bonding acetal copolymer to itself have yielded shear strengths of 600 - 800 psi (4.14 - 5.52 MPa). By subjecting adherend samples to cleavage stress (peel), a decrease of at least 25% in bond strength can be expected.

Non-structural adhesives are usually one-component, room-temperature-curing systems based either on thermoplastic resins or elastomeric materials dispersed in solvents. They are normally used in applications which will not have to sustain heavy and/or continuous loading and will not be exposed to temperatures above 180°F (82°C). Neoprene rubber adhesives have been used to provide shear strengths of 325 psi (2.24 MPa) to sanded surfaces and 300 psi (2.1 MPa) to unsanded surfaces. As in structural adhesives, a reduction in strength can be expected under peeling load.

**8.3.1.2 Acetal homopolymer (DELIN) (18).** Adhesives used to bond acetal homopolymer to itself and to other materials such as aluminum, steel, natural rubber, neoprene rubber, and Buna rubber include polyester and isocyanate curing agent, rubber-base adhesives, phenolics, epoxies, modified epoxies, and vinyls. Solvent cementing cannot be used for this type plastic unless the surfaces are specially roughened, because of the high solvent resistance of the material.

Other adhesive types sometimes used are:

Resorcinol

Vinyl phenolics

Ethylene vinyl acetate

Cyanoacrylates

Polyurethane

## MIL-HDBK-691B

**8.3.1.3 Acrylonitrile-Butadiene-Styrene (ABS).** ABS is usually bonded by bodied solvent cements. Adhesives recommended for ABS include epoxies, urethanes, thermosetting acrylics, elastomerics, vinyls, nitrile-phenolics and cyanoacrylates.(19)

**8.3.1.4 Cellulosics.** These plastics are usually solvent cemented. Polyurethane, epoxy and cyanoacrylate adhesives are commonly used to bond cellulosics. Cellulosic materials may contain plasticizers that are not compatible with the adhesive. The extent of plasticizer migration should be determined before an adhesive is recommended.(19)

Recommendations for conventional adhesives for specific cellulosic types are as follows:

Cellulose acetate - polyurethane, epoxy, synthetic resins, thermoplastic, and resorcinol-formaldehyde

Cellulose acetate butyrate (CAB) - natural rubber, polyisobutylene rubber, nitrile rubber, neoprene rubber, polyvinyl acetate, vinyl acetate/acrylic acid, vinyl chloride/vinyl acetate, polyacrylate, cyanoacrylate, polyamide, polyester & isocyanate, nitrile-phenolic.

Cellulose nitrate - epoxy, synthetic thermoplastic, nitrile rubber, polyurethane, and cyanoacrylate.

Cellulose propionate - same as CAB

Ethyl cellulose - epoxy, nitrile-phenolic, neoprene, synthetic rubber with the setting resin, synthetic thermoplastic resin, and resorcinol formaldehyde.

**8.3.1.5 Ethylene Tetrafluoroethylene copolymer (ETFE) (TEFZEL).** This material is usually thermally welded or spin-welded. The manufacturer (duPont) claims that a new treated film type has been developed that is receptive to many adhesives, although no information is given as to the types of adhesives recommended.(20)

**8.3.1.6 Ethylene-vinyl acetate (EVA).** No particular adhesives are recommended.

**8.3.1.7 Fluorinated ethylene propylene (FEP).** Epoxies and polyurethanes give good bond strengths to treated fluorocarbon surfaces.(19)

**8.3.1.8 Ionomer (Surlyn).** Epoxies or polyurethanes are recommended.(21)

**8.3.1.9 Nylon (Polyamide).** The best adhesives for bonding nylon to nylon are generally solvents, as discussed above in 7.2.4. Various commercial adhesives, especially those based on phenol-formaldehyde and epoxy resins are sometimes used for bonding nylon to nylon, although they are usually considered inferior to the solvent-type of bonding agents because they result in a brittle joint.

## MIL-HDBK-691B

Adhesives recommended by duPont for their nylons (mostly Nylon 6,6) are:

Nylon to Metal

Phenolweld #7 (Hardman, Inc.)

Nylon to Wood, Metal and Leather

Resiweld 7004 (M. B. Fuller Co.) (epoxy)

Nylon to Metal and Vinyl Stock

Resiweld 7006 (M. B. Fuller Co.) (epoxy)

General

APCO 5363 (Applied Plastics Co.)

Nylon-phenolic, nitrile-phenolic, nitriles, neoprenes, urethanes, epoxy rubber and epoxy are recommended for bonding nylon to metal and other materials (22).

8.3.1.10 Perfluoroalkoxy resins (PFA). Epoxies and polyurethanes give good bond strengths to treated fluorocarbon surfaces.(19)

8.3.1.11 Phenylene Oxide-based resins (NORYL). Although solvent cementing is the usual method of bonding these resins, conventional adhesive bonding can be used. Epoxies, polysulfide epoxy, polyurethane, silicone and cyanoacrylate are recommended by the manufacturer. The cure temperature of the adhesive must not exceed the heat-deflection temperature of the NORYL resin, which is 212-300°F (100-149°C), depending upon the formulation.(22)

8.3.1.12 Polyaryl ether (ARYLON T). This material is normally joined by solvent cementing.

8.3.1.13 Polyaryl sulfone (ASTREL 360). As indicated above under 5.3.5.2.2.13, HYSOL EA 9614 (modified epoxy on a nylon carrier) has been used to give very good bonds with this plastic. Curing is at 160°F (71°C) for 4 hours, or 1 hour at 200-250°F (93-121°C) at 30 psi (0.20 MPa) pressure. Bonds of strengths up to 2023 psi (14 MPa) have been obtained with solvent-washed surfaces.

A Picatinny Arsenal study (23) reported on the use of EPON 828/Versamid 140 (epoxy-polyamide) for bonding ASTREL 360. The ratio of epoxy to polyamide was 70:30 and the specimens were cured with contact pressure at 260°F (127°C) for 3 hours. Average shear strengths of 750 psi (5.16 MPa) were observed with adherend failure. Somewhat lower shear strengths (410 psi) (2.83 MPa) were obtained with a novalac epoxy system, CIBA EPN 1138. With this system there was some adhesive failure, usually 0 - 20%. The Picatinny study also evaluated a solvent cement, m-cresol, which was cured at 40 psi (8.28 MPa) at 212°F (100°C) for 10-15 minutes, followed by 420°F (216°C) for one hour. This solvent system is hazardous, however, and the curing and drying cycle is so long that it is not feasible for production line use. Shear strengths of 680 psi (4.69 MPa) were obtained with m-cresol, with adherend failure.

## MIL-HDBK-691B

**8.3.1.14 Polycarbonate (LEXAN) (MERLON) (TUFFAK).** Polycarbonate is usually solvent cemented, but it can be bonded to other plastics, glass, aluminum, brass, steel, wood and other materials using a wide variety of adhesives.

Silane primers may be used when joining polycarbonates with adhesives to promote adhesion and ensure a dry surface for bonding (21). Epoxy and polyurethane adhesives offer good bond strengths to polycarbonates. (19)

Adhesives recommended for polycarbonate include epoxies, urethanes, silicones, cyanoacrylates, some epoxy-polyamides, rubber or neoprene-based materials, and hot melts. Generally best results are obtained with solventless materials, such as epoxies and urethanes. However, each application has unique requirements for flexibility, temperature resistance, ease of application, and appearance, requiring careful adhesive selection.

Parts molded from polycarbonate resin can be cemented using epoxy systems containing room-temperature-curing hardeners, such as diethylene triamine, or with systems containing elevated-temperature-curing hardeners, such as anhydrides. When cementing polycarbonate parts to metal parts, use a room-temperature cure to avoid creating strains in the adhesive caused by the difference in coefficients of thermal expansion. This differential causes adherend cracking and considerably decreases expected bond strengths. Curing temperatures should not exceed 270°F (132°C), the heat-distortion temperature of standard polycarbonate resins. (24)

Epoxy formulations with amine hardeners, used at room or elevated temperatures, have a tendency to become hard and brittle. The addition of polysulfide modifiers increases elasticity, although generally at the expense of bond strengths. These adhesives permit a fairly thick cement line. Amine-cured or polyamide-cured epoxies are not generally recommended for hot-water or steam environments above 250°F (121°C). Anhydride-cured epoxies require a high-temperature cure. Before applying epoxy, parts should be predried for 2-3 hours at 250°F (121°C) in an air-circulating oven to drive out residual moisture. The cure temperature should not exceed 270°F (132°C). (24)

RTV silicone adhesives are recommended for applications requiring excellent bond strength, a high service temperature and good thermal expansion. Silicone adhesives may be used with all standard polycarbonate resins, including glass-reinforced grades. After light abrasion with fine emery and cleaning of the surface with methyl alcohol or other compatible cleaning solutions, the surfaces should be primed with GE silicone primer SS-4004 and allowed a minimum of one hour dry time. The silicone adhesive should be applied in the desired thickness. Final bond thickness may range from 0.005 to 0.030 inches (0.013 to 0.076 cm). (24)

Polyurethane adhesives are commonly recommended for bonding polycarbonate to metal, glass, ceramics, fluorocarbons and other plastics. These two-part adhesives are characterized by bonds which have excellent room-temperature shear and lap strength, high impact resistance and excellent low-temperature performance. However, polyurethane adhesives are generally limited to service temperatures under 200°F (93°C). At temperatures above 200°F (93°C) tensile lap shear values decline dramatically. They also suffer from excessive creep at room temperature and may exhibit undesirable changes in properties with aging. (24)



## MIL-HDBK-691B

H. B. Fuller Co. has developed a urethane adhesive for polycarbonate called FE 6039. This solvent-free adhesive can develop tensile-shear strengths of 1350 psi (9.31 MPa).

Cyanoacrylates cure at room temperature to a clear film and have the advantage of a wide use-temperature range. Some epoxy-polyamide one-part systems and rubber or neoprene-based systems also provide good adhesion. Hot-melt adhesives also produce excellent adhesion. These adhesives reach their ultimate strength seconds after applications, but may lose their strength at temperatures below 0°F (-18°C) or above 200°F (93°C). Some are also subject to cold flow under prolonged heavy loading. However, their resistance to hot water is excellent.

In a recent Army ARRADCOM study (25) both a two-part urethane (Uralane 5736) and a two-part epoxy (EPOH 828/Versamid 140) were evaluated, using two different surface-preparation techniques and various surface-exposure times (SET). The urethane gave better results than the epoxy-polyamide. Unaged bonds of 720 psi (4.96 MPa) were obtained for the urethane and 390 psi (2.69 MPa) for the epoxy/polyamide. Aged bond strengths were 560 psi (3.86 MPa) and 140 psi (0.97 MPa), respectively. SET's of up to 30 days did not affect the strength of either tested or aged specimens of the urethane bonds, but they did have an adverse effect on the epoxy/polyamide bonds. Aging was 30 days at 120°F (49°C) and 95% RH.

8.3.1.15 Polychlorotrifluoroethylene (PCTFE) (KEL-F). Epoxy/polyamide and epoxy/polysulfide adhesives have been used successfully for bonding properly treated PCTFE. EPOH 828/Versamid 125 (60:40 ratio) cured 16 hours at RT and followed by 4 hours at 165°F (74°C) has given tensile-shear strengths of 2840-3010 psi (19.6-20.6 MPa) for various KEL-F resins treated with sodium naphthalene etch solutions and also abraded.(26)(27)

8.3.1.16 Polyester (Thermoplastic).(28) (29) This grouping includes General Electric Company's VALOX and Celanese's CELANEX. Solvent cements used are hexafluoroacetone sesquihydrate and hexafluoroisopropanol. These are used with contact pressure with an 18-hour cure. Tensile strengths up to 1500 psi (10.3 MPa) have been reported with VALOX. The solutions are brushed on to the mating surfaces and the parts are held together under contact pressure. These solvents can be toxic.

Polyurethanes recommended include single-component AF 250 and AF 725 (Staley Chemical Co.) and two-component Uralane 5738, 5742, 8089 and 8615.

Cyanoacrylates such as LOCTITE's IS 06 and IS 12 and one-part modified epoxies such as 3M's Scotch-Weld 2214 and 2214 Hi-density, and two-part epoxies such as Scotch-Weld 3520 are also recommended. Adhesive-bonding tapes, such as USM's Bostik 10-253, can also be used. With the latter, the following results were obtained with CELANEX glass-reinforced polyester:

<u>Cure</u>	<u>Tensile Shear Strength</u>
2 hrs @ 275°F (135°C)	480 psi (3.31 MPa)
4 hrs @ 300°F (149°C)	600 psi (4.14 MPa)
2 hrs @ 350°F (177°C)	750 psi (5.17 MPa)



## MIL-HDBK-691B

A 1976 Picatinny Arsenal Study (31) compared hexafluoroacetone sesquihydrate (HFS) solvent welding with EPON 828/Versamid 140 epoxy/polyamide. After surface preparation by wiping with ethanol and sanding, the HFS gave shear strengths of 1160 psi (8.01 MPa), compared to 1090 psi (7.54 MPa) for the epoxy/polyamide. The Army workers felt that the 18-hour curing time for the HFS was too long to be practical in production, and the solvent was too hazardous for production use.

**8.3.1.17 Polyethylene.** Acceptable bonds have been obtained between polyolefin surfaces with polar adhesives, such as epoxies, and solvent cements containing synthetic rubber or phenolic resin. The adhesives are applied to both surfaces and the solvents allowed to evaporate before the parts are joined. Recommended epoxies are the anhydride-cured and the amine-cured. Also suitable is the two-component polyamide-modified epoxy compound. Other adhesives recommended include styrene-unsaturated polyester and solvent-type nitrile-phenolic. Table XXII gives results for an epoxy, a polyester, and nitrile-phenolic, using different surface treatments.

**8.3.1.18 Polyethylene - chlorotrifluoroethylene (E-CTFE) (HALAR).** The manufacturer of this copolymer recommends epoxy adhesives with either sodium etch or flame treatment. Adhesives suggested are 3M's Scotch-Weld 2214 Hi-Temp, Scotch-Weld 2216, and Chemplast's Chem-Grip Hi-Temp. Recent Picatinny Arsenal studies compared sodium etch and flame treatment for Scotch-Weld 2214 Hi-Temp room-temperature-curing Versamid-epoxy adhesive. Bond strengths of 995 psi (6.87 MPa) were obtained with the sodium etch, compared to 350 psi (2.43 MPa) for the flame treatment. (23)(31)

**8.3.1.19 Polymethylmethacrylate (PMMA) (PLEXIGLAS) (LUCITE).** Adhesive joints ordinarily provide lower bond strengths than solvent- or heat-welded joints with PMMA. Cyanoacrylates, epoxies, and second-generation acrylics offer good adhesion, but poor resistance to thermal aging. (19)

Other adhesives recommended are rubber-base adhesives (contact cements), silicones, and polysulfides (32). It is important to select adhesives which are flexible because frequently the differences in coefficient of expansion between the adhesive and the plastic present a problem. When it is necessary to cement PMMA to non-plastic, the dimensions of the cemented area should be as small as possible, especially if the material has a much smaller coefficient of expansion than PMMA. (33)

**8.3.1.20 Polymethylpentane (TPX).** No information has been found on recommended adhesives for this material.

**8.3.1.21 Polyphenylene Sulfide (RYTON).** Very little information has been found in adhesive bonding of PPS. In a Picatinny Arsenal study, (23), a mixture of 70 pbw EPON 828 epoxy and 30 pbw Versamid 140 was applied to both faying surfaces, assembled and cured under contact pressure at 260°F (127°C) for 3 hours. Shear strengths of 485 psi (3.35 MPa) were obtained, with 100% adherend failure.

**8.3.1.22 Polypropylene (PP).** As for polyethylene (see 8.3.1.17). Although rather poor results are obtained with polyolefins and cyanoacrylates, the results with PP are better than with PE. Bond shear strengths up to 411 psi (2.83 MPa) have been obtained with flame-treated PP and methyl cyanoacrylate. Without the flame treatment the strength was only 160 psi (1.25 MPa).

## MIL-HDBK-691B

A 1967 Navy report (34) evaluated seven adhesives for bonding polypropylene. Surfaces were prepared by abrasion and sometimes by further treatment with W. T. Bean's Metal Conditioner or sodium treating agent. Of the adhesives tested the most promising results were obtained with Armstrong A-2 epoxy and Devcon F (an 80% aluminum - 20% epoxy putty compound, not sold as an adhesive). The A-2 epoxy gave average bond tensile strengths of 191 psi (1.32 MPa) and the Devcon F gave strengths of 273 psi (1.94 MPa).

Besides epoxies, treated polypropylene can be bonded with nitrile-phenolics, polysulfide-epoxies, polyamide-epoxies, polyurethanes and hot melts. Silicone resin in xylene solvent has been recommended for untreated polypropylene. (21)

**8.3.1.23 Polystyrene (PS).** Polystyrene is usually bonded by solvent cementing. It can be bonded with vinyl acetate/vinyl chloride solution adhesives, acrylics, polyurethanes, unsaturated polyesters, epoxies, urea-formaldehyde, rubber-base adhesives, polyamide (Versamid-base), PMMA, and cyanoacrylate. (19)(21)(35)

For polystyrene foam, aromatic hydrocarbon solvent adhesives would result in collapse of the cellular materials, so it is advisable to use either 100%-solids adhesives, such as epoxies, urethanes and amino resins, or water-based emulsion adhesives such as vinyl acetate and acrylate copolymer emulsions (35). It is advisable that such adhesives be medium-to-heavy-viscosity and room-temperature and contact-pressure curing. (21)

Often it is desirable to contact the polystyrene manufacturer for details in bonding PS to specific adherends with conventional adhesives. One of the most comprehensive sources is a technical information bulletin by Monsanto Company (36) which recommends particular commercial adhesives for the following:

**Non-porous surfaces:**

Cellulosics, methacrylate (PMMA), ureas, phenolics, vinyls, glass, steel.

**Porous surfaces:**

Paper, wood, cork.

For these adherends adhesives are recommended in the fast-, medium-, and slow-setting ranges.

**8.3.1.24 Polysulfone (UDEL).** Solvent cementing of polysulfone can be carried out with chlorinated hydrocarbons (see 7.2.10). Conventional adhesives recommended include vinyl-phenolics, epoxy-nylons, epoxies, polyimides, rubber-based adhesives, styrene polyesters, resorcinol-formaldehyde, polyurethanes, and cyanoacrylate. Specific commercial adhesives reported used successfully are:

HYSOL EA 9614 epoxy film adhesive (160°F (71°C) cure; nylon carrier)  
3M Company SCOTCH-WELD epoxy-nylon Film Adhesive 42  
3M Company SCOTCH-WELD 2216 epoxy (room-temp cure)  
3M Company SCOTCH-GRIP 880 rubber adhesive (not a structural adhesive)  
American Cyanamid BR 89 and BR 92 (for high-temperature applications)  
Furane URALANE 5738 polyurethane (polyether type)

## NIL-MDBK-691B

8.3.1.25 Polytetrafluoroethylene (PTFE). Epoxies and polyurethanes give good bond strengths to treated fluorocarbon surfaces.(19) Other adhesives include two-part liquid epoxy or nitrile-phenolic adhesives. Polyisobutylenes and silicones function as pressure-sensitive adhesives.(35)

8.3.1.26 Polyvinyl chloride (PVC). Solvent cementing is usually used for PVC (see 7.2.3). Plasticizer migration from vinyls to the adhesive bond line can cause difficulty. Adhesives must be tested for their ability to resist the plasticizer. Nitrile rubber adhesives are very resistant to plasticizers. Polyurethanes and neoprenes are also used. PVC can be made with a wide variety of plasticizers. An adhesive suitable for a certain PVC formulation may not be compatible with a PVC from another supplier (19). Even rigid PVC contains some plasticizer (up to 5%) which makes it difficult to effect bonds produced with epoxy and other non-rubber types of adhesives. After proper surface preparation, most vinyls are fairly easy to bond with elastomeric adhesives. For laminating vinyl, solvent adhesives containing vinyl or synthetic rubber solids in a compatible solvent are adequate. Cyanoacrylate adhesives provide good bond strengths for bonding rigid vinyl to itself or to aluminum. The highest bond strengths for semi-rigid or rigid vinyl are achieved with two-component, RT-curing epoxies.

Other adhesives recommended for rigid PVC are: polyurethanes, modified acrylics, silicone elastomers, anaerobic structural adhesives, polyester-polyisocyanates, polymethylmethacrylate, nitrile-rubber phenolic, polyisobutyl rubber, nitrile rubber, neoprene rubber, epoxy-polyamide, polyhydroxy ether, polyvinyl acetate, and resin emulsion.

8.3.1.27 Polyvinyl fluoride (PVF) (TEDLAR). When the PVF film is supplied with an adherable surface, it may be bonded to a variety of substrates, including plastics, metals, foams, textiles, wood and other cellulose with many classes of adhesives, including acrylics, polyesters, epoxies, elastomers, and pressure-sensitive materials. In addition, TEDLAR can be heat-sealed to itself.(37)

8.3.1.28 Polyvinylidene fluoride (PVF<sub>2</sub>) (KYNAR). Epoxies and polyurethanes give good bond strengths to treated fluoroplastic surfaces.(19)

8.3.1.29 Styrene-acrylonitrile (SAN) (LUSTRAH). Solvent cements are frequently used for SAN. Conventional cements suggested for bonding this copolymer include cyanoacrylate, epoxy, 3M Co. SCOTCH-GRIP Plastic Adhesive 2262 (synthetic resin), 3M Co Industrial Adhesive 847 (nitrile rubber), 3M Co. Contact Cement 1357 (neoprene), and 3M Co. Rubber Adhesives 1300L and 1700 (neoprenes).

8.3.2 Thermosets. Most thermoset plastics are not particularly difficult to bond. Obviously, solvent cementing is not suitable for bonding thermosets to themselves, since they are not soluble. In some cases, solvent solutions can be used to join thermosets to thermoplastics. In general, adhesive bonding is the only practical method of joining a thermoset to a thermoset, or to non-plastic materials. In general, epoxies or modified epoxies provide good adhesion to thermosets.

8.3.2.1 Diallylphthalate (DAP). Suggested adhesives include urea-formaldehyde, epoxy-polyamine, neoprene, nitrile-phenolic, styrene-butadiene, neoprene, phenolic-nitrile, phenolic-polyvinyl butyral, polysulfides, furans, polyesters, and polyurethanes.(11)(21)

## MIL-HDBK-691B

**8.3.2.2 Epoxies.** For maximum adhesion to epoxies, primers, such as Hughson's CHEMLOK 607, are used. The strength obtainable in a good epoxy bond is similar to that of the base resin. In general, the curing temperature should be as high as possible, allowing for the distortion of temperature. In this way, maximum strength and heat resistance are obtained. Fast-bonding nitrile-phenolics with curing resins can give excellent bonds if cured under pressure at temperatures of 300°F (149°C). Bonds of lower strengths can be obtained with most rubber-based adhesives. Suggested adhesives include: modified acrylics, epoxies, polyesters, resorcinol-formaldehyde, furane, phenol-formaldehyde, polyvinyl formal-phenolic, polyvinyl butyral, nitrile rubber-phenolic, polyisobutylene rubber, polyurethane rubber, neoprene rubber, reclaimed rubber, melamine-formaldehyde, silicones, epoxy phenolic, and cyanoacrylates.

**8.3.2.3 Melamine-Formaldehyde (Melamines).** For bonding melamines to themselves or to other thermosets, epoxies, phenolic-polyvinyl butyral, epoxy-phenolic, phenolic-nitrile, polyurethanes, neoprene, butadiene-nitrile rubber, cyanoacrylates, resorcinol-polyvinyl butyral, furane, and urea-formaldehyde are suggested.

**8.3.2.4 Phenol-Formaldehyde (Phenolics).** Adhesive systems for bonding phenolics include both one-component and two-component types. Phenolics can be bonded to phenolics, to other thermosets, and to non-plastics with neoprene and urethane elastomers, epoxy and modified epoxy, phenolic-polyvinyl butyral, nitrile-phenolic and polyesters. Cyanoacrylates give adequate bond strengths between phenolics and other thermosets or non-plastics. With many types of phenolic molding compounds the best bonding medium is resorcinol-formaldehyde. Release agents can be a problem, especially the stearates, which are included in some phenolic formulations. Phenolic adhesives give good results, but require higher temperatures for cure and are less water-resistant than resorcinol-based adhesives. Other adhesives suggested include polyacrylate, modified acrylics, neoprene, polyvinyl acetate, and urea-formaldehyde.

**8.3.2.5 Polyesters.** Thermosetting polyester resins in their various product forms can be bonded satisfactorily with neoprene or nitrile-phenolic elastomer, epoxy, epoxy-polyamide, phenolic-epoxies, phenolic, polyesters, modified acrylics, cyanoacrylates, phenolic-polyvinyl butyral, polyurethanes, butyl rubber, polyisobutylene, and polymethylmethacrylates.

**8.3.2.6 Polyimide.** Little published literature is available on the bonding of high-performance composites (incorporating polyimide) for use at 600°F (316°C). A recent NASA study (38) (39) evaluated six adhesives for bonding polyimide. Candidate adhesive systems finally recommended are given in the list below. No significant differences in mechanical properties were observed among these adhesives.

PM-34 (Bloomington) polyimide tape

PM-34-B-18 (Bloomington) polyimide (arsenic-free)

LARC-13 - developed at the NASA Langley Research Center; made from benzophenone tetracarboxylic dianhydride (BTDA), *m*, *m'*-methylene diamine (*m,m'*-MDA) and nadic anhydride (NA) in dimethylformamide (DMF).

## MIL-HDBK-691B

NR056X - developed by duPont under a NASA contract; an adhesive version of the NR 150 polymer family (polyimide).

**8.3.2.7 Polyurethane.** Adhesives suggested for polyurethanes include urethanes, epoxies, nitriles, polysulfide epoxy, polyamide-epoxy, neoprene and resorcinol-formaldehyde. The latter offers excellent adhesion, but is somewhat brittle and can cause failure at high loads.

**8.3.2.8 Silicone resins.** Silicone resins are generally bonded with silicone adhesives, either silicone rubber or silicone resin.

**8.3.2.9 Urea-Formaldehyde.** Adhesives used are epoxies, nitrile-phenolics, phenol-formaldehyde, urea-formaldehyde, resorcinol-formaldehyde, furane, polyester, butadiene-nitrile rubber, neoprene, cyanoacrylate, and phenolic-polyvinyl butyral.

**8.3.3 Reinforced plastics/composites.** Adhesives which give satisfactory bonds to the base resin can be used to bond plastics which are reinforced with materials such as glass or organic fibers, asbestos, cotton, or paper. Reinforced thermoplastics can also be solvent cemented to themselves, or bonded to other thermoplastics by using a compatible solvent cement. As for reinforced thermosets, much of the information provided above under 8.3.2 thermosets applies. Certainly, the type of adhesive used should be governed, in part, by the type of resin used in the laminate.

A wide variety of adhesives are used with reinforced thermosetting plastics. In general, the following adhesives have been used: epoxies, epoxy-polyamides, urea-formaldehyde, vinyl-phenolic, unsaturated polyester-styrene, resorcinol-formaldehyde, phenolics, furanes, polyurethanes, nitrile rubber-phenolic, neoprene rubber, polyvinyl formal-phenolic, polyvinyl butyral-phenolic, modified acrylics, cyanoacrylates, butadiene-styrene rubber, silicone resins (RTV) and phenolic-epoxy.

#### **8.3.4 Plastic Foams.**

**8.3.4.1 Thermoplastic Foams.** Solvent cements are usually preferable to conventional adhesives for thermoplastic structural foams (see 7.2.12). Some solvent cements and solvent-containing pressure-sensitive adhesives will collapse thermoplastic foam. Water-based adhesives based on SBR, polyvinyl acetate, or neoprene are often used. Solvent cementing is not effective on polyethylene foams because of their inertness. Recommendations for adhesives are as follows:

- o Polyethylene - nitrile rubber, polyisobutylene rubber, flexible epoxy, nitrile rubber-phenolic, and water-based (emulsion) adhesives.

- o Modified polyphenylene oxide (MORYL) - epoxy, polyester-polyisocyanate, polyvinyl butyral, nitrile rubber, neoprene rubber, polyurethane rubber, polyvinylidene chloride, and acrylic.

- o Polystyrene - urea-formaldehyde, epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride-acetate copolymer, reclaim rubber, nitrile rubber, neoprene rubber and butadiene-styrene rubber are specific chemical adhesive for polystyrene. Polystyrene foam can be effectively bonded with any of the following general types of adhesives: (40)



## MIL-HDBK-691B

- water-based (emulsion) - best for bonding polystyrene foam to porous surfaces.

- contact bond - give optimum initial strength. Both water-base and solvent-base types may need auxiliary heating systems for faster drying. Solvent types are recommended for adhering to metal, baked enamel, or primed surfaces.

- pressure-sensitive adhesives - will bond to almost any substrate. Both water-base and solvent-base types are used. They cannot be used in applications requiring long-term resistance to stress or resistance to high levels of heat.

- 100% solids - These are 2-part epoxies and polyurethanes. They form an extremely strong, heat- and environmental-resistant bond.

o Polyvinyl chloride - epoxy, polyester-isocyanate, unsaturated polyester, vinyl chloride-acetate copolymer, polyvinyl acetate, polyvinyl alkyl ether, ethylene-vinyl acetate, nitrile rubber-phenolic, nitrile rubber, neoprene rubber, polyisobutylene rubber, polyurethane rubber and polysulfide rubber.

o Polycarbonate - urethane, epoxy, rubber-base adhesives.

o Polyethylene terephthalate (CLEARTUF) - urethane, epoxy.

#### 8.3.4.2 Thermosetting foams

o Polyurethane - epoxy, polyester, polyacrylate, polyhydroxyether, nitrile rubber, neoprene rubber, butyl rubber, water-based (emulsion), polyurethane rubber, melamine-formaldehyde and resorcinol-formaldehyde are specific types. Generally, a flexible adhesive should be used for flexible PU foams. Synthetic-elastomer adhesives with fast-tack characteristics are available in spray cans for these applications. Flexible urethane foams are commonly used for sound dampening in metal working, outboard motors, snowmobiles, tractor cabs, motorized golf carts, etc. Nearness to motors and exposure to outdoors calls for adhesives that are resistant to heat, fuel, oil, water and/or weathering. Flexible urethane foam is also used widely in comfort cushioning.

Solvent-base neoprenes are recommended for resistance to stress, water, and weathering. Solvent-base nitriles are recommended for resistance to heat, solvent and oil. Water-base adhesives generally dry too slowly for most industrial applications, unless accelerated equipment can be used. For immediate stress resistance contact bonding is preferred, in which adhesive is applied to the foam and the other substrate by spraying or brushing. Wet bonding can be used when the adhesive is applied to the other surface. This reduces soak-in on the highly absorbent and porous foam.(40)

o Phenolic - epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride-acetate copolymer, polyvinyl formal-phenolic, nitrile rubber, nitrile rubber-phenolic, reclaim rubber, neoprene rubber, polyurethane rubber, butyl rubber, melamine-formaldehyde, phenolic-neoprene and phenolic-polyvinyl formal.

o Urea formaldehyde - urea-formaldehyde, resorcinol-formaldehyde.



## NIL-HDBK-691B

o Silicone - silicone rubber.

o Epoxy - (including epoxy syntactic foams) - heat-curable epoxies (one-part).

8.4 Rubbers. Adhesives used for post-vulcanization bonding of rubbers include Hughson's CHEMLOK 236 and 234B, used for natural rubber, SBR, neoprene, butyl, nitrile and EPDM (see 5.3.5.3). These are unspecified types of rubber-base adhesives. In general, adhesives used for rubbers include natural, chlorinated, reclaim, butyl, nitrile, butadiene styrene, polyurethane, polysulfide, and neoprene-rubber adhesives, acrylics, cyanoacrylates, polyester-isocyanates, resorcinol-formaldehyde, phenolic-resorcinol formaldehydes, silicone resins, epoxies, polyisocyanates, furane resins, phenolic-nitriles, phenolic-neoprenes, phenolic-polyvinyl formals, and flexible epoxy polyamides. Bonding of vulcanized elastomers to themselves and other material is generally completed by using a pressure-sensitive adhesive derived from an elastomer similar to the one being bonded.(11)(19)

8.5 Wood. Adhesives (or glues) used for wood include animal or hide glues, starch, casein, soybean, blood glues, and fish glues, which have been used for many years, and synthetic resin adhesives. Resorcinol-formaldehyde resins are cold-setting adhesives for wood structures. Urea-formaldehyde adhesives, commonly modified with melamine-formaldehyde, are used in the production of plywood and in wood veneering for interior applications. Phenol-formaldehyde and resorcinol-formaldehyde adhesive systems have the best heat and weather resistance. Polyvinyl acetates are quick-drying, water-based adhesives commonly used for the assembly of furniture. These adhesives produce very strong bonds, but are not resistant to moisture or high temperatures.

Epoxies have been used for certain specialized applications, as in wood-to-metal bonds. Rubber-based adhesives (contact type) have also been used. Mastic adhesives have been used in construction work and are usually applied in caulking guns. These are based on elastomers, including reclaimed rubber, neoprene, butadiene-styrene, polyurethane, and butyl rubber.(19)(41)

8.6 Glass. Glass adhesives are generally transparent, heat-setting resins that are water-resistant to meet the requirements of outdoor applications. They include polyvinyl butyral, phenolic butyral, phenolic nitrile, neoprene, polysulfide, silicone, vinyl acetate, and epoxy adhesives.(19)

Optical adhesives used for bonding glass lenses are usually styrene-modified polyesters and styrene-monomer-based adhesives. Epoxies are also beginning to be used.(19)(42)

NIL-HDBK-691B

## REFERENCES

- (8-1) Reynolds Metal Company, Richmond, VA. "Adhesive Bonding Aluminum", booklet, 1966.
- (8-2) The Aluminum Association, N.Y., NY, "Adhesive Bonding of Aluminum Automotive Body Sheet Alloys", Publication T14, November 1975.
- (8-3) K. H. Miska. "New Epoxy Adhesive Systems Speed Assembly, Cut costs", Materials Engineering, 86(7): 30-32 (November 1977)
- (8-4) C. V. Cagle, Chapter 21, "Surface Preparation of Beryllium and Other Adherends", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, N.Y., NY, 1973.
- (8-5) H. St. Cyr, "Adhesive Bonding of Beryllium", Preprint Book, 15th. National SAMPE Symposium, pp. 719-731, 1970.
- (8-6) J. C. Bolger et al., "A New Theory for Improving the Adhesion of Polymers to Copper", Final Report, INCRA Project No. 172, International Copper Research Association, 708 Third Avenue, N.Y., NY 10017, August 16, 1971.
- (8-7) J. C. Bolger, Chapter 1, "Structural Adhesives for Metal Bonding", TREATISE ON ADHESION AND ADHESIVES, Vol. 3, edited by R. L. Patrick, Marcel Dekker, N.Y., NY, 1973.
- (8-8) J. C. Bolger et al. "Improving the Adhesion of Epoxies to Copper", Preprint Book, Part 1, Society of Plastics Engineers (SPE), 30th Annual Technical Conference, held at Chicago, IL, May 15-18, 1972.
- (8-9) L. C. Jackson, "Effects of Surface Preparation on Bond Strength of Magnesium", APPLIED POLYMER SYMPOSIA No. 3, Structural Adhesives Bonding, edited by M. J. Bodnar, pp. 341-351, Wiley-Interscience, 1966.
- (8-10) R. E. Keith et al., "Adhesive bonding of Nickel and Nickel-Base Alloys", NASA Technical Memorandum NASA TM X-53428, October 1965.
- (8-11) J. Shields, ADHESIVES HANDBOOK, 2nd Edition, Hwnes-Butterworth, London, 1976.
- (8-12) C. V. Cagle, Chapter 14, "Bonding Steels", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, NY, 1973.
- (8-13) A. T. Devine, "Adhesive Bonded Steel: Bond Durability as Related to Selected Surface Treatments", U. S. Army ARRADCOM Tech. Rept. ARLCD-TR-77027, December 1977.
- (8-14) G. W. Lively and A. E. Hohman, "Development of a Mechanical-Chemical Surface Treatment for Titanium Alloys for Adhesive Bonding", Preprint Book, 5th National SAMPE Technical Conference, held at Kiamesha Lake, N.Y., Oct 9-11, 1973, pp. 145-159.

## MIL-HDBK-691B

- (8-15) R. C. Walter et al., "Structural Bonding of Titanium for Advanced Aircraft", Preprint Book, 2nd National SAMPE Technical Conference, held at Dallas, TX, October 1971, pp. 321-330.
- (8-16) R. T. McIntyre, "Adhesive Bonding to Cadmium and Zinc Plated Steel Substrates", APPLIED POLYMER SYMPOSIA No. 19, edited by H. J. Bodnar, pp. 309-327, Wiley-Interscience, 1972.
- (8-17) Celanese Plastics Company, CELCON Acetal Copolymer Design Manual.
- (8-18) E. I. duPont de Nemours & Co., DELTRIN Acetal Resins Design Handbook, A-67041, 1967.
- (8-19) E. H. Petrie, Chapter 10, "Plastics and Elastomers as Adhesives", HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C. A. HARPER, McGraw-Hill, N.Y., NY, 1975.
- (8-20) E. I. duPont de Nemours & Co., TEFZEL Fluoropolymer Design Handbook, 1973.
- (8-21) C. V. Cagle, Chapter 19, "Bonding Plastic Materials", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, N.Y., NY, 1973.
- (8-22) General Electric Company, Plastics Department, Selkirk, NY, WORYL Thermoplastic Resins - Design - CDX-83A.
- (8-23) M. C. Ross, "A Preliminary Study of Adhesive Bonding of Newer Structural Plastics". Picatinny Arsenal Technical Report 2204, August 1976.
- (8-24) General Electric Company, Plastics Department, Pittsfield, MA, LEXAN Polycarbonate Resins Design Guide, CDC-536.
- (8-25) D. Levi et al., "Effects of Adhesive and Processing Parameters on Adhesive Bonding of Polycarbonate", U. S. Army ARRADCON Rept. ARLCD-TR-78054, August 1978.
- (8-26) N. J. DeLollis and O. Montoya, "Surface Treatment for Difficult to Bond Plastics", Adhesives Age, 6 (1): 32-36 (January 1963).
- (8-27) H. St. Cyr, "State of the Art - Methods of Bonding Fluorocarbon Plastics to Structural Materials", PLASTEC Rept. 6, May 1961
- (8-28) Celanese Plastics Company, "Properties and Processing - Glass Reinforced Grades - CELANEX Thermoplastic Polyester", May 1974.
- (8-29) General Electric Company, Plastics Department, Pittsfield, MA, VALOX Bonding Information, 6-page brochure, undated, rec'd Jan. 1975.
- (8-30) Not used
- (8-31) 3M Company literature.

## MIL-HDBK-691B

- (8-32) E. I. duPont de Nemours & Co., "LUCITE Design Handbook", A-63712, 1960
- (8-33) Rohm & Haas Company, Philadelphia, PA, "Cementing PLEXIGLAS", PL-7j.
- (8-34) "Investigation of Adhesive Bonding of Polypropylene", USL Technical Memorandum 2133-214-67, 10 March 1967.
- (8-35) J. Hiron and I. Skeist, "Bonding Plastics", Chapter 41, HANDBOOK OF ADHESIVES, 2nd Edition, Van Nostrand Reinhold, N.Y., NY, 1977.
- (8-36) Monsanto Company, "Fabrication Techniques for LUSTREX and LUSTRAN Styrene Plastics", Technical Bulletin 6422.
- (8-37) E. I. duPont de Nemours & Co., "Toughen it up with TEDLAR PVF Film", Designer's Information Kit, E-15871.
- (8-38) D. Pragar, "Polyimide Adhesive Bonding", pp. 123-138 in Graphite/Polyimide Composites, NASA Conference Publication 2079, Feb. 28-Mar.1, 1979.
- (8-39) P. S. Blatz, "MR 150B2 Adhesive Development", NASA CR 3017, July 1978.
- (8-40) 3M Company, "Adhesives Answer Book for Product Assembly". Z-CPSS (731)R
- (8-41) R. F. Blomquist, Chapter 17, "Adhesive Bonding of Wood", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, N.Y., NY, 1973.
- (8-42) C. V. Cagle, Chapter 18, "Bonding Glass, Optics, Ceramics, and Related Substrates", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, NY, 1973.

## MIL-HDBK-691B

## CHAPTER 9. THERMALLY AND ELECTRICALLY CONDUCTIVE ADHESIVES

9.1 Introduction. (See 4.4.3 for a general introduction to this subject.)

9.2 Filler choice. (See 4.4.3)

9.3 Filler content. (See 4.4.3)

9.4 Silver migration. (See 4.4.3)

9.5 Storage problems. Storage of uncured silver compounds in a warm area may cause the silver flakes to re-orient, thereby reducing the number of particle contacts and the electrical conductivity. Restoration of the normal conductivity can sometimes be accomplished by vigorous stirring before use.

9.6 Oxide coatings. Copper and aluminum powders readily form oxide coatings which reduce electrical conductivity by hampering particle-to-particle contact. For this reason these metal fillers are not generally used for electrically conductive adhesives. Silver coatings have been used on copper aggregates to inhibit copper oxide formation.

9.7 Curing schedules. Table XXXV shows how increasing cure temperature (and decreasing cure time) results in lower resistivities on a room-temperature-curing adhesive (Ablebond 463-1 with 66.7% by weight of coarse silver flake.)

TABLE XXXV. Effect of cure conditions on resistivity.

<u>Cure</u>	<u>Resistivity (ohm-cm)</u>
2 min @ 250°F (121°C)	0.00067
3 min @ 200°F (93°C)	0.00083
10 min @ 165°F (74°C)	0.00094
2 hrs @ room temp.	0.0035
3 days @ room temp.	0.0029
3 days @ room temp. + 30 min postcure @ 250°F (121°C)	0.0029

Postcuring after room-temperature curing has no advantage in this case. When a room-temperature-cured adhesive is postcured, resistivity may actually increase because of shrinkage.(1)

## MIL-HDBK-691B

Figure 30 shows graphically how cure time, cure temperature and resistivity are interrelated.

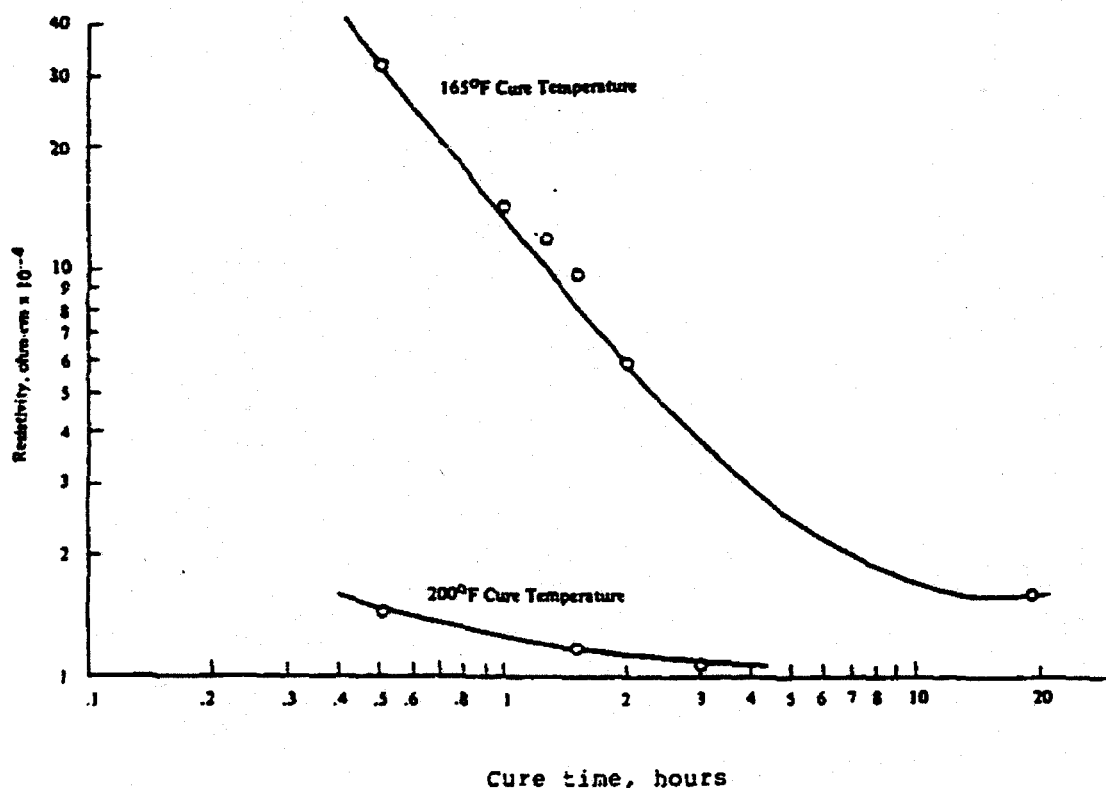


FIGURE 30. Resistivity of flexible 85% Silver conductive adhesive as a function of curing temperature.(1)

Figure 31 shows the effect of temperature and time of curing on a typical silver/epoxy adhesive. It is apparent that a cure for only 10 minutes at a higher temperature 390°F or (199°C) provides a much lower volume resistivity than curing for a much longer period (6 hours) at only 270°F (132°C). Aging temperatures are also shown in this figure. This type of result is quite typical of electrically conductive plastics. The variation in tensile adhesion of a well-known conductive adhesive with various cure times and temperatures is shown in Figure 32. In most typical conductive adhesives, the highest-temperature cure results in the highest strength. Note the reversion or apparent overcure at (160°F or 71°C.)



NIL-HDBK-691B

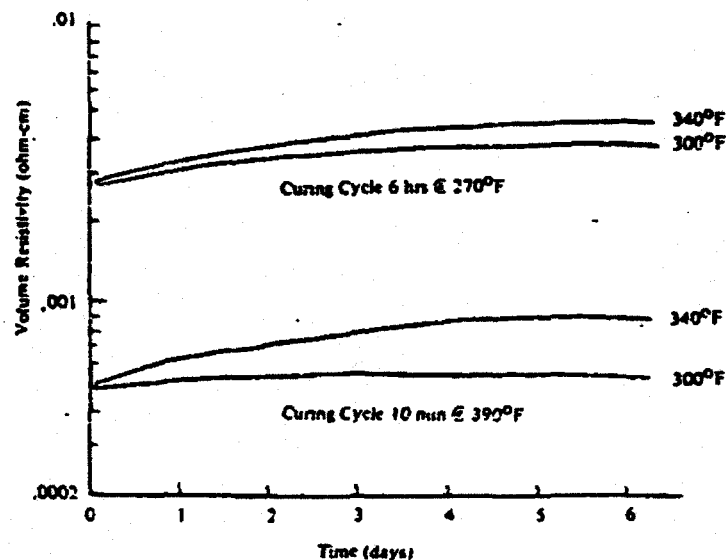


FIGURE 31. Volume resistivity of silver-epoxy adhesive (E-SOLDER 3012) as a function of temperature and time of curing.(1)

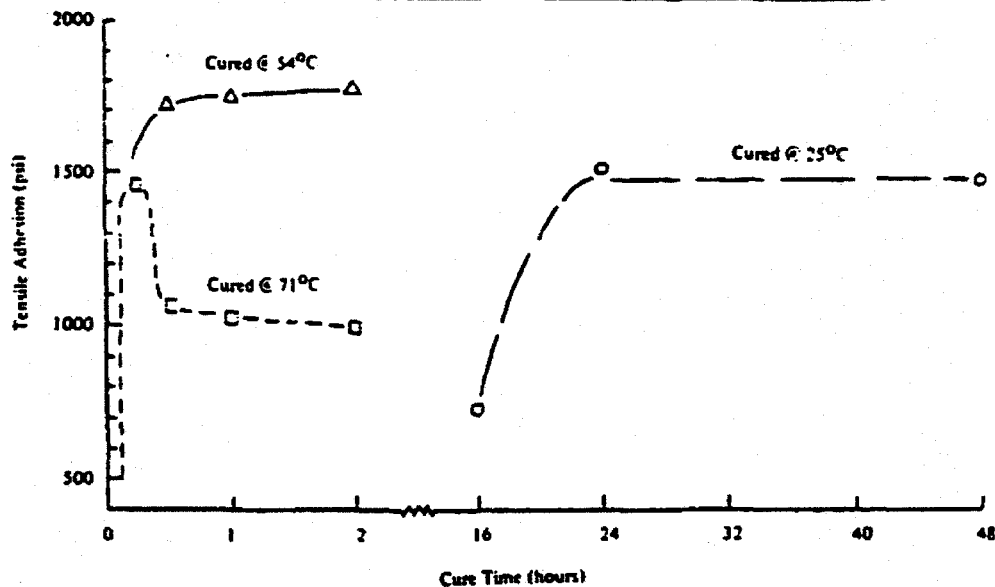


FIGURE 32. Tensile adhesion vs cure time and temperature for Hysol K8-4238 conductive cement.(1)

Room-temperature-curing conductive adhesives still leave much to be desired. Although the resistivity values of the better room-temperature-curing adhesives are good, they are not comparable to high-temperature curing for the same adhesives.

9.8 Hardener/resin ratio. The hardener/resin ratio is known to affect the flexibility of cured systems. Elastomeric properties may be obtained at one extreme (low hardener), while typical thermoset properties predominate at the other extreme. Hardener variations of + 10% can be tolerated with no serious adverse effects on tensile adhesion. Table XXXVI shows the results of an experiment in which a conductive epoxy adhesive was studied for the effect of hardener/resin rates in tensile adhesion and conductivity. The results show very little change in bond strength and no change in conductivity with high hardener. Samples with low hardener showed much more inconsistent and scattered results.

TABLE XXXVI. Effect of hardener/resin ratio on tensile adhesion and conductivity.(1)

Total Variation	Hardener Variation	Resin Variation	pbw Hardener	pbw Resin	Ratio Hardener/Resin	Tensile Adhesion psi	Conductivity ohms
15%	+7.5%	-7.5%	8.60	92.5	.0930	3150 ± 572	0.0001
10%	+5.0%	-5.0%	8.40	95.0	.0884	3201 ± 712	0.0001
5%	+2.5%	-2.5%	8.20	97.5	.0841	3278 ± 429	0.0001
(spec) 0%	0%	0%	8.00	100.0	.0800	3190 ± 466	0.0001
5%	-2.5%	+2.5%	7.80	102.5	.0761	2880 ± 414	0.0001
10%	-5.0%	+5.0%	7.60	105.0	.0724	4118 ± 727	0.0001
15%	-7.5%	+7.5%	7.40	107.5	.0688	3666 ± 478	0.0001

9.9 Mixing time. Viscosity increases rapidly with mixing time, reaching a maximum usable figure in a short time, such as 2 minutes for a typical conductive epoxy adhesive. Additional time results in lower tensile adhesion.

9.10 Time delay between mixing and use. After mixing, conductive adhesives are used over a period of time. The effect of time delay depends on the specific adhesive, but generally there is a drop-off in tensile adhesion with time. With one typical commercial adhesive there is a significant drop in tensile adhesion after only 10 minutes. Another common commercial adhesive is good for 30-45 minutes after mixing.

9.11 Surface preparation and solvent cleaning. Chapter 5 provides details for any surfaces likely to be encountered in conductive adhesive bonding. Conductivity test plugs (1" long x 0.565" diameter) (2.54 cm long x 1.44 cm diameter) of brass have been prepared by the following techniques:

- o Clean with MEK
- o Dip 3 min in the following solution:
  - 55% by vol. phosphoric acid, conc
  - 25% by vol. nitric acid, conc
  - 20% acetic acid, glacial
- o Rinse with distilled water

## HIL-HDBK-691B

o Dry 1/2 hour at  $150 \pm 10^{\circ}\text{F}$  ( $66 \pm 5.6^{\circ}\text{C}$ ).

Aluminum lap-shear and T-peel specimens have been prepared by cleaning and then chromic-sulfuric acid etched. Tensile adhesion test blocks of aluminum were cleaned with solvent, the faying surfaces grit-blasted with #80 aluminum oxide grit, and then brushed clean. Table 39 shows the effects of acid treatment on three conductive adhesives.<sup>(1)</sup>

**9.12 Interfacial resistance.** The term "interfacial resistance" means resistance to conductivity, whether thermal or electrical, caused by the interface between the metal adherend and the conductive adhesive. The interfacial resistance can be high if proper cleaning of the metal adherend is not performed. It is substantially lowered by curing at higher temperatures such as  $150\text{--}200^{\circ}\text{F}$  ( $66\text{--}93^{\circ}\text{C}$ ). The interfacial resistance also depends on the type of metal adherend used. A large resistance is introduced by the aluminum oxide present on aluminum adherends. The average resistivity for aluminum is 2140 ohm-cm vs 1 ohm-cm for brass, using identical curing conditions.<sup>(1)</sup>

In an evaluation of the difference in volume resistivity results obtained by the bulk method (glass tube) vs the bonded specimen (brass plug) technique, it was found that the volume resistivity is usually lower with the bulk method because of the adhesive-to-adherend interface and the resistance of the adherend itself. For a flexible silver/epoxy adhesive, the major factor contributing to the electrical resistance between metallic parts bonded with conductive adhesive is the resistance of the bond interface. Gold is frequently used to reduce the resistance at the interface. The ASTM procedure for volume resistivity of conductive adhesives recommends gold or silver plating for brass plugs.<sup>(1)</sup>

**9.13 Aging.** In general, volume resistivity rises in a fairly linear manner with thermal aging, particularly at higher temperatures. This can be seen in Figures 31 and 33, showing data up to a maximum of 8 days at  $302^{\circ}\text{F}$  ( $150^{\circ}\text{C}$ ). Whether or not thermal aging has a significant effect depends on the particular adhesive in question, and there is a wide variance in the results with different adhesives. For some adhesives, high-temperature (to  $257^{\circ}\text{F}$  or  $125^{\circ}\text{C}$ ) and/or high-humidity aging has a pronounced effect, while for other adhesives the effect is minimal.<sup>(1)</sup>

In a study involving a large number of adhesives it was found that aging for six months at room temperature and for two months at  $257^{\circ}\text{F}$  ( $125^{\circ}\text{C}$ ) had no adverse effect on conductivity, strength or adhesion properties. Generally, resistance values decreased slightly in the 30-day aging, and also decreased as temperatures increased. Conversely, certain adhesives broke down completely at temperatures of 212, 257 and  $302^{\circ}\text{F}$  ( $100$ ,  $125$  and  $150^{\circ}\text{C}$ ) and exhibited very large resistances, while others were very stable.<sup>(1)</sup>

In another study, aging up to nine weeks at  $185^{\circ}\text{F}$  ( $85^{\circ}\text{C}$ ) was evaluated. Again, the behavior was erratic. Most of the materials conditioned at  $185^{\circ}\text{F}$  ( $85^{\circ}\text{C}$ ) showed a dramatic decrease in volume resistivity for about two weeks, after which they remained at a fairly constant figure. One particular silver/epoxy conductive adhesive showed no change at all, even after nine weeks at  $185^{\circ}\text{F}$  ( $85^{\circ}\text{C}$ ).

## MIL-HDBK-691B

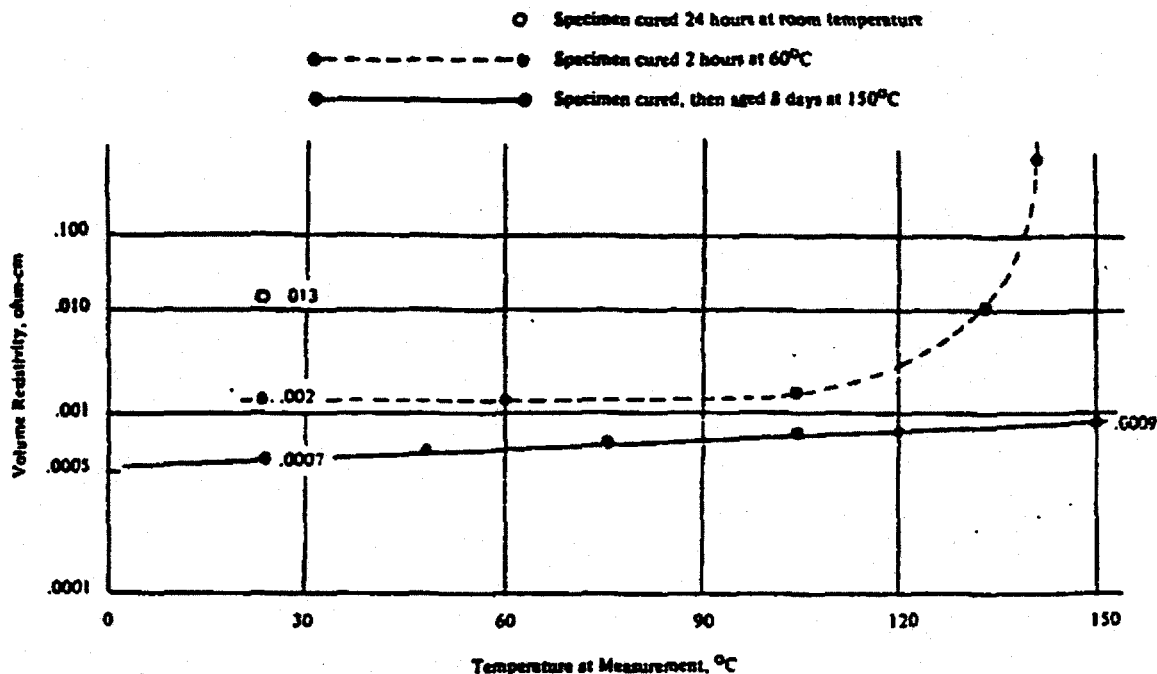


FIGURE 33. Relationship between volume resistivity, operating temperature and aging for hysol K20 epoxy conductive cement.(1)

Aging at high temperature is particularly likely to show an adverse effect on resistivity when combined with high relative humidity and salt spray (1).

9.14 Elevated-temperature testing. Table XXXVII shows a range of resistivities obtained after testing a copper-filled conductive adhesive at a range of temperatures between 77 and 200°F (25 and 93°C). Resistivity increased with high-temperature testing. Similar results were obtained with a silver/epoxy film adhesive where lap-shear strength decreased with increasing test temperature. Another reference shows a considerable reduction in bond strength of a thermally conductive adhesive when tested at 200°F (93°C). Similar reductions in bond strengths of three electrically conductive adhesives are shown in Table XXXVIII.

TABLE XXXVII. Resistivity of copper-filled epoxy adhesive after elevated-temperature testing.(1)

Cure and Subsequent Treatment	Resistivity (ohm-cm)
Cured 1 hr @ 225°F (107°C)	
Tested @ 77°F (25°C)	0.004
Tested @ 125°F (52°C)	0.005
Tested @ 150°F (66°C)	0.006
Tested @ 200°F (93°C)	0.009

## MIL-HDBK-691B

TABLE XXXVIII. Characteristics of Bacon Industries epoxy/silver electrically conductive adhesive. (1)

Adhesive	LCA-12		LCA-18		LCA-24	
Type	Two-part		Two-part equal volume or weight		Two-part	
Cure	2 hrs @ 160°F (24°C)		24 hrs @ 75°F (24°C) or 2 hrs @ 160°F (71°C)		24 hrs @ 75°F (24°C) or 4 hrs @ 160°F (71°C) or 2 hrs @ 200°F (93°C)	
Volume resistivity, ohm-cm after 6 mos @ 250°F (121°C)	0.010 0.010		0.015 0.015		0.005 0.010 @ 200°F or (93°C)	
Hardness, Shore D	88		75		64	
Bond strength to Al	(psi)	(MPa)	(psi)	(MPa)	(psi)	(MPa)
@ -65°F	2250	15.5	1700	11.7	1600	11.0
@ 75°F (24°C)	2250	15.5	1700	11.7	1600	11.0
@ 160°F (71°C)	2250	15.5	400	2.76	1600	11.0
@ 250°F (121°C)	1000	6.69	-	-	500	3.45
Thermal conductivity						
BTU-in/hr-ft <sup>2</sup> -°F	75		40		40	
W/m.K	10.8		5.77		5.77	
Chief features	Easily applied, good bond strength up to 250°F (121°C)		Easy mixing because of equal properties		More easily applied than LCA-12, good bond strength up to 250°F (121°C)	

9.15 Humidity environment. High temperature and high humidity have a pronounced negative effect in some conductive adhesives, and a minimal effect on others. Silver migration often takes place in silver/epoxy conductive adhesives under conditions of high humidity and DC potential. A Navy study showed a considerable reduction in bond tensile shear strength for three commercial adhesives exposed to (1) constant temperature and humidity (MIL-E-5272A, Para 4.4.3) and (2) temperature/humidity cycling (MIL-E-5272A, Para 4.4.1). Similar results are shown in Table XXXIX for the same adhesives with respect to electrical resistance.

## MIL-HDBK-691B

TABLE XXXIX Bond-tensile-shear strengths of conductive adhesives.(1)(2)

Property		Adhesive		
		E&C 56C <sup>a</sup>	E&C 57C <sup>b</sup>	Hysol 4238 <sup>c</sup>
Bond tensile shear strength, after:		(psi)		
No conditioning	Degreased panels	810	670	780
	Acid-dipped panels	960	640	2610
Salt spray		NIL	430	420
Constant temperature and humidity		440	500	470
Temperature/humidity cycling		440	420	290

Thickness of 56C adhesive between panels = 0.010 in. avg.

Thickness of 57C adhesive between panels = 0.021 in. avg.

Thickness of 4238 adhesive between panels = 0.011 in. avg.

<sup>a</sup> 40 parts 56C/1 part Catalyst 9; Cure 2 hrs @ 150°F (66°C)

<sup>b</sup> Equal parts A & B; Cure 3 hrs @ 150°F (66°C)

<sup>c</sup> 100 parts 4238/8 parts Hardener C; Cure 2 hrs @ 140°F (60°C)  
(Hysol 4238 is now K8-4238)

9.16 Salt spray. There appears to be considerable differences in results in studies carried out in this area. A series of five silver-filled conductive epoxy adhesives was exposed by a manufacturer to salt water for one week with no adverse effect on resistivity, as shown in Table XL. In another study, two commercial silver-filled adhesives, ECCOBOND 70C and HYSOL K16, were stored for periods up to 50 days under salt spray, resulting in a pronounced adverse effect on resistivity (3).

The Navy exposed three commercial silver-filled adhesives to salt spray and then evaluated them for tensile-shear strengths and electrical resistance. The salt spray weakened one particular adhesive to such an extent that the tensile shear samples fell apart in the exposure cabinet. Strengths were lowered significantly for the other two samples. The adverse effect on resistance was also extremely pronounced, as shown in Table XXXIX.



## MIL-HDBK-691B

TABLE XL. Volume resistivity of silver-filled conductive epoxy adhesives.(1)

Amicon Corp. Adhesive Designation	Special Features	Std. Cure	Volume resistivity, ohm-cm, after:	
			200 hrs @ 280°F (138°C)	1 week Salt water
UNISET C-409 <sup>a</sup>	High strength, good conductivity	.01	.01	.01
UNISET C-419 <sup>a</sup>	High strength, moderate cost	.02	.04	.01
UNISET C-429 <sup>a</sup>	Very low cost	2.0	2.0	2.0
AMICON C-13A/B <sup>b</sup>	Fast cure, resilient	.01	*	.01
AMICON C-14A/B <sup>b</sup>	High strength, 1:1 mix	.01	*	.01

\*Not recommended for service above 250°F (121°C)

a Cure schedule                      5 hrs @ 220°F (104°C) or  
for one-component                  1 hr @ 250°F (121°C) or  
adhesive                                30 min @ 280°F (138°C) or  
    10 min @ 320°F (160°C)

b Cure schedule                      16 hrs @ 72°F (23°C)  
for two-component                  20 min @ 150°F (66°C)  
adhesive

Salt spray is also known to be responsible for corrosion of silver-filled conductive sealants in aircraft applications. On the other hand, a silver/silicone rubber conductive adhesive has been reported to be unaffected by a salt-spray environment.(1)

9.17 Water immersion. Generally speaking, water immersion is not likely to change tensile lap-shear properties to any great extent, if at all. Water immersion may have an erratic effect on resistivity, although generally, resistivity decreases as immersion time increases.(1)

9.18 Outgassing. Stearic acid, which is used as a lubricant coating in silver flakes, will outgas at elevated temperatures and can contaminate critical parts. There is no problem with uncoated silver particles. In a study of the outgassing of organic binder in a silver-filled conductive adhesive, no loss is shown at 302°F (150°C), but the loss at 482°F (250°C) was 0.45%, and at 662°F (350°C) 3.6%. Poor processing of conductive adhesives in sealed-hybrid circuits and microcircuits results in chemical outgassing and contamination of thick-or-thin-film resistors and other electronic components.(1)

## MIL-HDBK-691B

**9.19 Pot life.** The pot life or working life of conductive adhesives can be controlled by a proper choice of curing agent. In most cases, a long pot life is desirable. The pot lives of most commercially available electrically conductive adhesives fall in the range of 3 to 8 hours, with a few falling in the 1/2-to 3/4-hour bracket. One highly reactive adhesive, ABLEBOND 463-1, has a pot life of only 14 minutes. This adhesive is sold premixed and frozen in 1-cc containers or in one-pound bulk units. With this short a pot life, the manufacturer recommends mixing of batches of 10 grams or less. An aerospace company has a process specification calling for a minimum working life of 40 minutes. Pot lives of thirteen electrically conductive adhesives evaluated in one study ranged from 1/2 hour for two-component pastes to one year for a one-component paste (1).

**9.20 Maximum service temperature.** Conductive adhesives based on silicones are useful up to about 500°F (260°C), while the maximum service temperature of epoxy-based electrically conductive adhesive is 572-662°F (300-350°C). The upper limit of this range is for brief exposures of two hours, while the lower limit is for twelve hours. After such exposure, acceptable volume resistivities are obtained.(1)

**9.21 Flexibility.** The flexibility of conductive adhesives is dependent upon the hardener/resin ratio (see 9.8). Systems with a low ratio have a high flexibility. There is a need for flexibility in electrically conductive adhesives for bonding materials of unlike coefficients of expansion, which are likely to fail when subjected to thermal cycling. Polyurethane, silicone and polysulfide conductive adhesives were evaluated in an AEC-sponsored study in 1964.(4) In this study the ideal flexible conductive adhesive was felt to be one with a maximum working temperature of 100°F (71°C), electrical resistivity of 0.10 ohm-cm, ultimate elongation at -65°F (-54°C) (strip) of 10 %, tensile strength of 500 psi (3.44 MPa), and peel strength of 20 pounds/inch (3.5 kN/m). None of the candidate materials approached these requirements.(1)(4)

MIL-HDBK-691B

REFERENCES

- (9-1) A. H. Landrock, "Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures - Part XVII, Thermally and Electrically Conductive Adhesives", Picatinny Arsenal Technical Report 4179.
- (9-2) F. M. Gahimer and P. M. Guhl, "Conductive Coatings and Adhesives, Evaluation of." Naval Avionics Facility Materials Test Report No. 108-60, 27 Dec. 1960.
- (9-3) R. M. Stone and H. G. Schlundt, "Evaluation of Conductive Adhesives", Douglas Aircraft Co., Materials and Process Lab Report MP 14, 358, 6 Dec. 1965.
- (9-4) L. W. Hartzell and S. S. Sakornbut, "The Development of Conductive Adhesives Flexible at Low Temperatures", paper presented at 7th National SAMPE Symposium on Adhesives and Elastomers for Environmental Extremes, held at Los Angeles, CA, May 20-22, 1964.

(WP# ID-7324A/DISK-0251A FOR MTL USE ONLY.)

## MIL-HDBK-691B

## CHAPTER 10. BONDING OF HONEYCOMB STRUCTURES

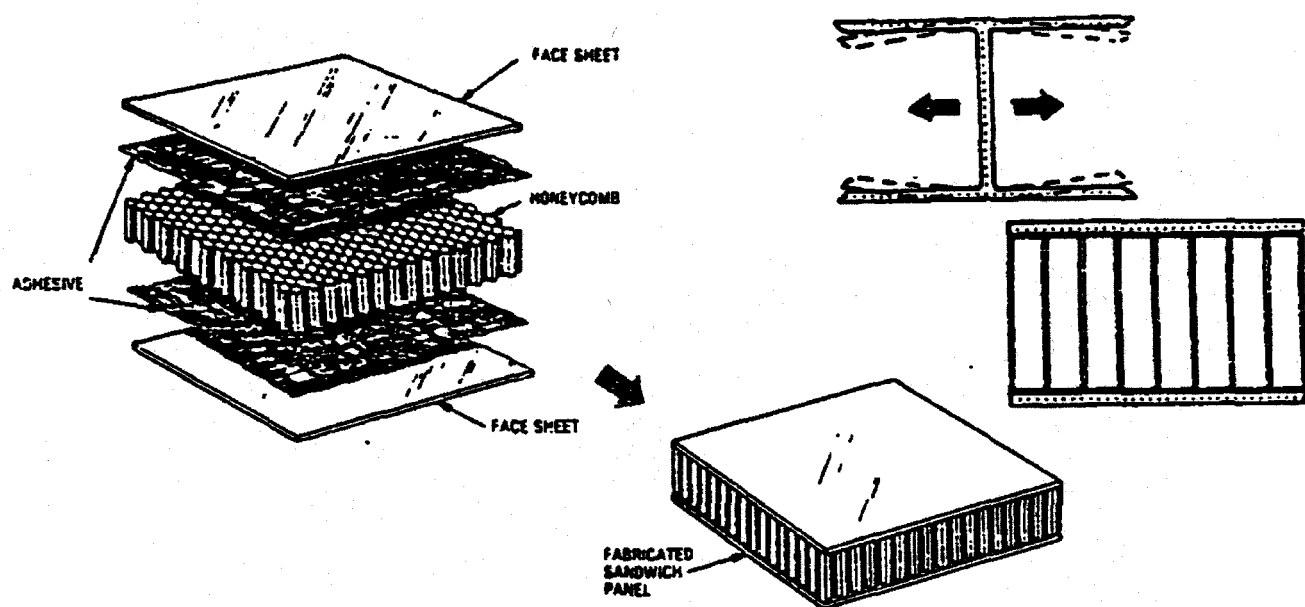
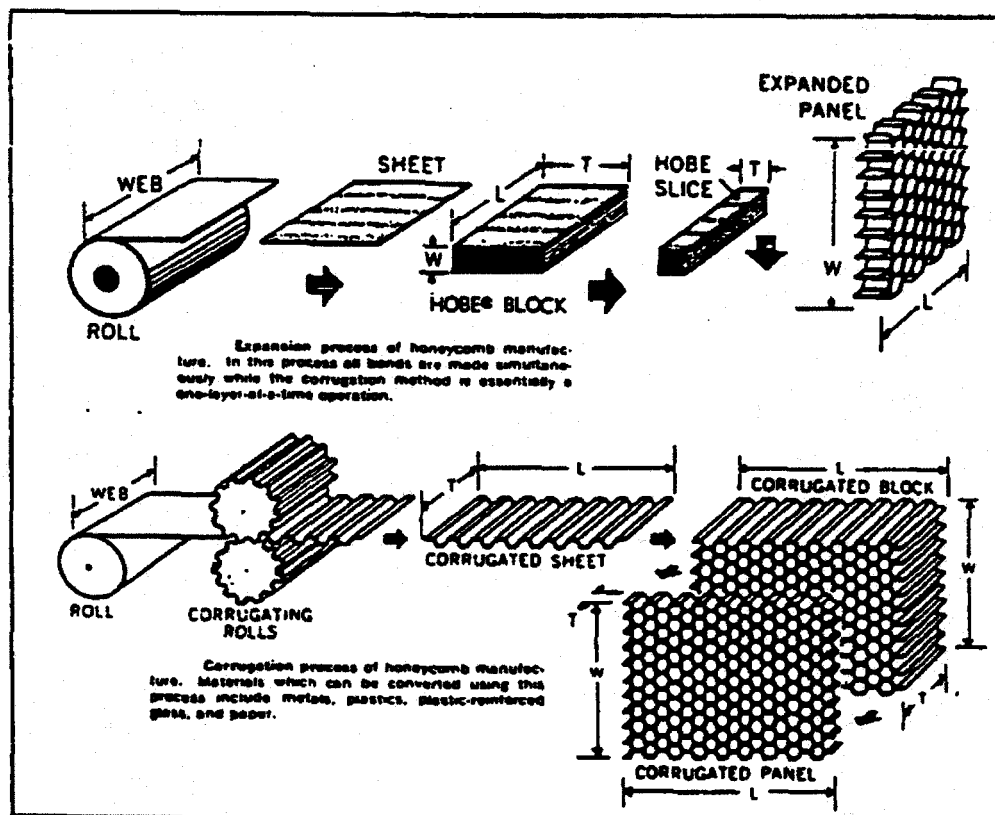
**10.1 Introduction.** Honeycomb is a series of hexagonal cells, nested together to form panels similar in appearance to a cross-sectional slice of a beehive. Honeycomb, in its expanded form, is 95 to 98 percent open space. Types of honeycomb include aluminum, made from alloys such as 5052, 5056 and 2024, used for service temperatures up to 420°F (216°C), fiberglass-reinforced phenolic honeycomb, which has excellent thermal stability and has been used from -423°F (-253°C) up to 400°F (204°C), polyimide resin honeycomb, with an upper limit of 600°F (316°C) for long-term exposure and 700°F (371°C) for short-term exposure, and paper honeycomb, used in building construction.

Figure 34 shows how honeycomb sandwich structures are assembled, using sheet adhesive, in this case. Other types of adhesive are used too, as will be explained below. Honeycomb is manufactured by one of two basic methods, expansion or corrugation, as shown in Figure 35. In the expansion process, material in web or roll form is fed into high-precision machines where continuous ribbons of structural adhesive are applied. Sheets are cut and stacked layer upon layer in HOBEX (Honeycomb Before Expansion) form, and slices are sawed from HOBEX to the required thickness. HOBEX slices are then expanded to honeycomb panels. The expansion process is most generally used in the manufacture of reinforced plastic, kraft paper and aluminum honeycomb. The corrugation process is used primarily for aluminum core with higher densities than can be obtained with the expansion process. Heavy foil gauges (up to 0.006 inch) can be made into honeycomb of 1/8 inch cell size or larger. Densities of up to 38 lbs/ft<sup>3</sup> (609 kg/m<sup>3</sup>) are available with this adhesive-bonded corrugation process. In addition, corrugated aluminum foil is used for making a cylindrical "honeycomb" configuration which has found many energy absorption applications.

Honeycomb is available made from aluminum, reinforced plastic, NOMEX (aromatic-polyimide) paper, and kraft paper. It is available with a cell-edge adhesive pre-applied to the honeycomb slices.

Adhesive-bonded aluminum-honeycomb sandwich structures have been used since about 1947, and their use is increasing. Applications include aircraft structures, missiles, space vehicles, military and naval ground support equipment, radar reflectors, electronic packaging, and building construction. Starting about 1954, the use of adhesive for honeycomb developed very rapidly because of increasing (1) thermosetting and thermoplastic polymers, (2) understanding of flow and filleting importance, (3) understanding of adhesion theory, (4) standardization of heat-pressure-cure procedures, and (6) standardization of test methods.

MIL-HDBK-691B

FIGURE 34. Sandwich construction.FIGURE 35. Methods of manufacturing honeycomb.  
(Courtesy of Hexcel Corporation)

## MIL-HDBK-691B

Until approximately 1964 DOD was responsible for most of the important development work on honeycomb adhesives. After 1964, the adhesives manufacturers began extensive development on their own for non-military markets.(2)

Reinforced polyimide honeycombs and related 3D woven structures are currently being used as radar housing and microwave transmission windows in advanced aerospace vehicles. They are also being used for high-temperature acoustical panels for commercial jet engine nacelle inlets, compression sections, and discharge ducts. They are also being evaluated for structural applications because of their superiority to titanium and aluminum alloy honeycomb cores in shear modulus, long-term durability at high temperatures, and resistance to corrosive attack.(3)

**10.2 Adhesive types.** The adhesive used to bond the honeycomb core to the facing material (as in Figure 34) is usually a modified phenolic or modified epoxy system tailored to develop the desired temperature, impact and strength requirements. Adhesives are available in paste, cell edge, film, and liquid forms. Tables XLI and XLII describe the adhesives available for various applications of honeycomb materials.(1)

**10.3 Filletting.** Figure 36 shows the location of adhesive fillets in honeycomb construction. The proper flow and filletting of the adhesive is a key characteristic of adhesive bonding facing sheets to honeycomb cores. A small-fillet (0.09 lb/ft<sup>2</sup> or 0.44 kg/m<sup>2</sup>) modified epoxy adhesive, UARMCC Metlbond 328, was found to give the core less "effective strength" and "effective stiffness" than the medium-fillet 0.135 lb/ft<sup>2</sup> (0.66 kg/m<sup>2</sup>) epoxy-phenolic (Bloomington BT-424). Adhesive weight and fillet size are related. This is generally true for the same, or same type adhesive, assuming that adhesive manufacturing, use processing, and aging effects can be held constant. When comparing two different adhesives types, the most important characteristic is the fillet size. The weight of the adhesive within each type is also important, but not so much as the fillet size.



## MIL-HDBK-691B

TABLE XLI. Classifications of honeycomb adhesive systems.(1)

Adhesive Code	Adhesive Type	Service Requirements and Comments
A	Modified Epoxy, 350°F (177°C) Cure	350°F (177°C) Service Low Bond Pressure, No Shrinkage
B	Modified Epoxy, 250°F (121°C) Cure	250°F (121°C) Service Low Bond Pressure, No Shrinkage
C	Modified Epoxy, Room-Temp. Cure	150°F (66°C) Service Simplified Bonding, No Shrinkage
D	Nitrile phenolic, 350°F (177°C) Cure	350°F (177°C) Service High Peel
E	Polyester, Room-Temp Cure	Inexpensive
F	Urethane, Room-Temp Cure	Bonds Plastics, High Impact

TABLE XLII. Adhesive selection matrix for honeycomb.(1)

Core Materials	Skin Materials			
	Aluminum	Steel	Reinforced Plastics	Plywood
Aluminum-Honeycomb	ABCD*	ABCD	BCF	BCEF
Kraft Paper Honeycomb	BC	BC	BCEF	BCF
Aluminum Close-Outs	ABC	ABC	BCF	BCF
Plastic Close-Outs	BCF	BCF	BCF	BCEF

\*Letters refer to Adhesive Code in Table XLI above

Fillet size is the most important physical factor in obtaining the maximum properties of honeycomb and sandwich constructions. The modulus of elasticity of the adhesive appears to have little or no importance in obtaining maximum properties.

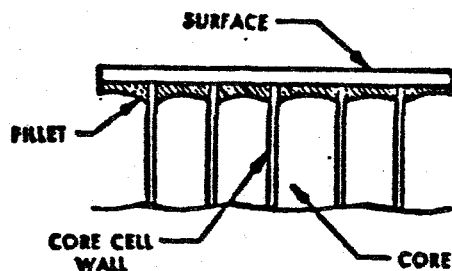


FIGURE 36 Honeycomb bonded to face sheet showing location of adhesive fillet.(4)

10.4 Adhesive application techniques. Adhesives used in bonding honeycomb cores to facing materials are available in many forms, liquids (solutions/emulsions), pastes, and films and tapes.

10.4.1 Films and tapes. Films and tapes are the most popular forms of adhesive used in the aerospace industry. They provide several advantages, including positive bond-line control, thickness uniformity, and ease of storage. They require no special application equipment and provide ready-to-use convenience. However, they are restricted to a limited range of available weights, are difficult to handle in light weights, and are high in cost. Reticulating films, which have recently become popular, offer the same advantages, plus an extra advantage. They have the possibility of optimum utilization of adhesive or honeycomb cell applications.(5) The application of powders to both flat sheet stock and honeycomb cell edge by electrostatic spray and fluidized-bed techniques has been suggested by one company, but the development has been dropped due to lack of interest, probably because of the high cost of capital equipment.

10.4.2 Solutions/emulsions. The advantages of solutions/emulsions include moderate cost, ability to apply adhesive in varying weights, low loss potential, and performance equivalent to films and tapes. The disadvantages lie in the problems of solvent removal. These disadvantages include cost and availability of solvent, energy required to remove the solvent, potential pollution problems, difficulty in obtaining high weight application due to the problem of incomplete solvent removal from thick films, and the possibility of advancement or staging of the adhesive due to the flashing conditions required to remove the solvent. The equipment costs can also be excessive (5).

Although the initial cost of a curtain coater or roller coater is not high, a continuous drying system can be. Both solvent and hot-melt curtain coaters are available. However, because of the low viscosities required for

## MIL-HDBK-691D

application (400-500 cps or 0.4-0.5 Pa.s normally), the use of a 100%-solids thermal setting system is difficult because of the relatively short shelf life at the required application temperature. Solution systems applied at ambient conditions have the advantage of long latency and a viscosity which can be adjusted by addition of solvents.(5)

10.4.3 Pastes. One hundred percent solids adhesives offer many advantages, including those of solvent-free systems, low cost and good performance. On the debit side, some special processing equipment is needed, including a roller coater, material handling and metering and mixing equipment. Roller coating with paste adhesive has been used to apply adhesive to flat skin materials and honeycomb cell edge at ambient and elevated temperatures. The choice of an adhesive for this technique depends on adhesive rheology, viscosity and use life at the application temperature. The latter parameter restricts, to some extent, the use of ambient-curing adhesives. Because of the relatively short pot lives that most paste adhesives have, application temperatures of 120-160°F (49-71°C) are used with curing temperatures of 250°F (121°C).(5)

MIL-HDBK-691B

REFERENCES

- (10-1) Hexcel Products, Inc., "The Basics on Bonded Sandwich Construction", TSB 124, Rev. 1984.
- (10-2) G. L. Grimes, Chapter 20, "Honeycomb Structures", HANDBOOK OF ADHESIVE BONDING, edited by C. V. Cagle, McGraw-Hill, NY, NY, 1973.
- (10-3) I. Serlin et al., Chapter 37, "Aromatic Polyimide Adhesives and Bonding Agents", HANDBOOK OF ADHESIVES, 2nd Edition, edited by I. Skeist, Van Nostrand Reinhold, NY, NY, 1977.
- (10-4) Bloomingdale Division, American Cyanamid Co., Handbook of Adhesives.
- (10-5) G. H. Green, "Advancements in Applications of Adhesive to Core Cell Edges and Flat Sheet Material", Preprint Book, 7th National SAMPE Technical Conference, held at Albuquerque, NM, Oct. 14-16, 1975, pp. 118-125.

(WP# ID-7333A/DISK-0251A. FOR AMMRC USE ONLY.)

## MIL-HDBK-791B

## Chapter 11. REPAIR OF ADHESIVE-BONDED STRUCTURES

**11.1 Introduction.** Repairing adhesive-bonded structures is of interest in two main areas, (1) fiberglass-reinforced plastics (FRP) for general applications, and (2) composite structures, primarily involving aircraft. Currently the greatest interest is in honeycomb structures. Typical uses of honeycomb construction in Army Aircraft Weapons Systems are rotor blades, bulkheads, transverse shear webs, torsional shear webs, floors, work desks and work platforms, ramps, access doors, fuel-cell bladder-containment panels, wing skins, flaps, stabilizers, cabin roofs, and cockpit-containment panels.(1)

**11.1.1 General applications.** Usually four types of damage are found:

- o Cracks or fractures
- o Delamination
- o Small holes
- o Demolished sections requiring replacement

**11.1.2 Factors to be considered.** Three aspects of major importance in repairs are:

- o Method of surface preparation
- o Choice of adhesive and other materials
- o Method of pressure application

**11.2 Field repair.** The development of a field-repair system ranges from a system of classifying damage into categories, to packaging repair materials and equipment into a complete semi-portable kit. Types of damage found include:

- o Minor dent, scratches, punctures and delaminations within specific design limitations, which require only minor rework
- o Dents, scratches, punctures and delaminations affecting one face only, possibly accompanied by some core damage, and which exceed the limitations of the paragraph above
- o Dents, scratches, punctures and delaminations which exceed the limitations of the second paragraph, or which affect both faces and the core
- o All damage which exceeds the limitations of the third paragraph.

Field repairs are carried out with an epoxy adhesive which cures at lower pressure and temperature than the original bonding adhesive. The epoxy adhesive is used as a filler to replace damaged core, and to bond on a patch plate to the panel surface. Curing of the adhesive is effected by means of a flexible electrical-resistance heating blanket and vacuum pressure. A vacuum pump and automatic temperature controller are contained in the repair kit.(2)

## MIL-HDBK-791B

Sandwich panels in aircraft are subject to damage from gunfire, contact with objects on runways, or in the water, or accidents in ground handling, such as dropped tools, contact with ground vehicles, and mishandling by personnel. Field repair for this type structure must be as simple as possible and must be carried out in a relatively short time without removal of the panel from the aircraft. Such repairs must have adequate strength to carry design loads and must be capable of withstanding all environments encountered in service.(2)

A recent Army publication(1) covers standardized adhesive repair of honeycomb structures. Part I of this publication covers field level repairs. These repairs are to be made at the Aviation Intermediate Maintenance (AVIM) level, and in some cases, when approval is granted, at the Aviation Unit Maintenance (AVUM) level. The repair methods are intended for honeycomb structure fabricated with skin, i.e., aluminum, titanium, fiberglass, etc. (smooth and rigidized), of thicknesses ranging from 0.008 inch (0.020 cm) to 0.040 inch (0.10 cm).

**11.3 Depot repair.** A program has recently been sponsored by the Naval Air Development Center to develop and validate depot-level repair procedures for graphite/epoxy structures for use at Naval Air Rework Facilities (NARF's). While no decrease in the original stiffness is permitted within the structure, moderate local increases in stiffness due to the repairs are acceptable. Weight increase must be minimized, especially on honeycomb sandwich structures. Repairs need not be aerodynamically smooth, although forward-facing steps beyond the outer moldline are to be ramped or chambered, and are not to exceed 0.10 inches (2.5 mm) for most repairs. Repair procedures to be used for depot-level use are generally assumed to use bonded or cocured repairs for most composite material applications.(3)

The recent Army publication(1) discussed under 11.2 covers Standardized Depot Repair Procedures for Adhesive Bonded Honeycomb Structures - On-Aircraft Repair in Part II and Off-Aircraft Repair in Part III.

**11.4 Materials.** Materials used for field or depot repair include (1)(4)(5)(6):

- o Alloys (titanium and aluminum)
- o Fiberglass
- o Honeycomb replacement material
- o Prepregs
- o Sealants (polysulfide)
- o Peel-ply fabric
- o Adhesives (various types of RT or high-temperature curing epoxies, in various forms)
- o Aerodynamic smoothers (used on the external surface of the aircraft)
- o Potting compounds (core filler) - used to fill dents and core damage. These are usually resin adhesives containing an inert filler. They typically are cured at RT, or quick-cured at moderate temperatures. Application is usually by trowel or spatula.
- o Potting compounds (injectable honeycomb) - similar to above, but with a lower viscosity for injection applications



## MIL-HDBK-791B

- o Sealants/aerodynamic smoothers (both corrosion and noncorrosion inhibiting types are available for general application and for service to 350°F (177°C)
- o Paints and paint primers
- o Alkaline cleaners
- o Sandpaper
- o Gloves (rubber, cotton)
- o Solvents (MEK, TCE, Safety - Fed Spec O-T-620)
- o Vacuum bagging repair kit
- o Injection needle, stainless steel
- o Drill
- o Release film
- o Speedtape, masking tape
- o Breather fabric
- o Metal patches
- o Thermoplastic repair materials and hot melts

### 11.5 Repair techniques.

11.5.1 General procedures for FRP. The basic steps in making repairs of sandwich structures are (7):

- o Remove paint or other surface coatings completely
- o Remove broken material and feather the edge around the damaged area
- o Using mat, fabric and resin (or pre-mix), duplicate the original construction, where possible.
- o Apply heat and pressure, where applicable
- o Sand, buff and paint

11.5.2 Small cracks. These are usually repaired with chopped strands mixed in with catalyzed resin. Mineral fillers added to the resin provide a putty-like consistency that is desirable for working on vertical surfaces. Pigments or dyes may also be used.(7)

11.5.3 Delamination. Delamination without surface rupture can be caused by impact on FRP parts. If the damage is severe, it is advisable to cut out the delaminated area as if it were a hole. Where the delamination is only slight, small holes can be drilled into the material and catalyzed resin can then be forced through the holes and into the delaminated areas. Pressure is then applied and the resin cured.(7)

11.5.4 Small holes. These are usually repaired by using fabric or mat cut to size, impregnated with resin, held in place and cured. Often an additional ply of impregnated fabric is applied to each side of the repair and is cured in place. If the damage is extensive, sometimes the opening can be covered with a thin, flexible, cured laminate in a manner simulating the use of metallic plate to repair punctured areas in boilers. This is followed by a wet lay-up on top, with subsequent pressure and heat application.(7)

11.5.5 Radomes and antenna housings. The repair of these items is more specialized and requires more precision. It is almost always necessary to maintain the exact original wall thickness, since any changes will increase electronic reflective and absorptive losses in the radome. The precise

matching of wall thickness can be achieved with thin fabrics. If the damaged part is made from glass-cloth honeycomb, a replacement piece must be tailored to fit, and roughened to produce a fuzzed edge. The edges of the replacement honeycomb piece should be coated with a thin layer of resin prior to combining it with the fabric facing.<sup>(7)</sup>

11.5.6 Polyester-glass. Where repair of polyester-glass combinations is considered, polyester resins are usually used. This is because a wide variety of cure rates can be achieved by the use of appropriate catalyst systems. Room-temperature cures are possible and an infrared lamp is sufficient to provide heat for rapid curing.<sup>(7)</sup>

11.5.7 FRP/metal. In those cases where FRP is to be bonded to metal sections, epoxy resins are normally employed because of their great bond strengths to metals, especially aluminum.<sup>(7)</sup>

11.5.8 Pressure application. In order to obtain smooth repairs with high glass loadings, some pressure should be applied during cure. Specific universal methods to obtain pressure cannot be recommended, as each job presents its own problem. Standard procedures are used for clamping joints during curing of the adhesive. These include beam bracing, sand bags, rubber bands, and tape. Vacuum bags are currently in widespread use.<sup>(7)</sup>

11.5.9 Air exclusion. Because the cure of the resins employed tends to be inhibited by the pressure of air, it is wise to place a layer of cellophane or other similar barrier over the repair area during the cure. The film will also impart a smooth surface to the molding.<sup>(7)</sup>

11.5.10 Repair of metals. FRP can be used for the emergency repair of tanks, boilers and pipes. The techniques are similar to those employed in the repair of glass-plastic parts. This method of repair can be used to repair war battle damage in both civilian and military applications.<sup>(7)</sup>

11.5.11 Phosphoric acid anodize. In adhesive bonded aircraft structures there have been a large number of failures due to corrosive delamination of the bonds. The problem has been especially severe in honeycomb panels, where delamination of peripheral bonds has allowed moisture to penetrate to the thin foil core. The core is frequently destroyed, usually as a result of freeze-and-thaw conditions caused by ground-air-ground cycling of the aircraft, or solely because of the presence of the moisture.<sup>(8)</sup>

The phosphoric acid-anodize method<sup>(5)</sup> (see also 5.3.5.1.2) has been one of the most significant recent developments in adhesive bonding aluminum aircraft structures. This procedure has eliminated the bond surface as a weak bond-durability link. This technology has been extended to maintenance applications. At large repair depots, autoclaves, surface-preparation tanks, and clean rooms are readily available. However, the damaged components themselves cannot ordinarily be placed in the cleaning tanks and their surfaces must be hand-cleaned. Autoclaves can rarely be used. In repair operations with aircraft structures curing pressure is applied by a vacuum bag or other means. The heating required to obtain durable bonds is usually obtained by heating blankets or forced hot air.<sup>(8)</sup>

MIL-HDBK-6191B

When parts to be repaired are so large that they cannot be removed from the aircraft, phosphoric acid-anodizing can be adapted to a hand or non-tank procedure. This can be done by using the acid as a paste, rather than as a liquid, as shown in Figure 37. The acid paste is used to saturate several layers of gauze, which serve to insulate the surface to be anodized from a stainless steel screen. A rectifier or battery, connected to the screen, is used to supply the necessary direct current. Durability of bonds prepared in this way approaches that of the best tank processes.(8)

Detailed procedures are given in an Air Force-sponsored report prepared by Boeing<sup>(9)</sup> for the Phosphoric Acid Non-Tank Anodize (PANTA) process.

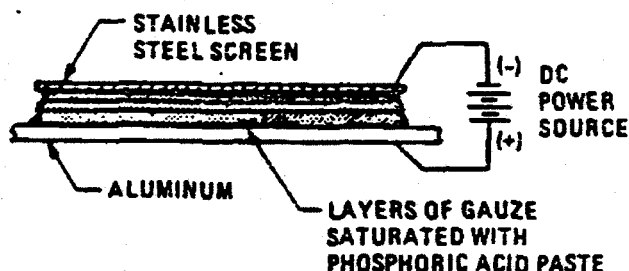


FIGURE 37. Set-up for non-tank phosphoric acid anodizing of aluminum.<sup>(8)</sup>

Phosphoric acid non-tank anodize (PANTA)<sup>(9)</sup>

- (a) Solvent wipe with MEK, trichloroethane, or equivalent
- (b) Abrade with nonwoven abrasive, such as nylon abrasive pads, or equivalent
- (c) Dry-wipe with clean gauze to remove dust and debris
- (d) Apply uniform coat of gelled 12% phosphoric acid\* or PR 50\*\* to aluminum surface
- (e) Place two or three layers of gauze over top of coating; apply another coat of gelled phosphoric acid to completely saturate and wet out the gauze.
- (f) Secure a piece of stainless steel over the coating. Apply another coating of the gelled phosphoric acid. (NOTE: Be sure that the stainless steel screen does not contact any part of the aluminum surfaces being anodized.)
- (g) Connect screen as cathode (-) and aluminum as anode (+), as shown in Figure 37.
- (h) Apply a DC potential of 6 volts for 10 minutes (4 to 6 volts for 10-12 minutes are satisfactory). (NOTE: A rectifier may be used to supply the voltage and current during anodizing.) Current density should be in the range of 1 to 7 amps/ft<sup>2</sup>. In an emergency, a fresh or fully charged dry or wet cell battery may be used to anodize small areas.
- (i) At the end of the anodizing time, open the circuit and remove the screen and gauze.

## MIL-HDBK-6191B

- (j) Moisten clean gauze with water. Lightly wipe off the gelled acid with the moistened gauze without delay. The rinse-delay time is limited to less than 5 minutes. Do not rub the anodized surface. Immersion- or spray-rinsing should be used, if possible.
  - (k) Air-dry a minimum of 30 minutes at RT, or force-air oven-dry at 140-160°F (60-71°C).
  - (l) Check quality of prepared surface. A properly anodized surface will show an interference color when viewed through a polarizing filter rotated 90° at a low angle of incidence to fluorescent light or daylight. An inspection being accomplished is shown in Figure 38.
  - (m) If no color is observed, repeat steps (d) through (l). (NOTE: Machined surfaces or abraded surfaces are sometimes difficult to inspect for color. Rotation of the polarizing filter is required because some pale shades of yellow or green are so close to white that without a color-change inspection, they might be considered "no color," which would falsely indicate no anodic coating. (NOTE: Do not touch the dried anodized surface. Do not apply tape to the surface.)
- \* can be made by adding Cab-O-Sil to acid until thickened  
 \*\* ready-made product available from Products Research Corporation

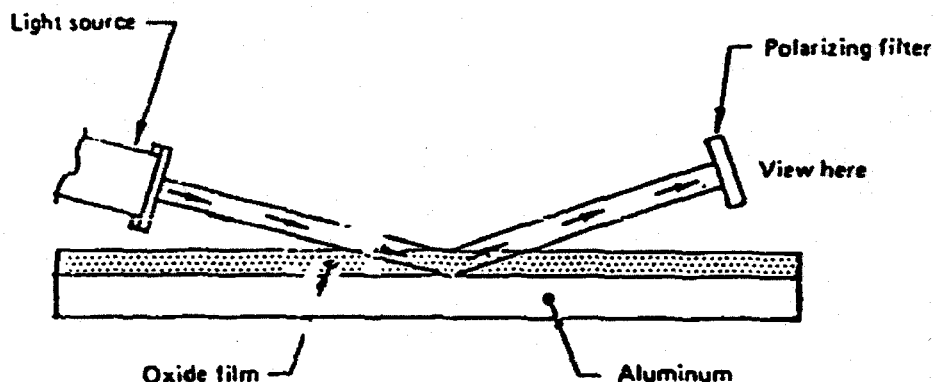


FIGURE 38. Polarized light test-verification of anodic oxide film.(9)

11.5.12 Large-area composites. Large damage areas on graphite/epoxy panels can be repaired by using techniques outlined in an Air Force-sponsored guide.(10) The recommended repair configuration uses a scarf joint machined into the parent panel as the damaged panel is removed. Repair plies of prepreg are stepped to fit the scarfed surface and made to extend slightly beyond the end of the scarf, leaving an essentially flush surface. The repair plies are cocured in place with a layer of film adhesive. Alternatively, a precured external patch can be used, which may be simpler to install, in some cases, although at the expense of aerodynamic smoothness and with some loss in strength.(3)(6)

## MIL-HDBK-6191B

Such a patch may consist of 8-mil titanium foil interleaved with layers of film adhesive to form a bonded patch external to the outer surface. This type of repair, limited to a 2-inch diameter damage, has been used for many repairs on the empennage structure of F-14 aircraft. Other repair configurations that have been developed include external patches made of aluminum, titanium, and precured composite materials.

**11.5.13 Army aircraft weapons systems honeycomb structures.** Repairs of damaged honeycomb structures are accomplished by the following steps:

- o Classification of damage
- o Surface finish removal from repair area
- o Layout of damage area
- o Selection of proper repair method
- o Removal of the damaged skin and core
- o Core replacement
- o Preparation of skin surfaces for bonding
- o Repair of skins
- o Surface refinishing and sealing after repairing

Detailed repair procedures are given in (1).

**11.5.14 Air Force Repair Guide.** An Air Force repair guide (6) gives details on two kinds of repairs used in large-area composite repairs:

- o A nearly flush repair for which a scarf joint surface is machined in the parent laminate, and replacement plies with adhesive are cocured into place.
- o An external patch which is precured and subsequently bonded over the damaged area.

**11.5.15 Commercial airline practice.** An airline operations center has six categories of repair techniques.<sup>(10)</sup> While not military, this operation may be of interest to users of this handbook.

- o Small area line maintenance rework where fiberglass overlay patches or rivet-bonded sealant (polysulfide) patches suffice.
- o Life-limited repairs necessary for aircraft dispatch, but requiring short time inspection intervals and replacement at the first maintenance opportunity.
- o Partial repairs using a heating blanket and vacuum-bag techniques for localized areas, or when the chance of damaging the original bond with more extensive heat application is a factor. The structure can be acid paste-etched and primed with a corrosion-resistant coating. The repair patch can be acid-etched, phosphoric acid-anodized, and painted with corrosion-inhibiting primer. Perforated metal repair skins are sometimes used.

**MIL-HDBK-6191B**

- o Partial repairs using the autoclave when time constraints do not permit anodizing and corrosion inhibiting priming. These parts are monitored for deterioration and rebuilt as time permits.
- o Partial repairs using the autoclave to repair one side of the part with honeycomb core replacement as needed. Structure which cannot be immersed in cleaning and anodizing tanks is acid paste-etched and primed with a corrosion-inhibiting coating.
- o Fully repaired or rebuilt parts where the old spar, end ribs, etc. are used as the basis for building a reconditioned structure. All surfaces are hot acid-etched, anodized and corrosion inhibiting primed prior to bonding. Different primers and adhesives are used in the 250°F (121°C) vs. 350°F (177°C) curing systems.



MIL-HDBK-6191B

REFERENCES

- (11-1) R. F. Wegman, M. C. Ross and E. A. Garnis, "Standardized Adhesive Repair of Honeycomb Structure," U. S. Army ARRADCOM, Dover, NJ, unnumbered report, Nov. 1980.
- (11-2) J. P. Reese, The Martin Co., Baltimore, MD, "Field Repair of Bonded Sandwich Construction," in Proceedings, WADC-University of Dayton Joint Symposium, Structural Adhesives and Sandwich Constructions 12-13 June 1957, Dayton, Ohio, pp. 336-362 in WADC-TR 57-513, 12 June 1957.
- (11-3) J. D. Labor, Northrop Corp., "Composite Repair Concepts for Depot Level Use," 26th National SAMPE Symposium, Apr. 28-30, 1981; proceedings, Vol. 26, pp.705-715.
- (11-4) Proceedings-Composite Material Maintenance/Repair Workshop, sponsored by Naval Air Systems Command, San Diego, CA, Sept 1978.
- (11-5) R. E. Morton, et al, Boeing Commercial Airplane Co., "Adhesive Bonded Aerospace Structures Standardized Repair Handbook," AFML-TR-77-206/ AFFDL TR-77-159, Oct. 1977.
- (11-6) J. D. Labor and S. M. Myhre, Northrop Corp., "Repair Guide for Large Area Composite Structure Repair, AFFDL-TR-79-3039, March 1979. (USGO)
- (11-7) R. H. Sonneborn et al, FIBERGLAS REINFORCED PLASTICS, Reinhold Publishing Corp., NY, 1954.
- (11-8) R. E. Horton, The Boeing Co., "Demonstration of an Improved Method of Repair of Bonded Aircraft Structures," SAMPE Quarterly, 10(4) :20-26 (July 1979).
- (11-9) M. C. Locke et al, Boeing Commercial Airplane Co., "Anodize Optimization and Adhesive Evaluation for Repair Applications," AFML-TR-78-104, July 1978.
- (11-10) M. H. Kuperman, United Airlines, "Structural Adhesive Bond Repair of Aircraft Flight Control Surfaces," 24th National SAMPE Symposium, San Francisco, CA, May 8-10, 1979; proceedings. Vol. 24, Book II, pp. 1126-1139.

## MIL-HDBK-691B

## Chapter 12. WELDBONDING

**12.1 Introduction.** Spot-weld adhesive bonding, more commonly called weldbonding, is a method of fabricating hardware that uses both welding and adhesive-bonding techniques. A layer of adhesive, either in paste or film form, is applied to one of the metal members to be joined. The other metal member is placed on top, forming a lap-type joint, and the assembly is clamped or resistance-tack-welded to maintain part alignment. The two members are then joined by resistance welding through the adhesive, using a conventional spot or seam welder. The welds are commonly spaced 1 to 2 inches (2.5 to 5.1 cm) apart, center-to-center (Fig. 39). After curing at ambient or elevated temperature, the adhesive forms a gas-tight seal. Hardware fabricated by this method has higher tensile-shear strength, increased fatigue life, higher buckling strength, and improved corrosion resistance, compared to equivalent resistance-welded structures. Both cost and weight savings are significant compared to riveted or mechanically fastened structures.<sup>(1)</sup>

Weldbonding was initially developed in the Soviet Union and used in the fabrication of transport aircraft (AN 22, AN 24 and YAK 40). In recent years several American aircraft manufacturers (Lockheed-Georgia, Northrup, Martin-Marietta, TRW) have studied the process and written reports, some in-house, and some sponsored by NASA and the Air Force. Annotated bibliographies have been prepared covering developments in weldbonding.<sup>(2)(3)</sup>

When properly applied, weldbonding will provide a joint structurally comparable to an adhesive bonded joint, while eliminating the complex and expensive tooling generally required for adhesive bonding.<sup>(4)</sup> Weldbonding may be accomplished by applying the adhesive to the faying surfaces prior to welding, (weld-thru) or a low-viscosity adhesive may be used to infiltrate the faying surfaces by capillary action after the welding has been accomplished. Both techniques have been used in Russia.<sup>(4)(5)</sup>

**12.1.1 Weldbond configuration.** Figure 39 is a schematic (not to scale) detail of a spotweld and the surrounding adhesive-bonded region of a single-lap weldbonded joint. In the most-used process, a paste adhesive is applied to the metal sheet material and the metal is then spotwelded through the uncured adhesive. The spotwelding pressure and heat result in displacement of the adhesive and fusion of the metal to form a solid weld nugget. In Figure 39, the solid circle represents the visible mark at the edge of the surface of contact between the spotwelding electrode and the metal sheet. The inner dashed circle outlines the weld nugget. The area between the two dashed circles, or "halo," is effectively unbonded due to their displacement and heating of the adhesive during the spotwelding process. Beyond the halo is a region of transition to full adhesive thickness. The exact shape and dimensions of the features are functions of several variables. These include stiffness and thickness of the metal sheet and uncured adhesive and such welding parameters as pressure, current, resistance, time, and electrode shape.<sup>(6)(7)</sup> Figure 40 shows a single-lap and comparable double-lap weldbonded joint.

MIL-HDBK-691B

Large helicopters contain over 5000 fasteners of various types and sizes, so intense installation labor is necessary. Over half of an airframe's direct support maintenance cost presently is related to fasteners and secondary structures. For this reason it is very desirable to reduce the number of fasteners. Rivet bonding decreases the number of rivets, but does not eliminate them. Resistance spot welded parts undergo melting in the weld zone, which can result in wrinkling when the pieces are clamped. Also, the recast metal in the area of the weld is susceptible to fatigue.<sup>(8)</sup>

High-strength weldbond joints are necessary for aircraft applications, using aluminum alloys and titanium. For such applications special surface preparation treatments, special adhesives, and carefully controlled curing conditions must be used. For automotive applications using steel and aluminum, the requirements and procedures are much less stringent. Elaborate surface preparation techniques are not necessary and adhesives such as vinyl plastisols and modified epoxies may be used, resulting in strengths 67% stronger with weldbonds than with spotwelds.<sup>(9)</sup>

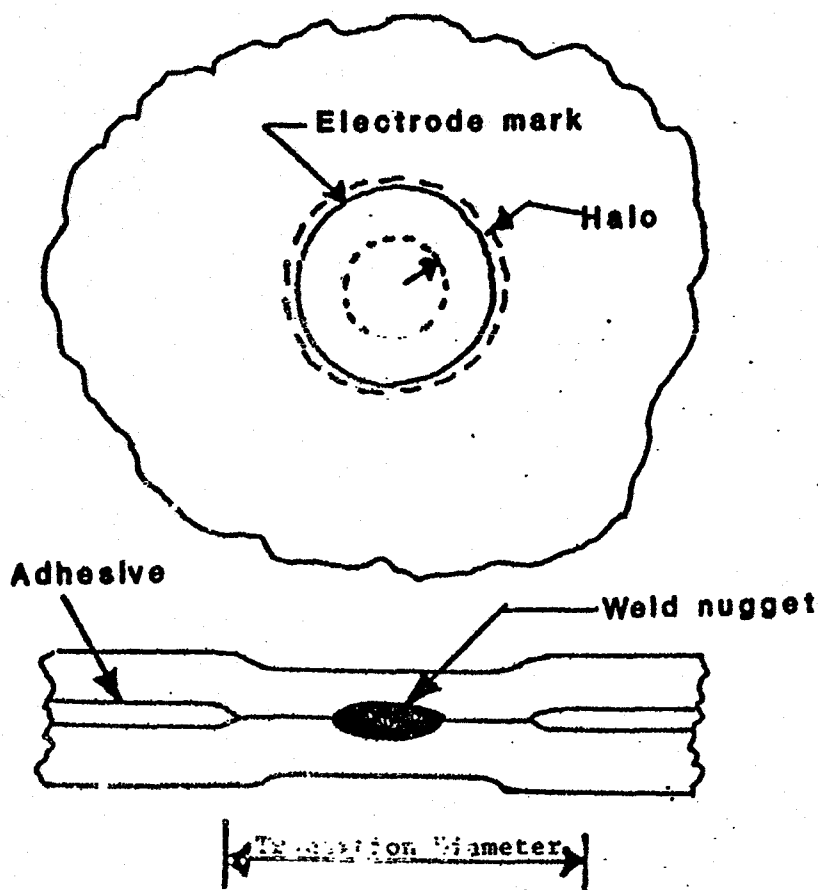


FIGURE 3b. Schematic cross-section of a spotweld in a single-lap weldbonded joint.

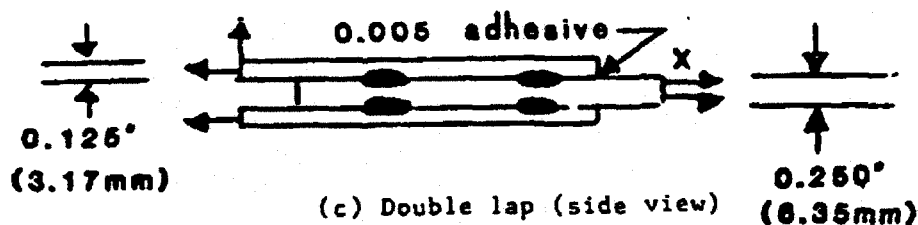
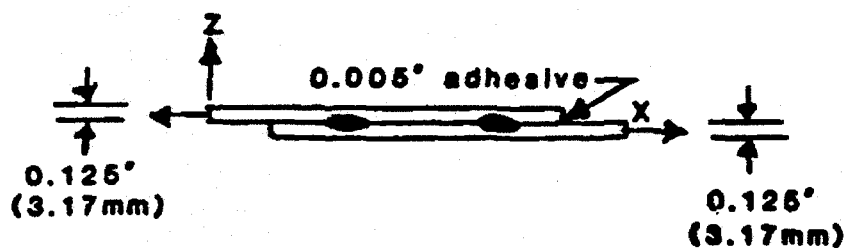
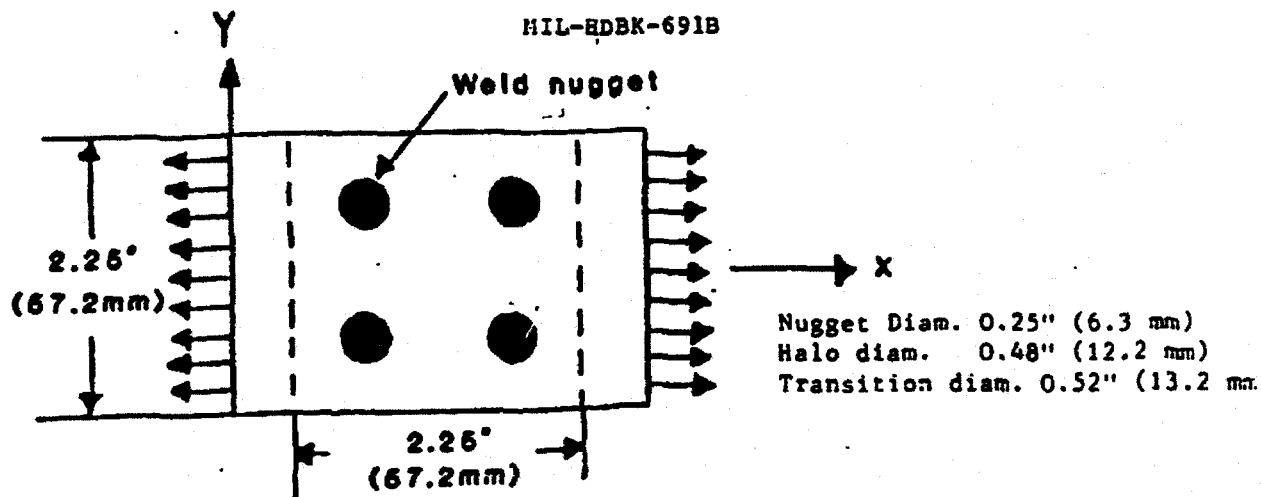


FIGURE 40. Comparable single-lap and double-lap weldbonded joint.(6)(7)

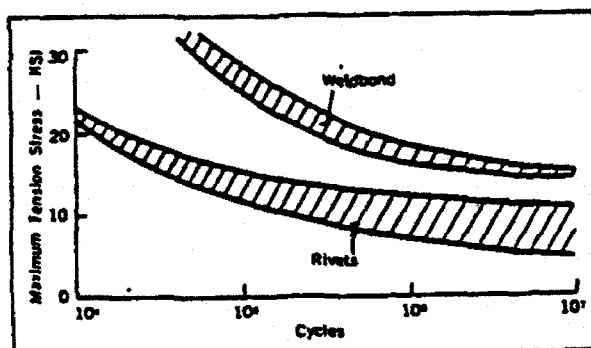


FIGURE 41. Axial load fatigue strength of aluminum alloy weldbond, as compared to rivets. (10)

NIL-HDBK-691B

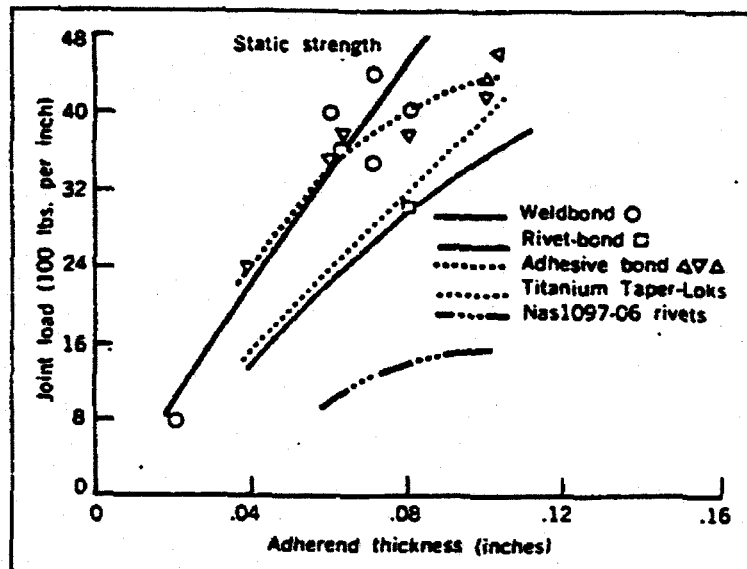


FIGURE 42. Static joint strength of weldbond as compared to other types of joints. (10)

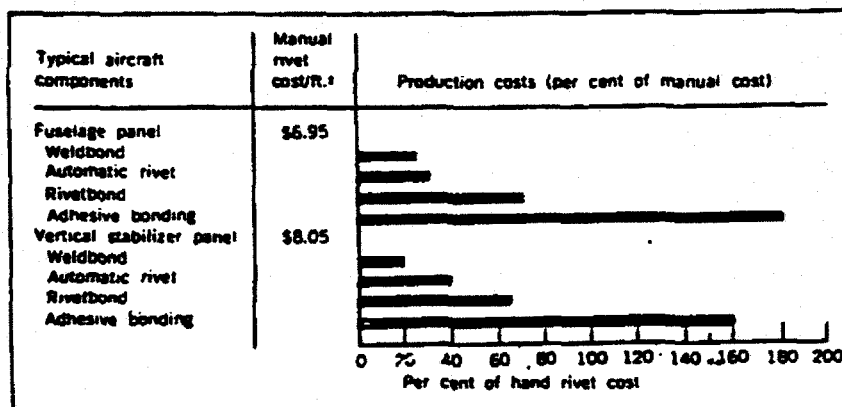


FIGURE 43. Comparative joining technique on typical aircraft structure. (1973 prices) (10)

MIL-HDBK-691B

Weldbond is competitive in static strength with titanium fasteners in sheet thicknesses up to 0.156 inch (0.40 cm). Beyond this point, the spot-welding limitations and static-strength capacity make weldbond less desirable. The weight advantage for weldbond is significant. It is lighter than mechanical fasteners because of its lack of additional fastening material. Joint overlaps are reduced because of the closer spacing between spot-weld rows permitted with weldbond.(12)

Figure 44 is a plot of ultimate tensile load against temperature for different joining methods, using titanium. It is plotted in this way to obtain a direct strength comparison of the various techniques. Weldbond joints show a superior strength at room temperature in all categories tested and, except for two temperature levels, a superiority to all categories at all temperatures.(13)(14)

The greatest obstacle to the use of weldbonding in aircraft primary structures is the previous bad reputation attributed to resistance spot welding in the aircraft industry. This reputation is primarily emotional opinion and is generally believed to be unsupported by facts.(10)

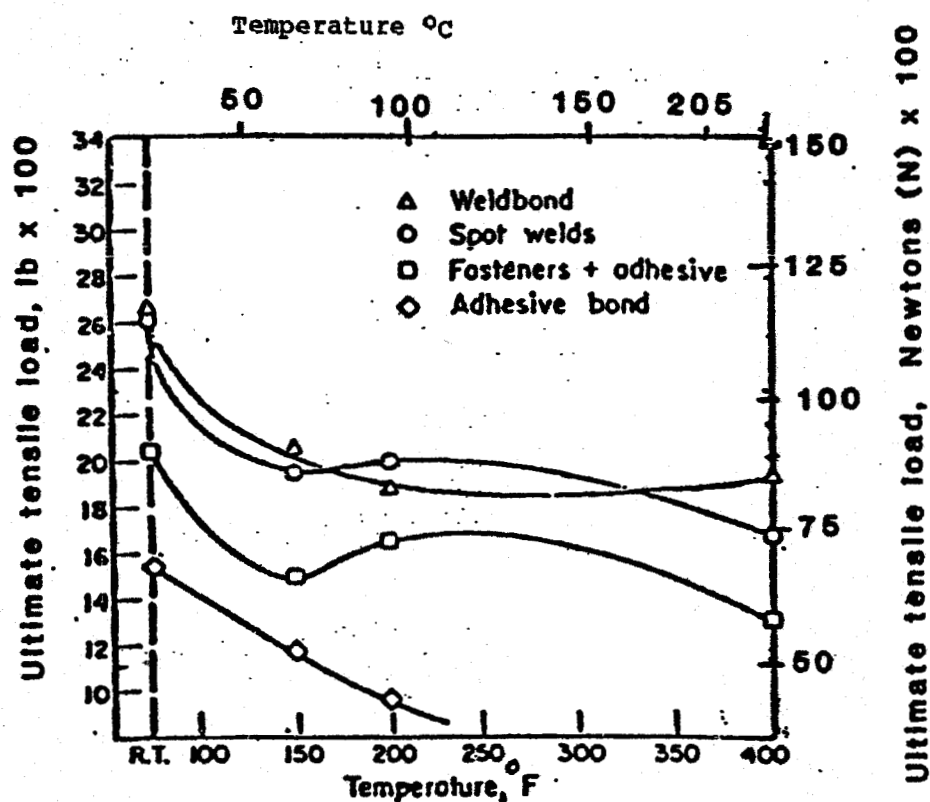


FIGURE 44. Comparative joint strength, butt shear double row, for 0.025" to 0.063" titanium alloy (Ti-6Al-4V). (13)(14)



## MIL-HDBK-691B

It has been demonstrated that high-quality welds can be made in high-strength aluminum alloys up to 72 hours after layup of the parts with adhesive at the parts interface. Figure 41 shows how the axial-load fatigue endurance of weldbond joints is increased many times over that of mechanical fasteners. Figure 42 shows the advantage of the joint static strength of weldbond joints over other types of joints.

Because the weldbond process is highly adaptable to mechanization and automation, a substantial production cost savings is realized when compared to other joining methods, as shown in Fig. 43.

**12.2 Advantages and limitations.** The advantages of a weldbond structure over a similar structure joined by rivets or mechanical fasteners are listed as follows:(11)

- o Increased tensile-shear strength (static strength)
- o Increased fatigue life
- o Gas-tight structure suitable for gas or liquid containers
- o Increased rigidity
- o Improved corrosion resistance of the lap-type joint
- o Inexpensive tooling requirements for fabrication
- o Weight savings
- o Smooth hermetically sealed inner and outer surfaces improve aerodynamics and simplify hardware attachments
- o Complete interface bond improves load transfer between inner and outer members.

**12.3 Surface preparation.** (See 5.3.5.1.17 above for details of methods for aluminum and titanium.)

Chemical cleaning of surfaces for welding and adhesive bonding is necessary to assure high-strength joints. Welding and bonding each require different specialized surface preparation techniques. To produce Class A resistance welds it is essential to have a low surface resistance. On the other hand, to produce maximum-strength adhesive-bonded joints, it is necessary to have a chemically active surface which may have a high surface resistance. Final selection of the cleaning process should be based on the end use of the hardware and on consideration as to the relative importance of weld quality and adhesive joint strength.(11)(15)

As discussed above under 12.1, it has been shown that for non-critical weldbonds used in automotive applications involving aluminum alloys and steel, no cleaning or special surface preparation is necessary.(9)(16)

The low-voltage phosphoric acid/sodium dichromate (P/SD) anodize described above under 5.4.5.1.17.1 is a versatile process, since it is capable of producing the required boehmite oxide layer ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), which is tenaciously bonded to the aluminum alloy substrate on a variety of alloys. However, it is essential to remove the "as received" oxide layer (bayerite) before anodization to assure maximum corrosion resistance and bond durability. Since the boehmite layer thickness is controllable, Class A spot welds can be produced consistently, even with corrosion-inhibited weld-bond paste adhesive in place. With the addition of chromates to adhesives improved

## MIL-HDBK-691B

corrosion resistance under salt spray and humid environments has been possible. With the P/SD anodize process adhesives bondability and weldability have been achieved, even after 300 hours exposure to these environments.

**12.4 Adhesive selection.** Epoxy, modified epoxy, and urethane adhesives are commonly employed in weldbonding aluminum. Epoxy and polyimide adhesives are used for titanium. Polyimides are particularly suitable for titanium because of their very high temperature resistance (matching the resistance of titanium). Epoxy and modified epoxy adhesives are available in one- or two-part liquid, paste, capillary, or unsupported film form.(11)

The most suitable adhesive for general weldbond applications is the modified epoxy one-part paste type containing metal filler. Most adhesives used for weldbonding are arbitrarily selected from adhesives that were developed for other purposes, resulting in a compromise when used for weldbonding. Adhesives specifically developed for weldbonding should show improvements over those presently available.(11)

General requirements for a good adhesive system for weldbonds are as follows:(15)

- o Good lap-shear strength - 3000 psi or 20.7 MPa minimum
- o Adequate peel strength - 10 in-lbs/in or 4.44 J/m minimum
- o Good durability
- o Bondline filling capability - does not starve the joint by draining, and fills voids easily
- o Surface preparation capable of maintaining stability for 3 weeks minimum before adhesive is applied and cured
- o Multiple cure capability - 1-3 cures can be applied to a completed structure requiring several curing cycles without damage to the adhesive and surface properties.
- o Class A weld-through capability - Class A welds can be made through the prepared surface and adhesive with the resistance spot-welding machine.

Fillers used in epoxy-type adhesives include silica (CAB-O-SIL, 7% by wt) to prevent run off, 3% strontium chromate to provide corrosion inhibition, and conductive metal powders. Viscosity of adhesives in paste form has an important effect on the weld and bonded joint. The viscosity must be low enough to allow the force of the electrodes to push the adhesive out of the interface contact area, yet sufficiently high or thixotropic so that it will not flow out of the joint during the cure cycle.(17)

Film adhesives have been found by some workers to be impractical because spot welds could not be made consistently, due to the carrier.(18) On the other hand, film adhesives have been found to give substantial benefits because they improve workmanship in the production facility. Bondline thickness can be controlled easily. Complete adhesive coverage can be obtained and placement easily controlled. Cleanup is also easier. The eutectic welding equipment incorporated into the use of film adhesives provides a total weldbonding system capable of reproducible nugget quality without inhibiting the benefits of highest quality adhesive bonding.(19)

## MIL-HDBK-691B

The first requirement of any adhesive for the weld-through process of weldbonding is that the adhesive have the capability of being moved under pressure of the welding electrodes in order for metal-to-metal contact to occur at the joint interface. A second requirement is that the heat resulting from the spot weld cause only limited detrimental effect on the strength of the bond.(19)

Film adhesives generally have higher peel strengths (5060 in-lbs/in or 22.2-26.7 J/m) than paste adhesives, and assembly time can be saved by applying film adhesives to the joint. However, to resistance spot-weld through a film adhesive, a method must be used to melt the adhesive before spot welding so that the adhesive can be squeezed out of the joint. Accurate temperature control of the film adhesive is critical if good welds are to be made. Poor temperature control within large parts greatly increases the problem of expulsion. (Expulsion in a weldbonded joint produces a black patch of mixed aluminum oxide and charred adhesive. This mixture is expelled from the nugget rather than the spike-shaped molten aluminum expelled during normal spot welding.) Furthermore, the flowability of film adhesives is poor. This may result in the formation of pores in the joint if the adhesive does not close up gap areas. Therefore, the selection of either a paste or film adhesive for weldbonding is essentially a matter of selecting the proper adhesive form for a given application.(15)

One of the advantages of a paste-form adhesive in the weldbonding process is the mobility or flow of the paste, which allows the use of low curing pressures (spot weld assembly pressures) to produce good strength levels. As mentioned above, the flow of the paste should be low enough that it will not flow out of the joint during the cure cycle and leave a starved joint.(15)

**12.5 Tooling for weldbonding.** Tooling for weldbonding falls into four general categories as follows:

- o Part handling
- o Adhesive application
- o Tacking
- o Welding

Since three of these categories are commonly used in industry, only tooling for adhesive application need be discussed. Tooling for paste adhesive application must fixture the parts and control location, width and thickness of the adhesive stripe. The tooling should have a platen to locate the part, and a moveable head consisting of gridded shim stock to control width and thickness of the adhesive stripe. The adhesive can be applied with an air-actuated caulking gun and spread to a uniform thickness (.006"-.016") (.15-.41 mm) and width by drawing a plastic spreader along the shim stock. The open position of the fixture should provide accessibility for solvent cleaning of the shim stock prior to the next adhesive application. Automatic adhesive application and spreading can be incorporated into the fixture if high production rates are required.(11)

## MIL-HDBK-691B

**12.6 Weldbonding techniques.** Class A resistance spot or seam welds can be made through the adhesive in weldbond structures when recommended spot weld cleaning or surface preparation techniques are used. When a modified epoxy paste adhesive containing a conductive powder filler is used, the welding parameters are nearly the same as those used for welding without adhesive. Welding through an adhesive causes a higher percentage of irregularly shaped nuggets, but the strength of the weldbond joint is not adversely affected. When welding through adhesive on material prepared by the recommended surface preparation, there is a tendency for a high percentage of the spot welds to exhibit expulsion (see 12.4), resulting in lower-quality and lower-strength welds.(11)

Weldbond process specifications have been prepared by several contractors for use by government agencies.(19)(20)(21) These process specifications give detailed steps to be taken to provide optimum weldbonds. The actual joining of parts by weldbonding is relatively straightforward. Most of the processes involved in resistance spot welding are applicable to weldbonding. The parts are chemically cleaned as for spot welding (see 12.3), wrapped and stored for up to 36 hours, if required, and removed for welding. Paste adhesive of the consistency of room-temperature honey is applied to the parts by laying a small bead of adhesive on the part surface and spreading it, using a nylon spatula. The parts are then brought together and temporarily clamped. The parts are then placed between the electrodes of a conventional three-phase, variable pressure-type spot welder and welded together. The weld setup used to join the parts is only slightly modified from a conventional setup. After welding, the structure is placed in a low-temperature oven and the adhesive cured for approximately one hour. Time and temperature are dependent on the type of adhesive and method involved.(10)(22)

**12.7 Quality control.** The extent of process and quality control must be based on the end use of the hardware. Methods in current use should be selected to fit a specific application. Consistent joint strength can be assured by evaluating cured weldbond tensile shear specimens, cleaned with each batch of parts, for strength and bond quality. Consistent weld quality can be assured by hourly evaluation of uncured tensile shear and macro specimens for strength and weld quality. Higher assurance can be obtained from the use of an in-process weld monitor that will detect unacceptable welds. The extent of the inspection of the production item must be determined from or based on the end use of the part, and will also be affected by size and complexity of the part. If the parts are small, visual inspections for surface defects and surface adhesive irregularities may be adequate. If the parts are large and complex and the end use is critical, radiographic inspection may be used for determination of weld quality and ultrasonic inspection for determination of bond quality.(11) X-ray radiography will reveal weld nugget defects such as cracking, expulsion and porosity.(15)

Infrared nondestructive inspection methods cannot be used for weldbonded structural assemblies.(21) Process specifications prepared by leading aerospace corporations under government contract have sections covering quality assurance provisions and should be consulted.(19)(20)(21)

## MIL-HDBK-691B

## REFERENCES

- (12-1) R. C. Hall, "Environmental Resistance of a Weldbond Joint," SAMPE Journal, 10(4): 10-14 (Aug/Sept. 1974).
- (12-2) J. A. Kizer and T. J. Kopkin, "Weldbond Joining Process Bibliography," September 1970. Lockheed-Georgia Company.
- (12-3) R. W. Winans et al, "Weldbonding in the United States: An Annotated Bibliography and History," PLASTEC Note M26, December 1974. AD A008048
- (12-4) J. A. Kizer, "Development of Weld-Thru Weldbond Process Surface Preparation," 5th National SAMPE Technical Conference, Kiamasha Lake, NY, Oct 9-11, 1973. Proceedings, Vol. 5, pp. 124-130.
- (12-5) W. J. Russell and W. C. Tanner, "Component Parts Assembly with Joints: Adhesive-Mechanical Part 1. Surface Preparation of Aluminum for Weldbonding," Picatinny Arsenal PATR 4610, Feb. 1974. AD 919514L.
- (12-6) R. A. Mitchell et al, "Finite Element Analysis of Spotwelded Bonded and Weldbonded Lap Joints," National Bureau of Standards NBSIR 75-957, Dec. 1975.
- (12-7) R. A. Mitchell et al, "Component Parts Assembly with Joints: Adhesive-Mechanical - Part 4. Analysis and Test of Bonded and Weldbonded Lap Joints," Picatinny Arsenal PATR 4965, March 1976. AD A029426. (Prepared by NBS)
- (12-8) Anonymous, "Bonding Replaces Fasteners," U.S. Army ManTech Journal, 2(1): 35-36 (Winter 1977).
- (12-9) Anonymous, "Spot Welding Teams Up with Adhesives for Stronger Metal-to-Metal Bonds," Product Engineering, 46(5): 22-23 (May 1975).
- (12-10) D. Fields, "Summary of the Weldbonding Process," Adhesives Age, 16(9): 41-44 (Sept. 1973).
- (12-11) R. D. Beemer, "Introduction to Weld Bonding," SAMPE Quarterly, 5(1): 37-41 (Oct. 1973).
- (12-12) R. H. Evans, "Titanium," DHIC Review of Recent Developments, Aug. 25, 1971. 2 pp.
- (12-13) D. Fields, Lockheed-Georgia Co., "Manufacturing Methods Development of Spot-Weld-Adhesive Bonded Joining for Titanium," AFHL-TR-71-93, June 1971. Final Report Nov. 70 - May 71. AF Contract F33615-71-C-1099. AD 725029.
- (12-14) R. H. Evans, "Advances in Joining Technology - The 60's and Beyond," MCIC 73-13, January 1973.

## MIL-HDBK-691B

- (12-15) K. C. Wu and B. B. Bowen, Northrop Corp., Aircraft Div., "Advanced Aluminum Weldbond Manufacturing Methods," AFML-TR-76-131, Sept. 1976. Final Report June 1975 - March 1976. AF Contract F33615-71-C-5083. AD CAB016865. Also in Preprint Book, 22nd National SAMPE Symposium, Vol. 22, San Diego, CA, Apr. 26-28, 1972. pp. 536-554.
- (12-16) J. D. Minford et al, "Weldbond and its Performance in Aluminum Automotive Body Sheet," SAE Paper No. 750462, presented at Automotive Engineering Congress and Exposition, Detroit, Michigan, Feb. 24-28, 1975.
- (12-17) B. B. Bowen, "Preparation of Aluminum Alloy Surfaces for Spot Weld Bonding," 7th National SAMPE Technical Conference, Albuquerque, New Mexico, Oct. 14-16, 1975. Proceedings, Vol. 7, pp. 374-385.
- (12-18) H. J. Salkind, "Spot-Weld Bonding on the Blackhawk Helicopter," Proceedings, Symposium on Welding, Bonding and Fastening, sponsored by NASA, George Washington University and ASM, May 1972. Paper No. 2, 6 pp.
- (12-19) R. L. Szabo, General Dynamics Convair Div., "Feedback-Controlled Spotwelding," AFML-TR-76-35, April 1976. Final Report June 15, 1975 - April 15, 1976. AF Contract F33615-75-C-5229. AD B014690L.
- (12-20) B. B. Bowen et al, Northrup Corp., Aircraft Div., "Improved Surface Treatments for Weldbonding Aluminum," AFML-TR-76-159, Oct. 1976. Final Report April 1975 - June 1976. AF Contract F33615-74-C-5027. AD CAB017811L.
- (12-21) J. J. Grosko and J. A. Kizer, Lockheed-Georgia Co., "Weldbond Flight Component Design/Manufacturing Program, AFML-TR-74-179, AFFDL-TR-74-106, Dec. 1974. Final Report July 15, 1971 - July 15, 1974. AF Contract F33615-71-C-1716. AD B002822L.
- (12-22) P. R. Miller, "Advanced Fusion Welding Processes, Solid State Joining and a Successful Marriage," Proceedings, Symposium on Welding, Bonding and Fastening, sponsored by NASA, George Washington University and ASH, May 1972. Paper No. 29. 45 pp.

(WP # ID-7344A/DISK-0034A FOR MTL USE ONLY.)



## MIL-HDBK-691L

## Chapter 13. TEST METHODS

13.0 Test methods.

13.1 Organization. There are a considerable number of test methods used to evaluate adhesives and adhesive joints. Most of those that will be of interest to the users of this handbook can be found in the methods developed by ASTM Committee D-14 on Adhesives. A total of 62 methods standards have been published to date in this field. In some (16) cases, standards dealing with methodology have been issued as Recommended Practices, or more recently, as Practices. These do not have quite the status of Methods. Of the 78 ASTM standards involving adhesives test methods or practices, a total of 26 (33%) have been adopted by DOD. In these cases DOD agencies can obtain copies free on request from the Naval Publications and Forms Center. The ASTM standards of interest are tabulated below under 13.2, followed by 13.3, a section covering the four Federal Test Method Standards under FTHS 175B still in effect.

13.2 ASTM standards.(1)

13.2.1 ASTM D816-82. \*Standard Methods for Testing RUBBER CEMENTS, 8 pp. (DOD Adopted) ASTM Committee D-11 on Rubber.

This method covers adhesives that may be applied in plastic or fluid form and that are manufactured from natural rubber, reclaimed rubber, synthetic elastomers, or combinations of these materials. Tests include: adhesion strength, bonding range, softening point, cold flow, viscosity, cold brittleness, density and plastic deformation (for heavy doughs or putties).

13.2.2 ASTM D896-64. Standard Test Method for RESISTANCE OF ADHESIVE BONDS TO CHEMICAL REAGENTS, 3pp. (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the testing of all types of adhesives for resistance to chemical reagents. Includes provisions for reporting loss in strength in accordance with ASTM methods of test for strength properties of adhesives. Standard chemical reagents described in ASTM D543 and oil and fuels from ASTM D471 are used, along with specially formulated supplementary reagents (1 hydrocarbon mixture, 2 jet fuel mixtures, and 1 silicone fluid).

13.2.3 ASTM D897-78 (1983). Standard Test Method for TENSILE PROPERTIES OF ADHESIVE BONDS, 5 pp. (DOD Adopted). ASTM Committee D-14 on Adhesives.

This is known as the "butt" joint adhesion tensile test. Blocks or rods of wood or metal are shaped or machined to specified dimensions of 1-13/16 in. (40 mm) diameter for wood and 1-7/8 in. (47.5 mm) diameter for metal. Two of these machined circular contact surface "buttons" are then bonded together with the adhesive under test. A tensile testing machine is used under standardized conditions and the maximum load at failure is recorded with the force normal to the contact area. This test is not as commonly used as the lap shear strength.

## MIL-HDBK-691B

13.2.4 ASTM D898-69 (1980). Standard Test Method for APPLIED WEIGHT PER UNIT AREA OF DRIED ADHESIVE SOLIDS, 3 pp (DOD Adopted). ASTM Committee D-14 on Adhesives.

Covers the determination of the quantity of adhesives solids applied in a spreading or coating operation.

13.2.5 ASTM D899-51 (1984). Standard Test Method for APPLIED WEIGHT PER UNIT AREA OF LIQUID ADHESIVES, 2 pp. (DOD Adopted). ASTM Committee D-14 on Adhesives.

Covers the determination of the quantity of liquid adhesive applied in a spreading or coating operation. Intended to be applied only to adhesives used for bonding wood.

13.2.6 ASTM D903-49 (1983). Standard Test Method for PEEL OR STRIPPING STRENGTH OF ADHESIVE BONDS, 4 pp. (DOD Adopted). ASTM Committee D-14 on Adhesives.

This test is essentially a 180° peel/stripping test where only one member of the laminate couple is bent. This is in contrast to the peel tests which apply force to both laminated structure members and in which both laminated members deform - e.g. the T-peel Test (D 1876). The test is especially useful for comparative testing of adhesive materials and provides practical data for the evaluation of vinyl-to-metal adhesives for example.

13.2.7 ASTM D904-57 (1981). Standard Recommended Practice for EXPOSURE OF ADHESIVE SPECIMENS TO ARTIFICIAL (CARBON-ARC TYPE) AND NATURAL LIGHT, 3 pp. ASTM Committee D-14 on Adhesives.

This recommended practice defines conditions for the exposure of adhesives in the form of glued transparent or translucent assemblies to (1) artificial, and (2) natural light sources. Where such information is of value, the same exposure conditions may be used on adhesive film or any other suitable form in which light may be a deteriorating factor. The practice is limited to the method of obtaining the exposure conditions and outlines the procedure to be followed, but does not cover methods of test to be used in evaluating the effects of the exposure. The artificial light is provided by a carbon-arc apparatus, and the natural light is provided by sunlight beamed at a 45-degree angle facing south.

13.2.8 ASTM D905-49 (1981). Standard Test Method for STRENGTH PROPERTIES OF ADHESIVE BONDS IN SHEAR BY COMPRESSION LOADING, 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method is used to determine the comparative shear strengths of adhesives for bonding wood and similar materials. The materials must be conditioned. The adhesive is evaluated in terms of the maximum and minimum stresses required to fail the specimens, as well as the degree of wood failure. The test is most adaptable for furniture woods and composites. In the test standard-size test blocks are placed in a small shearing tool so that the load may be applied with a continuous motion.

13.2.9 ASTM D906-82. Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN PLYWOOD TYPE CONSTRUCTION IN SHEAR BY TENSION LOADING, 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

## MIL-HDBK-691B

This test is often used to measure comparative shear strength of adhesively bonded plywood-type construction. If applied specifically to wood-to-wood adhesives, specimens of plywood in the form of strips 1 inch wide and approximately 4 inches long are cut from a test panel. The test samples are placed in the jaws of the grips of the testing machines, aligned, clamped in place, and the machine is loaded to failure.

**13.2.10 ASTM D950-82. Standard Test Method for IMPACT STRENGTH OF ADHESIVE BONDS, 6 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.**

In this test, which measures pendulum-impact resistance, the specimen is mounted in a special grip and placed in a standard impact machine. One adherend is struck with a pendulum hammer travelling at a prescribed speed, and the energy of impact reported in pounds per square inch of bonded area.

**13.2.11 ASTM D1002-72 (1983). Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING (METAL-TO-METAL), 5 pp., (DOD Approved). ASTM Committee D-14 on Adhesives.**

This lap-shear or tensile-shear test is the most commonly used shear test for metal-to-metal structural adhesive. Two sections of grid sheet material (e.g. metal) with suitably treated surfaces, usually 4 inches long x 1 inch wide and 0.064 inch thick (101.6 x 25 x 1.65 mm) are used to fabricate the specimens. The ends are overlapped 1/2 inch (12.7 mm) and adhesively bonded together to form a half-square-inch (323 square mm) contact area. In the test, both ends of the bonded specimen are firmly clamped into the jaws of a tensile testing machine. The jaws are moved apart at a prescribed speed until failure occurs. The failing load is reported, as well as the mode of failure (adhesive, cohesive or mixed).

**13.2.12 ASTM D1062-78 (1983). Standard Test Method for CLEAVAGE STRENGTH OF METAL-TO-METAL ADHESIVE BONDS, 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.**

Cleavage tests are carried out by prying apart one end of a rigid bonded joint and measuring the load necessary to cause rupture. The test is a subjective measure of the cleavage strength of an adhesive material and a quantitative measure of the fracture toughness of the adhesive. Cleavage values are reported in pounds per inch of adhesive width. Because cleavage test specimens involve considerable machining, peel tests are usually preferred.

**13.2.13 ASTM D1084-63 (1981). Standard Test Method for VISCOSITY OF ADHESIVES, 6 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.**

These methods, four in number, cover the determination of the viscosity of free-flowing adhesives. Method A is a cup method applicable only to adhesives capable of delivering 50 ml in a steady stream from a standard cup. The time required to move the adhesive is recorded for each cup size. Method B is intended for measuring the viscosity of adhesives covering a range from 50 to 200,000 cP. It is limited to materials that have or approach Newtonian flow characteristics. The apparatus is the Brookfield viscosimeter, an instrument with revolving spindles. Method C is intended primarily as a control method

## MIL-HDBK-691B

for determining the viscosity of adhesives that have or approach Newtonian flow characteristics. A Stormer viscosimeter with double flag paddle-type rotor, as specified in ASTM D562, is used. The latter test is used for measuring paint consistency. Method D is intended primarily as a control method for determining the viscosity of materials which have an equivalent viscosity no greater than approximately 3000 cP, and is limited to materials that have or approach Newtonian flow characteristics. (For a non-Newtonian flow method use ASTM D 2256). In this method five Zahn cups are used. These are so designed that the sample will flow through the calibrated orifice in approximately 1 minute or less.

**13.2.14 ASTM D1144-84.** Standard Recommended Practice for DETERMINING STRENGTH DEVELOPMENT OF ADHESIVE BONDS, 2 pp. ASTM Committee D-14 on Adhesives.

This recommended practice covers the determination of the strength development of adhesive bonds when tested on a standard specimen and under specified conditions of preparation and testing. It is applicable to all adhesives requiring curing at specified conditions of time and temperature agreeable to both the manufacturer and the purchaser. It covers all types of adhesives. Any ASTM test method for determining strength properties of adhesive bonds may be used, particularly the spool-type tension specimens (ASTM D 897) or the lap-type shear specimens (ASTM D 1002).

The specimens are prepared in accordance with ASTM D1002. The manufacturer's recommended curing time and temperature are used to determine the strength values. In addition, tests are run at the same temperature and time intervals to determine fixture time (set time) at 20, 50 and 80% strength. Testing is normally carried out immediately after the specimens reach room temperature.

**13.2.15 ASTM D1146-53 (1981).** Standard Test Method for BLOCKING POINT OF POTENTIALLY ADHESIVE LAYERS, 3 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the determination of the blocking point of a thermoplastic or hygroscopic layer or coating of potentially adhesive materials (materials in a substantially non-adhesive state which may be activated to an adhesive state by application of heat or solvents. Two degrees of blocking (first degree and second degree) and two types of blocking (cohesive and adhesive) are covered. Thermoplastic blocking is measured in a desiccator over 50% RH at 38°C.

**13.2.16 ASTM D1151-84.** Standard Test Method for EFFECT OF MOISTURE AND TEMPERATURE ON ADHESIVE BONDS, 3 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method defines conditions for determining the performance of adhesive bonds when subjected to continuous exposure at 22 specified conditions of moisture and temperature. The performance is expressed as a percentage based on the ratio of strength retained after exposure, to the original strength. Any desired strength property may be used. Test conditions of temperature and moisture only are prescribed in this standard. The duration of the exposure is dependent upon the nature of the adhesive and type of specimens and will, therefore, be covered by material specifications.

## MIL-HDBK-691B

13.2.17 ASTM D4299-83. Standard Test Method for EFFECT OF BACTERIAL CONTAMINATION ON PERMANENCE OF ADHESIVE PREPARATIONS AND ADHESIVE FILMS, 6 pp. ASTM Committee D-14 on Adhesives. Supersedes ASTM D1174-55(1981)

These test methods cover the determination of the effect of bacterial contamination on the permanency of: adhesive preparations, by determining the comparative viscosities and observing the appearance of the uncontaminated and the contaminated adhesives when tested under defined conditions; and adhesive films, by exposure to cultures of selected species of bacteria growing on agar plates. The test for the resistance of adhesive preparations to bacterial contamination is used to determine susceptibility of the adhesive to biodegradation. These methods are useful in demonstrating whether an adhesive preparation is sufficiently protected with biocide to resist attack by bacteria during its shelf life.

13.2.18 ASTM D1183-70 (1981). Standard Test Method for RESISTANCE OF ADHESIVES TO CYCLIC LABORATORY AGING CONDITIONS, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

These methods cover the determination of the resistance of adhesives to cyclic accelerated service conditions by exposing bonded specimens of high and low temperatures and high and low relative humidities. The extent of degradation is determined from changes in strength properties as a result of exposure to the test conditions.

13.2.19 ASTM D1184-69 (1980). Standard Test Method for FLEXURAL STRENGTH OF ADHESIVE BONDED LAMINATE ASSEMBLIES, 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the determination of the comparative properties of adhesive assemblies when subjected to flexural stresses with standard shape specimens and under defined conditions of pretreatment, temperature, relative humidity, and testing techniques. The test specimens and testing technique were designed to develop a large portion of shear forces between the laminate of the test piece when the load is applied, rather than to reduce shear stress to a minimum, as is done in other ASTM test methods for flexural properties. The method is useful only for assemblies made with rigid adherends.

13.2.20 ASTM D4300-84. Standard Test Method for EFFECT OF MOLD CONTAMINATION ON PERMANENCE OF ADHESIVE PREPARATIONS AND ADHESIVE FILMS, 6 pp. ASTM Committee D-14 on Adhesives. (Supersedes ASTM D1286-57(1979))

These test methods cover the determination of the effect of mold contamination on the permanency of adhesive preparations and adhesive films, as follows: adhesive preparations, by determining the comparative viscosities and observing the appearance of the uncontaminated and the contaminated adhesives when tested under defined conditions; and adhesive films, by exposure to cultures of selected species of mold growing on agar plates. The test for the resistance of adhesive preparations to mold contamination is used to determine susceptibility of the adhesive to biodegradation. This method is useful in demonstrating whether an adhesive preparation is sufficiently protected with biocide to resist attack by molds during its shelf life.



## NIL-HDBK-691B

Laboratories not equipped to handle a more accurate microbiological determination are generally capable of using this procedure. The test for resistance of adhesive films to mold attack provides an indication of whether the adhesive will carry into the glue sufficient anti-mold properties to prevent attack by molds which occur naturally in wood.

13.2.21 ASTM D1304-69 (1983). Standard Test Method of Testing ADHESIVES RELATIVE TO THEIR USE AS ELECTRICAL INSULATION, 3 pp. ASTM Committee D-14 on Adhesives.

These methods cover procedures for testing adhesives in liquid, highly viscous, solid or set states, that are intended to be cured by electronic heating, or that are intended to provide electrical insulation, or that are intended for use in electrical apparatus. The following procedures are used:

- (1) Procedures for Testing Adhesives Before Use:
  - Power Factor and Dielectric Constant of Liquid Adhesives
  - Direct-Current Conductivity
  - Extract Conductivity
  - Acidity and Alkalinity
  - pH Value
- (2) Procedure for Testing Properties of Adhesives as Used:
  - Power Factor and Dielectric Constant of a Dried or Cured Adhesive Film
  - Dielectric Strength
  - Volume and Surface Resistivity
  - Arc Resistance

In general, ASTM Methods are cited for each procedure, with some slight modifications.

13.2.22 ASTM D1337-56 (1984). Standard Test Method for STORAGE LIFE OF ADHESIVES BY CONSISTENCY AND BOND STRENGTH, 3 pp. ASTM Committee D-14 on Adhesives.

This method is applicable to all adhesives having a relatively short storage life. It is intended to determine whether the storage life conforms to the minimum specified storage life required of an adhesive by consistency tests (Procedure A) or by bond strength tests (Procedure B), or by both. A viscosimeter is used for the consistency tests and a standard testing machine for the bond strength tests.

13.2.23 ASTM D1338-56 (1982). Standard Test Method for WORKING LIFE OF LIQUID OR PASTE ADHESIVES BY CONSISTENCY AND BOND STRENGTH, 3 pp. ASTM Committee D-14 on Adhesives.

This method is similar to ASTM D1337 above, except that it covers working life instead of storage life.

13.2.24 ASTM D1344-78. Standard Test Method for CROSS-LAP SPECIMENS FOR TENSILE PROPERTIES OF ADHESIVES, 4 pp. ASTM Committee D-14 on Adhesives.



## MIL-HDBK-691B

This method covers a simplified tension test procedure for determining the comparative strength of adhesives by the use of a cross-lap assembly under specified conditions of pretreatment, temperature, and testing machine speed. The test has been specially designed for adhesion of glass, either to itself or to other materials. Two test pieces 1 inch x 1 1/2 inch (25 mm x 38 mm) 1/8 inch to 1/2 inch (3 to 12.7 mm) thick are assembled by bonding them together at right angles in such a way that a 1 inch<sup>2</sup> (650 mm<sup>2</sup>) contact bonded area is formed. A 1/4 inch (6 mm) overlap region is present on all four sides of the bonded area. The test is carried out in a tensile testing machine, using a special jig. Specimen formation is simple. Breaking strength is reported in psi and MPa and the type of failure (adhesive, cohesive, mixed) is noted. The test is useful for quality control and comparative purposes.

13.2.25 ASTM D1382-64 (1981). Standard Test Method for SUSCEPTIBILITY OF DRY ADHESIVE FILMS TO ATTACK BY ROACHES, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the damage American roaches carry out on adhesive-impregnated paper. The method may be adapted, with appropriate changes, to other vermin. In the test, filter paper is dipped in a freshly prepared adhesive and drained, then dried for 24 hours. Starved American roaches (*Periplaneta americana*), both male and female, are used in the testing. The percent destruction of the impregnated filter paper is determined by weighing before and after exposure.

13.2.26 ASTM D1383-64 (1981). Standard Test Method for SUSCEPTIBILITY OF DRY ADHESIVE FILMS TO ATTACK BY LABORATORY RATS, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the evaluation of the susceptibility of dry adhesive films to attack by rodents. Laboratory-bred white rats are used to determine the comparative damage to adhesive-impregnated paper and blanks. In the test, filter paper is dipped in freshly prepared adhesive and drained, then dried for 24 hours. Starved healthy male albino white rats are used. The test assemblies, with blanks, are placed in wire mesh cages and exposure carried out. The degree of destruction is determined by weight loss and converted to percentage damage.

13.2.27 ASTM D1488-60 (1981). Standard Test Method for AMYLACEOUS MATTER IN ADHESIVES, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This test covers the determination of the presence or absence of amylaceous (starch-like) material in phenol-, resorcinol-, and melamine-resin glues. These are quick spot tests, using iodine test solution or ethyl alcohol for testing phenol and resorcinol adhesives, and iodine test solution and acetic acid-ethyl alcohol solution for testing melamine resins.

13.2.28 ASTM D1489-69 (1981). Standard Test Method for NONVOLATILE CONTENT OF AQUEOUS ADHESIVES, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

## NIL-HDBK-691B

This method covers the determination of the nonvolatile content of aqueous adhesive, such as dextrin, starch, casein, animal gelatin, etc. Ten-gram samples of the adhesive under test are weighed into a small beaker to the nearest 0.01 g. The adhesive is dispersed in 50 ml of hot distilled water and transferred into the 200-ml volumetric flask. Ten-ml aliquots are then pipetted from the flask into a tared weighing bottle filled 3/4 full of silica sand dried to constant weight. The sample in the bottle is dried at  $105 \pm 1^\circ\text{C}$  to constant weight, then covered and cooled in a desiccator to room temperature before weighing to the nearest 0.001 g. The percentage of nonvolatile matter is then calculated.

**13.2.29 ASTM D1490-82.** Standard Test Method for NONVOLATILE CONTENT OF UREA-FORMALDEHYDE-RESIN SOLUTIONS, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the determination of the apparent nonvolatile content of urea-formaldehyde resin solutions intended for use as wood adhesives. A portion of resin solution is placed in a tared Lunge weighing pipet and weighed to  $\pm$  mg. An aliquot of this solution is transferred into a tared aluminum foil drying dish, 5 ml of water added, and the solution mixed. The solution is then dried at  $105^\circ\text{C}$  ( $221^\circ\text{F}$ ) for 3 hours. The percentage of nonvolatile matter is then calculated.

**13.2.30 ASTM D1579-60 (1981).** Standard Test Method for FILLER CONTENT OF PHENOL, RESORCINOL, AND MELAMINE ADHESIVES, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method is suitable for measuring the filler content of phenol-, resorcinol-, and melamine resin-base adhesives mixed with hardener or catalyst that set at room, intermediate, and high temperatures. Results are expressed on the basis of the nonvolatile content of the mixed, liquid adhesive. The procedure involves weighing samples of the adhesive into suitable solvent solutions, stirring, and then filtering the mixture with all its contents. In the case of melamines, acid-washed diatomaceous earth is added. Drying is carried out at  $105^\circ\text{C}$  to constant weight, except for melamines, where a 16-hour period is used. The filler content is then determined by calculation.

**13.2.31 ASTM D1581-60 (1984).<sup>e\*</sup>** Standard Test Method for BONDING PERMANENCY OF WATER- OR SOLVENT-SOLUBLE LIQUID ADHESIVES FOR LABELING GLASS BOTTLES, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the bonding permanency of dextrin, casein, starch, animal gelatin, and other liquid adhesives (excluding pressure-sensitive types) used for applying printed paper labels to glass bottles. A total of nine (9) exposure conditions are provided to simulate typical storage conditions. A uniform adhesive film is applied to a clean glass plate to give a wet film thickness of 0.025 to 0.038 mm. The label is applied and the adherend unit stored at RT and 50% RH for at least 24 hours, or until it is no longer sticky to touch. Then the specimens are stored under test conditions for the prescribed period, usually 7 days. At the end of that time, they are examined for permanency of bond.

\*The symbol e means the standard has been editorially revised.

## MIL-HDBK-691B

**13.2.32 ASTM D1562-60 (1981).** Standard Test Method for NONVOLATILE CONTENT OF PHENOL, RESORCINOL, AND MELAMINE ADHESIVES, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the nonvolatile content or total solids of phenol, resorcinol, and melamine adhesives with or without hardener added and containing high-boiling and low-boiling volatile organic solvents or water or both (Note: in some cases low-molecular-weight materials in the adhesive may be lost if hardener is not used). Basically, samples are weighed out and dried at 70°C, 105°C, or 150°C, with slightly differing procedures, depending on the presence or absence of hardener.

**13.2.33 ASTM D1583-61 (1981).** Standard Test Method for HYDROGEN ION CONCENTRATION OF DRY ADHESIVE FILMS, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers determination of the hydrogen ion concentration (pH), acidity or alkalinity, of organic adhesives in the dry-film form. It is not designed for use with pressure-sensitive adhesives. The pH is important because the adhesive itself may be adversely affected in time by the acidity or alkalinity. These conditions often arise from the catalysts used to cure the adhesive. A pH meter capable of making measurements to  $\pm 0.05$  pH is used. Samples of the adhesive are ground, then weighed out and placed in small standard-size glass vials to which freshly boiled, cooled distilled water is added. The pH is then read at 23°C.

**13.2.34 ASTM D1584-60 (1984).<sup>e</sup>** Standard Test Method for WATER ABSORPTIVENESS OF PAPER LABELS, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the selection of paper labels of uniform water absorptiveness for use in determining the bonding permanency of adhesives for labeling glass bottles. This method is used in conjunction with ASTM D 1581. A Cobb sizing tester is used. Ten ml of distilled water is introduced to the inside of the test ring and the water then poured off after 110 seconds. After 120 seconds, the surface moisture is blotted from the label with a soft towel and the label reweighed. The water absorptiveness is calculated from the amount of weight gain.

**13.2.35 ASTM D1713-65 (1981).** Standard Test Method for BONDING PERMANENCY OF WATER- OR SOLVENT-SOLUBLE LIQUID ADHESIVES FOR AUTOMATIC MACHINE SEALING TOP FLAPS OF FIBERBOARD SPECIMENS, 2 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the bonding permanency of dextrin, casein, starch, resin base, and other water- or solvent-soluble liquid adhesives (excluding pressure-sensitive types) used for sealing the top flaps of fiberboard shipping cases.

**13.2.36 ASTM D1780-72 (1983).** Standard Recommended Practice for CONDUCTING CREEP TESTS OF METAL-TO-METAL ADHESIVES, 5 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This recommended practice covers the determination of the amount of creep of metal-to-metal adhesive bonds due to the combined effects of temperature, tensile shear stress, and time.

## MIL-HDBK-691B

13.2.37 ASTM D1781-76 (1981). Standard Test Method for CLIMBING DRUM PEEL TEST FOR ADHESIVES, 6 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the determination of the peel resistance of adhesive bonds between a relatively flexible adherend and a rigid adherend, and the relatively flexible facing of a sandwich structure and its core, when tested under specified conditions. The specimen consists of a laminated assembly of two adhesively bonded layers 1 inch to 3 inches wide (25-76 mm) and 10 inch to 12 inches long (254-305 mm). The specimen may be in the form of a sandwich construction. The peeling apparatus consists of a flanged drum onto which the end tabs of the specimens are clamped, with the help of flexible loading straps or cables to guide the specimen on the drum during peeling.

The outside radius of this drum is 2 inches (51 mm). One tab of the test specimen is securely clamped to the drum, which is secured in the lower jaw of tensile testing machine through the flexible metal bonds or cables. The other end is clamped, through a self-clinching device to the upper joint of the testing machine. The peel resistance over a distance of at least 6 inches (152 mm) of the bond is measured, in tension, at a crosshead speed of 1 inch/minute (25.4 mm). At this specific drum-peel configuration, the flexible member is peeled from the assembly at a rate of 4 inches/minute (102 mm). The average load to peel of the laminar specimen is recorded.

This type of test is well regarded among peel tests. The force required to deform the peeled-away layer material is factored out of the measurement. This test is considered a better evaluation of peel adhesive of laminar and sandwich construction than the more popular T-peel method (ASTM D1876). In addition, the deformation of the specimen is controlled during the performance of the test, leading to a more direct measure of peel adhesion.

13.2.38 ASTM D1828-70 (1981). Standard Recommended Practice for ATMOSPHERIC EXPOSURE OF ADHESIVE-BONDED JOINTS AND STRUCTURES, 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This recommended practice defines the procedure for the direct exposure of adhesive-bonded joints and structures to natural atmospheric environments. The procedure for sheltered atmospheric exposure, such as a Stevenson screen, of adhesive-bonded joints and specimens is the same, except for the requirements of facing south and measurement of solar radiation. The recommended practice is limited to the procedure by which samples (exposed joints in structure) are exposed and does not cover the tests that may be used to evaluate the effects of atmospheric exposure in these adhesive-bonded joints and structures. The latter test methods may be any that are suitable, destructive or nondestructive. In the case of metal adherends, four types of test sites are recommended as:

1. Rural-pure atmosphere
2. Industrial-sulfurous gases present
3. Marine-seacoast sites where chlorides are deposited
4. Tropical or southern Florida where heat and high humidities are present.

## MIL-HDBK-691B

Suggestions are given as to suitable exposure racks and climatological instruments. Details are given as to specimen preparation, exposure duration, and report preparation.

13.2.39 ASTM D1875-69 (1980). Standard Test Method for DENSITY OF ADHESIVES IN FLUID FORM, 2 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

This method covers the measurement of density (weight per gallon) of adhesives and components thereof, when in liquid form. It is particularly applicable where the fluid has too high a viscosity, or where a component is too volatile for a specific gravity determination. A weight-per-gallon cup (83.2 ml capacity at 25°C) is used. The weight in grams of the contents, divided by 10, is the weight per gallon in pounds.

13.2.40 ASTM D1876-72 (1983). Standard Test Method for PEEL RESISTANCE OF ADHESIVES (T-PEEL TEST), 4 pp., (DOD Adopted). ASTM Committee D-14 on Adhesives.

The T-peel test is a popular peel test applied to measure the peel resistance between two adhesively bonded laminated panels. The specimen preparation and test procedure are relatively simple. Test panels are 6 inches wide (152 mm) by 12 inches (305 mm) long and bonded only over 9 inches (241 mm) of their length. These bonded panels are cut into 1-inch wide (25 mm) specimens and then the 3-inch (75 mm) unbonded ends of the specimen are spread apart, perpendicular to the bond line. The bent tabs of the prepared specimens are placed in the grips of the tensile testing machine and the load applied at 10 inches/minute (254 mm/minute). The peel resistance is measured over at least a 5-inch (127 mm) length. The data is reported as the average load per unit width of bond line required to produce progressive separation of the two bonded, flexible adherends.

13.2.41 ASTM D1877-77.<sup>e</sup> Standard Test Method for PERMANENCE OF ADHESIVE-BONDED JOINTS IN PLYWOOD UNDER MOLD CONDITIONS, 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the resistance of wood adhesives in plywood under conditions conducive to mold growth under controlled laboratory conditions using a culture of unselected organisms under the jurisdiction of ASTM Committee D-14 on Adhesives. This test method was withdrawn in 1984 and replaced by ASTM D4300 for Effect of Mold Contamination on Permanence of Adhesive Preparations and Adhesive Films (see 13.2.20).

13.2.42 ASTM D1879-70(1981) Standard Practice for EXPOSURE OF ADHESIVE SPECIMENS TO HIGH-ENERGY RADIATION, 5 pp. ASTM Committee D-14 on Adhesives.

This practice defines conditions for the exposure of polymeric adhesives and bonded specimens to high-energy radiation prior to determination of radiation-induced changes in physical or chemical properties. The recommended practice covers gamma or X-Ray-radiation, electron or beta radiation, neutrons, and mixtures of these, such as reactor radiation. The practice specifies only the conditions of irradiation, but does not cover the preparation of test specimens, testing conditions, or the evaluation of tests.



## MIL-HDBK-691B

Five procedures are given:

- Procedure A - Exposure at ambient conditions
- Procedure B - Exposure at controlled temperature
- Procedure C - Exposure in a medium other than air
- Procedure D - Exposure under load
- Procedure E - Exposure combining two or more of the variables listed in Procedures A to D.

**13.2.43 ASTM D1916-69 (1980).** Standard Test Method for PENETRATION OF ADHESIVES, 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the penetration under pressure of adhesives used in systems where at least one of the adherends is porous. It is particularly adaptable to use with starch or starch-base adhesives commonly used on the paper converting industry. The penetration testing apparatus is so constructed as to allow a section of round steel bar stock 25 mm (1 inch) in diameter and weighing 700 grams (the hammer) to fall freely through a distance of 0.8 m (31 inches) upon a steel disk (the anvil) 6 mm (1/4 inch) thick and 51 mm (2 inches) in diameter, in such a manner as to strike the anvil at right angles. Dimensions of the guiding tube and the section of bar stock permit free fall of the bar stock without undue sideways movement.

In the test five sheets of filter paper are stacked, one on top of another upon the anvil at the bottom of the tube. One-tenth ml of the adhesive under test is applied to the center of the bottom end of the hammer, using a 1 ml syringe. Thirty seconds after the adhesive is applied to the hammer, it is released and allowed to fall freely. The hammer is then raised and the filter papers removed, then stained with a slight excess of staining solution suitable for the adhesive being tested (e.g. KI-I<sub>2</sub> for starch). The stained papers are allowed to air-dry for one hour, after which a densitometer and planimeter are used to calculate the density and stained areas. The results are expressed as Ja, density times area.

**13.2.44 ASTM D2095-72 (1983).** Standard Test Method for TENSILE STRENGTH OF ADHESIVES BY MEANS OF BAR AND ROD SPECIMENS, 4 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the relative tensile strength of adhesives by the use of bar- and rod-shaped butt-joined specimens under defined conditions of preparation, conditioning and testing. The method is applicable to the testing of adhesives with various adherend materials in either similar or dissimilar combinations. Bar specimens 1.5 inch (38 mm) long by 0.5 inch x 0.5 inch (12.7 x 12.7 mm) square contact area (end), or rod specimens 1.5 inches (38 mm) long with a contact diameter (end) of 0.5 inch (12.7 mm) are used in the test. The specimens are matched with a 0.1875-inch (4.76 mm) diameter hole through the side of one end. The specimens are bonded together at the machined control surface. The prepared bar or rod specimen is placed in a tensile testing machine fitted with a special self-aligning holding jig. Steel dowel pins are used to secure the specimen. The crosshead speed is adjusted to 2400-2800 psi (170-195 kg/cm<sup>2</sup>) per minute. The maximum load carried by the specimen at failure is recorded. The percentages of the various types of failure (adhesive, cohesive, contact, or adherend) are also reported.

## MIL-HDBK-691B

13.2.45 ASTM D2182-72 (1978). Standard Test Method for STRENGTH PROPERTIES OF METAL-TO-METAL ADHESIVES BY COMPRESSION LOADING (DISK SHEAR), 3 pp. ASTM Committee D-14 on Adhesives. (Discontinued 1985)

This method covers the determination of the shear strength of adhesives when tested in a standard specimen under specified conditions of preparation and loading in compression. The method is intended primarily as an evaluation of adhesives for metals, but it is also useful for other substrates and materials. The test specimen consists of a metal disk having an area of 1 square inch ( $6.45 \text{ cm}^2$ ) with a radius of 0.564 inch (14.32 mm) and a thickness of 0.25 inch (6.35 mm), bonded to a strip of metal 4.25 inch (107.95 mm) long, 1.128 inch (28.66 mm) wide and 0.250 inch (6.35 mm) thick. The strip and disk may be of similar or dissimilar metal. The bonded surfaces must be well machined and polished before bonding is attempted.

Using a special holding jig known as a shearing tool, the specimen is held upright in the jig and placed in the testing machine. An anvil section of the shearing tool is fitted in such a way that the load on the disk, when a compressive force is applied by the testing machine, shears the disk along the plane of the plate section of the specimen. The test rate, in compression, is 1200-1400 psi ( $84\text{-}98 \text{ kg/cm}^2$ ) per minute to failure. The shear stress at failure is determined in psi or  $\text{kg/cm}^2$  of the shear area. The nature of the failure, including the average estimated percentages of failure (adhesive, cohesive, contact) is reported.

13.2.46 ASTM D2183-69 (1982). Standard Test Method for FLOW PROPERTIES OF ADHESIVES, 5 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the flow properties of adhesives under prescribed heating or curing conditions. The method is intended for adhesives that are dried in the form of a film and adhesives that are dried to a relatively tack-free state prior to assembly of the adherends and curing or setting of the adhesive. In the method, flow is calculated from a determination of the weight of adhesive flowing from a given area of the adhesive film during curing or setting. The test provides reasonably accurate information on the flow of an adhesive during cure or setting under pressure. This information is useful in determining pressure requirements for optimum bond thickness. It can also be used to determine advancement of cure during shelf aging of an adhesive. A special flow-test apparatus is used to apply pressure to the flow test specimen. Unsupported film adhesives are tested in the as-received condition. With liquid adhesives, a film for testing is prepared by casting onto uncoated cellophane, TFE film, or other suitable parting surfaces. The adhesive is then dried but not cured. Weight ratios are determined by the use of circular-disk specimens cut with dies. In the flow test, circular-disk specimens of 40.53 mm (1.596 inch) diameter are dried. These are placed between two disks of uncoated cellophane or other suitable parting film. This "sandwich" is placed in the flow-test apparatus and pressure applied according to the manufacturer's recommendations by compression of the spring. The entire assembly is placed in an oven to flow and cure the adhesive according to the manufacturer's recommendations of time, temperature and pressure.



## MIL-HDBK-691B

The flow is determined after the required exposure after removal of the test unit from the oven, removal of the cellophane, and drying of the specimens with a lint-free cheesecloth. A specified-size circular disk is cut from the center of the cured adhesive specimen and weighed after drying. The percentage flow is then calculated.

13.2.47 ASTM D2293-69 (1980). Standard Test Method for CREEP PROPERTIES OF ADHESIVE IN SHEAR BY COMPRESSION LOADING (METAL-TO-METAL), 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the creep properties of adhesives for bonding metals when tested on a standard specimen and subjected to certain conditions of temperature and compressive stress in a spring-loaded testing apparatus. The specimens are similar to the ASTM D1002-type tension lap-shear specimens, except that the length of either side of the shear area is 1/4 inch (6.35 mm), rather than 3 1/2 inch (88.9 mm). Specimens have polished bond area edges containing three scribe lines for creep measurement. A special slotted spring jig is used to hold the specimen. The short-stub-overlap test specimen is placed in the slot made by compressing the spring. The specimen is confined between two washers. The correct compression load on the specimen is controlled by the degree of compression of the calibrated spring. With a static load on the specimen, the creep of the bond line is measured by following the movement of the scribe lines with a travelling microscope. Creep is followed as a function of time. Static load and temperature may be varied for a particular test.

13.2.48 ASTM D2294-69 (1980). Standard Test Method for CREEP PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING (METAL-TO-METAL), 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the creep properties of adhesives for bonding metals when tested on a standard specimen and subjected to certain conditions of temperature and tensile stress in a spring-loaded testing apparatus. The method can be used in the temperature range of -55 to  $\pm 260^{\circ}\text{C}$  (-67 to  $\pm 500^{\circ}\text{F}$ ). The test specimens are similar to ASTM D1002-type tension lap shear specimens, except that holes are drilled in the end tab about 1/2 inch (12 mm) from each end. The overlap edges are polished and have three scribe lines for creep measurement. Using a special tension creep test jig, the specimen is loaded into the jig while it is being "compressed" at a given loading by a testing machine. The specimen is locked into place by pins placed through the holes in the specimen end tabs. When the compression is released, the lap-shear joint is under tension by the action of a spring in the test apparatus. The tensile creep of the lap joint is measured by a travelling microscope by following the movement of the scribe lines. Creep is followed as a function of time. Static load and temperature may be varied for a particular test.

13.2.49 ASTM D2295-72 (1983). Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING AT ELEVATED TEMPERATURES (METAL-TO-METAL), 4 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the comparative shear strengths of adhesives for bonding metals when tested on a standard specimen and under specified conditions of preparation and testing at elevated temperature (315 to  $850^{\circ}\text{C}$  or 600 to  $1500^{\circ}\text{F}$ ). A testing machine conforming to ASTM D638 is

## NIL-HDBK-691B

used, except that pin-type grips are used to hold the specimens. The specimens are similar to the tension lap-shear specimens described in ASTM D1002, except that pin-type grips are used. Unless otherwise specified, the test specimens are loaded to failure at a rate of 8.3 to 9.7 MPa (1200-1400 psi) per minute. The load at failure is recorded and the amount of this failure (cohesive, adhesive, substrate, etc.) reported in MPa or psi.

13.2.50 ASTM D2339-82. Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN TWO-PLY WOOD CONSTRUCTION IN SHEAR BY TENSION LOADING, 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the comparative shear strengths of adhesives when tested in a standard specimen and under user-specified conditions of preparation, conditioning and testing. The method is intended to be applied only to adhesives used in bonding wood to wood. Sweet or yellow birch veneer is used in the method.

13.2.51 ASTM D2556-69 (1980). Standard Test Method for APPARENT VISCOSITY OF ADHESIVES HAVING SHEAR-RATE-DEPENDENT FLOW PROPERTIES, 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the measurement of the apparent viscosity of shear-rate-dependent adhesives. The principle of measurement is based upon a reversible isothermal change in apparent viscosity with change in rate of shear. Measurement is performed in a spindle, disk, T-bar, or coaxial cylinder rotational viscometer under standardized conditions, with rigid control of time intervals of measurement. Readings are obtained on the viscometer dial scale at the end of 1 minute for each rotational speed.

13.2.52 ASTM D2557-72 (1983). Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING IN THE TEMPERATURE RANGE FROM - 267.8 to -55°C (-450 to -67°F), 4 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the comparative shear strength of adhesives for bonding metals when tested on a standard specimen and under specified conditions of preparation and testing at extreme sub-zero temperatures. The testing equipment shall conform to ASTM D1002, except that pin-type grips shall be used to hold the test specimen. The cooling equipment is a cold box or a cryostat filled with a gaseous or liquid refrigerant in which the standard specimen is immersed prior to and during the test.

13.2.53 ASTM D2558-69 (1964). Standard Test Method for EVALUATING PEEL STRENGTH OF SHOE SOLE-ATTACHING ADHESIVES, 4 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the peel strength of the adhesive bond on shoe-soling materials. The shoe-soling materials are bonded to standard control materials (rubber composition or vinyl plastic) under controlled conditions. The peel strength measurements are made under specified conditions and intervals. Apparatus required is (1) a tension testing machine, (2) source of infrared heat to produce temperatures of 225°F (107°C) in the adhesive films within 60 seconds, (3) cushioned

## MIL-HDBK-691B

pressure device, and (4) constant-temperature oven to provide 105°F (41°C) or 120°F (49°C). The test piece consists of an 8 inch x 1 inch (203 x 25.4 mm) x 1/8 inch (3.18 mm) thick sample of shoe-soling material laminated to a control adherend of the same dimension. For vinyl plastic soling materials, specimens are of the same thickness, but have standard specified hardness, tensile strength, specific gravity, elongation, abrasive index and 100% modulus. In the test, the 8 inch x 1 inch strips of material are bonded together, with one end of the specimen then being opened up 1/2 inch (12.7 mm) for clamping in the test grips of the tensile-testing machine. A load is applied at a rate of 2 inches (50 mm) per minute, or 12 inches (305 mm) per minute. The peeling force is measured during the test and the average peel strength as lbs/inch (kg/cm) of width is recorded, as well as the mode of failure of the test specimen (adhesive, cohesive or contact failure due to voids in bond line).

13.2.54 ASTM D2739-72 (1984). Standard Test Method for VOLUME RESISTIVITY OF CONDUCTIVE ADHESIVES, 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the volume resistivity of resin-based conductive adhesives in the cured condition. The test is made on a thin adhesive layer as prepared in a bonded specimen. The method is used for conductive adhesives that are cured either at room temperature or at elevated temperatures. The volume resistivity of adhesive layers between metal adherends is measured on a resistance bridge. Tensile adhesion plugs are described in the standard for this method. Any other test specimens and materials can be used as long as similar precautions are observed regarding preparations and tolerances. Usually brass tensile-adhesion plugs coated with gold or silver are used.

13.2.55 ASTM D2918-71 (1981). Standard Recommended Practice for DETERMINING DURABILITY OF ADHESIVE JOINTS STRESSED IN PEEL, 4 pp. ASTM Committee D-14 on Adhesives.

This test is useful for determining the durability of adhesive joints in the peeling mode while the specimen is in contact with air, air in equilibrium with certain solutions, water, aqueous solutions, or other environments at various temperatures. The test is considered an accelerated test for adhesive joint durability.

The combination of stress and moisture decreases the durability of most adhesive joints. Stresses in the presence of water or water vapor may cause some adhesive joints to fail at some fraction of the stress required to break the dry joint. The time to failure for a given adhesive joint tested under moist conditions generally decreases with increasing stress, temperature and relative humidity.

The test, intended primarily for metal-to-metal laminated assemblies, typically uses 1/2 inch (12.7 mm) wide specimens, each 8 inches (200 mm) long and any convenient width. The 8 inch (203.2mm) length has a 1 inch (25.4 mm) long delaminated (previously shinned) end that can be spread apart, forming a "T" until the cross bar measures 4 inches (100 mm). This requires separating the bond 1 inch beyond the delaminated end. In the test one "T" tab portion of the specimen is securely clamped, while the other is stressed statically by

## MIL-HDBK-691B

an attached weight. The procedure can be carried out under ambient conditions as well as under water, if a suitable apparatus is built. The distance peeled as a function of time is recorded. The rate of peeling is averaged over six sequential portions of the distance vs. time curve.

13.2.56 ASTM D2919-84. Standard Test Method for DETERMINING DURABILITY OF ADHESIVE JOINTS STRESSED IN SHEAR BY TENSION LOADING, 6 pp. (DOD Adopted) ASTM Committee D-14 on Adhesives.

This test is primarily for metal-to-metal bonding. The data obtained are most useful as a measure of qualitative stress endurance. The combination of stress and moisture used in the procedure decreases the durability of most adhesive joints. Stresses in the presence of water or water vapor may cause some adhesive joints to fail at some small fraction of the stress required to break the dry joint. The time to failure for a given adhesive joint generally decreases with increasing stress, temperature, and relative humidity.

A tensile-lap-shear specimen of the ASTM D1002 type is used. Two coupons of 5 inches (127 mm) in length x 1 inch (25.4 mm) wide x 0.064 inch (1.6 mm) thick sheet metal are overlapped at the 1-inch-wide end and bonded together with 1/2 inch (12.7 mm) overlap. Holes are located 1/2 inch (12.7 mm) from the end of the tab to accommodate the gripping bolt. The test requires the construction of a special double-steel-spring jig. As in the ASTM D2294 static load fatigue test, the specimen is held in the spring-compressed jig, the end tabs are gripped, clamped and the compression on the spring released, leaving the lap-shear specimen under a static tensile load. The maximum, minimum and average length of time to failure of the stressed specimen exposed to various environments is recorded. The test is carried out at various levels of fractional stress below the "short-term" failure stress and static stress, as time-to-failure curves are plotted.

13.2.57 ASTM D2979-71 (1982). Standard Test Method for PRESSURE-SENSITIVE TACK OF ADHESIVE USING AN INVERTED PROBE MACHINE, 4 pp. ASTM Committee D-14 on Adhesives.

This method covers measurement of the pressure-sensitive tack of adhesives. The method is applicable to those adhesives which form a bond of measurable strength rapidly upon contact with another surface, and which can be removed from that surface cleanly without leaving a residue visible to the naked eye. For such adhesives, tack may be measured as the force required to separate an adhesive and the adherend at the interface shortly after they have been brought into contact under a defined load of known duration at a specified temperature.

The method involves bringing the tip of a cleaned stainless steel probe of defined surface roughness into contact with the adhesive at a controlled rate, under a fixed pressure, for a short time, at a given temperature. The bond formed between the probe and adhesive is subsequently broken, also at a controlled rate. Tack is measured as the maximum force required in breaking the adhesive bond.

## HIL-HDBK-691B

**13.2.58 ASTM D3111-76 (1982). Standard Practice for FLEXIBILITY DETERMINATION OF HOT MELT ADHESIVES BY MANDREL BEND TEST METHODS, 4 pp. ASTM Committee D-14 on Adhesives.**

This practice covers the determination of the flexibility of a hot-melt adhesive in sheet form under specific test conditions. The results of this working test are useful for comparing adhesives, not for absolute characterization of adhesives. Test strips of a hot-melt adhesive properly sized and conditioned are bent 180° over a mandrel (rod). Using a fresh specimen for each test, the test is repeated with smaller diameter mandrels until the adhesive fails on bending. The flexibility of the adhesive is the smallest diameter mandrel over which 4 out of 5 test specimens do not break. Usually rod diameters are 1/8 inch (3.2 mm), 1/4 inch (6.4 mm), and 1/2 inch (12.8 mm) and rod lengths are 3-6 inches (75-150 mm) long and are made from brass or stainless steel.

**13.2.59 ASTM D3121-73 (1984). Standard Test Method for TACK OF PRESSURE-SENSITIVE ADHESIVES BY ROLLING BALL, 3 pp. ASTM Committee D-14 on Adhesives.**

This method covers measurement of the comparative tack of pressure-sensitive adhesives by a rolling ball, and is most appropriate for low-tack adhesives. The method is only one of several available for the measurement of tack. In the test, a steel ball 1/16 inch (11.1 mm) in diameter is released at the top of an incline, allowed to accelerate down the incline and roll onto a horizontal surface covered with a pressure-sensitive adhesive. Tack is determined by measuring the distance that the ball travels across the adhesive before stopping. The test specimen is a substrate centered with a pressure-sensitive adhesive. It is generally about 2 inches (51 mm) wide and approximately 15 inches (381 mm) long.

**13.2.60 ASTM D3163-73 (1984). Standard Test Method for DETERMINING THE STRENGTH OF ADHESIVELY BONDED RIGID PLASTIC LAP-SHEAR JOINTS IN SHEAR BY TENSION LOADING, 3 pp. ASTM Committee D-14 on Adhesives.**

This method is intended to complement ASTM D1002 on metals and extend its application to single-lap shear adhesive joints of rigid plastic adherences. The practice is useful for generating comparative shear strength data for joints made from a number of plastics. It can also provide a means by which several plastics surface treatments can be compared. The method is limited to test temperatures below the softening point of the subject adhesives and is not intended for use in anisotropic adherends such as reinforced plastic laminates. Where possible, test specimens should conform to the form and dimensions of ASTM D1002. However, adherends thicknesses and joint overlaps must be chosen so that failure will preferably occur in the joint and not in the substrate. It is important to use the optimum surface preparation techniques for the plastic adherends under test. Failing stress is reported in pounds-force per square inch (or megapascals) of shear area.

**13.2.61 ASTM D3164-73 (1979). Standard Test Method for DETERMINING THE STRENGTH OF ADHESIVELY BONDED PLASTIC LAP-SHEAR SANDWICH JOINTS IN SHEAR BY TENSION LOADING, 4 pp. ASTM Committee D-14 on Adhesives.**



## MIL-HDBK-691B

This method is intended to complement ASTM D1002 on metals and extend its application to single-lap-shear adhesive joints employing plastic adherends. The method is useful for generating comparative shear-strength data for joints made from a number of plastics. It can also provide a means by which several plastics surface treatments can be compared. The method is limited to test temperatures below the softening point of the subject adherends and is not intended for use on anisotropic adherends such as reinforced-plastic laminates.

Specimens shall conform to the form and dimensions shown on a figure. Alloy 2024-73 aluminum of 0.064 inch (1.62 mm) thickness is recommended for the metal specimens. The recommended length of overlap is 0.5 inch (12.7 mm). The sandwich under test is a metal/adhesive/plastic/adhesive/metal. It is important to use the optimum surface-preparation technique for the plastic and metal adherends under test.

13.2.62 ASTM D3165-73 (1979).\* Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING OF LAMINATED ASSEMBLIES, 4 pp. ASTM Committee D-14 on Adhesives.

This method is intended for determining the comparative shear strengths of adhesive in large area joints when tested on a standard specimen and under specified conditions of preparation and testing. Adhesives respond differently in small areas than they do in large areas. It is intended for use in metal-to-metal application, but may be specially adapted for plastic adherends. The method is useful in that the joint configuration closely simulates the actual joint configuration of many bonded assemblies and can be used to develop design parameters for such assemblies. It can also be used as an in-process quality control test for laminated assemblies. In practice, the laminated assembly is either made oversize and test specimens removed from it, or a percentage of the assemblies are destructively tested.

In the test with metals, two 0.064 inch (1.62 mm) thick layers of metal are adhesively bonded together in the form of a laminated panel. One inch (25.4 mm) wide strips of laminate 7 inch + L inches long (77.8 + Lmm) must be machined from this laminated panel. The panel is molded or cut through at opposite but displaced sides so that when the panel is tensile stressed an overlap length of L occurs. This length defines the shear area in the fabricated specimen.

In the procedure the ends of the 1-inch wide specimen are placed in the grips of a tensile testing machine so that the long axis of the test specimen coincides with the direction of applied stress. The load is applied at a rate of 1200-1400 psi (8.3 - 9.7 MPa) of the shear area per minute. The crosshead speed is 0.05 inches/minute for a 1/2 in<sup>2</sup> shear area. The load is automatically applied until failure of the joint occurs. The maximum, minimum, and average values for the failing load are reported, along with comments as to the nature of the failure, including the average estimated percentages of failure in cohesion of the adhesive, contact failure, voids, and apparent adhesion to the metal.



## HIL-HDBK-691B

13.2.63 ASTM D3166-73 (1979). Standard Test Method for FATIGUE PROPERTIES OF ADHESIVES IN SHEAR BY TENSION LOADING (METAL/METAL), 3 pp. ASTM Committee D-14 on Adhesives.

This method covers the measurement of fatigue strength in shear by tension loading of adhesives on a standard specimen and under specified conditions of preparation, loading and testing. It is intended for use in metal-to-metal applications, but may be specially adapted for plastic adherends. The data obtained by this method, although useful, are limited in scope because the complex nature of the single lap shear tensile test specimen configuration renders precise analyses impossible. Comparative fatigue data may be obtained, but the test cannot be considered of direct engineering design significance.

The single-lap-shear specimen of the ASTM D1002 test is issued. The specimen is placed in the jaws of a special tensile testing machine capable of imposing a cyclic or sinusoidal stress on the specimen. The test is carried out at 1800 cycles/minute unless otherwise noted. The cyclic load shall range from a maximum (to failure) to approximately 10% of the maximum, the maximum load being selected from previous "static" tests such as ASTM D1002. The number of cycles to failure at a given level is recorded and so-called S-N curve is constructed to display the fatigue behavior of the adhesive material and the joint.

13.2.64 ASTM D3167-76 (1981). Standard Test Method for FLOATING ROLLER PEEL RESISTANCE OF ADHESIVES, 5 pp. ASTM Committee D-14 on Adhesives.

This method covers the determination of the relative peel resistance of adhesive bonds between one rigid adherend and one flexible adherend when tested under specified conditions of preparation and testing. A variation in thickness will generally affect the results. When no thickness is specified, the flexible adherend shall be 0.63 mm (0.025 inch) thick and the rigid adherend 1.63 mm (0.064 inch) thick. The test is primarily for metal-to-metal peel resistance. The specimen is a thin laminated structural strip 0.5 inch (12.7 mm) wide with unbonded ends suitable for clamping into the test jig. The ideal specimen is composed of one rigid and one flexible adherend.

In the test, a special two-roller, drum-like fixture, each roller 1 inch (25.4 mm) in diameter, is placed in the testing machine. The flexible tab of the specimen is inserted between the two rollers, leaving the rigid portion of the specimen to rest on the top part of the rollers. The specimen-holding configuration thus forms a "T"-like shape. The flexible tab of the specimen is then clamped in the bottom jaw of the tensile machine, while the top of the roller-drum fixture is clamped in the top jaw of the testing machine. With the flexible tab on the specimen curled over one of the rollers, the specimen is peeled at a crosshead speed of 6 inches/minute (153 mm/min). The results are obtained in terms of average peel strength in pounds force per inch (or kilonewtons per metre) of width of each combination of materials and construction under test.

This test is similar to the T-peel test (ASTM D1876), but with the provision that the peeling angle is kept constant for all adhesive types relative to given adherends. It is a more controlled test than ASTM D1876.

## MIL-HDBK-691B

13.2.65 ASTM D3236-73 (1983). Standard Test Method for VISCOSITY OF HOT MELT ADHESIVES AND COATING MATERIALS, 11 pp. ASTM Committee D-2 on Petroleum Products and Lubricants

This method covers the determination of the apparent viscosity of hot-melt adhesive and coating materials compounded with additives and having apparent viscosities up to 200,000 millipascal seconds (mPa·s) at temperatures up to 175°C (347°F). (Higher viscosities and temperatures may be practical, although their precision has not been studied.) In the test a representative sample of the molten material to be tested is maintained in a thermally controlled sample chamber. Apparent viscosity is determined under temperature equilibrium conditions using a precision rotating spindle-type viscometer (Brookfield). Data obtained at several temperatures can be plotted on appropriate semi-logarithmic graph paper and apparent viscosity at intermediate temperatures can be estimated.

13.2.66 ASTM D3310-74 (1983). Standard Practice for DETERMINING CORROSIVITY OF ADHESIVE MATERIALS, 2 pp. ASTM Committee D-14 on Adhesives.

The practice is intended to determine whether an adhesive material, cured or uncured is corrosive to a metal. It is a general method intended to screen out those materials that give a visible sign of corrosion. The metal under test is enclosed in a glass container with the adhesive material. The containers are stored in a temperature-controlled oven at various temperatures with and without water present. A control consisting of glass jars containing samples (strips) of the same metal with and without water, but with no adhesive, is stored in the same oven for comparison. Results are reported after various exposure periods as degree of corrosion on the scale of five. Unless corrosion is rapid, when 1-hour exposure periods may be used, exposure is usually for 1, 3 and 7 days.

13.2.67 ASTM D3482-76(1981). Standard Practice for DETERMINING ELECTROLYTIC CORROSION OF COPPER BY ADHESIVES, 4 pp. ASTM Committee D-14 on Adhesives.

This practice covers the determination of whether an adhesive has any corrosive effect on copper. It is ordinarily intended to distinguish materials that might cause corrosion in electrical and electronic equipment. This procedure is a subjective test for which precision and accuracy have not been established. It is not recommended for adhesives on backing. Metals other than copper may be used if desired. In the practice two parallel helices of fine copper wire are laid in etched grooves on a glass tube. The adhesive material is coated over the wires and the tube and then allowed to set or cure. The wired tube is exposed to high humidity with a d-c potential applied between the wires. Corrosion products are observed visually, usually after 1, 3, and up to 15 days.

13.2.68 ASTM D3528-76 (1981). Standard Test Method for STRENGTH PROPERTIES OF DOUBLE LAP SHEAR ADHESIVE JOINTS BY TENSION LOADING, 6 pp. ASTM Committee D-14 on Adhesives.

## MIL-HDBK-691B

This method covers the determination of the tensile shear strengths of adhesives for bonding metals when tested on an essentially peel-free standard specimen that develops adhesive stress distribution representative of those developed in a typical low-peel production-type structural joint. The reproducibility of the strengths achieved is directly related to conformance with specified conditions of preparation and testing. The test specimens must conform to one of the alternative types, A or B, as specified in the procedure. A testing machine meeting the requirements of ASTM E4 is used. The maximum, minimum and average failing stresses shall be reported in terms of kilograms per square centimeter ( $\text{kg}/\text{cm}^2$ ) or pounds-force per square inch (psi) of total shear area. The nature of failure, including percentages of various types (cohesive, adhesive, metal) is also reported.

13.2.69 ASTM D 3632-77 (1982).<sup>e</sup> Standard Practice for ACCELERATED AGING OF ADHESIVE JOINTS BY THE OXYGEN-PRESSURE METHOD, 12 pp. ASTM Committee D-14 on Adhesives.

This practice is a method of estimating the relative resistance to deterioration of adhesive films and adhesive-bonded joints placed in a high-pressure oxygen environment. The instructions include both wood-to-wood and wood-to-metal joints as well as free films of adhesive. The effects of chemicals such as fire retardants, preservatives, or wood extractives can be evaluated by using materials containing these chemicals for adherends. The practice is primarily intended for elastomer-based construction adhesives, but is also applicable to other types of adhesives that may be susceptible to oxygen degradation. The results of this accelerated test are only comparative and must be evaluated against the performance of bonded joints whose natural and accelerated aging characteristics are known. The practice entails subjecting specimens with known physical properties to a controlled aging environment for specific time periods, then observing the physical properties again and noting any changes. The controlled environment consists of elevated temperature ( $70^\circ\text{C}$ ) ( $158^\circ\text{F}$ ) and oxygen at elevated pressure (2.07 MPa) (300 psi). Three types of specimens are used: Type A is for wood-to-wood lap and tests shear strength; Type B is for wood-to-metal lap and also tests shear strength; Type C is for unsupported film and tests flexibility. Three different oxygen-pressure aging exposures are used. Exposure is for (1) 500 hours, at the end of which a single physical property is tested, (2) 1000 hours, at the end of which a single physical property is tested, and (3) 1000 hours, with tests of the physical property after 200, 400, 600, 800 and 1000 hours. The practice is useful to the adhesive manufacturer in research and development and in manufacturing control. The results are also used for specification acceptance or as a guide in adhesive selection.

13.2.70 ASTM D3658-78 (1984).<sup>e</sup> Standard Practice for DETERMINING THE TORQUE STRENGTH OF ULTRAVIOLET (UV) LIGHT-CURED GLASS/METAL ADHESIVE JOINTS, 5 pp. ASTM Committee D-14 on Adhesives.

This method covers the simplistic comparison of strengths of glass/metal joints when the adhesive is cured by ultraviolet (UV) radiation and standard specimens are used and tested under specific conditions of preparation, radiation and load. The practice involves torque loading of UV-bonded hexagonal metal blocks to glass plates. The practice may be used to obtain comparative torque strength-to-failure data for other bonded joint systems, radiation cured or not.

## MIL-HDBK-691B

13.2.71 ASTM D3762-79 (1983). Standard Test Method for ADHESIVE-BONDED SURFACE DURABILITY OF ALUMINUM (WEDGE TEST), 5 pp. ASTM Committee D-14 on Adhesives.

This method simulates in a qualitative manner the forces and effects on an adhesive bond joint at metal-adhesive/primer interface. It has proven to be highly reliable in determining and predicting the environmental durability of adherend surface preparations. The method has proven to be correlatable with service performance in a manner that is much more reliable than conventional lap-shear or peel tests. The method is ordinarily used in aluminum-to-aluminum applications. In the method, a wedge is forced into the bondline of a flat-bonded aluminum specimen, thereby creating a tensile stress in the region of the resulting crack tip. The stressed specimen is exposed to an aqueous environment, usually at an elevated temperature, or to an appropriate environment relative to the use of the bonded structure. The resultant crack growth with time and failure modes is then evaluated. Variations in adherend surface quality are easily observable when the specimens are forcibly, if necessary, opened at the test conclusion.

13.2.72 ASTM D3807-79 (1984).<sup>e</sup> Standard Test Method for STRENGTH PROPERTIES OF ADHESIVES IN CLEAVAGE PEEL BY TENSION LOADING (ENGINEERING PLASTICS-TO- ENGINEERING PLASTICS), 4 pp. ASTM Committee D-14 on Adhesives.

This practice covers the determination of the comparative cleavage/peel strength of adhesives for bonding engineering plastics when tested on a standard specimen and under specified conditions of preparation and testing. The bonded test panels are cut into 25 mm (1 inch) wide and 177 mm (7 inches) long test specimens. These specimens are bonded for only approximately 76 mm (3 inches) of their length. A tension-testing machine is used to apply load at a contact crosshead speed of 12.7 mm (0.5 inches) per minute. The average load in kilonewtons per metre width of specimen required to separate the adherends is determined for the first 50.8 mm (2 inches) of cleavage/peel after the initial peak.

13.2.73 ASTM D3808-79 (1984).<sup>e</sup> Standard Practice for QUALITATIVE DETERMINATION OF ADHESION OF ADHESIVE TO SUBSTRATES BY SPOT ADHESION METHOD, 2 pp. ASTM Committee D-14 on Adhesives.

This practice provides a simple qualitative procedure for quickly screening whether an adhesive will, under recommended application conditions, bond to a given substrate without actually making bonded assemblies. It can be used to determine whether or not an adhesive will continue to adhere to the substrate under specified environmental conditions. It can also be used to evaluate adhesion of a particular adhesive to a variety of substrates, or to obtain "subjective" comparative data between several adhesives on a given substrate by noting the relative ease of failure between the adhesives tested. It is particularly applicable to adhesives that cure or set when exposed to "air" (ambient, heated, etc.) and can be used for anaerobic adhesives if testing is carried out in an oxygen-free atmosphere.

## MIL-HDBK-691B

In the practice spots of adhesive, usually about 1/4 inch (6 mm) in diameter are placed onto a substrate using the applicable procedure at curing conditions acceptable to both user and supplier of the adhesive. The substrate preparation and environmental exposure of the spot of adhesive after cure or setting can be varied as described. The determination of whether an adhesive bonds to the substrate is made by simply trying to pry the spot of adhesive from the substrate. The mode of failure is readily evident by examining whether the bond separated adhesively or cohesively, either in the adhesive or substrate.

13.2.74 ASTM D3929-80 (1984). Standard Practice for Evaluating the STRESS CRACKING OF PLASTICS BY ADHESIVES USING THE BENT-BEAM METHOD, 5 pp. ASTM Committee D-14 on Adhesives.

This is a procedure for determining the compatibility of adhesives with plastics, based on whether the adhesive causes cracking of stressed samples. It can be used for sheets or strips of plastics. It can also be used on injection-molded tensile specimens or flexural bars. The practice involves the qualitative determination of the compatibility of adhesives with plastics by observing the effect of adhesives applied in the liquid state on stressed plastic specimens. Bars of plastic are bent in a three-point loading fixture to cause a determined initial tensile stress in the surface of the bar. The liquid adhesive is then applied to the area of maximum stress, which is checked periodically for crazing or cracking. Initial stress only can be determined, and the stress level may decrease significantly during the course of the test. Suggested stress levels of testing are 1000, 2000, and 3000 psi (7, 14 and 21 MPa). For initial screening the 3000 psi level is suggested. Test results are reported as the presence or absence of cracks or crazes at a given level.

13.2.75 ASTM D3931-80 (1984). Standard Practice for Determining STRENGTH OF GAP- FILLING ADHESIVE BONDS IN SHEAR BY COMPRESSION LOADING, 5 pp. ASTM Committee D-14 on Adhesives.

This practice covers the determination of comparative shear properties of gap-filling adhesives in wood-to-wood joints at specified thicknesses of bondline in the dry condition, when tested on standard specimens under specified conditions of preparation, conditioning and loading in compression. This practice is intended as an evaluation of gap-filling adhesives such as those used to bond plywood to lumber, lumber to lumber, and other similar materials in building construction. In the practice, a testing machine having a capacity of about 15,000 lb (6818 kg) in compression, or of sufficient capacity to test the adhesive in use, is used.

13.2.76 ASTM D3983-81. Standard Practice for MEASURING STRENGTH AND SHEAR MODULUS OF NONRIGID ADHESIVES BY THE THICK ADHEREND TENSILE LAP SPECIMEN, 17 pp. ASTM Committee D-14 on Adhesives.

This practice describes a method of measuring the shear modulus and rupture stress in shear of adhesives in bonded joints. The method employs lap-shear specimens with wood, metal, or composite adherends, with adhesives having a shear modulus ranging up to 700 MPa (100,000 psi). The practice is suitable generally for joints in which the ratio of adherend tensile modulus to adhesive shear modulus is greater than 300 to 1. It is not suitable for adhesives that have a high shear modulus in the cured state and that also



## NIL-HDBK-691B

require elimination of volatile constituents during cure. In the procedure lap-shear specimens are prepared with the adhesive in question, using selected adherends. The load-deformation properties of the specimens are measured under specific recommended conditions to yield a "first estimate" of adhesive shear modulus. This estimate is used to determine the optimized joint geometry for best attainable uniformity of stress distribution in the joint. A second set of specimens is prepared having the optimized joint geometry. The final values for load-deformation properties are then measured under a variety of controlled environmental and experimental conditions. The practice is based upon the theoretical analysis by Goland and Reissner relating stress concentrations in single-lap joints to the geometry of the joint and the mechanical properties of the materials involved.

**13.2.77 ASTM D4027-81. Standard Practice for MEASURING SHEAR PROPERTIES OF STRUCTURAL ADHESIVES BY THE MODIFIED-RAIL TEST, 12 pp. ASTM Committee D-14 on Adhesives.**

This practice describes equipment and procedures to measure shear modulus and shear strength of adhesive layers between rigid adherends. The equipment may also be used for determining the adhesive's shear creep compliance, the effects of strain history, such as cyclic loading, upon shear properties, and a failure criterion for biaxial stress conditions, such as shear plus tension and shear plus compression. High-density wood is the preferred substrate, but woodbase composites, metal, plastic, reinforced plastics, and other common construction materials, may also be used as adherends. In the practice shear force is applied to the adhesive through the adherends by a modified-rail shear tool. The adherends are firmly clamped between two pairs of rigid rails, one of which is fixed and the other movable. The rigid rails limit undesired adherend deformation. The pair of movable rails is fixed to two counter-movement pivot arms. These arms restrict the attached rails (and clamped adherend) to collinear motion with respect to the fixed rails (and clamped adherend). The results are nearly uniform stress and strain distribution and the reduction of normal stress in the adhesive layer under load. A known amount of uniform tensile or compression force can be applied to the adhesive layer by the shear tool in order to develop a fracture criterion for the adhesive under combined states of stress, such as shear plus tension, or shear plus compression, which commonly occur in bonded structures. The basic output of the practice is the bond shear strength determined as the shear stress at failure, and the stress-strain diagram determined from the plot of load on the shear tool versus the shear displacement of the bond line. Bond strength and the stress-strain diagram may be obtained for a variety of environmental and loading conditions.

**13.2.78 ASTM E229-70 (1981). Standard Test Method for SHEAR STRENGTH AND SHEAR MODULUS OF STRUCTURAL ADHESIVES, 7 pp. ASTM Committee D-14 on Adhesives.**

This method covers the determination of the shear strength and shear modulus of structural adhesives as they occur in thin gluelines restrained by the relatively higher-modulus adherends.



## MIL-HDBK-691B

The test is intended for high-modulus adherends like most structural metals. The specimen consists of two large loading blocks with a thin narrow ring between them. This simulates the torque loading of a large-diameter, thin-walled tube. Between the loading blocks is an adherend ring made of the material under test. The load block is fitted with an alignment shaft and a suitable pin/jig arrangement to apply torque to the adherend ring area of the specimen.

In the method, torsional shear forces are applied to the adhesive through the circular specimen, producing a peripherally uniform stress distribution. The maximum stress in the adhesive at failure represents the shear strength of the adhesive. By measuring the adhesive strain as a function of load, a stress-strain curve can be established. The test specimen should be made from the same materials as are to be used in production. Production cleaning and bonding processes should be used when applicable.

### 13.3 Federal Test Methods. (2)

13.3.1 Federal Test Method Standard No. 175B. "Adhesives: Methods of Testing", September 1, 1983. 25 pp. This document currently consists of only four (4) test methods. The large number of test methods in earlier issues have been replaced by ASTM methods. The current four methods are as follows: The standard indicates the ASTM methods superseding each of the old methods.

#### 13.3.1.1 Method 1081. FLEXIBILITY OF ADHESIVES, 2 pp.

This method provides a means for determining the flexibility (elasticity) of single films or systems of films of adhesives. A uniform coating of the adhesive is applied to the clean surface of the test panel or coating system. The adhesive is dried and the test panel then placed with the adhesive side up on a mandrel of specified diameter at a point equally distant from the top and bottom edges of the panel. The panel is then bent double (180°) or 90°, as specified in the materials specification, in approximately one second. The specimen is then checked for cracks, flakes and chips.

#### 13.3.1.2 Method 4032.1 ASH CONTENT OF ADHESIVES, 4 pp.

These two procedures, A and B, are intended for use in measuring the ash content of adhesives. They are not applicable to adhesives containing decomposable salts, such as zinc chloride. Procedure A is for use of a glue or starch adhesive, or one where there is no danger from the nonvolatile content forming a rubbery residue when ignited. Procedure B employs nitric acid to prevent the nonvolatile residue from being transformed into a viscous foam when ignited. Procedure A uses a crucible with a capacity of 30 ml or more. A muffle furnace kept at 550-600°C (1022-1112°F) is used to combust the sample. Procedure B uses an evaporating dish of 150-ml capacity and a muffle furnace kept at 600°C (1112°F).

13.3.1.3 Method 4041.1. GRIT OR LUMPS (OR UNDISSOLVED MATTER) IN ADHESIVES, 1 pp.

## MIL-HDBK-691B

This method is for determining whether an adhesive a liquid, water-based adhesive such as starch, dextrin, casein, latex, or resin base contains grit, lumps, or undissolved matter. Unless otherwise specified, approximately 10 grams of the adhesive material are used in the test. The adhesive components are mixed in the proper proportions and a thin layer of the resultant adhesive product is applied to a sheet of white bond paper. The sheet is placed face-down on a piece of glass and rolled with a paper or print roller to eliminate air bubbles and wrinkling. The sheet is then felt by hand to determine any unevenness caused by grit of undissolved matter.

**13.3.1.4 Method 4051.1 ODOR TEST FOR ADHESIVES, 3 pp.**

This method is completely different from the earlier Method 4051. In the method 20 grams of adhesive sample are placed into a wide-mouth glass bottle, covered with aluminum foil, and the cap screwed on. The bottle with sample is then aged for at least 24 hours at 73°F (23°C) and 50% RH, along with a control containing a reference adhesive known to have an acceptable odor. Heating to higher temperatures for 2 hours or longer may be used. The bottles are then opened and smelled by a panel of at least five members. The sample is rated as to whether the odor of the test adhesive is less than, equal to, or greater than the reference material.

## MIL-HDBK-691B

## REFERENCES

- (13-1) The ASTM standards listed in this Chapter are published in the Annual Book of ASTM Standards, available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19120. The standards issued by Committee D-14 on Adhesives are all found in Volume 15.06-Adhesives. Single copies, called "separates", are also available from ASTM. The abstract entries in this Chapter were adapted from the actual ASTM standards, and, in some cases, from the section on ASTM Tests, pp. XXXI-XLIII, in Adhesives, edition 3, Desk-Top Data Bank<sup>R</sup>, Cordura Publications, Inc., 1984.
- (13-2) Federal Test Method Standard No. 175B, Adhesives, Methods of Testing, with the latest revisions, is available from General Services Administration, Specifications Unit (WFSIS), 7th and D Streets, SW, Washington, D.C. 20407, or from the Naval Publications and Forms Center, 5801 Tabor Avenue, Philadelphia, PA 19120.

## MIL-HDBK-691B

## Chapter 14. QUALITY CONTROL

**14.1 Introduction.** Processing control and quality control are usually the final considerations in the design of an adhesive-bonding system. These decisions are very important, however, because they alone may:

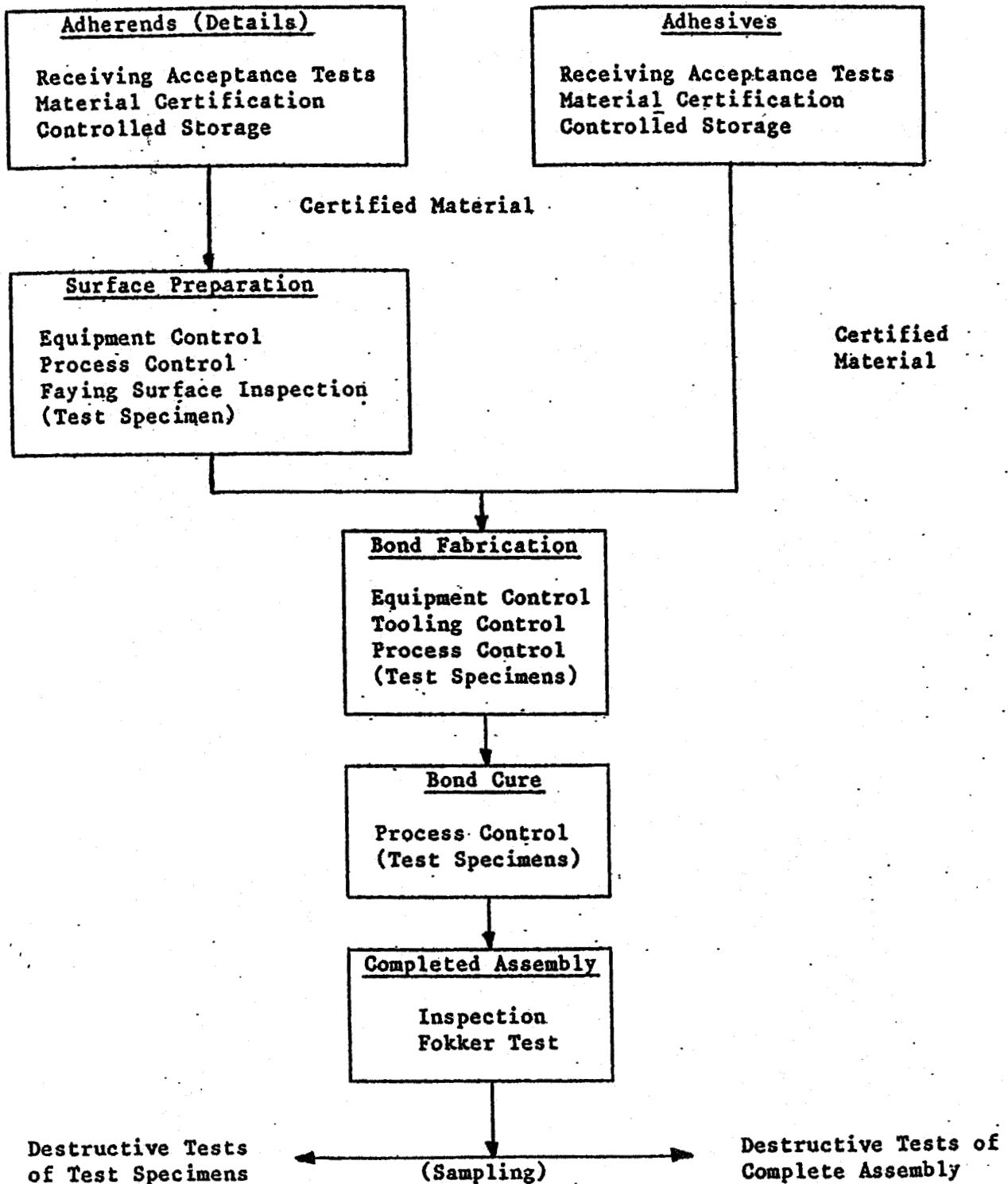
1. restrict the degrees of freedom in designing the end product
2. widen or narrow the types of adhesives that can be considered
3. affect the quality and reproducibility of the joint
4. affect the total assembly cost.(1)

A flow chart of a quality-control system for a major aircraft manufacturer is shown in Figure 45. This system is designed to detect substandard bonds before they are shipped, and to recommend methods of correcting the causes. It combines nondestructive Pokker tests of individual joints with rigid controls over process operations, and destructive tests of sample bonded parts and test specimens. The level of quality control applied to a particular bonded assembly depends upon its structural requirements. Critical joints are controlled by high sampling levels for destructive testing, and tight acceptance requirements. Less critical bonds are controlled by less stringent procedures.

The first phase of the quality-control system outlined in Fig. 45 controls the quality of adhesive material and adherend details making up the joint. Inspections and tests are performed upon incoming materials to assure their meeting acceptance requirements. Shortly before use, destructive tests (in which the test specimens are damaged) are conducted on specimens bonded with each particular batch of adhesive to be used, to insure their capability of developing bond strength after proper cure. Carefully controlled storage insures that only certified adherend details and adhesive materials are used in each joint.(2)

Rigid process controls insure that each batch of bonded joints receives proper processing during the surface preparation, fabrication and cure processes. Surface preparation processes are controlled with respect to temperature and composition of baths and immersion time of parts, which are followed by inspection of treated faying surfaces to determine wettability. Fabrication operations are regulated by process controls in conjunction with tests and controls over dimensions, alignment, and pressurization provided by the tooling. Cure conditions are generally controlled by incorporating thermocouples into the glue line to monitor actual cure temperature and time. Although these rigid controls do not completely assure proper processing, there is a high level of assurance that each batch of parts is processed to develop acceptable bond quality in the lot.(2)

## MIL-HDBK-691B

FIGURE 45. Flow chart of a quality-control system for adhesive bonding. (2)

## MIL-HDBK-691B

Test coupons, or preferably extensions of the actual parts, pass through the entire bonding process with the particular lot of assemblies they represent. These specimens are destructively tested in shear, tension, or peel (see Chapter 13 for test methods applicable), and the strength of each joint within the lot is assumed to be that of the accompanying test specimens. Test specimens having substandard bond strength cause rejection of the entire lot. In addition, destructive tests are conducted to qualify the first article produced, and subsequently upon a sampling of assemblies, produced from each piece of tooling during the production run, to insure that the process and tooling remain under control. These process control and sampling methods are capable of detecting discrepancies affecting the entire lot of assemblies, but cannot evaluate factors affecting individual joints or specific areas of a particular joint.(2)

Incorporating the nondestructive Fokker test method into the inspection and test system provides the capability of evaluating many of the factors affecting bond strength of individual joints.(2)

The major limitation of existing quality-control systems for adhesive bonding is lack of ability to detect weak bonds caused by local areas of poor adhesion. The major causes of such discrepancies are inadequate surface preparation in particular areas, nonhomogeneous adherend surfaces, or contamination of prepared adherend surfaces or adhesive material during processing. Process controls are incapable of detecting weak bonds caused by such discrepancies. The incidence of substandard bonds can be decreased by rigid controls over materials and processes, and by particular care being taken by production personnel. Such methods are not capable of providing complete assurance of high-quality bonds. The solution to this problem would be the development of a nondestructive test method capable of measuring the properties of adhesive-adherend interfaces and the adhesion of films to adherend surfaces. Until such a nondestructive test method is developed, the present combination of rigid process controls, destructive tests of specimens, and nondestructive tests of each completed joint, will remain the most reliable means of assuring the quality of adhesive bonds and bonded structures.(2)

**14.2 Incoming material control.** Quality control starts with the receipt of raw materials, such as adhesives and catalysts. The purchase order normally defines the required quality properties of the material by virtue of an actual statement of requirements, or by what is called out in the Material Specification. The inspection requirements are normally specified in the Material Specification as Quality Acceptance Tests or as Receiving Inspection Requirements. (Military and Federal specifications on adhesives are listed in Chapter 17).(3)

**14.2.1 Containers.** The first inspection requirement is normally the condition of the container. The following items should be looked for when inspecting the container.(3)

- o **Damage.** Physical damage to a container of film adhesive can rupture its sealed wrapper, allowing moisture, dirt, etc. to reach and contaminate the adhesive. Damage can render a pail of liquid measure unusable in automatic measuring equipment.



## MIL-HDBK-691B

o Leakage. Leakage of liquid adhesive components can change the ratio of the catalyst to the base resin if premeasured kits are involved. It can also result in the receipt of less material than the purchaser needs and is paying for.

o Identification. Identification of a container should include:

- o Product number
- o Manufacturer's name
- o Date of manufacture
- o Batch or lot numbers
- o Shelf life
- o Recommended storage conditions
- o Manufacturer's instructions for use
- o Safety precautions

14.2.2 Adhesives. Incoming adhesive material control includes two types of tests: physical properties, such as percent flow and gel time, and percent volatiles, that are of interest to the process engineer in assuring the bond quality. For example, the test on percent flow is of value in maintaining the bonding process so the adhesive flow won't be too great, which could cause a thick or inadequately filled bond.<sup>(4)</sup> Test methods used for physical properties include the following, which are described in Chapter 13.

ASTM Methods

D816	Rubber Cement (includes test methods on adhesion strength, bonding range, softening point, cold flow, viscosity, cold brittleness, density, and plastic deformation.)
D898	Applied Weight Per Unit Area of Dried Adhesive Solids
D899	Applied Weight Per Unit Area of Liquid Adhesives
D1084	Viscosity of Adhesives
D1337	Storage Life of Adhesives by Consistency and Bond Strength
D1488	Amylaceous Matter in Adhesives
D1489	Nonvolatile Content of Aqueous Adhesives
D1490	Nonvolatile Content of Urea-Formaldehyde Resin Solutions
D1579	Filler Content of Phenol, Resorcinol and Melamine Adhesives
D1582	Nonvolatile Content of Phenol, Resorcinol and Melamine Adhesives
D1583	Hydrogen Ion Concentration of Dry Adhesive Films
D1584	Water Absorptiveness of Paper Labels (not on adhesives, but adhesive-related)
D1875	Density of Adhesives in Fluid Form
D1916	Penetration of Adhesives
D2183	Flow Properties of Adhesives
D2556	Apparent Viscosity of Adhesives Having Shear-Rate-Dependent Flow Properties
D2979	Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine
D3121	Tack of Pressure-Sensitive Adhesives by Rolling Ball
D3236	Viscosity of Hot Melt Adhesives and Coating Materials

## MIL-HDBK-691B

Federal Test Method Standard No. 175B: Adhesives: Methods of Testing

Method 1081 Flexibility of Adhesives  
 Method 4032.1 Ash Content of Adhesives  
 Method 4041.1 Grit or Lumps (or Undissolved Matter) in Adhesives  
 Method 4051.1 Odor Test for Adhesives

The mechanical properties of the incoming material are of interest, since they are indicative of the structural results to be obtained in the final bonded assembly. The various tests and requirements for mechanical strength properties of structural adhesives are adequately described in various specifications and standard tests methods described in Chapter 13. The test methods covering mechanical strength properties (including durability, flexibility and fatigue) are as follows:

ASTM D897, D903, D905, D906, D950, D1002, D1062, D1144,  
 D1184, D1344, D1781, D1876, D2095, D2182, D2295, D2339, D2557,  
 D2558, D2918, D2919, D3111, D3163, D3164, D3165, D3166, D3167,  
 D3527, D3528, D3568, D3762, D3807, D3808, D3931, D4027, E229  
 Fed. Test Method Std. No. 175B, Method 1081.

Other miscellaneous properties, including creep, are covered in the following:

D896, D904, D1146, D1151, D1183, D1304, D1382, D1383, D1581,  
 D1713, D1780, D1828, D1877, D1879, D2294, D2739, D3310, D3482,  
 D3632, D3929, D4299, D4300

**14.3 Surface preparation control.** The second step, after determining the quality of incoming materials, is adherend surface preparation. Surface preparations must be carefully controlled for reliable production of adhesive-bonded parts. Adherend surface preparation is discussed in considerable detail in Chapter 5 and in Chapter 12 (Section 12.3) on Weldbonding. Section 5.1 discusses quality control aspects to some extent.

If a chemical surface treatment is required, the process must be monitored for proper sequence, bath temperature, solution concentration, and contaminants. If sand- or grit-blasting is employed, the abrasive must be changed regularly. An adequate supply of clean wiping cloths for solvent cleaning is also required. Checks should be made to determine if cloths or solvent containers have been contaminated. The specific surface preparation used can be checked for effectiveness by the water-break-free test described in 5.3.3.1. After the final treatment step, the substrate surface is checked for its ability to form a continuous film of water when deionized water droplets are applied to the surface. After the adequacy of the surface treatment has been determined, precautions must be taken to assure that the substrates are kept clean and dry until bonding. The adhesive or primer should be applied to the treated surface as quickly as possible.(1)

**14.4 Process control of bonding.** In addition to surface preparation, considered in 14.3, production of adhesive-bonded parts involves (1) prefit, (2) adhesive application, (3) assembly, and (4) cure.

## MIL-HDBK-691B

**14.4.1 Prefit.** All detail parts must be dry-fitted together to insure a close contact of the faying surfaces. If two or more detail parts do not fit prior to being bonded, they are not likely to fit well enough after being bonded to produce a good joint. If a high production rate exists where a reproducible fit accuracy can be established, the prefit can sometimes be omitted. First-article fits can be checked by using tool-proofing films which produce an imprint or image of the joint fit. This can greatly reduce the risk factor or poor fit where expensive or critical components are involved. After prefit conditions are verified, each detail part fitted in that assembly should be identified as such to facilitate mating of those specific parts after adhesive application. Process-control test panels or excess tag end portions of the assembly should be included with the kit of prefitted details at this point and verified at the time of prefit inspection. These process-control test specimens must be processed through all operations simultaneously with the end product. They should be tested after curing to verify the adhesive batch, surface preparation, and other processing conditions used on that end item.(3)

**14.4.2 Adhesive application.** Most structural film adhesives require a primer to protect prepared surfaces, resist peel loads, and promote wetting of the substrate surfaces by the adhesive when low-flow adhesives are involved (see Primers, Sect. 5.2). Adhesive primers are usually spray-applied by air or by airless spray systems. Roller or brush application is sometimes used on small areas, or where spray equipment is not available. The primer coat must be air-dried and sometimes oven-baked to remove solvents. The thickness of the prime coat will usually affect the adhesive bond strength and must be controlled and verified. This is usually done by periodically certifying the primer applicator and by monitoring part primer thickness after drying.(3)

Film adhesives are applied by removing a paper or plastic separator/protective film and laying the adhesive on the faying surface smoothly, taking care not to allow wrinkles to develop nor air to become entrapped between the adhesive and the substrate surface. A common workmanship error is made by not removing the separator film before assembly of the detail parts. Some bonders utilize special check-off points to insure separator film removal.

The batch number, lot number, time and date of application and adhesive type should be logged with the inspection record for traceability should a failure occur. The shop-life expiration date and time should also be logged to aid in controlling assembly and care of adhesive-coated parts within the prescribed working life of the adhesive.(3)

**14.4.3 Assembly.** The adhesive-coated detail parts are usually joined in a tool or holding fixture. Cleanliness and proper preparation of the tools should be verified. Time limits on the surface preparation, pot life of the adhesive, and remaining time during which the adhesive must be cured need verification at the point of assembly.(3)

Assembly of detail parts in their proper sequence and fit should be verified. Maintenance of cleanliness and atmosphere control is important. The atmosphere to which the parts and the adhesive are exposed must be controlled from the time the detail parts are prepared for adhesive application until the cure is initiated. Controlling the atmosphere normally involves:

## MIL-HDBK-691B

- (1) keeping the temperature between 65-90°F (18-32°C)
- (2) keeping relative humidity between 20% and 65%
- (3) filtering of all incoming air to preclude airborne contaminants
- (4) maintaining a slight positive pressure differential between the controlled environment area and all surrounding areas.

Temperature and humidity indicators of the recording type should be used for verification.(3)

**14.4.4 Curing.** Curing an adhesive in any joint is usually a time-temperature-pressure function. Regardless of the means of controlling each of these three variables, the documentation-verification means are basically the same. Controlling the length of cure time can be by manual or automatic timing devices. Verification is usually documented on a cure chart taken from a temperature and/or pressure recorder; recordings of pressure and temperature are obtained in the same manner.(3)

The facility for applying heat must be certified for its basic capabilities and uniformity with respect to its intended use. Points that must be considered are: (1) heat-up rate, (2) maximum temperature limits, (3) temperature range or spread during heat-up and at cure temperatures, and (4) cool-down characteristics. This certification should make the facts clear as to the curing facility. The same degree of verification is needed for the pressure characterization of the facility if it is an autoclave, a vacuum system, or a press.(3)

**14.4.5 Standard test specimen.** It is very desirable to fabricate a standard test specimen in the same cycle as the part being bonded. This specimen should be designed for a test method that is indicative of the prime structural loading requirement. For example, if the critical item is normally loaded in tensile shear, the specimen should be of the lap-shear type.

#### **14.5 Final inspection**

**14.5.1 General.** After the adhesive is cured, the joint area can be inspected to detect gross flaws or defects. This inspection procedure can be either destructive or nondestructive in nature (See Section 14.1 for general discussion of the testing procedure for quality control). Destructive testing generally involves placing samples of the production run in simulated or accelerated service and determining if it has properties similar to a specimen that is known to have a good bond and adequate service performance. The causes and remedies for faults revealed by such mechanical tests are described in Table XLIII. Section 14.2.2 lists the destructive (mechanical) tests that can be carried out on adhesive bonds. Nondestructive tests are far more economical, and every assembly can be tested, if desired.(1)

#### **14.5.2 Nondestructive tests**

**14.5.2.1 Visual inspection.** Visual inspection, with the help of a strong light, can be used to detect gross flaws and defects. Table XLIV lists the characteristics of faulty joints that can be detected visually. The most difficult to detect by any means are those defects related to improper curing and surface treatments. For this reason, great care and control must be given to surface-preparation procedures and shop cleanliness.(1)

## MIL-HDBK-691B

14.5.2.2 Sonic methods

14.5.2.2.1 Tap test. One of the first methods used to evaluate the soundness of an adhesive-bonded structure was the tap test, in which a coin is used as a special tapping hammer. The experienced inspector analyzes the resulting tone. Tone differences indicate inconsistencies in the bonded joint. Sharp, clear tones indicate that adhesive is present and adhering to the substrate in some degree; dull, hollow tones indicate a void or unattached area. Some improvement in the tap test can be achieved by using a solenoid-operated hammer and a microphone pickup. The resulting electrical signal can be analyzed on the basis of amplitude and frequency. (1)(3)

14.5.2.2.2 Sonic resonator. This technique uses a vibrating crystal to excite a structure acoustically at sonic frequencies (5-28 KHz). The elastic properties of the structure are changed by unbonds or other structural defects. Resulting changes in the crystal loading are processed electronically to obtain an electrical signal for display or recording. The technique can be used to test bonded honeycomb structure without regard to the material of either the facing sheet or the honeycomb core. It requires comparison standards and a liquid for coupling the probe to the specimen. The apparatus used is capable of detecting unbonds, crushed core, fracture core, and water content. (5)

14.5.2.2.3 Eddy-sonic test method. This method is based on the phenomenon that a mechanical force is inherently associated with flow of eddy currents. Since the eddy current field is time-variant, the mechanical force is also time-variant. Thus an acoustic vibration can be induced in the proper sample. To use this principle as an NDT technique for honeycomb materials, some constituents must be electrically conductive. The major advantage is that no liquid-energy couplant is needed, since air serves as a satisfactory coupling medium. The system is useful for detecting both near-side and far-side unbonds in thin honeycomb structures. It can also be used to detect crushed core, fractured core and voids in the adhesive.

14.5.2.2.4 Pulsed eddy-sonic test method/Shurtronic harmonic bond tester. This method can detect both near-side and far-side unbonds in many types of honeycomb and laminar structures. It can also detect crushed core, fractured core, and excessive adhesive build-up in repaired structures. At least one of the surfaces must be electrically conductive to some extent. (5)

14.5.2.2.5 Arvin acoustic analysis system. This is an indicator system which produces and detects acoustical vibrations in metal surfaces. It is useful for bond inspection of aluminum honeycomb materials. No acoustic coupling is needed.



## MIL-HDBK-691B

TABLE XLIII. Faults in adhesive-bonded joints revealed by mechanical tests.(1)

Fault	Cause	Remedy
Thick, uneven glue line	Clamping pressure too low	Increase pressure. Check that clamps are seating properly
	No follow-up pressure	Modify clamps or check for freedom of moving parts
	Curing temperature too low	Use higher curing temperature Check that temperature is above the minimum specified throughout the curing cycle
	Adhesive exceeded its shelf life, resulting in increased viscosity	Use fresh adhesive
Adhesive residue has spongy appearance contains bubbles	Excess air stirred into adhesive	Vacuum-degas adhesive before application
	Solvents not completely dried out before bonding	Increase drying time or temperature. Make sure drying area is properly ventilated
	Adhesive material contains volatile constituent	Seek advice from manufacturers
	A low-boiling constituent boiled away	Curing temperature is too high
Voids in bond (i.e., areas that are not bonded), clean bare metal exposed, adhesive failure at interface	Joint surfaces not properly treated	Check treating procedure; use clean solvents and wiping rags. Wiping rags must not be made from synthetic fiber. Make sure cleaned parts are not touched before bonding. Cover stored parts to prevent dust from settling on them
	Resin may be contaminated	Replace resin. Check solids content. Clean resin tank
	Uneven clamping pressure	Check clamps for distortion
	Substrates distorted	Check for distortion; correct or discard distorted components. If distorted components must be used, try adhesive with better gap-filling ability
Adhesive can be softened by heating or wiping with solvent	Adhesive not properly cured	Use higher curing temperature or extend curing time. Temperature and time must be above the minimum specified throughout the curing cycle. Check mixing ratios and thoroughness of mixing. Large parts act as a heat sink, necessitating larger cure times.



## MIL-HDBK-691B

TABLE XLIV. Faults in adhesive-bonded joints revealed by visual inspection.(1)

Fault	Cause	Remedy
No appearance of adhesive around edges of joint or adhesive bond line too thick	Clamping pressure too low Starved joint Curing temperature too low	Increase pressure. Check that clamps are seating properly Apply more adhesive Use higher curing temperature. Check that temperature is above the minimum specified
adhesive bond line too thin	Clamping pressure too high Curing temperature too high Starved joint	Lessen pressure Use lower curing temperature Apply more adhesive
Adhesive flash breaks easily away from substrate	Improper surface treatment	Check treating procedure; use clean solvents and wiping rags. Make sure cleaned parts are not touched before bonding
Adhesive flash is excessively porous	Excess air stirred into adhesive Solvent not completely dried out before bonding Adhesive material contains volatile constituent	Vacuum-degas adhesive before application Increase drying time or temperature Seek advice from manufacturer
Adhesive flash can be softened by heating or wiping with solvent	Adhesive not properly cured	Use higher curing temperature or extend curing time. Temperature and time must be above minimum specified. Check mixing

14.5.2.3 Ultrasonic methods. Ultrasonic testing basically measures the response of the bonded joint to loading by low-power ultrasonic energy.(1) These methods appear to be particularly suitable for the detection of unbonds of the following types:(5)

- o Unbonds between the facing sheet to adhesive interfaces in honeycomb structures
- o Unbonds between the adhesive-to-core interfaces in honeycomb structures
- o Unbonds between adherends in adhesive-bonded laminate structures

## MIL-HDBK-691B

**14.5.2.3.1 Ultrasonic pulse echo and contact impedance testing.** The contact impedance technique is based on the fact that when a vibrating crystal is placed in a composite structure, the characteristic impedance or elastic properties of the structure determine the manner in which it is loaded. Changes in loading will change the amplitude or phase of the crystal with respect to the applied voltage. Such a change can be indicated by a suitable meter readout, or can be displayed on a cathode ray tube. The pulse echo technique can be evaluated by observing energy reflection from defects and from the back surface of the structure under inspection. These methods can be used to detect unbonds in honeycomb and laminar structures. They can also detect crushed core, fractured core, and adhesive build-up in repair areas. A disadvantage of both methods is that their response to a completely unbonded area in a honeycomb panel is difficult to differentiate from some other anomaly. Water, for example, shows the same response as an unbond.(5)

**14.5.2.3.2 Sweep-frequency resonance method (Fokker bond tester is an example).** This method has the advantage of producing a quantitative estimate of bond strength in metal-to-metal and metal-to-core structures, as well as similar structures made from nonmetallic materials. The energy that is introduced into the structure is varied over a wide range of frequencies; the resonance set up by the probe, face sheet, adhesive, and the remainder of the structure is observed.(3) The Fokker Bond Tester is believed to be the only system currently capable of providing an accurate direct quantitative reading of the quality of an adhesive bond. The principle is that when a crystal resonating at its natural frequency is placed on a composite structure, the characteristic impedance or elastic properties of the structure determine the manner in which it is loaded. Changes in loading are shown by the combination of the two instrument readings, resonance frequency shift and a change in amplitude of the resonant frequency. Such a change is indicated by a meter readout and displayed on a cathode-ray tube. A light oil is used as a couplant. The Fokker Bond Tester has been successful in determining near-side unbonds in a wide variety of adhesively bonded structures. It does not give good results in detecting unbonds in honeycomb panels with laminated facing sheets. Besides unbonds, it detects crushed core, fractured core, and voids in the adhesives.(5) The Fokker Bond method is most sensitive to properties which physically affect adhesion, such as voids, porosity, and incomplete wetting. It is not capable of detecting incomplete cure, poor surface preparation, or contamination of the interface.(1)

**14.5.2.4 Liquid crystals.** Cholesteric liquid crystals are compounds that go through a transition phase where they possess the flow characteristics of a liquid, while retaining much of the molecular order of the crystalline solid. Since liquid crystals have the ability to reflect iridescent colors, depending on the temperature of their environment, they may be applied to the surfaces of bonded assemblies and used to project a visual color picture of minute thermal gradients associated with bond discontinuities. Cholesteric crystals are potentially a simple, reliable, and economical method for evaluating bond defects in metallic and nonmetallic composite structures.(6) Materials with poor heat-transfer properties are difficult to test by this technique, and the joint must be accessible from both sides.(1)

## MIL-HDBK-691B

**14.5.2.5 Holography.** The science of holography has also been used for NDT of adhesive bonds. Holography is a method of producing photographic images of flaws and voids, using coherent light, such as that produced by a laser. The major advantage of holography is that it photographs successive "slices" through the scene volume. A true three-dimensional image of a defect or void can then be reconstructed.<sup>(1)</sup> It is now possible, using stored-beam holographic techniques, to make real-time differential interferometric measurements to a precision of the order of one-millionth of a centimeter on ordinary surfaces. A simple method of inspecting bonded panels is to place them horizontally and to apply a thin sand layer on the upper surface. When the panel is vibrated, any unbonded areas will be revealed by the pattern resulting from the movement of the sand particles. Bond quality can also be determined by making circular cuts through one adherend down to the bond line in a zone where the strength of the assembly will not be affected. The disks are pried out to expose the adhesive to visual inspection. Plugs may be inserted later in the cut-outs. In certain cases, test specimens are treated and bonded simultaneously with the production parts under the same conditions. These specimens are then tested for strength.<sup>(6)</sup>

Holographic techniques are well-known for their ability to measure differential displacements. This property of holography makes it a useful tool for detecting nonbonds in laminar structures. If such a structure is stressed by any of several means (heat, differential pressure, or mechanical), then the displacement of the surface can be related to the integrity of the bonded layers below the surface. A laminar material which is well-bonded will have a uniform surface displacement which is a function of the physical properties of the material, the means of stressing and the holographic techniques. If, however, the material has a nonbonded region somewhere in the different layers, then the surface above that region will displace differently than the rest of the surface due to the change in the boundary conditions. This change in the surface displacement is a microscopic differential change, and would normally not be visible. Holography, however, with its remarkable sensitivity, makes such microscopic changes clearly visible. The means of acquiring the surface displacements and thereby the integrity of the bond is called double-exposure holography.<sup>(7)</sup>

**14.5.2.6 Thermal image inspection.** In this technique bond discontinuities are revealed through temperature differences on the assembly surface. The use of ultraviolet radiation permits the direct visual detection of these discontinuities as dark regions in an otherwise bright (fluorescent) surface. For practical purposes, to preclude thermal damage to the adhesive and/or heat-sensitive adherends, a phosphor is used that shows a large change in brightness with a small change in temperature in the near-room-temperature range (25 to 65°C). The coatings used for this purpose provide a stable (non-settling) suspension of the phosphor in the vehicle that can be applied by conventional paint-spray equipment.<sup>(6)</sup>

## MIL-HDBK-691B

**14.5.2.7 Thermal infrared inspection (TIRI).** This technique has been used for detection of internal voids and unbonded areas in solid-propellant rocket engines and in large, panel-shaped components.<sup>(6)</sup> The technique uses a dynamic heating principle with continuous injection of thermal energy from an induction generator into the exposed surface of the specimen along a line of scan. Continuous radiometric detection of the emission from contiguous surface regions along the line of scan, after a fixed time interval following heat injection, results in temperature gradients at the outer surface. The depth of the flaw below the surface of the material (interface level) is determined by comparison of inspection recordings taken at pre-established exposure times. Destructive sectioning of representative specimens following TIRI examination indicated a correlation of 95% for first and second interface defects.<sup>(8)</sup>

**14.5.2.8 Radiography.** Radiographic inspection techniques have proven to be successful for the detection of defects in adhesive-bonded metal-to-metal joints and metal sandwich structures. In the case of metal-to-metal joints, the adhesive must contain some metal powder or other suitable filler to create enough contrast to make defects visible. The same procedure can be used with nonmetallic adhesive bonded joints. An experienced inspector, using radiography, can often detect undesirable concentrations of adhesive, or evaluate the quality of adhesive-bonded sandwich structures. Damage can occur in handling, or may be the result of unequal pressure during the bonding cycle.<sup>(3)</sup> Radiography will not detect lack of bond areas where the adhesive is present, but not bonded to one or both adherends.<sup>(5)</sup>

**14.5.2.8.1 X-ray techniques.** These may be used only if fillers are added to the adhesive. This results from the slight weakening of the rays in the penetration through unfilled adhesive, because the density of the latter is low. Excellent results may be obtained by adding lead oxide. In this case it is possible to detect even the smallest air and gas bubbles. Conventional X-ray equipment for flaw detection is used. Because of the thinness of the adhesive layer, very long rays must be used.<sup>(6)</sup>

**14.5.2.8.2 Radioisotope methods.** For inspecting the toughness of combined bonded and spot-welded joints radioactive isotopes may be used to check the possibility of electrolyte penetrating to the bond line during subsequent anodizing in sulfuric acid. A radioactive sodium isotope, such as sodium-22, with a half-life of 2.5 years, is introduced into the most active electrolyte. If there are voids in the adhesive layer the electrolyte penetrates into the clearance between the adherends. The joint is then washed clean and examined with a radiometer. If there are voids, radioactive substance is retained in them and the radiation intensity is higher. However, the application of this method in industry is limited by the danger of radiation.<sup>(6)</sup>

**14.5.2.8.3 Neutron radiography.** If the adhesive used is not X-ray opaque, neutron radiography may be used. The hydrogen atoms in the adhesive absorb neutrons, making the adhesive opaque.<sup>(4)</sup> The neutron radiographic technique detects defects within adhesive bondlines and predicts the lap-shear strength, usually within 5 to 10%. A portable system permits the method to be applied

## MIL-HDBK-691B

to aircraft with adhesively bonded parts. Although ultrasonic and X-ray techniques can determine void content and joint strength, neutron radiography appears to have more sensitivity. In addition, it seems to be more nearly independent of metal thickness than X-ray and less dependent on scattering and geometric complexity than the ultrasonic method.(9)

**14.5.2.9 Penetrant inspection.** This method is used for local examination of sections of seam joints. First, the surface of the specimens must be cleaned and degreased. Then a penetrant solution is applied along the joint. Capillary action pulls the solution into any defect open to the surface. The penetrant on the surface is rinsed with a solvent, leaving the penetrant in the defects. A developer is then applied to draw the penetrant back to the surface. Because the penetrants are brilliantly colored, each defect is easy to see.(6)



## HIL-HDBK-691B

## REFERENCES

- (14-1) E.M. Petrie, "Plastics and Elastomers as Adhesives," Chapter 10 in HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A. Harper, McGraw-Hill, New York, N.Y., 1975.
- (14-2) D.F. Smith and C.V. Cagle, "A Quality-Control System for Adhesive Bonding Utilizing Ultrasonic Testing," Applied Polymer Symposia, (3): 411-434 (1966).
- (14-3) Society of Manufacturing Engineers, ADHESIVES IN MODERN MANUFACTURING, E.J. Bruno, Editor, 1970.
- (14-4) W. Bandaruk, "Process Control Considerations for Adhesive Bonding in Production," Journal of Applied Polymer Science, 6 (20): 217-220 (March/April 1962.)
- (14-5) I.R. Kraska and H.W. Kamm, General American Transportation Corporation, "Evaluation of Sonic Methods for Inspecting Adhesive Bonded Honeycomb Structures," AFHL-TR-690283, August 1970. (AD 876 977) (Currently not limited).
- (14-6) S. Semerdjiev, METAL-TO-METAL ADHESIVE BONDING, Business Books, Ltd., London, 1970.
- (14-7) M.J. Barbarisi, B.R. Chisholm and P.J. Kisatsky, "Evaluation of the Adhesive Bonding Process Used in Helicopter Manufacture - Part 4, Nondestructive Inspection of Adhesive Bonds Using Holographic Techniques," Picatinny Arsenal Technical Report 4419, October 1972. (AD 765 455).
- (14-8) P.R. Yettito, "A Thermal, Infrared Inspection Technique for Bond-Flaw Inspection," Applied Polymer Symposia, (3): 435-454 (1966). Editor, H.J. Bodnar, Picatinny Arsenal.

(WP# ID-7346A/DISK-0034A. FOR MTL USE ONLY)



## MIL-HDBK-691B

Chapter 15. ENVIRONMENTAL EFFECTS  
(Durability of Adhesive Joints  
in Adverse Environments)

### 15.0 ENVIRONMENTAL EFFECTS.

15.1 Introduction. For an adhesive bond to be useful, it not only must withstand the mechanical forces acting on it, but must also resist the service environment. Adhesive strength is influenced by many common environments, including temperature, moisture, chemical fluids, and outdoor weathering. Table XLV summarizes the relative resistance of various adhesive types to a number of common environments (1)(2).

In applications where possible degrading elements are present, candidate adhesives must be tested under simulated service conditions. Common ASTM environmental test methods often reported on in the literature include the following, described in Chapter 13:

ASTM D896  
ASTM D1151  
ASTM D1183  
ASTM D1828

ASTM D1879  
ASTM D2295  
ASTM D2557  
ASTM D4299

ASTM D4300

The service environments to which adhesive-bonded assemblies are exposed vary from highly protected sealed systems to exterior unprotected systems. The latter may include semi-arid locations, such as New Mexico or Arizona, and highly corrosive tropical jungle or marine locations. The question of durability is meaningless unless it is linked with the intended service environment. At the same time, the durability of an adhesive bond to an extreme environmental condition is highly dependent on the surface treatment of the adherends and adhesive additives which are interfacially active.(3)

Another factor which must be considered is the durability of bonds under stress. While this is a valid consideration for bonds representative of primary bonded structures as used in aircraft construction, many bonds have negligible very low permanent loads, while the actual high-stress environment, if any, is of very short duration.(3)

Laboratory ambient storage studies revealed no degradation in bond strength for epoxy/aluminum bonds stored for up to 11 years, and for elastomeric adhesive sealant bonds to aluminum and cold-rolled steel stored for up to five years.(3)

Applied stress will cause an adhesive bond to degrade at a faster rate than an unstressed bond, although stress-relief primers, such as vinyl phenolic, or stress-relief adhesives, such as nitrile-modified phenolics, will minimize bond degradation due to stress.(3)

## MIL-HDBK-691B

TABLE XLV. Relative resistance of synthetic adhesives to common service environments. (2)

Adhesive type	Shear	Peel	Heat	Cold	Water	Hot water	Acid	Alkali	Oil, grease	Fuels	Alcohols	Ketones	Esters	Aromatics	Chlorinated solvents
<b>Thermosetting Adhesives</b>															
1. Cyanoacrylate.....	2	6	5	...	6	6	6	6	3	3	5	5	5	4	4
2. Polyester + isocyanate.....	2	2	3	2	1	3	3	2	2	2	2	2	2	6	2
3. Polyester + monomer.....	2	6	5	3	3	6	3	6	2	2	2	6	6	6	6
4. Urea formaldehyde.....	3	6	3	3	2	6	3	2	2	2	2	2	2	2	2
5. Melamine formaldehyde.....	2	6	2	2	2	5	2	2	2	2	2	2	2	2	2
6. Urea-melamine formaldehyde..	2	6	2	2	2	2	1	1	2	2	2	2	2	2	2
7. Resorcinol formaldehyde.....	2	6	2	2	2	2	2	2	2	2	2	2	2	2	2
8. Phenol-resorcinol formaldehyde	2	6	2	2	2	2	2	2	2	2	2	2	2	2	2
9. Epoxy (+ polyamine).....	2	5	3	5	2	2	2	2	2	2	1	6	6	1	
10. Epoxy (+ polyanhydride).....	2	5	1	4	3	3	2	2	...	2	2	6	6	2	
11. Epoxy (+ polyamide).....	2	2	6	2	2	6	3	6	2	2	1	6	6	2	
12. Polyimide.....	2	4	1	1	2	4	2	2	2	2	2	2	2	2	2
13. Polybenzimidazole.....	2	4	1	1	2	4	2	2	2	2	2	2	2	2	2
14. Acrylic.....	2	6	5	3	1	3	2	2	2	2	2	2	2	2	2
15. Acrylate acid diester.....	2	6	3	3	4	4	6	6	3	3	5	5	5	4	4
<b>Thermoplastic Adhesives</b>															
16. Cellulose acetate.....	2	6	2	3	1	6	1	2	...	2	4	6	6	6	6
17. Cellulose acetate butyrate....	2	3	3	3	2	...	3	3	...	...	6	6	6	6	6
18. Cellulose nitrate.....	2	6	3	3	3	3	3	6	2	2	6	6	6	6	6
19. Polyvinyl acetate.....	2	6	6	...	2	6	2	2	2	2	6	6	6	6	6
20. Vinyl vinylidene.....	2	3	3	3	3	3	...	...	2	2	2	2	2	2	2
21. Polyvinyl acetal.....	2	6	5	2	2	...	6	3	2	2	3	3	6	3	2
22. Polyvinyl alcohol.....	...	2	3	...	6	6	3	3	2	1	3	1	1	1	1
23. Polyamide.....	2	3	5	...	5	6	6	2	2	2	6	2	2	2	6
24. Acrylic.....	2	2	4	3	3	3	...	...	2	...	...	4	4	...	4
25. Phenoxyl.....	2	3	4	3	3	4	3	2	3	5	5	...	...	6	
<b>Elastomer Adhesives</b>															
26. Natural rubber.....	2	3	3	...	3	...	3	3	6	6	2	4	4	6	6
27. Reclaimed rubber.....	2	3	3	...	2	...	3	3	6	6	2	4	4	6	6
28. Butyl.....	3	6	6	3	2	6	1	2	6	6	2	2	2	6	6
29. Polyisobutylene.....	6	4	6	3	2	6	2	2	6	6	2	2	2	6	6
30. Nitrile.....	2	3	3	3	2	5	5	6	2	2	3	6	6	3	6
31. Styrene butadiene.....	3	3	3	3	1	...	3	2	...	5	2	6	5	6	6
32. Polyurethane.....	2	3	3	2	2	3	3	3	2	2	2	5	5	...	5
33. Polyurethane.....	3	2	2	2	1	6	2	2	2	2	2	6	6	2	6
34. Silicone (RTV).....	3	5	1	2	2	2	3	3	2	3	3	3	3	3	3
35. Silicone resin.....	2	2	1	2	2	2	...	2	2	2	2	4	4	3	6
36. Neoprene.....	2	3	3	3	2	...	2	2	2	2	2	6	6	6	6
<b>Alloy Adhesives</b>															
37. Epoxy-phenolic.....	1	6	1	3	2	2	2	2	3	3	2	6	6	2	
38. Epoxy-polyurethane.....	2	2	6	2	1	6	2	2	2	2	2	6	6	2	6
39. Epoxy-nylon.....	1	1	6	2	2	6	...	...	...	2	3	6	6	6	6
40. Phenolic-nitrile.....	2	2	2	3	2	2	2	2	2	2	2	6	6	6	6
41. Phenolic-neoprene.....	2	3	3	2	2	...	3	2	2	2	3	6	6	6	6
42. Phenolic-polyvinyl butyral....	2	3	3	3	2	3	4	2	2	2	4	6	6	6	6
43. Phenolic-polyvinyl formal.....	2	3	6	6	2	6	4	2	2	2	4	6	6	6	6

Key: 1. Excellent 2. Good 3. Fair 4. Poor 5. Very poor 6. Extremely poor

The ranking of adhesives as to their durability is very much dependent upon the type of exposure conditions employed. Table XLVI compares the resistance of seven common adhesives to (1). typical laboratory accelerated testing environments and (2). typical weathering environments. Some workers have concluded that artificial aging ranks adhesives with respect to their resistance to penetration of water into the adhesive, with corresponding influence on the cohesive strength of the adhesive. The normal outdoor weathering tests, however, rank the adhesives with respect to their resistance to penetration of corrosion of the metal along the interface. (4)

Adhesive type	Shear	Peel	Heat	Cold	Water	Hot water	Acid	Alkali	Oil, grease	Fuels	Alcohols	Ketones	Esters	Aromatic solvents	Chlorinated solvents
<b>Thermosetting Adhesives</b>															
1. Cyanoacrylate.....	2	0	5	...	0	0	0	0	3	3	5	5	5	4	4
2. Polyester + isocyanate.....	2	2	3	3	1	3	3	2	2	2	3	2	2	0	2
3. Polyester + monomer.....	2	0	5	3	2	0	3	0	2	2	0	0	0	0	0
4. Urea formaldehyde.....	2	0	2	2	2	0	2	2	2	2	2	2	2	2	2
5. Melamine formaldehyde.....	2	0	2	2	2	5	2	2	2	2	2	2	2	2	2
6. Urea-melamine formaldehyde.....	2	0	2	2	2	2	1	1	2	2	2	2	2	2	2
7. Resorcinol formaldehyde.....	2	0	2	2	2	2	2	2	2	2	2	2	2	2	2
8. Phenol-resorcinol formaldehyde.....	2	0	2	2	2	2	2	2	2	2	2	2	2	2	2
9. Epoxy (+ polyamine).....	2	5	3	5	2	2	2	2	2	2	1	0	0	1	2
10. Epoxy (+ polyamhydrine).....	2	5	1	4	3	3	2	0	2	2	1	0	0	3	3
11. Epoxy (+ polyamide).....	2	4	0	2	2	0	3	0	2	2	1	0	0	2	2
12. Polyimide.....	2	4	1	1	2	4	2	2	2	2	2	2	2	2	2
13. Polybenzimidazole.....	2	4	1	1	2	4	2	2	2	2	2	2	2	2	2
14. Acrylic.....	2	4	5	3	1	4	2	0	2	2	2	2	2	2	4
15. Acrylate acid diester.....	2	5	3	3	4	4	0	0	2	2	5	5	5	4	4
<b>Thermoplastic Adhesives</b>															
16. Cellulose acetate.....	2	0	2	3	1	0	1	2	...	2	4	0	0	0	0
17. Cellulose acetate butyrate.....	2	3	3	3	2	...	2	0	...	...	6	0	0	0	0
18. Cellulose nitrate.....	2	0	3	3	2	2	3	2	2	2	0	0	0	0	0
19. Polyvinyl acetate.....	2	0	0	...	2	0	3	...	2	2	2	2	2	2	2
20. Vinyl vinylidene.....	2	3	3	3	3	3	...	...	2	2	2	2	2	2	4
21. Polyvinyl acetal.....	2	6	5	2	2	...	6	3	2	2	3	2	0	3	2
22. Polyvinyl alcohol.....	...	2	3	...	0	0	5	5	2	1	3	1	1	1	1
23. Polyamide.....	2	3	5	...	5	0	0	0	2	2	0	2	2	2	0
24. Acrylic.....	2	3	4	3	3	2	...	...	...	...	...	4	4	...	4
25. Phenoxyl.....	2	3	4	3	3	4	2	2	2	...	5	...	...	...	...
<b>Elastomer Adhesives</b>															
26. Natural rubber.....	2	3	3	...	3	...	3	3	6	6	2	4	4	0	0
27. Reclaimed rubber.....	2	3	3	...	2	...	3	3	6	0	2	4	4	0	0
28. Butyl.....	3	6	0	3	2	6	1	2	6	0	2	2	2	0	0
29. Polyisobutylene.....	6	0	0	3	2	6	2	6	6	0	2	2	2	0	0
30. Nitrile.....	2	3	3	3	2	5	5	6	2	2	3	6	0	0	0
31. Styrene butadiene.....	3	6	3	3	1	...	3	3	...	5	2	5	5	5	5
32. Polyurethane.....	3	3	3	2	2	3	3	3	2	2	2	5	0	0	0
33. Polyurethane (RTV).....	3	2	0	2	1	0	2	2	2	2	2	0	0	2	3
34. Silicone (RTV).....	3	5	1	1	2	2	...	2	2	3	3	3	3	3	3
35. Silicone resin.....	2	2	1	3	2	2	...	2	2	2	3	4	4	6	6
36. Neoprene.....	2	3	3	3	2	...	2	2	2	2	3	6	6	6	6
<b>Alloy Adhesives</b>															
37. Epoxy-phenolic.....	1	6	1	3	2	2	2	2	3	3	2	6	6	2	6
38. Epoxy-polyurethane.....	2	2	6	3	1	0	2	2	2	2	2	0	0	0	0
39. Epoxy-nylon.....	1	1	0	2	2	0	...	...	...	...	3	0	0	0	0
40. Phenolic-nitrile.....	2	2	2	2	2	2	...	2	2	2	2	0	0	0	0
41. Phenolic-neoprene.....	2	3	3	3	2	...	3	2	2	2	3	0	0	0	0
42. Phenolic-polyvinyl butyral.....	2	3	3	3	2	...	4	2	2	2	4	0	0	0	0
43. Phenolic-polyvinyl formal.....	2	3	0	0	2	0	4	2	2	2	4	0	0	0	0

Key: 1 Excellent 2 Good 3 Fair 4 Poor 5 Very poor 6 Extremely poor

## MIL-HDBK-591B

TABLE XLVI. Environmental failure resistance of different adhesive-aluminum joints.(4)

Adhesive Type	Laboratory Exposure* (Picatinny Arsenal Tests)	Outdoor Exposure** (Hockney, UK)
Nitrile-phenolic (with primer)	Excellent	Excellent
Epoxy-phenolic	Good	Excellent
Epoxy-polyamide	Good	Very Poor
Vinyl-phenolic	-----	Good
Modified epoxy paste	Average	Good

\*Chromic acid solution or paste-treated. Lap-shear 1-yr storage at 160°F (71°C) and MIL-STD-304 conditioning

\*\*Chromic acid etched Al adherends. Lap-shear, 90° peel and honeycomb joint geometries. Two years exposure in temperate, hot-dry, and hot-wet regions (MIL-STD-304 conditioning consists of 30-day cycles under the following conditions: -65°F (-54°C), 160°F (71°C) dry heat, 160°F (71°C) and 95% RH-heat and humidity)

The strength and stiffness (modulus of elasticity) of adhesives are strongly dependent upon the test or use temperature of the adhesive.(5) The strength of three representative adhesives as a function of test temperature is plotted in Figures 46 and 47. Dogbone samples were used for the studies resulting in Figure 46. For Figure 47 standard ASTM lap-shear specimens were prepared using 2024-T3 aluminum adherends. The shear-test specimens used for this study were very similar to the tensile specimens used in Figure 46. A shear stress is developed across the interface between notches when the specimen is tested in tension.(5)

The following general conclusions about durability of adhesive systems can be made (6):

- o Heat-curing systems possess greater durability than RT-cure systems.
- o Surface-preparation is an important factor and it is important in making comparisons between adhesive systems to use the same surface preparation techniques

## MIL-HDBK-691B

- o All systems do have an endurance limit. The RT-cure systems have a low endurance limit, 100 psi (0.7 MPa), but they do have one
- o The chemistry of adhesive systems does have an effect on durability, i.e., highly crosslinked systems such as aromatic amine-cured systems and phenolic systems generally possess superior durability
- o Materials such as nylon that show hydrogen bonding tend to have lower durability
- o Materials such as vinyl polymers which can break down to form HCl are detrimental to durability
- o The use of chromate-pigmented primer systems greatly enhances durability

Many factors influence the durability of adhesive-bonded joints. For this reason a durability test should be conducted on all systems before they are selected for any particular application. This test should include the adherends, surface preparation, adhesive, and cure parameters needed for each application.(6)

## 15.2 High temperature.

15.2.1 General. All polymeric materials are degraded to some extent by exposure to elevated temperatures. Physical properties are lowered as a result of testing at high temperatures, but they also degrade during thermal aging. Newly developed polymeric adhesives have been found capable of withstanding 500-600°F (260-316°C) continuously. To use these materials, the designer must pay a premium in adhesive cost and must also be capable of providing long, high-temperature cures.(1)

For an adhesive to withstand elevated-temperature exposure it must have a high melting or softening point and resistance to oxidation. Materials with a low melting point, such as many of the thermoplastic adhesives, may prove to be excellent adhesives at room temperature. However, once the service temperature approaches the glass transition point of the adhesive, plastic flow results in deformation of the bond and degradation in cohesive strength. Thermosetting materials, exhibiting no melting point, consist of highly cross-linked networks of macromolecules. Many of these materials are suitable for high-temperature applications. When considering thermosets, the critical factor is the rate of strength reduction due to thermal oxidation and pyrolysis.(1)

High-temperature adhesives are usually characterized by a rigid polymeric structure, high softening temperature, and stable chemical groups. The same factors also make these adhesives very difficult to process. Only epoxy-phenolic — , polyimide-, and polybenzimidazole-based adhesives can withstand long-term service temperatures greater than 350°F (177°C).(1)

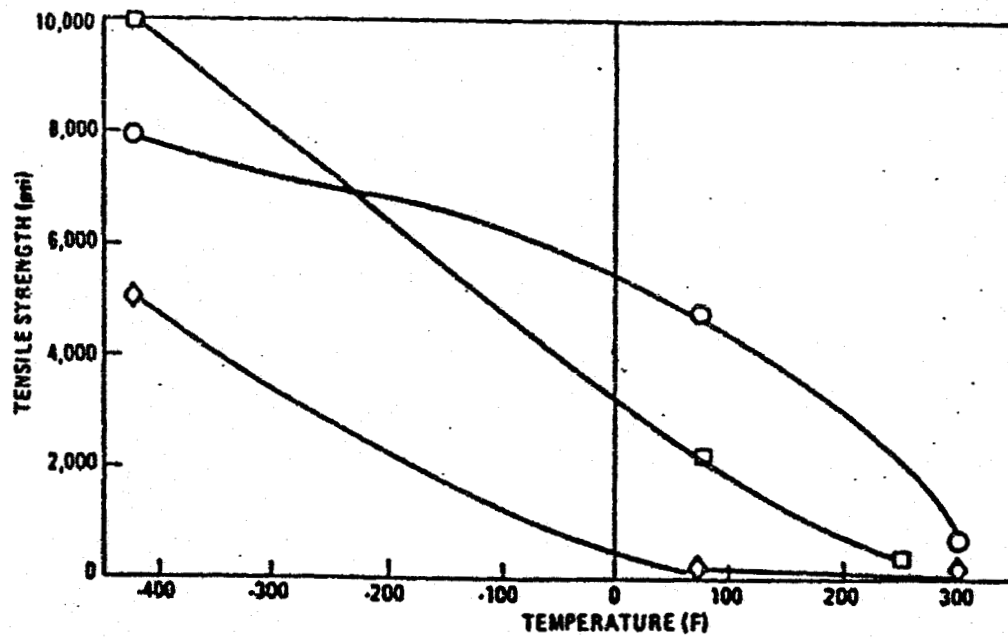


FIGURE 46. Tensile strength vs Temperature of adhesives.  
(Dogbone specimens) (5)

- Hysol EA 934 RT-cure two-part paste epoxy
- ◇ GE RTV 560 silicone two-part elastomer
- Crest 7343 polyurethane (MOCA-cured)

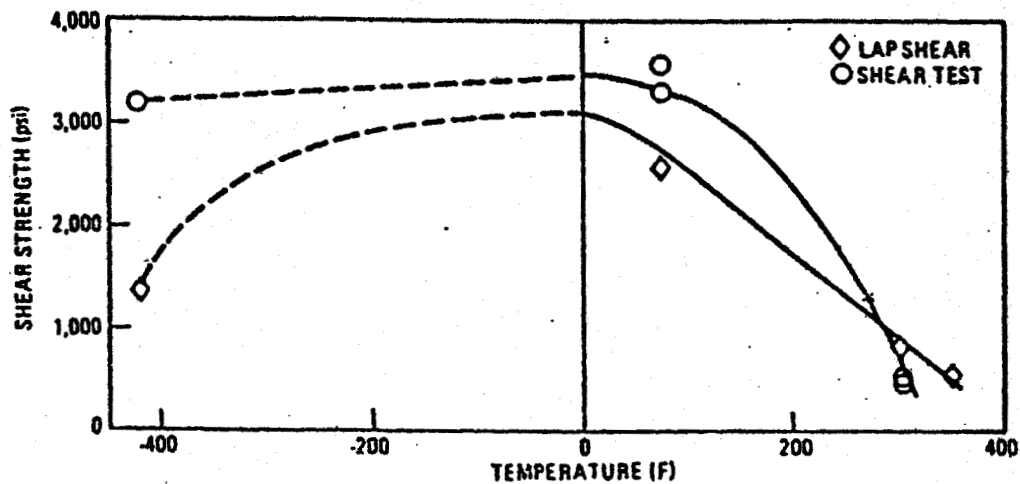


FIGURE 47. Shear strength vs Temperature for HYSOL EA 934  
RT-cure two-part paste epoxy adhesive.(5)



## MIL-HDBK-691B

Tape and film adhesives provide different high-temperature properties than paste adhesives, as shown in Figure 24 and 25 above. The distinguishing compositional feature of tape and film adhesives is that they contain a high proportion of a high-molecular-weight polymer. On the other hand, typical 100% solids paste adhesives or liquid adhesives must, to remain fluid and usable, contain only low-molecular-weight resins. Tape and film adhesives (discussed above under 4.2.5 and 6.3.5) frequently contain polymers with a degree of polymerization of 600 or more and molecular weights of 20,000 or higher. Network polymers made from these high-molecular-weight linear polymers can be very much tougher and more resilient and can provide more recoverable elongation than the highly branched network formed by curing the low-molecular-weight resins used in paste adhesive (7). Figures 24 and 25 above illustrate this point by comparing typical tensile shear data reported by manufacturers of a variety of adhesive types. The best of the tape and film adhesives have higher peak values and broader service temperature-ranges than the best of the "100%-solids" types.(7)

**15.2.2 Epoxies.** Epoxy adhesives are generally limited to applications below 250°F (121°C). Certain epoxy adhesives have been able to withstand short-term service at 500°F (260°C) and long-term service at 300 to 500°F (149 to 260°C). These systems were formulated especially for thermal environments by incorporation of stable epoxy coreactants or high-temperature curing agents into the adhesive (See 4.2.1.1.1, 4.2.1.3.2 and 4.3.1.5).(1)

One of the most successful epoxy coreactant systems is an epoxy-phenolic alloy (See 4.2.5.2). The excellent thermal stability of the phenolic resins is coupled with the adhesion properties of epoxies to provide an adhesive capable of 700°F (371°C) short-term operation and continuous use at 350°F (177°C). The heat resistance and thermal aging properties of an epoxy-phenolic adhesive cure are compared with those of other high-temperature adhesives in Figure 48.(1)

Anhydride curing agents give unmodified epoxy adhesives greater thermal stability than most other epoxy curing agents. Phthalic anhydride, pyromellitic dianhydride, and chloroendic anhydride allow greater crosslinking and result in short-term heat resistance to 450°F (232°C). Long-term thermal endurance, however, is limited to 300°F (149°C).(1)

Advantages of epoxy-based systems include relatively low cure temperatures, no volatiles formed during cure, low cost, and a variety of formulating and application possibilities. The higher-temperature resistant adhesives lose these advantages in favor of improved thermal-aging characteristics.(1)

### 15.2.3 Modified phenolics

**15.2.3.1 Nitrile-phenolics** Of the common modified phenolic adhesives, the nitrile-phenolic blend has the best resistance to elevated temperatures. Nitrile-phenolics have high shear strengths up to 250 to 350°F (121 to 177°C), and the strength retention on aging at these temperatures is very good. Nitrile-phenolic adhesives are extremely tough and provide high peel strength (See Figure 48) (1). Nitrile-phenolics are available in solvent solutions and unsupported and supported film. Nitrile-phenolic adhesives are discussed above under 4.2.5.3. See also Figure 48.

MIL-HDBK-691B

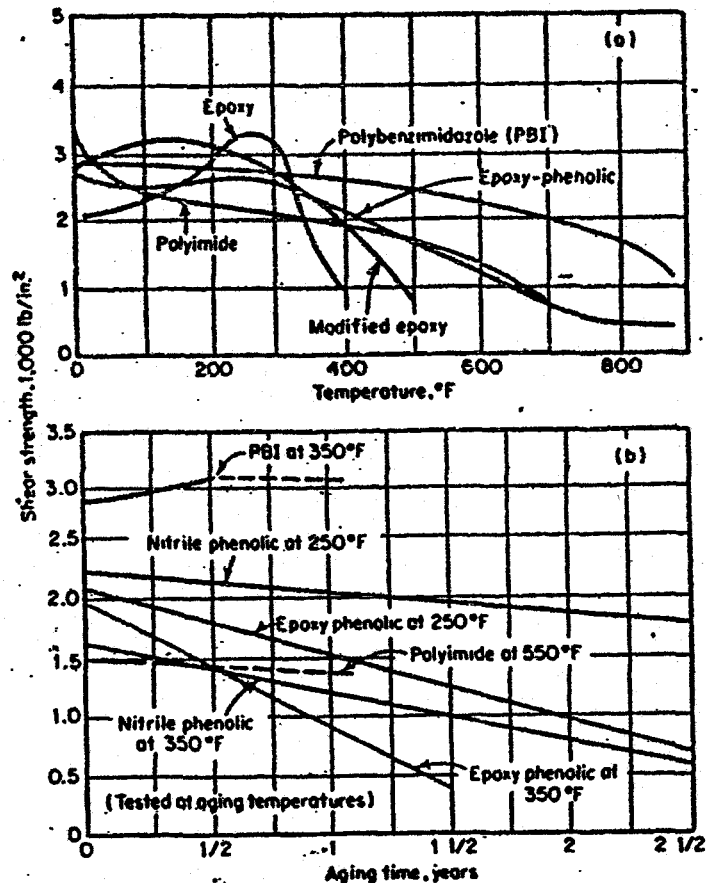


FIGURE 48. Heat resistance (a) and thermal aging (b) of high-temperature structural adhesives (1)

**15.2.3.2 Epoxy-phenolics.** These adhesives, which are used almost exclusively for the military market, are designed for service between 300° and 500°F (149 and 260°C). However, epoxy-phenolics do not withstand exposure to 350°F (177°C) as well as nitrile-phenolics. Since 350°F (177°C) cures tend to cause outgassing and foaming, 200°F (93°C) cures for 24 hours are recommended (See 4.2.5.2).

**15.2.4 Polysulfone.** A high-temperature hot-melt thermoplastic that has been used as an adhesive is polysulfone. This material is capable of adhering to hot metals, has a high softening point (190°F or 88°C) and outstanding heat stability. It has a 345°F (174°C) heat-distortion temperature and a 375°F (193°C) second-order glass-transition temperature. Flexural modulus is retained fairly constant over a wide temperature range. This material is supplied as dry pellets. Metal-to-metal joints exhibit high peel and shear strength. Polysulfone maintains its structural integrity up to 375°F (193°C). Greater than 60% of its room-temperature shear strength, as well as excellent creep resistance, is retained at 300°F (149°C). Since this is a hot melt, long cure cycles are unnecessary. The cycle need only be long enough to introduce sufficient heat for adequate wetting of the substrate by the polysulfone. Polysulfone hot melt has been used successfully with clad aluminum alloy, stainless steel and cold-rolled steel. Adequate surface preparation is necessary before bonding. Table XLVII shows bond strength from -67°F (-54°C) to 400°F (204°C) on aluminum alloy. (8)

## MIL-HDBK-691B

TABLE XLVII Effect of temperature variation on tensile-lap-shear strength of hot-melt polysulfone adhesive (UDEL P-1700) on 2024-T3 clad aluminum alloy (0.002-0.003" glue line), (8).

Test Temperature		Tensile-Lap-Shear Strength	
°F	°C	psi	MPa
-67	-54	3,300	22.8
+77	25	3,500	24.1
180	82	2,700	18.6
300	149	2,200	15.2
350	177	1,950	13.4
400	204	520	3.6

For unprimed aluminum, a temperature of 700°F (371°C) should be used to allow the polysulfone to flow sufficiently to wet the substrate. With this temperature and a pressure of 80 psi (0.6 MPa), joints with tensile-lap-shear strengths above 3000 psi (20.7 MPa) are developed in 5 minutes. Stainless steel has also been bonded with good results at 700°F (371°C). Shear strengths above 4000 psi (27.6 MPa) are obtained. With both carbon steel and aluminum, a bonding temperature of 500°F (260°C) can be used with satisfactory results if the metal is first primed with a dilute solution (5-10%) of polysulfone, applied by spray or flow-coated, and baked for 10 minutes at 500°F (260°C). The primed metal surfaces can then be bonded by pressing for 1 minute at 500°F (260°C). (8)

**15.2.5 Silicones.** Silicone adhesives have very good thermal stability, but low strength. Their chief application is in nonstructural uses, such as high-temperature pressure-sensitive tapes. Attempts have been made to incorporate silicones in the other adhesives, such as epoxies and phenolics, but long cure times and low strength have limited their use. (1) The maximum service temperature for silicone adhesive/sealants is 500°F (260°C) for continuous operation and up to 600°F (316°C) for intermittent exposure, depending on the type used. (See 4.2.1.1.7).

**15.2.6 Polyaromatics.** The polyaromatic resins, polyimide and polybenzimidazole, offer greater thermal resistance than any other commercially available adhesives. The rigidity of their molecular chains decreases the possibility of chain scission caused by thermally agitated chemical bonds. The aromaticity of the structures provides high bond-dissociation energy and acts as an "energy sink" to the thermal environments (See Figure 23 and 4.2.1.3.1).

**15.2.6.1 Polyimides** The strength retention of polyimide adhesives for short exposures to 1000°F (538°C) is slightly better than that of an epoxy-phenolic alloy. However, the thermal endurance of polyimides at temperatures greater than 500°F (260°C) is unmatched by other commercially

## MIL-HDBK-691B

available adhesives. Polyimide adhesives are usually supplied as glass-fabric reinforced film having a limited shelf life. A cure of 90 minutes at 500 to 600°F (260 to 316°C) and 15 to 200 psi (0.10 to 1.4 MPa) pressure is necessary for optimum properties. High-boiling volatiles are released during cure, which causes a somewhat porous adhesive layer. Because of the coherent rigidity of polyimides, peel strength is low (1).

**15.2.6.2 Polybenzimidazole (PBI).** As illustrated in Figure 48, polybenzimidazole (PBI) adhesives offer the best short-term performance at elevated temperatures. However, PBI resins oxidize rapidly and are not recommended for continuous use at temperatures over 450°F (232°C). PBI adhesives require a cure at 600°F (316°C). Release of volatiles during cure contributes to a porous adhesive bond. Supplied as a very stiff, glass-fabric reinforced film, this adhesive is very expensive and applications are limited by a long, high-temperature curing cycle (1).

**15.3 Low temperatures and cryogenic temperatures** Cryogenic adhesives have been defined as those capable of retaining shear strengths above 1000 psi (6.89 MPa) at temperatures varying from room temperature to -423°F (20K) (-253°C). With space vehicles carrying cryogenic fluids and travelling through outer space and re-entering the earth's atmosphere at speeds greater than Mach 3, adhesives encounter temperatures varying from -423°F (-253°C) to 1500°F (816°C) (9).

The major use of adhesives for cryogenic applications is for bonding external insulation for both metallic and non-metallic substrates. Other applications are listed in Ref. 9. Adhesives can also act as sealants. Many wing structures utilize adhesive-sealed tanks and pressure-type bulkheads. RTV silicones have been evaluated as sealants and adhesives for cryogenic applications (9). The adhesives strength values obtained with methyl-phenyl RTV silicones were only 1/4 to 1/10 the values for the better structural cryogenic adhesives. These values are adequate, however, for nonstructural bonding applications where low tensile and shear forces are anticipated. The RTV silicones may find use where high-temperature extremes up to 600°F (316°C) are encountered for short periods. The better cryogenic adhesives will not tolerate these high temperatures (9).

Many of the problems associated with bonded joints at cryogenic temperature are the result of stress concentrations and gradients developed within the bond. There are a number of causes of stress concentrations in adhesive joints. Many of these are aggravated at cryogenic temperatures. Some of the principal causes are: (9)

- o Difference in thermal coefficient of expansion between adhesive and adherends
- o Shrinkage of adhesive in curing
- o Trapped gases or volatiles evolved during bonding
- o Difference in modulus of elasticity and shear strengths of adhesive and adherends

## MIL-HDBK-691B

- o Residual stresses in adherends as a result of the release of bonding pressure
- o Inelasticity in the adhesive or adherend
- o Plasticity in the adhesive or adherend

At room temperature, a low-modulus adhesive may readily relieve stress concentration by deformation. At cryogenic temperatures, however, the modulus of elasticity may increase to a point where the adhesive can no longer effectively release the concentrated stresses. The modulus of elasticity generally increases with decreasing temperature. More constant properties are usually obtained when attempts are made to match the coefficient of expansion of the adhesive to that of the adherends. The thermal conductivity is important in minimizing transient stresses during cooling. Thinner glue lines and higher thermal conductivity minimize these stresses.

A PLASTECH report (9) provides considerable data on a number of cryogenic adhesives.

Room-temperature-curing polyurethane adhesives in current use provide higher ultimate shear and tensile stress and higher peel and shock properties at  $-423^{\circ}\text{F}$  ( $-253^{\circ}\text{C}$ ) than the earlier polyurethanes. This situation is the inverse of what happens to most structural adhesives. The polyurethane adhesives increase in strength at  $-423^{\circ}\text{F}$  ( $253^{\circ}\text{C}$ ), but become weaker at ambient and higher temperature, as shown in Table XLVIII. No drop-off in strength is observed before  $180^{\circ}\text{F}$  ( $82^{\circ}\text{C}$ ) and  $300^{\circ}\text{F}$  ( $149^{\circ}\text{C}$ ), however (9).

TABLE XLVIII Comparison of "tough" cryogenic adhesives at liquid hydrogen and ambient temperatures.(10)

Adhesive Type	Tensile Shear Strength				T-Peel Strength			
	$-423^{\circ}\text{F}$ (20 K)		Ambient		$-423^{\circ}\text{F}$ (20 K)		Ambient	
	psi	MPa	psi	MPa	lbf/in	N/m	lbf/in	N/m
Polyurethane (RT-curing paste)	7500	51.7	1500	10.3	70	12,260	20-40	3502-700X
Nylon-epoxy film ( $300-350^{\circ}\text{F}$ - $149-177^{\circ}\text{C}$ cure)	3600	24.8	5000	34.5	4	700	104	18,200



MIL-HDBK-691B

The shear strength properties of several classes of adhesives suitable for cryogenic applications are shown in Figure 49. Although bond strengths are reasonably good, the unmodified epoxy resins suffer from brittleness and corresponding low peel and impact strength at cryogenic temperatures. The epoxy-phenolics have excellent cryogenic-temperature strengths, as well as good high-temperature properties. The epoxy-nylons give consistently high strength at cryogenic temperatures. The flexibility of the nylon imparts greater peel strength to the epoxies and produces systems with unusual low-temperature properties. Epoxy-polyamides are readily mixed, easily applied, have good pot life, and can be cured at room temperature to yield a flexible system. Their low-temperature performance, however, is not as good as that of the epoxy-nylons. Vinyl acetal-phenolic adhesives are available as supported and unsupported films, solutions, and solutions with powder, and show reasonably good low-temperature strength. Their strength falls off, however, with decreasing temperature due to the increasing modulus of elasticity characteristic of thermoplastics.(11)

Rubber phenolics are of value because of their high peel strengths, but their shear strengths are relatively low. Nitrile-phenolics are examples of this type. The polyurethane adhesives have excellent adhesion to a number of substrates, along with inherently good low-temperature flexibility. Peel strength is excellent. Epoxy-nylon adhesives, mentioned above, have higher strength in the low-temperature ( $-100^{\circ}\text{F}$  or  $-73^{\circ}\text{C}$ ) range, as seen in Figure 49, than any other cryogenic adhesive. At liquid-nitrogen temperature ( $-321^{\circ}\text{F}$  or  $77\text{K}$ ) there is little difference in the shear strengths of the polyurethane and epoxy-nylon types. At liquid-hydrogen temperature ( $-423^{\circ}\text{F}$  or  $20.4\text{K}$ ), however, the newer polyurethane adhesives surpass the epoxy-nylons. (11)

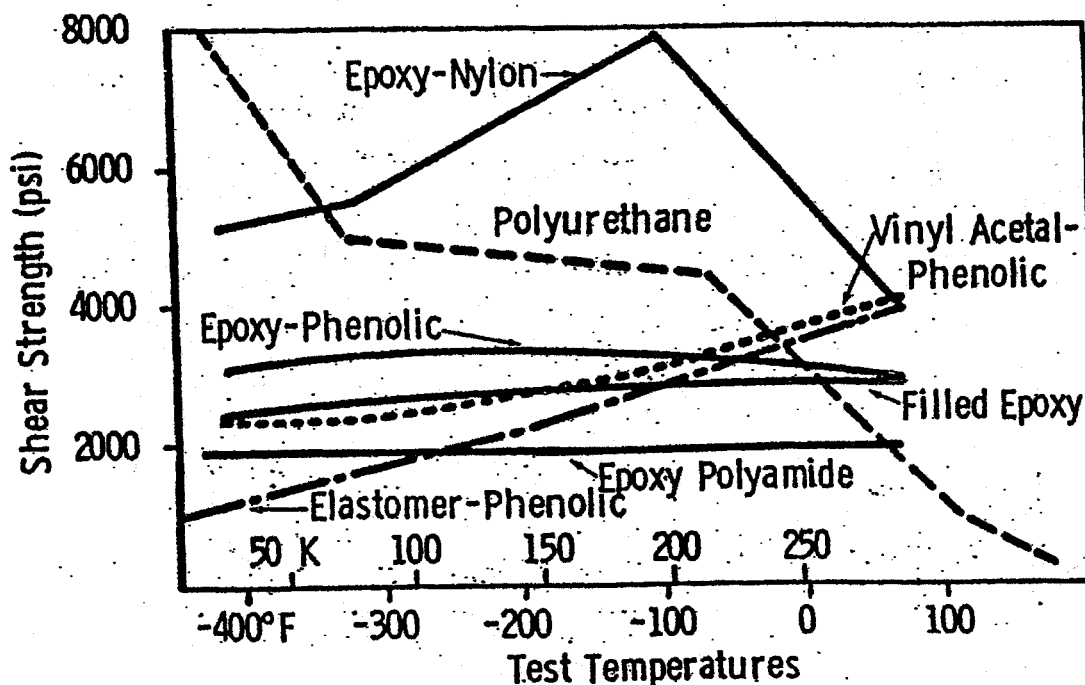


FIGURE 49. Comparison of cryogenic and low-temperature adhesive types.(11)



## MIL-HDBK-691B

The National Bureau of Standards (NBS) at Boulder, Colorado has prepared an excellent survey for NASA on available reports and publications on cryogenic adhesives and sealants.(12)

A 1974 contractor report describes work performed on the development of a structural adhesive system for use over a  $-423^{\circ}\text{F}$  (20 K) to  $600^{\circ}\text{F}$  (589 K) range. Two polyimide adhesive systems, BR 34/FM 34 (American Cyanamid) and P4/A5F or P4/A5FA (TRW Systems), were found to provide excellent results with both titanium alloy and stainless steel substrates.(13)

**15.4 Humidity and water immersion.** Moisture can affect adhesive strength in two significant ways. Some polymeric materials, notably ester-based polyurethanes, will "revert", i.e., lose hardness, strength, and in the worst cases, liquify during exposure to warm, humid air. Water can also permeate the adhesive and preferentially displace the adhesive at the bond interface. This mechanism is the most common cause of adhesive-strength reduction in moist environments.(1)

The rate of reversion, or hydrolytic instability, depends on the chemical structure of the base adhesive, the type and amount of catalyst used, and the flexibility of the adhesive. Certain chemical linkages, such as ester, urethane, amide and urea, can be hydrolyzed. The rate of such attack is fastest for ester-based linkages. Such linkages are present in certain types of polyurethane and anhydride-cured epoxies. Generally amine-cured epoxies offer better hydrolytic stability than anhydride-cured types. The reversion rate of hydrolytic materials also depends on the amount of catalyst used in the formulation. The best hydrolytic properties are obtained when the proper stoichiometric ratio of base material to catalyst is used. Reversion is usually much faster in flexible materials because water permeates them more easily.(1)

Structural adhesives not susceptible to the reversion phenomenon are also likely to lose adhesive strength when exposed to moisture, particularly at high temperatures. The mode of failure in the initial stages of exposure under these conditions is cohesive. After 5 to 7 days the failure becomes one of adhesion. Water vapor apparently permeates the adhesive through its exposed edges and concentrates in weak boundary layers at the interface. This effect is very much dependent on the type of adhesive. Table XLIX illustrates that a nitrile-phenolic adhesive does not succumb to failure through the mechanism of preferential displacement at the interface. Failures occurred cohesively within the adhesive, even when tested after 24 hours of immersion in water. A nylon-epoxy adhesive degrades rapidly under the same conditions, owing to permeability and preferential displacement by moisture. Adhesive strength deteriorates more quickly in an aqueous-vapor environment than in liquid water, because of the more rapid permeation of the vapor. Because of the importance of the interface, primers and surface treatments tend to hinder adhesive strength degradation in moist environments. A fluid primer that easily wets the interface presumably tends to fill in minor discontinuities on the surface. Chemical etching, which removes surface flaws, also results in improved resistance to high humidity.(1)

## MIL-HDBK-691B

Stress accelerates the effect of environments on the adhesive joint. Few data are available on this phenomenon because of the time and expense involved with stress aging tests. However, it is known that moisture, as an environmental burden, markedly decreases the ability of an adhesive to bear prolonged stress.<sup>(1)</sup>

**15.4.1 Effects of surface preparation on moisture exposure.** The Aluminum Company of America (ALCOA) has carried out studies on unstressed joint durability after room-temperature water immersion and after 100%-RH exposure at 125°F (52°C). Table I gives results on the room-temperature tests in water. Direct comparison of durability for all joints can only be made after one year's soaking exposure. The two-year exposure test had not been completed for the chromic acid-anodized and phosphoric acid-anodized surface joints at the time of the report. After one year in this moderately accelerated laboratory weathering exposure, the relative bond retention averages were similar for all but the vapor-degreased surface joints, and ranged between 70-80% of initial bond strength values. The vapor degreased surface joints averaged only 46.2% of their initial bond strength values. Table LI gives the results after exposure to condensing humidity (100% RH) at 125°F (52°C). After 12 months exposure all of the anodized surface joints showed significantly high retained bond strength, ranging from a high of 73% for the sulfuric acid-anodized surface joints to a low of 54.8% for the phosphoric acid-anodized surface joints. The average bond strength retention for the acid-etched surface joints in high humidity ranged from 31% for the inhibited alkaline cleaned (RIDOLINE 53) and chromic-sulfuric acid etched surface joints to 16.1% for the alcohol-phosphoric acid etched surface joints (15). ALCOA has also studied the effects of stress with the system described above.

**15.4.2 Stressed temperature/humidity test.** One of the earlier methods used by the Army for evaluating the durability of adhesive-based joints is the stressed temperature/humidity test described in ASTM D 2919-84 (See 13.2.56). ARRADCOM workers have used an environmental condition not listed in the standard test environments of this standard, 140°F (60°C) and 95 to 100% RH. These conditions were selected during an evaluation of adhesive-bonding processes used in helicopter manufacture. This stressed method is very time-consuming and often expensive, since it requires environmental test chambers. (16) Figures 50 and 51 show the stressing jig used in this procedure and how it is used with multiple units. (17).

Figures 52 and 53 show the degradation of the epoxy adhesive bond due to the effect of temperature on the anodic aluminum joint at 95% RH.<sup>(18)</sup> The plots show that those joints exposed at 73°F (23°C) and 95% RH had degraded rapidly when the stress level exceeded 880 lbs, which would be equal to approximately 40% of the room-temperature tensile-shear strength of the joint. At 120°F (49°C) rapid deterioration occurred at a stress level of 440 lbs (1957 N), or approximately 20% of the room-temperature strength of the joint. The durability or stress vs log time to failure curves are shown in Figure 53 for the various temperatures at 95% RH. The resultant curves are straight lines and are close to being parallel, indicating that the effect of temperature at a constant RH is constant, and, as the temperature increases, the durability will decrease as a function of the strength change caused by

TABLE XLIX. Effect of water (liquid and vapor) on tensile shear strength of structural adhesive bonds on aluminum. (14)

## Tensile Shear Strength Exposure (Months).

Adhesive Type	Environment	Controls (psi) (MPa)	2		6		12		18		24		
			(psi)	(MPa)	(psi)	(MPa)	(psi)	(MPa)	(psi)	(MPa)	(psi)	(MPa)	
Nylon-epoxy <sup>a</sup>	High Temp. High RH Cycle <sup>b</sup>	4,370	30.1	1,170 <sup>c</sup>	8.07	950	6.55	795	5.48	1,025	7.07	850	5.86
Nylon-epoxy <sup>a</sup>	Immersion in distilled water	4,370	30.1	2,890 <sup>c</sup>	19.9	1,700	11.7	500	3.45	200	1.38	120	0.83
Nitrile d rubber	High Temp. High RH Cycle <sup>b</sup>	3,052	21.0	2,180	15.0	2,370	16.3	2,830	3.45	2,350	1.38	120	0.83
Nitrile d rubber phenolic	Immersion in distilled water	3,052	21.0	2,740	18.4	2,280	15.7	2,380	16.4	2,640	18.2	2,390	16.5

<sup>a</sup>Used with compatible tack primer-air dried minimum of 30 min. - cure 90 min. at 350°F (177°C), 25 psi (0.17 MPa)  
<sup>b</sup>Humidity cycle 93% RH plus temperature cycles 149 to 89°F (65 to 31.7°C) in 48-hr period  
<sup>c</sup>Starting with the two-month test specimens, all nylon-epoxy failures were adhesive  
<sup>d</sup>Used with compatible liquid primer air-dried plus 30 min. bake at 280°F (138°C) before assembly-cure at 350°F (177°C), 25 psi (0.17 MPa)

Note: Aluminum treated with a sulfuric acid-dichromate etch per MIL-A 9067 before priming

## MIL-HDBK-691B

TABLE L. Effects of surface treatment on the durability of 6061-T6 aluminum alloy joints exposed to inversion in RT water in the unstressed condition (nitrile-modified epoxy paste adhesive).(15)

Surface Treatments	Initial Shear Strength psi	Avg. % Retained Bond Strength After Indicated Exposure Time			
		3 Mos.	6 Mos.	12 Mos.	24 Mos.
Vapor Degreased	4330	70.9	59.4	46.2	27.0
Deoxidine 526 (5 min., 25% conc. at R.T.)	4970	83.1	84.5	73.8	56.9
Chromic-sulfuric (5 min., 180°F (82°C))	5330	83.9	82.6	78.2	66.2
Chromic acid anodize	5513	85.6	83.6	70.9	N.A.
Phosphoric acid anodize (Boeing procedure, 5-10 volts, 20 min.)	6480	89.8	80.2	74.4	N.A.
Sulfuric acid anodize (12 asf, 60 min., boiling water seal)	3550	69.6	66.8	67.6	68.5

TABLE LI. Effects of surface treatment on the durability of 6061-T6 aluminum alloy joints exposed to 100% RH (condensing humidity) at 125°F (52°C) in the unstressed condition (nitrile-modified epoxy paste adhesive).(15)

Surface Treatments	Initial Shear Strength psi	Avg. % Retained Bond Strength After Indicated Exposure Time			
		3 Mos.	6 Mos.	12 Mos.	24 Mos.
Deoxidine 526 (5 min., 25% conc. at R.T.)	4970	46.1	30.2	16.1	10.9
Chromic-sulfuric (5 min., 180°F (82°C))	5330	39.9	23.8	16.6	12.4
Ridoline 53 (3 min., 180°F (82°C))	5430	51.4	36.3	31.3	26.3
Chromic-sulfuric (5 min., 180°F (82°C))					
Chromic acid anodize	5513	70.7	69.8	60.9	N.A.
Phosphoric acid anodize (Boeing procedure, 5-10 volts, 20 min.)	6480	70.7	62.8	54.8	N.A.
Sulfuric acid anodize (12 asf, 60 min., boiling water seal)	3550	74.9	74.1	72.7	67.6

## MIL-HDBK-691B

the temperature change. Similar results are obtained with titanium. Thus, an increase in % RH will cause a decrease in the joint durability, and appears to be a significant factor in joint failures.(18)

This ASTM method has some drawbacks, such as the large scatter of data, the inability to check stress level at environmental conditions, and the inability to run very low loads because of the high k-factor of the springs. Springs with lower k-factors could be used, however.(19)

**15.4.3 Hot-water-soak test.** With this newer method developed by ARRADCOM, the durability curves for a large number of adhesive/adherend combinations can be predicted simultaneously. The method involves the soaking of test specimens in a tank of deionized water at 140°F (60°C). The specimens are allowed to soak for periods up to 100-1000 hours in the 140°F (60°C) water. At the end of the soak period the specimens are removed and placed in a container of water at 140°F (60°C). This container is then placed into the test chamber of a universal tensile testing machine. The chamber is also kept at 140°F (60°C). The test specimens are removed, one at a time, from the water and placed in the grips of the test machine. A thermocouple is attached to the specimen and the temperature monitored. When the temperature of the specimen reaches 140°F (60°C) the test is started. The load is applied at a rate of 1200-1400 lbs/min (270-315 N/min) until the specimens fail. This test is carried out on at least four specimens and the results are plotted on semi-logarithmic paper.(16)(19)

When the data is plotted as a function of the residual strength vs log of exposure time, the resulting plot is a straight line similar to the stressed durability curves shown in Figure 52.(19)

Figure 54 depicts the data obtained on an epoxy-nitrile film adhesive on 5052-H34 aluminum alloy after immersion in the hot water for 50, 100, 300, 500 and 1000 hours. This test is very useful because it permits a large number of adhesive-bonded specimens with different adhesives, adherends and surface pretreatments to be tested at the same time with a relatively small investment in man hours and equipment. Figure 55 shows a comparison of the stressed durability data and unstressed hot water-soak data on the same epoxy-nitrile film adhesive, using 2024-T3 aluminum alloy. Note the parallelism of the plots. The curve in the lower left was obtained when lap-shear specimens were subjected to various levels of stress and then exposed to an environment of 140°F (60°C) and 95% RH until failure. The failure time is plotted as a log function. The curve in the upper portion is a plot of the data when the same types of lap-shear specimens were subjected to 140°F (60°C) water for prescribed periods of time and then tested for their residual strength. In the first case failure time was recorded. In the latter case, residual strength was determined. The same type data is obtained with both curves.(19)

**15.4.4 Fatigue-life data.** Bonded joints in helicopters are subjected to constant fatigue. The operation of a helicopter puts the aircraft in a constant state of vibration. The mission of the Army's helicopter fleet subjects them to conditions of elevated temperatures and frequently high humidity. Environmental exposure is believed to have a strong detrimental effect upon the fatigue endurance of bonded joints in these aircraft.(20)



MIL-HDBK-691B

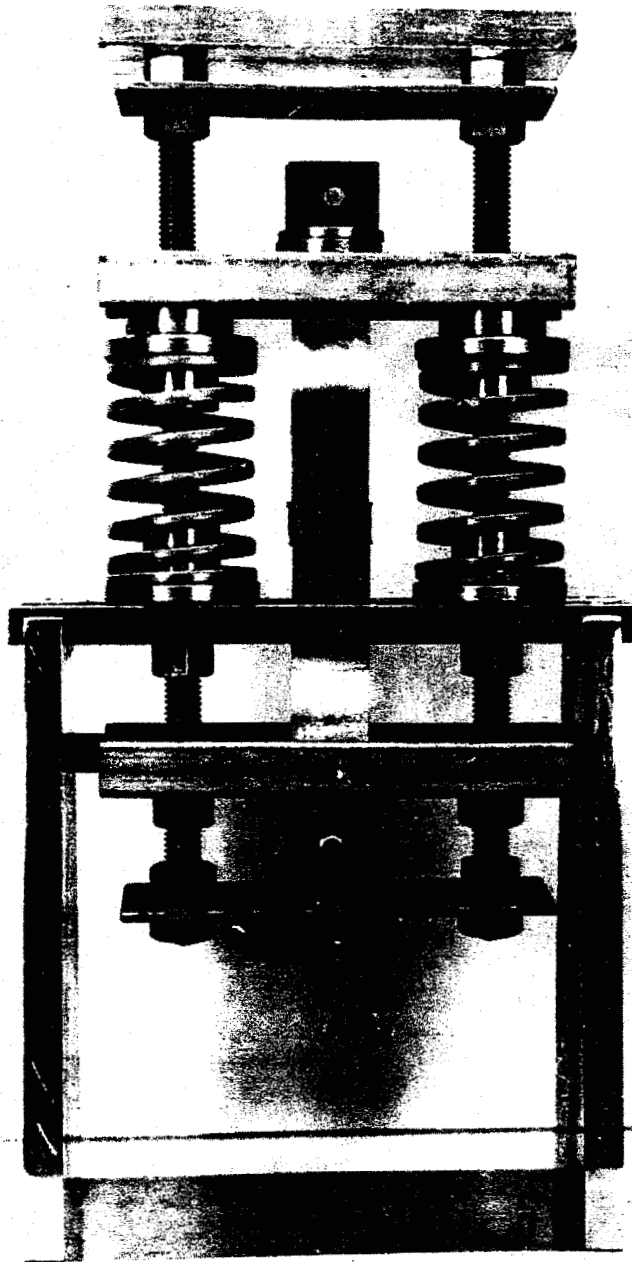


FIGURE 50. Stressing jig used in loading test fixture (ASTM D2919).(17)





FIGURE 51. Stressing jigs used at ARRADCOM with automatic failure recording device (microswitch timing monitor).

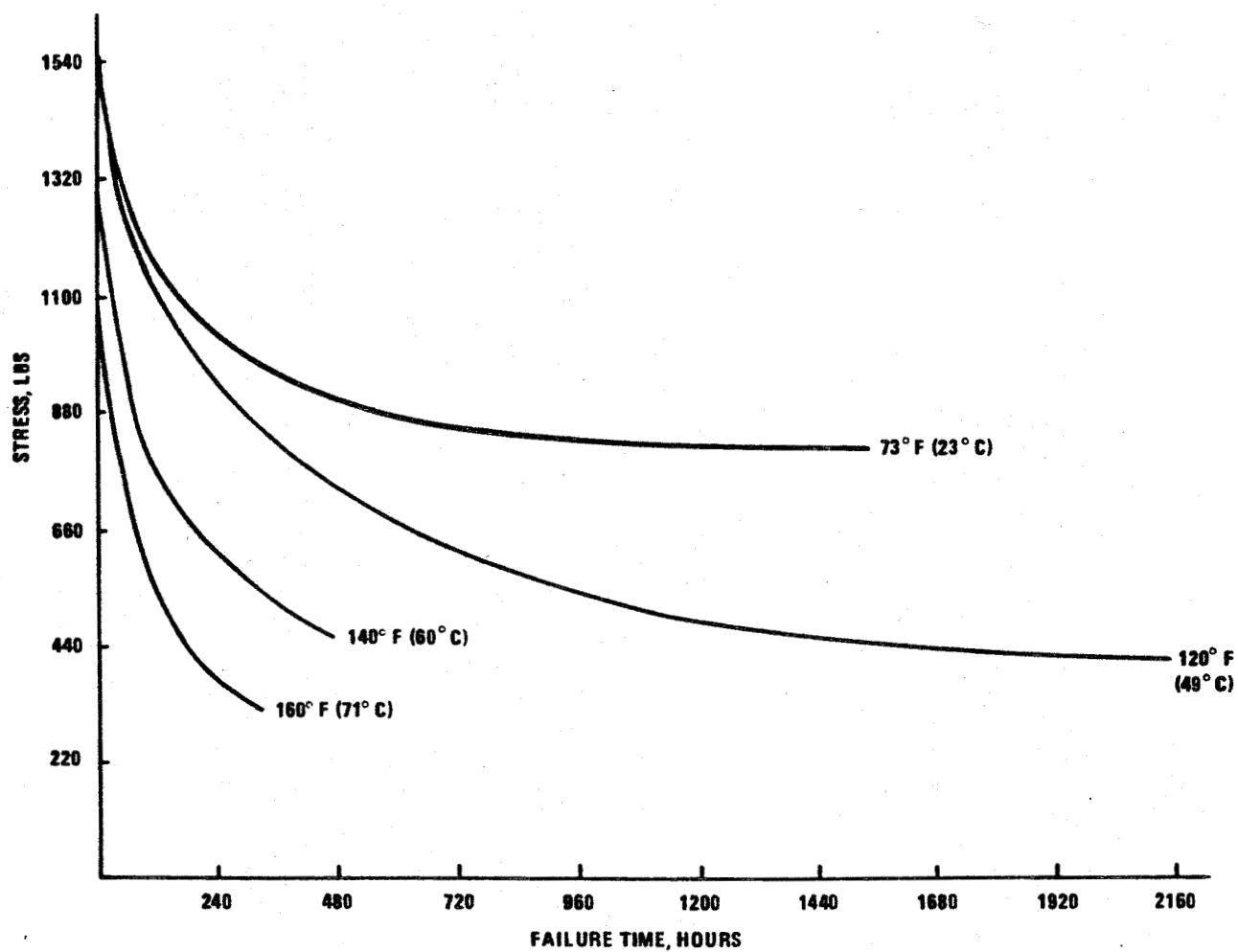


FIGURE 52. Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH (modified epoxy film adhesive). (18)

MIL-HDBK-691B

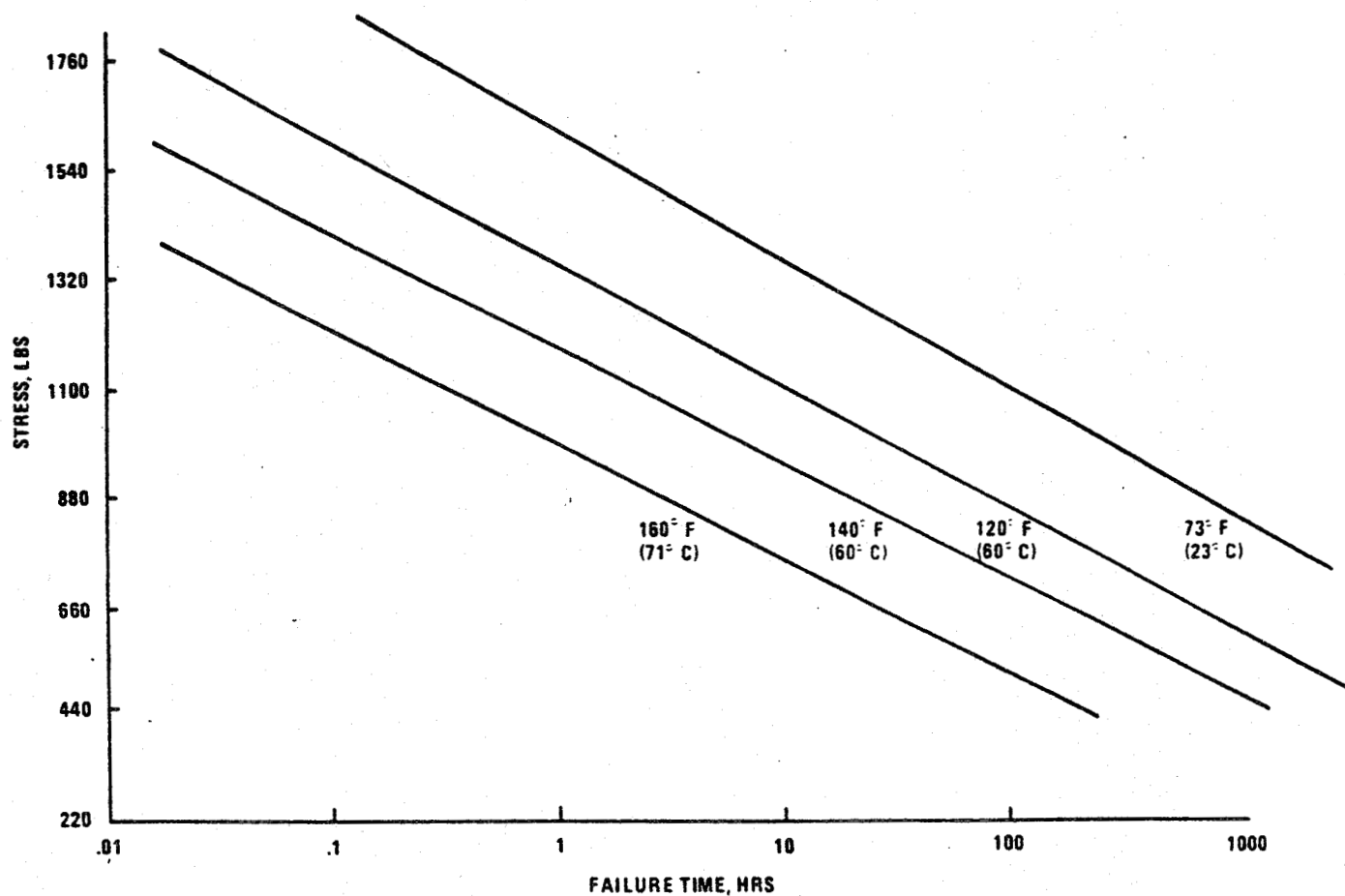


FIGURE 53. Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH (log plot) (modified epoxy film adhesive).(18)

## MIL-HDBK-691B

A vibration frequency of 1000 cycles per minute is considered representative of the vibration of Army aircraft during flight. Accordingly, ARRADCOM workers have designed a test for determination of fatigue-life data in the tension stress cycle from zero to a specific maximum stress of 2800 psi (19.3 MPa). Endurance curves were determined at room temperature, 140°F (60°C) (dry) and 140°F (60°C) with 95% RH. (20)

Figure 56 compares the stress vs log of cycles to failure (S/Log N) curves for an epoxy-nitrile film adhesive used for bonding sulfuric-dichromate etched 2024-T3 aluminum at a frequency of 1000 cycles per minute at RT, 140°F (60°C) (dry) and at 140°F (60°C) with 95% RH (20). In general, the fatigue curves obtained at these environments follow the trend shown in Figures 52 and 53, where a noticeable drop is experienced when the environment is changed from 73°F (23°C) to 140°F (60°C), and again when the environment becomes more drastic with the addition of 95% RH to the 140°F (60°C) environment. (21)

#### 15.5. Salt water and salt spray.

15.5.1 Introduction. Salt water and salt spray are known to have a deleterious effect on adhesive joints, particularly the latter. Testing for the effects of salt spray (salt fog) is usually carried out using ASTM B117, "Standard Method of Salt Spray (Fog) Testing". This method has been approved for use by DOD agencies to replace Method 811.1 of Federal Test Method Standard 151B.

Bond durability results on an aluminum alloy are shown in Table LII for chromic acid-anodized and four variations of phosphoric acid-anodized surfaces, plus two variations of sulfuric acid-anodizing, i.e. sealed and unsealed. The excellent resistance to surface corrosion in salt-water exposure shown by unbonded anodized surfaces is also manifested in the bonded joints. All chromic acid and phosphoric acid-anodized surface joints were highly resistant to bond failures, which ordinarily occur by undercutting corrosion of the bondline in this environment. The essential absence of any such undercutting was noted visually in joints failed deliberately after 12 months exposure, and was confirmed by the high percentage of retained bond strength in the range of 79-96%. Although thicker sulfuric acid-anodized coatings would be expected to offer the highest degree of corrosion resistance to salt spray in the sealed and unbonded state, the only bond failure encountered when tested weekly to 50% of initial bond strength was with a sealed sulfuric acid-anodized pretreated joint. This is not surprising, since it is known that an unsealed sulfuric acid anodized surface can be bonded with higher initial bonding strength and better bond durability. The good bond durability in salt water-exposure of anodized surface-pretreated joints is a positive basis for selecting this type of pretreatment over the acid-etching procedures for marine applications. (15)

15.5.2 Seacoast weathering environment. Important bond durability results between vapor-degreased, acid-etched, and sulfuric acid-anodized surface joints are shown in Table LIII for periods as long as 8 years. This type of natural weathering test environment is highly discriminating between the various surface pretreatments. The surprisingly high 62% bond strength retention for the sealed sulfuric acid-anodized surface joints after 8 years

MIL-HDBK-691B

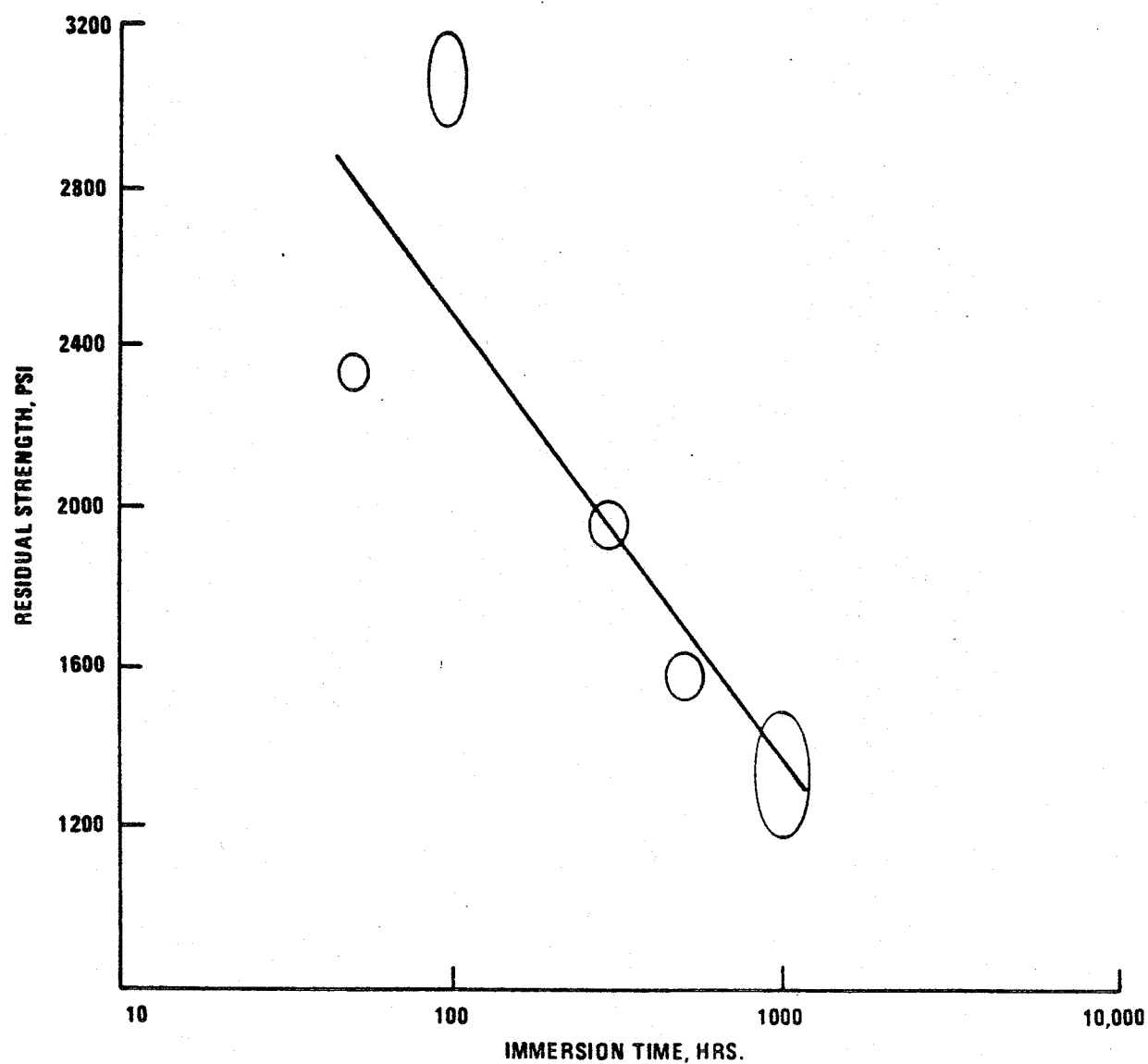


FIGURE 54. Hot water soak data with epoxy-nitrile film adhesive on 5052-H34 aluminum joints.(19)

MIL-HDBK-691B

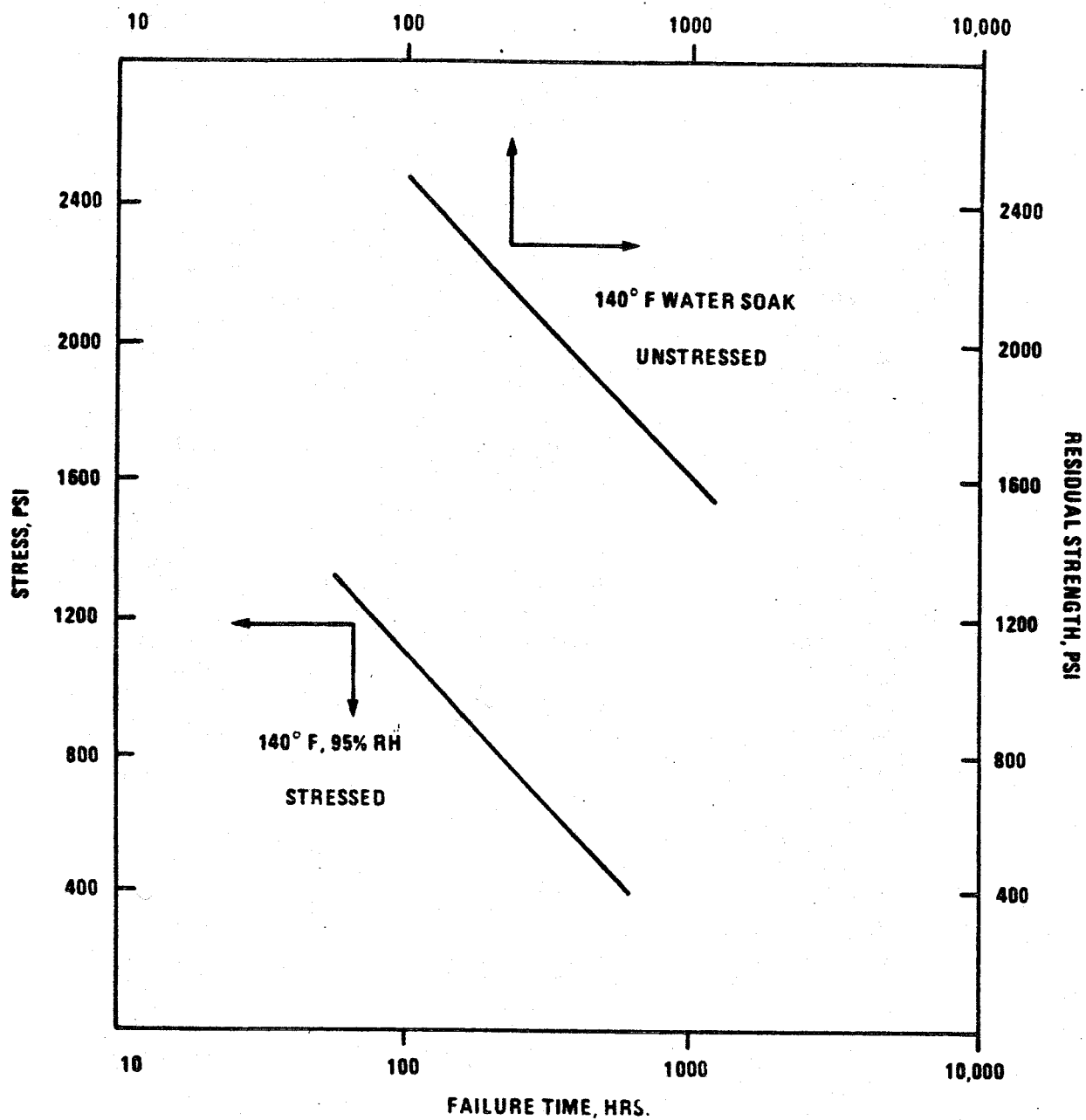


FIGURE 55. Comparison of stressed durability data and unstressed hot water soak data with epoxy-nitrile film adhesive on anodized 2024-T3 aluminum joint.(19)



MIL-HDBK-691B

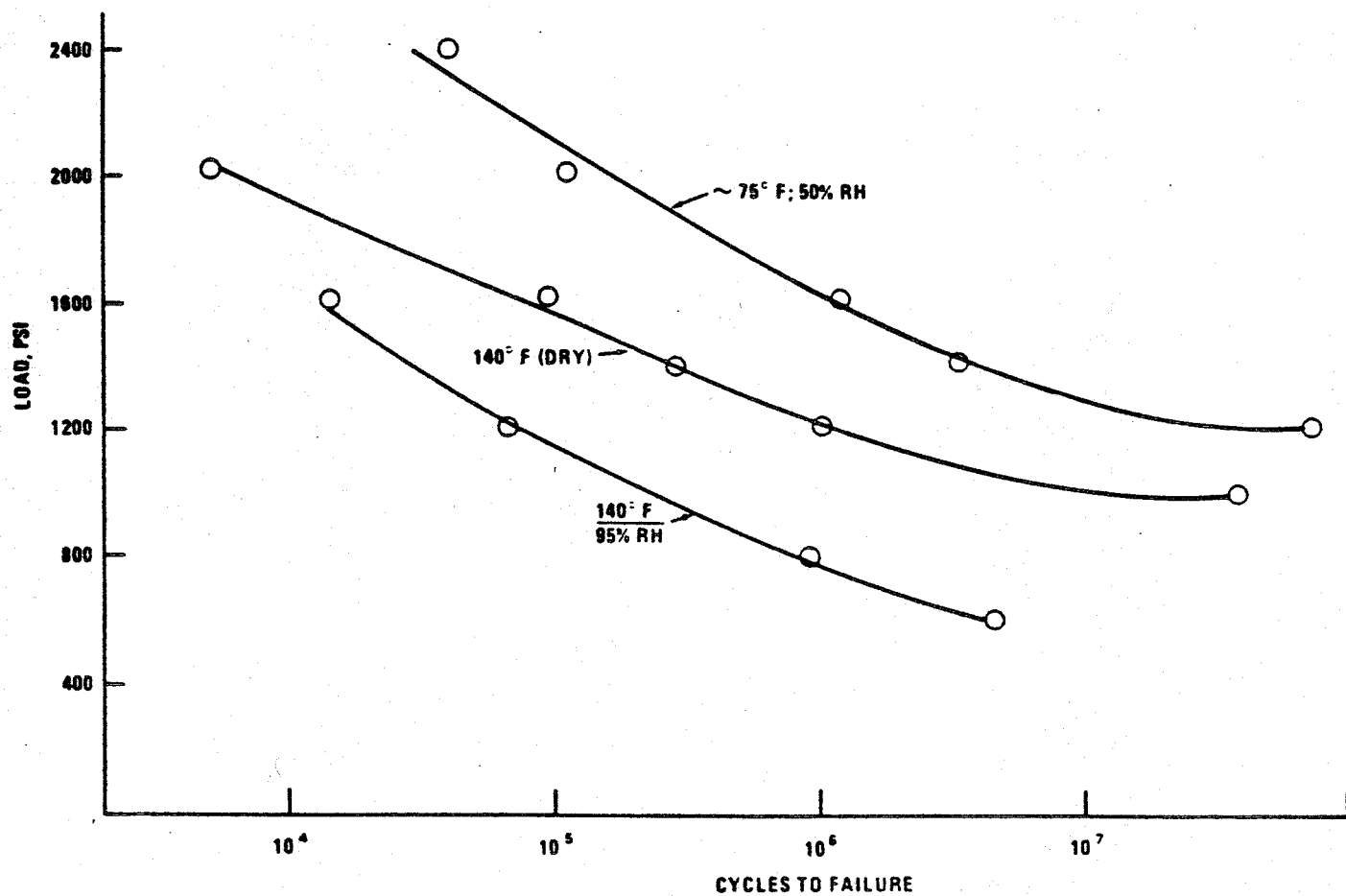


FIGURE 56. Environmental S-log N curves for nitrile-epoxy film adhesive - bonded 2024-T3 aluminum joints at 1000 cycles/minute.(20)

## MIL-HDBK-691B

TABLE LII. Effect of surface treatment and exposure to 3 1/2% salt water intermittent spray on the durability of 6061-T6 aluminum alloy joints exposed in the unstressed condition (nitrile-modified epoxy paste adhesive).(15)

Surface Treatments	Initial Shear Strength psi	Avg. % Retained Bond Strength After Indicated Exposure Time*			
		3 Mos.	6 Mos.	9 Mos.	12 Mos.
Chromic acid anodize	5513	50	50	50	82.0
Phosphoric acid anodize (30 volts, 30 min.)	5700	50	50	50	89.8
Phosphoric acid anodize (60 volts, 18.5 min.)	6030	50	50	50	92.9
Phosphoric acid anodize (110 volts, 6 min.)	6070	50	50	50	95.9
Phosphoric acid anodize (Boeing procedure)	6480	50	50	50	79.3
Sulfuric acid anodize (12 asf, 60 min., unsealed)	3940	50	50	50	75.1
Sulfuric acid anodize (12 asaf, 60 min., boiling water seal)	3550	50	50	50	49.6

\*The procedure used was to stress the specimens weekly to 50% of initial shear strength and return to the exposure conditions, providing no bond failures occurred. After 52 weeks testing the joints were deliberately failed for quantitative determination of the actual retained bond strength as shown.

TABLE LIII. Effect of surface treatment and exposure to seacoast environment<sup>a</sup> on the durability of 6061-T6 aluminum alloy joints exposed in the unstressed condition (nitrile-modified epoxy paste adhesive).(15)

Surface Treatment	Initial Shear Strength psi	Avg. % Retained Bond Strength After Indicated Exposure Time			
		1 Yr.	2 Yrs.	4 Yrs.	8 Yrs.
Vapor degreased	4330	0(1)			
Deoxidine 526 (5 min., 25% conc. at R.T.)	4970	72.4	10.9	0(2)	
Chromic-sulfuric (5 min., 180°F (82°C))	5330	91.2	63.2	0(3)	

## MIL-HDBK-691B

TABLE LIII. (Continued)

Surface Treatment	Initial Shear Strength psi	avg. % Retained Bond Strength After Indicated Exposure Time			
		1 Yr.	2 Yrs.	4 Yrs.	8 Yrs.
Chromic acid anodize	5513	82.5			
Sulfuric acid anodize (12 asf, 60 min., boiling water seal)	3270	69.4	68.2	85.4	62.3

<sup>a</sup>Exposed at Point Judith, Rhode Island.

- (1) Time span of bond failures 71-270 days.
- (2) Time span of bond failures 720-1440 days.
- (3) Time span of bond failures 760-1440 days.

exposure is especially significant when compared to the less-than-one-year survival time for vapor-degreased surface joints and the approximately 720 to 1440 day survival times for alcohol-phosphoric and chromic-sulfuric etched surface joints.(15)

Minford (22) showed that the seacoast atmosphere is the most deteriorating to heat-cured epoxies as a group, many failing completely after the end of four years exposure. Anhydride-cured epoxies gives better results and retain roughly half of their initial shear strength after four years in this aggressive marine environment. Nitrile-modified epoxies give better results than the non-modified, as is the case with phenolics and nitrile-phenolics.  
(15)

Two-part epoxy adhesives (RT-curing) do not give good results in seacoast atmospheres, unless a compatible organic sealer is placed over the edge of the bondline. In the case of tape and film adhesives, nylon or nylon-modified epoxy adhesive bonds either failed to survive four years exposure, or lost 73% of initial strength. Excellent performances were shown by all nitrile-phenolic and phenolic-type adhesives. As a group all joints fabricated from ten of twelve tape and film adhesives tested in a seacoast atmosphere survived for the total test period of 48 months. By contrast, no two-part epoxy joints lasted longer than 30 months, and only one heat-cured, one-part epoxy survived 48 months exposure (15).

15.5.3 Salt-water immersion. Figure 57 presents results for four different phosphoric acid-processing conditions under stress and intermittent salt-water immersion testing. None of the joints pretreated by varying phosphoric acid-anodizing conditions have failed after 480 days exposure, even under 2268 psi (15.6 MPa) stress. A few of the stressed joints pretreated by chromic acid-anodizing failed during the 480 days of exposure, but only at a stress level of approximately 2000 psi (13.8 MPa), or approximately 35% of the initial

## MIL-HDBK-691B

bond strength. Because of the lower initial bond strength of the sulfuric acid anodized surface joints, the highest stress levels imposed were 1379 psi (9.5 MPa) (35%) for the unsealed and 1242 psi (8.6 MPa) (35%) for the sealed joints. After about 100 days, the sealed sulfuric anodized joints failed in exposure, while the corresponding unsealed joints survived after 482 days exposure.(15)

15.5.4 Nitrile-phenolic adhesives. Minford has shown the exceptional strength retention of nitrile-phenolics, such as FM-61, on aluminum after extended salt spray, water immersion, and other long-term exposure tests. It is probably true that no other adhesive type exceeds the ability of the nitrile-phenolics to maintain good strength on steel or aluminum after extended exposure to water, salts, or other corrosive media, and to prevent undercutting through corrosion of the metal substrate.(7)

15.5.5 Boeing/Air Force studies. An Air Force-sponsored study in 1976 reported on the effects of the corrosive salt-spray environment on bondlines of different bonded systems.(23) The system variations included clad and bare alloys, surface treatments, adhesive primers, and adhesives. Five specimens were fabricated for each of the bonded systems. The specimens were then placed in a salt-spray environment of 5% NaCl at 95°F (35°C). The change in crack length of each specimen was recorded periodically. At the end of 1 month, one specimen was randomly selected from each bonded system and opened for visual inspection of the bondline condition, both in the stressed zone (crack-tip zone) and in the unstressed zone. This same procedure was carried out after 2, 3, 6, and 12 months, when the last specimen was removed from test. The average crack lengths at the end of each time period are shown in Table LIV, a, b, and c. The conclusions were as follows:(23)

- o The phosphoric acid-anodize process provides markedly improved stressed-bond joint durability and retards bondline crevice corrosion (started at an edge) in severely corrosive environments when compared to chromic acid-anodize and FPL etch.
- o Stressed-bond-joint durability is markedly affected by the adherend prebond surface treatment and the adhesive/primer system in contact with it. This is evidenced by the poor performance of FM 123-L/BR 123 (non-CIAP) adhesive/primer system on FPL-etched and chromic acid-anodized 2024-T3, clad and bare, and the better performance of the same systems when BR 127 (CIAP) is substituted for BR 123 (non-CIAP).
- o The wedge test method is discriminating and provides a relative ranking for many of the parameters that affect bond joint durability.
- o The data confirm that clad aluminum in the bondlines is undesirable under the severely corrosive salt-spray environment.

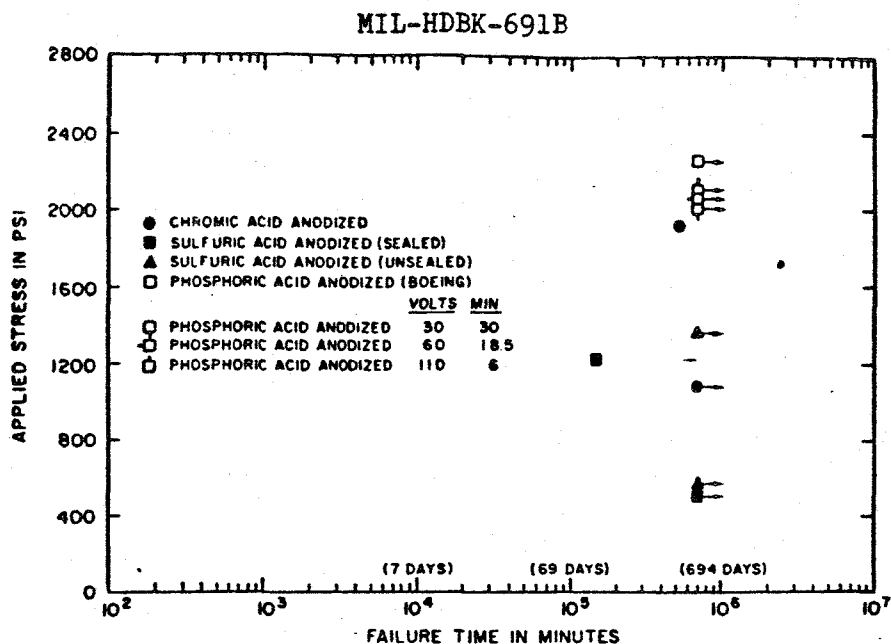


FIGURE 57. Effect of surface treatment and intermittent immersion in salt water under stress on the durability of 6061-T6 aluminum alloy.(15)

## 15.6 Weathering.

15.6.1 General. By far the most detrimental factors influencing adhesives aged outdoors are heat and humidity. Thermal cycling, ultraviolet radiation, and low temperatures are relatively minor factors. When exposed to weather, structural adhesives rapidly lose strength during the first 6 months to 1 year. After 2 to 3 years, the rate of decline usually levels off at 25 to 30% of the initial joint strength, depending on the climate zone, adherend, adhesive, and stress level. The following generalizations are important in designing a joint for outdoor service (1):

- o The most severe locations are those with high humidity and warm temperatures
- o Stressed panels deteriorate more rapidly than unstressed panels
- o Stainless-steel panels are more resistant than aluminum panels because of the corrosion in the latter
- o Heat-cured adhesive systems are generally more resistant to severe outdoor weathering than room-temperature-cured systems
- o Using the better adhesives, unstressed bonds, are relatively resistant to severe outdoor weathering, although all joints will eventually exhibit some strength loss.

15.6.2 Simulated weathering/accelerated testing. Picatinny Arsenal has carried out a number of experiments in the laboratory (accelerated testing) using MIL-STD-304 conditioning, and in actual weathering sites throughout the world.(24) MIL-STD-304 has now been replaced by MIL-STD-331, but the MIL-STD-304 conditions were: exposure to alternating cycles of cold (-65°F) (-54°C), dry heat (160°F) (71°C), and heat and humidity (95° RH) for 30 days. After the exposure period, the aluminum-alloy panels used in the studies (2024-T3) were cut into individual specimens and tested at the

## MIL-HDBK-691B

TABLE LIV Effect of salt spray- 5% NaCl at 95°F (35°C) on bonded aluminum alloy joints with different surface preparations, (23)

(a) Phosphoric acid anodize

Adhesive system	Alloy	$a_o$ , in. <sup>a</sup> (a)	$a_o + \Delta a_1$ <sup>b</sup> 1 day (a)	$a_o + \Delta a_2$ 7 days (a)	$a_o + \Delta a_3$ 30 days (a)	$a_o + \Delta a_4$ 60 days (b)	$a_o + \Delta a_5$ 90 days (c)	$a_o + \Delta a_6$ 183 days (d)	$a_o + \Delta a_7$ 365 days (e)
FM 123-2/BR 123 <sup>c</sup> <sup>d</sup>	2024 clad	1.32	1.38	1.38	1.49	1.53	1.50	1.62	1.84
	2024 bare	1.43	1.43	1.50	1.54	1.57	1.56	1.68	1.64
FM 123-2/BR 127 <sup>e</sup>	2024 clad	1.33	1.36	1.36	1.52	1.53	1.43	1.48	1.48
	2024 bare	1.40	1.40	1.51	1.55	1.60	1.56	1.55	1.73
EA 9628/BR 127 <sup>f</sup>	2024 clad	1.37	1.37	1.44	1.44	1.46	1.46	1.47	1.47
	2024 bare	1.48	1.50	1.53	1.58	1.59	1.59	1.64	1.62
	7075 clad	1.44	1.51	1.56	1.63	1.65	1.54	1.53	1.66
	7075 bare	1.47	1.50	1.55	1.60	1.58	1.59	1.57	1.57

(b) Chromic acid oxidize

Adhesive system	Alloy	$a_o$ , in.	$a_o + \Delta a_1$ 1 day	$a_o + \Delta a_2$ 7 days	$a_o + \Delta a_3$ 30 days	$a_o + \Delta a_4$ 60 days	$a_o + \Delta a_5$ 90 days	$a_o + \Delta a_6$ 183 days	$a_o + \Delta a_7$ 365 days
FM 123-2/BR 123	2024 clad	1.31	2.68	2.68	2.78	2.80	2.77	2.84	3.48
	2024 bare	1.41	2.66	3.06	3.06	3.38	3.52	3.97	3.66
FM 123-2/BR 127	2024 clad	1.33	1.34	1.44	1.49	1.47	1.40	1.45	3.86
	2024 bare	1.42	1.47	1.56	1.71	1.73	1.73	1.86	2.16
EA 9628/BR 127	2024 clad	1.42	1.45	1.80	2.37	2.63	2.47	2.48	2.44
	2024 bare	1.47	1.52	1.53	1.69	1.79	1.76	2.10	2.82
	7075 clad	1.40	1.43	1.43	1.45	1.46	1.45	1.42	1.42
	7075 bare	1.46	1.48	1.54	1.59	1.67	1.58	1.59	1.64



## MIL-HDBK-691B

TABLE LIV (Continued)

(c) FPL etch

Adhesive system	Alloy	$a_0$ , in.	$a_0 + \Delta a_1$ 1 day	$a_0 + \Delta a_2$ 7 days	$a_0 + \Delta a_3$ 30 days	$a_0 + \Delta a_4$ 60 days	$a_0 + \Delta a_5$ 90 days	$a_0 + \Delta a_6$ 183 days	$a_0 + \Delta a_7$ 365 days
A 123-2/BR 123	2024 clad	1.40	2.64	3.26	3.56	3.50	3.66	Total disbond	
	2024 bare	1.43	2.95	3.23	3.53	3.74	3.66	Total disbond	
A 123-2/BR 127	2024 clad	1.35	1.35	1.45	1.48	1.50	1.53	1.53	2.20
	2024 bare	1.37	1.41	1.50	1.57	1.65	1.63	2.08	2.31
A 9628/BR 127	2024 clad	1.40	1.40	1.54	1.62	1.76	1.77	2.20	2.47
	2024 bare	1.45	1.46	1.52	1.62	1.72	1.73	1.94	2.46
	7075 clad	1.43	1.52	1.73	3.55	3.42	3.03	Total disbond	
	7075 bare	1.49	1.53	1.69	1.90	1.88	1.88	1.94	2.10

a - Original crack length

b -  $a_1$ ,  $a_2$  etc. are crack extensions at the end of various time intervals

c - Fm 123-2 modified nitrile epoxy film adhesive (250°F)(127°C) cure

d - BR 123 non corrosion-resistant primer

e - BR 127 corrosion inhibiting adhesive primer (CIAP)

f - EA 9628 modified epoxy film adhesive (250°F)(127°C) cure

temperatures indicated in Table LV. A number of different types of adhesives were tested. Only one adhesive actually failed. Virtually all the adhesives showed a loss in strength when tested at 160°F (71°C), some being affected more than others. One adhesive, No. 7, the epoxy-anhydride RT-cured system, lost approximately 70% of its joint strength at 73°F (23°C) after cycling. The room-temperature-cured epoxy-polyamide system (No. 1) seemed to be the least affected of the adhesive types tested. Picatinny Arsenal carried out the tests in conjunction with actual field weathering studies. It should be noted that the testing was carried out at -65°F (-54°C), 73°F (23°C) or 160°F (71°C), after MIL-STD-304 cycling.(24)

15.6.3 Outdoor weathering. Picatinny Arsenal Studies. The results of weathering exposure up to one year on the adhesives covered in Table LV, along with several additional adhesives, are given in Table LVI.(25) The results are given as % retention of original joint strength. In addition to controls, the following climates were used:

- o Hot, dry (Yuma, Arizona)
- o Hot, humid (Panama Canal Zone)
- o Temperate (Picatinny Arsenal, Dover, N.J.)

## MIL-HDBK-691B

TABLE LV Effect of MIL-STD-304\* conditioning (JAN cycle) on strength of bonded aluminum alloy 2024-T3 joints.(24)

Adhesive Type (MPa)	Test Temperatures		Average Shear Strength			
	(°F)	(°C)	Control		MIL-STD-304*	
			(psi)	(MPa)	(psi)	(MPa)
1. Epoxy-polyamide, RT-cured	-65	-54	1700	11.7	2100	14.5
	73	23	1800	12.4	2100	14.5
	160	71	2700	18.6	1800	12.4
2. Epoxy-polyamide w/mica filler, RT-cured	-65	-54	2200	15.2	3080	21.2
	73	23	2500	17.2	3140	21.7
	160	71	2200	15.2	1120	7.7
3. Resorcinol epoxy-polyam- ide, RT-cured	-65	-54	2600	17.9	2440	16.8
	73	23	3500	24.1	3120	21.5
	160	71	3300	22.8	2720	18.8
4. Epoxy aromatic amine, RT-cured	-65	-54	1700	11.7	Panels fell apart	
	73	23	2000	13.8	Panels fell apart	
	160	71	720	5.0	Panels fell apart	
5. Epoxy-polysulfide, RT-cured	-65	-54	1800	12.4	1940	13.4
	73	23	1900	13.1	1640	11.3
	160	71	1700	11.7	1070	7.4
6. Nylon-epoxy, RT- cured	-65	-54	2400	16.6	3020	20.8
	73	23	2600	17.9	1730	11.9
	160	71	220	1.5	80	0.6
7. Epoxy-anhydride, RT-cured	-65	-54	2400	16.6	1900	13.1
	73	23	3000	20.7	920	6.3
	160	71	3300	22.8	1330	9.2
8. Modified epoxy, cured 1 hr at 350°F (177°C)	-65	-54	3700	25.5	2700	18.6
	73	23	4900	33.8	3400	23.4
	160	71	4100	28.3	3200	22.1
9. Epoxy-phenolic, cured 45 min at 330°F (166°C)	-65	-54	2800	19.3	2610	18.0
	73	23	2900	20.0	2350	16.2
	160	71	2900	20.0	2190	15.1
10. Nitrile-phenolic, cured 1 hr at 350°F (177°C)	-65	-54	4700	32.4	5300	36.6
	73	23	4600	31.7	3900	26.9
	160	71	3070	21.2	2900	20.0
11. Polyurethane, RT- cured	-65	-54	3500	24.1	4200	29.0
	73	23	2600	17.9	1970	13.6
	160	71	1600	11.0	1560	10.8

\* Alternating cycles of cold (-65°F) (-54°C), dry heat 160°F (71°C) and heat and humidity (160°F) (71°C) (95% RH) for 30 days. MIL-STD-304 has been superseded by MIL-STD-331.

Table LVI Percent Retention of Original Adhesive Joint Strength\* After Weathering One Year (2024-T3 Aluminum Alloy). (25)

Adhesive Designation and Type														
Weathering	Epoxy 350°F (177°C)	Epoxy 250°F (121°C)	Polyamide- Epoxy	Epoxy- Anhydride	Poly- Epoxy	Epoxy Powder	Filled Epoxy- Nylon	Epoxy- Resorcinol	Epoxy- Nylon	Epoxy- Phenolic	Nitrile- Phenolic	Silicone (RTV)	Polyure- thane	Polyester
Tested at 73°F (23°C)														
Control	92	115	115	91	107	82	99	87	100	89	103	200	168	80
Picatinny	76	84	88	84	76	71	93	80	93	80	90	184	98	95
Panama	60	90	90	34	74	104	96	74	98	76	90	208	24	0
Yuma	91	112	137	90	100	117	96	81	102	78	100	300	183	61
MIL-STD-304	58	89	135	32	83	68	105	92	69	72	92	107	135	47
Tested at 160°F (71°C)														
Control	96	124	113	100	139	72	158	98	115	85	98	230	130	138
Picatinny	88	103	77	71	122	81	82	86	101	82	98	140	57	102
Panama	55	83	76	30	90	117	65	65	95	73	88	220	87	0
Yuma	97	127	100	91	174	99	120	89	90	80	103	220	155	162
MIL-STD-304	62	86	84	46	181	69	90	77	22	72	100	170	130	40
Tested at -65°F (-54°C)														
Control	95	98	123	83	110	68	112	89	74	94	107	171	102	81
Picatinny	67	62	119	90	108	68	92	90	78	83	104	172	45	89
Panama	67	74	114	85	77	84	107	78	119	78	104	145	27	0
Yuma	67	90	130	98	140	71	97	86	85	85	93	172	64	109
MIL-STD-304	64	83	143	93	145	73	110	76	115	82	119	109	119	121

\*based on each testing temperature

Table LV12 Percent Retention of Original Adhesive Joint Strength\* After Weathering Three Years (2024-T3 Aluminum Alloy), (26)

Weathering	Adhesive Designation and Type									
	1	2	3	4	5	6	7	8	9	10
	Epoxy paste, Al-filled (350°F) (177°C)	Epoxy paste, filled (350°F) (177°C)	Epoxy paste, filled (250°F) (121°C)	Polyamide-Epoxy RT	Epoxy Anhydride RT	Poly-sulfide Epoxy RT	Modified Epoxy RT	Epoxy Powder (300°F) (149°C)	Epoxy Nylon RT	Epoxy Resorcinol RT
Tested at 73°F (23°C)										
Control	79	94	108	102	109	100	102	No data	92	93
Picatinny	70	68	77	78	58	35	65	63	54	58
Panama	22	9	53	39	0	0	0	87	90	64
Yuma	90	80	103	91	94	103	102	90	95	88
MIL-STD-304 Control	96	90	128	115	105	96	105	80	85	104
MIL-STD-304	58	51	89	135	32	83	0	68	105	92
Tested at 160°F (71°C)										
Control	84	100	107	83	100	256	274	No data	142	94
Picatinny	75	75	89	65	65	95	100	61	70	51
Panama	39	0	46	43	0	0	0	84	54	59
Yuma	103	93	103	85	87	324	154	83	71	84
MIL-STD-304 Control	93	94	129	125	114	289	89	95	176	93
MIL-STD-304	62	56	86	84	46	181	0	69	90	77
Tested at -65°F (-54°C)										
Control	79	110	108	118	97	139	97	No data	102	74
Picatinny	73	78	70	111	91	52	59	58	71	64
Panama	22	0	72	75	0	0	0	69	113	73
Yuma	76	73	72	130	111	150	76	70	98	84
MIL-STD-304 Control	97	88	109	115	118	122	119	73	85	81
MIL-STD-304	64	63	83	143	93	145	0	73	119	76

\*based on each testing temperature

## MIL-HDBK-691B

11 Epoxy-Nylon Paste HT	12 Epoxy-Nylon film (3750F) (1900C)	13 Epoxy-Phenolic film (3300F) (1660C)	14 Nitrile- Phenolic Film (3500F) (1770C)	15 Silicone Rubber HTV	16 Polyether- based (1800F) (820C)	17 Styrene- modified Polyester HT
36	110	81	103	250	117	159
65	110	67	95	102	24	22
100	0	68	127	250	165	0
85	77	77	147	183	70	74
103	--	89	108	208	180	95
69	--	72	92	167	135	47
108	84	80	106	276	195	147
97	109	76	107	115	50	70
94	0	70	88	204	71	0
129	120	85	108	200	84	80
56	--	95	107	250	135	140
22	--	72	100	170	130	40
81	154	81	128	153	121	97
94	83	68	111	31	44	66
98	0	63	121	136	47	0
95	98	80	137	115	64	86
91	--	88	106	208	99	85
115	--	82	119	109	119	170

## MIL-HDBK-691B

Results in JAN cycling (MIL-STD-304), as described, were also given. Table LVI shows that, in general, most of the adhesive joints, when stored in the laboratory (controls), retain most of their original joint strength for one year. The joints that were stored in the hot, dry area (Yuma) generally retained most of their original strength. Two adhesives, epoxy-resorcinol and epoxy-phenolic, show a trend towards decreased joint strength. Where climatic conditions subject the bond to humidity and precipitation, i.e., at Picatinny and in Panama, most of the joints show a decrease in joint strength. Four adhesive joints, those with filled epoxy-nylon, unfilled epoxy-nylon, nitrile-phenolic, and silicone, do not appear to be affected to any large degree by weathering, regardless of the site and climatic conditions.<sup>(25)</sup> Further study of Tables LV and LVI indicate that the MIL-STD-304 temperature and humidity cycle (now MIL-STD-331) can, in general, be used to predict the changes that occur in panels which expose them to high humidity.<sup>(25)</sup>

Table LVII shows the results of three years of weathering tests carried out by Picatinny Arsenal workers on aluminum joints, using seventeen different adhesives (26). Of those seventeen adhesives, thirteen were epoxies or modified epoxies, since epoxy types are most widely used in structural adhesive-bonding applications. In the study, only five of the original seventeen adhesives retained a minimum of 50% of their original joint strength and approximately 2000 psi (13.8 MPa) shear strength at all test temperatures after two years of weathering, regardless of the test site. After three years, only two adhesives, the phenolic-epoxy film (#13) and the nitrile-phenolic film (#14) met these requirements. Table LVI shows the percentage of retention of the original adhesive-joint strength for the seventeen adhesives after three years of weathering at the three test sites and after MIL-STD-304 cycling. It can be seen that the joints stored in the laboratory (controls) retained most of their original strength for the three years. So did most of the joints weathered at Yuma. Where humidity and moisture were prevalent, i.e. at Picatinny and in Panama, most of the joints showed a decrease in joint strength.

The joints made with an aluminum-filled one-component epoxy paste, 350°F (177°C) curing adhesive (#1) showed very good durability at Yuma. However, these joints showed a marked decrease in joint strength in the high humidity of Panama. At the end of three years there was some evidence of corrosion of the aluminum beneath the bond line. The joints made with another filled, one-component modified-epoxy paste, 350°F (177°C) curing adhesive (#2) showed good retention of joint strength during the three-year exposure at all sites other than Panama. After two years, the Panama joints had lost more than 50% of their original strength due to corrosion of the aluminum; after three years they were so badly corroded that they fell apart in the racks. In general, the joints formed with a 250°F (121°C) curing, one-component epoxy paste adhesive (#3) showed a good retention of the original bond strength. However, here again, the higher-humidity sites appeared to have an adverse effect after three years. This effect was also noted on the joints made with the polyamide-modified epoxy (#4).



## MIL-HDBK-691B

The joints with the two-part epoxy-anhydride adhesive (#5), the two-part aliphatic-amine-cured polysulfide-modified epoxy (#6), and the two-part mixed-amine-cured, filled epoxy (#7) fell apart on the racks at the Panama site. Numbers 5 and 7 both fell apart during the second year of the program. The #6 adhesive joints fell apart during the third year, and also showed a sharp decrease in strength after three years at the Picatinny site. Joints #8, 9, 10, and 11 retained better than 50% of their original joint strength after three years at all test temperatures and sites. For some unknown reason, the three-year laboratory control of #11 fell sharply to 36% retention at 73°F (23°C).

The joints made using the epoxy-nylon film adhesive (#12) fell apart on the racks in Panama due to crevice and exfoliation corrosion. The epoxy-phenolic film adhesive (#13) and the nitrile-phenolic film adhesive (#14) retained better than 50% of their original joint strength with average joint strengths of approximately 3000 psi (13.8 MPa) under all test conditions after exposure to the environments of all the test sites. The joints made with the RTV silicone rubber adhesive (#15) showed a general increase in bond strength in the early stages of exposure, probably due to further cure. They also demonstrated a general retention of the initial bond strength throughout the three-year period. The joints made with polyurethane (#16) showed signs of degradation at all the outdoor sites. The joints made with the polystyrene-modified unsaturated polyester fell apart in Panama after two years exposure. The panels at the other sites generally retained a fair percentage of their original joint strength.(26)

In summary, the joints that retained better than 50% of their original bond strengths at all test temperatures after exposure to three years at any of the test sites were #8, 10, 13, and 14. Of these, only #13 and #14 retained approximately 2000 psi (13.8 MPa) shear strength at all test temperatures after three years at any of the test sites. Five of the joints retained better than 50% of their original bond strength and approximately 2000 psi (13.8 MPa) shear strength at all test temperatures after exposure to MIL-STD-304 cycling. These were #1, 2, 3, 13 and 14. Subjection of bonded panels to the temperature and humidity aging of MIL-STD-304 does, in general, tend to show up those adhesive systems which will not form joints that will give satisfactory performance in highly humid atmospheres.(26)

15.6.4 Australian Studies. In another experiment carried out in Australia in conjunction with Picatinny Arsenal, studies were carried out under hot/wet and hot/dry conditions. A room-temperature vulcanizing (RTV) silicone showed excellent weather resistance, especially if not heavily loaded. A room-temperature-curing acrylic adhesive showed relatively small declines in properties upon weathering. A room-temperature-curing modified epoxy adhesive weathered well under hot/dry conditions, but results under a hot/wet environment were inconsistent. A room-temperature-cured polyamide-epoxy weathered poorly under hot/wet conditions. The hot/dry results were somewhat anomalous. Generally, this system would not be recommended for outdoor use.

## MIL-HDBK-691B

15.7 Chemicals and solvents. Most organic adhesives tend to be susceptible to chemicals and solvents, especially at elevated temperatures. Among the standard test fluids and immersion conditions (other than water, high humidity and salt spray) are the following:

- 7 days in JP-4 jet engine fuel
- 7 days in anti-icing fluid (isopropyl alcohol)
- 7 days in hydraulic oil (MIL-H-5606)
- 7 days in HC test fluid (70/30 v/v isooctane/toluene)

Unfortunately, exposure tests lasting less than 30 days are not applicable to many service-life requirements. Practically all adhesives are resistant to these fluids over short time periods and at room temperatures. Some epoxy adhesives even show an increase in strength during aging in fuel or oil (1). Hysol Division (Dexter Corporation) reported studies in their Aerospace Adhesive EA 929, a fast-curing, one-part thixotropic epoxy paste adhesive. With gasoline at 75°F (24°C) and gear oil at 250°F (121°C) there was a definite increase in 250°F (121°C) tensile shear strength in etched 2024-T3 Al clad cured 20 minutes at 400°F (204°C). This increase tended to level off after 4-6 months immersion.(27) This effect is possibly due to postcuring or plasticizing of the epoxy by the oil.(1)

Epoxy adhesives are generally more resistant to a wide variety of liquid environments than other structural adhesives. However, the resistance to a specific environment is greatly dependent on the type of epoxy curing agent used. Aromatic amines, such as metaphenylene diamine, cured systems are frequently preferred for long-term chemical resistance.(1)

Urethane adhesives generally show good resistance to most chemicals, solvents, oils and greases.

There is no generally "best" adhesive for all chemical environments. As an example, maximum resistance to bases almost axiomatically means poor resistance to acids. It is relatively easy to find an adhesive that is resistant to one particular chemical environment. Generally, adhesives which are most resistant to high temperature have the best resistance to chemicals and solvents.(1)

The temperature of the immersion medium is a significant factor in the aging properties of adhesives. As the temperature increases, more fluid is generally adsorbed by the adhesive and the degradation rate increases. In summary (1):

- o Chemical resistance tests are not uniform in concentrations, temperature, time, or properties measured.
- o Generally, chlorinated solvents and ketones are severe environments.
- o High-boiling solvents, such as dimethylformamide, dimethyl sulfoxide, and Skydrol (Monsanto Corp.) are severe environments.
- o Acetic acid is a severe environment.

## MIL-HDBK-691B

- o Amine curing agents for epoxies are poor in contact with oxidizing acids.
- o Anhydride curing agents are poor in contact with caustics.

ASTM D896-84, "Standard Test Method for Resistance of Adhesive Bonds to Chemical Reagents" (see 13.2.2) covers the testing of all types of adhesives for resistance to chemical reagents. The standard chemical reagents are those listed in ASTM D 543 and the standard oils and fuels are given in ASTM D 471. Additional supplementary reagents, for which the formulations are given, are: Hydrocarbon Mixture No. 1, Standard Test Fuel No. 2, and Silicone Fluid (Polydimethylsiloxane).

15.8 Vacuum. The ability of an adhesive to withstand long periods of exposure to a vacuum is of primary importance for materials used in space travel. The degree of adhesive evaporation is a function of its vapor pressure at a given temperature. Loss of low-molecular-weight constituents such as plasticizers or diluents could result in hardening and porosity of adhesives or sealants. Since most structural adhesives are relatively high-molecular weight polymers, exposure to pressures as low as  $10^{-9}$  torr ( $1.33 \times 10^{-7}$  Pa) is not harmful. However, high temperatures, nuclear radiation, or other degrading environments may cause the formation of low-molecular-weight fragments which tend to bleed out of the adhesive in a vacuum.(1)

The space vacuum is one of the more important components of the space environment. Although, volatility of materials at high vacuum is certainly an important consideration, volatility of the polymer is usually not high enough to be significant. Polymers, including adhesives, will not volatilize as a result of vacuum alone. Incomplete polymerization often results in the presence of residual lower-molecular-weight specimens, which, in turn, are responsible for observed outgassing of polymeric materials. The vacuum is no real problem in itself when the molecular weight of the polymer is reasonably high and the polymer is free of low-molecular-weight components. The effect of vacuum on polymers is not one of evaporation or sublimation, but is a degradation caused by the breaking down of the long-chain polymers into smaller, more-volatile fragments. Chain length, (molecular weight), extent of branching, and cross-linking have a direct effect upon the rate of decomposition.(28)

Polymers which show high decomposition rates in vacuum near room temperature are nylon, polysulfides and neoprene.(28)

Douglas Aircraft carried out a study (29) on outgassing of commercially available structural adhesives, sealants and seal materials at  $10^{-9}$  torr ( $1.33 \times 10^{-7}$  Pa). Disks of 1-inch diameter were punched from nineteen adhesives, sealants and seal materials. The disks were dried in a desiccator over phosphorous-pentoxide, weighed on an automatic balance, and placed in a vacuum at  $10^{-9}$  torr ( $1.33 \times 10^{-7}$  Pa) for 7 days. At the conclusion of the exposures, each specimen was immediately placed in a desiccator and reweighed for determination of any weight change. After this second weighing the specimens were exposed to the atmosphere for one week and again weighed to determine any additional weight change. Table LVIII shows a few results of this study and indicates that under ambient conditions a high vacuum does not cause significant weight loss in the materials.

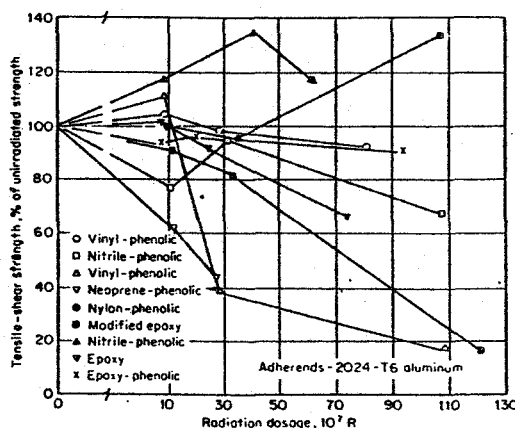
MIL-HDBK-691B

TABLE LVIII Effect of  $10^{-7}$  Torr ( $1.33 \times 10^{-5}$  Pa) on commercial adhesives/sealants.(29)

Adhesive	Type	Weight change %	Moisture change, %
Lefkowied 109	Modified epoxy	-0.03	+0.60
EC2216B/A	Flexibilized epoxy	-0.06	+0.61
Adiprene L-100 + Moca	Polyurethane	+0.01	+0.38
PR1535	Polyurethane	+0.01	+0.44
EC1605	Polysulfide	-0.23	+0.39

15.8.1 Higher temperature and vacuum. To show the significant effect of temperature on the rate of decomposition and volatilization, over vacuum, the same experiment as described above was conducted at 225°F (107°C) on the two polyurethane materials. The Adiprene L-100 and Moca formulation now showed a weight change of -0.75% and the PR 1535 showed a weight change of 1.45%. The 225°F(107°C) test temperature was considerably higher than intended for the urethane formulas available at the time of testing.(29)

15.9 Radiation. High-energy particulate and electromagnetic radiation including neutron, electron, and gamma radiation, have similar effects on organic adhesives. Radiation causes molecular-chain scission of polymers used in structural adhesives, which results in weakening and embrittlement of the bond. This condition is worsened when the adhesive is simultaneously exposed to elevated temperatures and radiation. Figure 58 shows the effect of radiation dosage on the tensile shear strength of structural adhesives. Generally, heat-resistant adhesives have been found to resist radiation better than less thermally stable systems. Fibrous reinforcements, fillers, curing agents, and reactive diluents affect the radiation resistance of adhesive systems. In epoxy-based systems, aromatic curing agents offer greater radiation resistance than aliphatic types.(1)(30)

FIGURE 58. Effect of nuclear radiation (gamma rays) dosage on structural adhesives. (1)(30)

## MIL-HDBK-691B

ASTM D1879-70 (1981), "Standard Practice for Exposure of Adhesive Specimens to High Energy Radiation" is the test method currently in use. This method was originally adopted in 1961. It is described briefly in 13.2.42. Polyester resins and cured anaerobic products have high radiation resistance based on a radiation spectrum for electrical insulation and materials. Research surveys class anaerobic resins in a radiation exposure category with all dose rates based on 100 hours up to 1000 Mrad with a dose rate of  $10^6$  to  $10^7$  rads/hour, or  $10^{11}$  to  $10^{12}$  neutrons/hour. Thread-locking grades of anaerobic adhesives have sustained  $2 \times 10^7$  rads without molecular change or loss in locking torque. Anaerobic threaded connections have been exposed to radiation in a reactor for several years with no apparent loss in holding strength.(31)

Adhesives generally react to radiation in much the same manner as the plastics or elastomers from which they are derived. Generally, those containing aromatic compounds show good resistance to radiation. Fillers and reinforcing materials improve the radiation stability of these products substantially, while also improving other properties.(32)

The following conclusions were made by Battelle workers on sterilizing-radiation effects on polymers that might be used in adhesives (32):

Polysulfones - can withstand radiation doses greater than 1000 Mrads without significant effect

Phenol-formaldehyde or Urea-formaldehyde - these are usually filled or reinforced. The addition of mineral fillers increases the radiation stability significantly, by as much as 100 fold. Filled resins of this type usually show good radiation resistance up to 500 Mrads or higher (General radiation resistance - good)

Epoxies - these materials are above average in radiation resistance of polymers, although this may be varied somewhat, depending upon the hardeners used. Resins using aromatic curing agents generally are more stable than those using aliphatic hardeners. These polymers are stable to radiation doses above 1000 Mrads. (General radiation resistance-excellent)

Unsaturated Polyesters - these thermoset materials have quite good radiation resistance, especially if they contain mineral fillers or glass fibers. They can be expected to withstand greater than 1000 Mrads. (General radiation resistance - good)

Polyimides - these materials are well-known for their very high thermal and radiation resistance. They can be expected to withstand radiation doses of about 1000 Mrads at high temperatures (500° F or 260°C). (General radiation resistance - excellent)

Polyurethanes - their properties vary from those of an elastomer to those of hard, rigid cross-linked polymers whose mechanical properties show no reduction after an exposure to 1000 Mrads. (General radiation resistance - excellent).



## MIL-HDBK-691B

In 1962 a study was carried out on the effects of gamma radiation on the performance of several structural adhesive bonds.<sup>(33)</sup> The general conclusions were:

- o Nitrile-phenolic adhesives are more resistant to radiation damage than epoxy-based adhesives
- o The peel strength of adhesives deteriorates more rapidly than other properties
- o Thick adhesive layers retain useful strength better than thin glue lines. Ten mils (0.01 inch or 0.25 mm) is recommended as the minimum glue-line thickness.

Figure 59 shows the effect of radiation on the overlap shear strength of four rigid adhesives used primarily for metal-to-metal bonding in 1962. Radiation does not appear to have serious effects on the overlap-shear strength of these highly cross-linked adhesives. In each case they seem to benefit slightly from the additional cross-linking caused by the low orders of irradiation, but eventually begin to degrade after 500-600 megarads. The principal effect noted was embrittlement due to high (800-900 megarads) amounts of radiation. Very probably there is a loss of cohesive strength in the adhesive due to a considerable amount of chain scission, as well as cross-linking.<sup>(33)</sup>

Figure 60 shows the effect of radiation in the bond performance over a wide temperature range. The high-temperature performance of structural adhesives appears to fall off in a manner parallel to the room-temperature performance. The modified-epoxy adhesive maintains its properties up to about 600 megarads and the modified phenolic is relatively unaffected by very high doses of radiation. The elastomer-phenolic films, as might be expected, are more greatly affected by radiation, since they have a greater flexibility and more sites for cross-linking. These films maintain their performance at room temperature up to 400 megarads, but fall below the old MIL-A-5090D, type II requirements of 2,250 psi (15.5 MPa) after about 100 megarads of radiation.<sup>(33)</sup>

As long as an adhesive maintains its adhesion to the substrate and a certain amount of cohesive strength, its performance is relatively unaffected by radiation. The results obtained with a more complex mechanical response like peel strength are shown in Table LIX.

The question arises as to what the probable radiation dose will be for exposure to the space environment. In outer space unshielded structures might be exposed to as much as 3500 megarads per day during a solar storm. Organic structures with the minimum amount of shielding will be exposed to perhaps 10 to 50 rads per hour. Even at the upper level of 50 rads per hour (Van Allen belt), it would take two million hours to reach the 100-megarad dosage level, and it is expected that most missions would be completed by that time.<sup>(33)</sup>

Most structural adhesives will perform well under radiation encountered in outer space over any reasonable time period. The rigid metal-to-metal adhesives will perform under fairly high radiation dosages, although it is not recommended that they be exposed directly to the space environment. The other major requirement for radiation resistance of adhesives is for nuclear reactors and related equipment with high radiation-flux zones.<sup>(33)</sup>



MIL-HDBK-691B

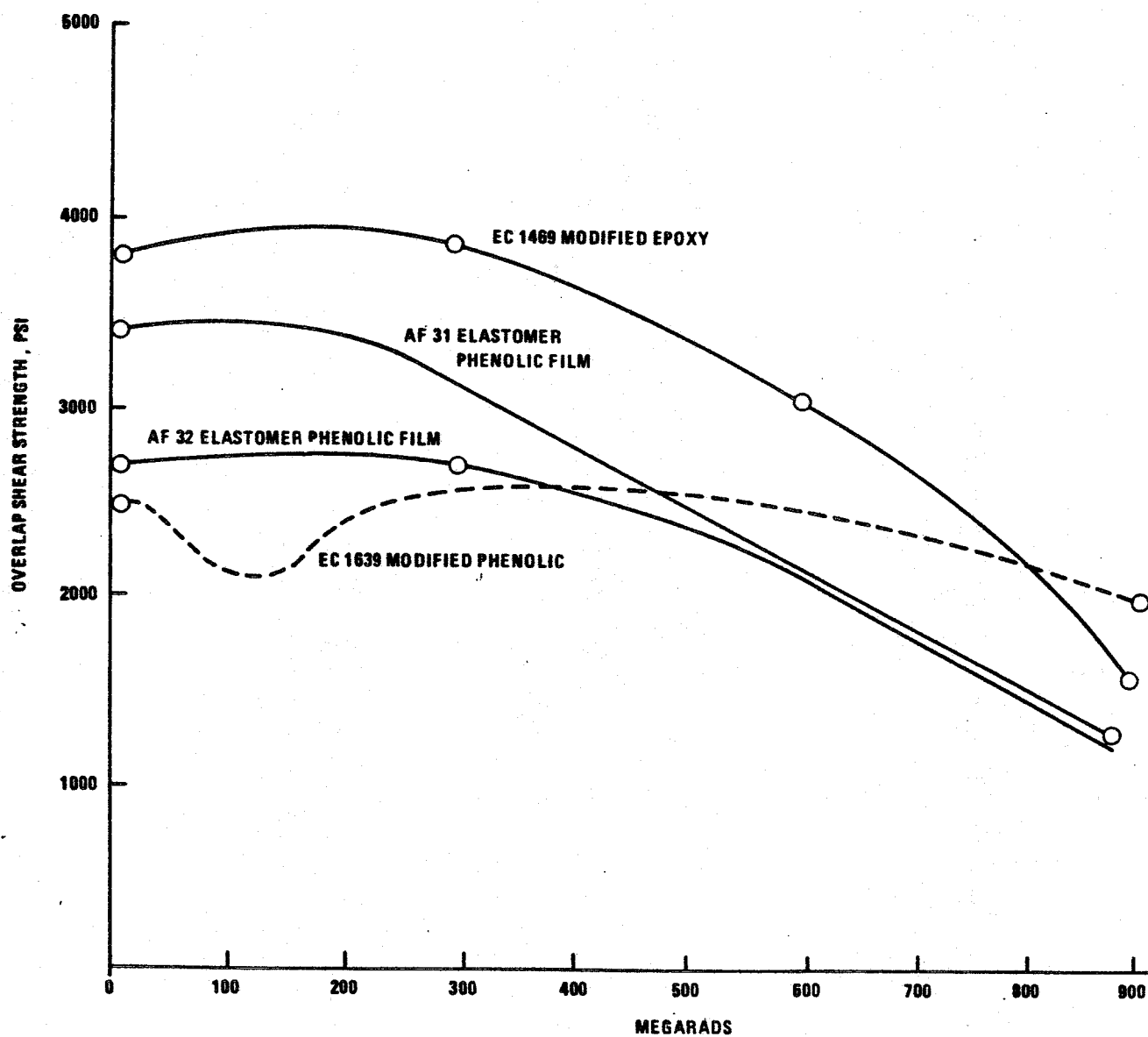


FIGURE 59. Effect of gamma radiation on overlap shear strength of structural adhesive bonds at 75°F (24°C).(33)

MIL-HDBK-691B

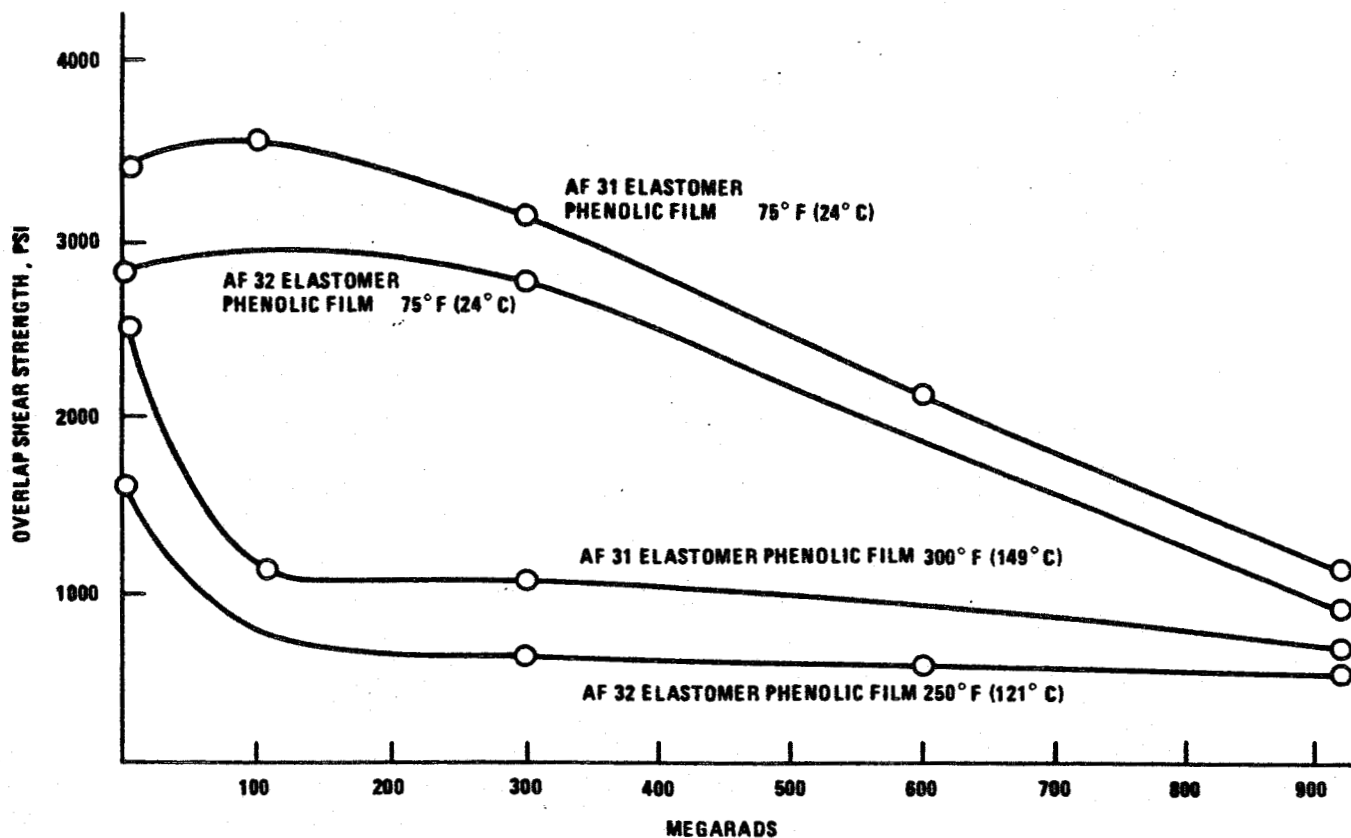


FIGURE 60. Effect of gamma radiation on structural adhesive bonds over temperature range 75-300°F (24-149°C).(33)

TABLE LIX. Effect of gamma radiation on T-peel strength of elastomer-phenolic film adhesives.(33)

Adhesive	Radiation dose, megarads				
	0	100	300	600	900
AF-30 4	48.5 pli	34 pli	12 pli	5 pli	5 pli
AF-31 (most rigid)	30 pli	20 pli	8 pli	4.5 pli	4 pli
AF-32	34 pli	10 pli	4 pli	3 pli	3 pli

## 15.10 Biological.

15.10.1 General. Adhesives in bonded joints may or may not be attacked and degraded by biological organisms (fungi, bacteria, insects and rodents), depending on how attractive the adhesives are to these forms. Adhesives based on animal or plant materials (animal or fish glues, starch, dextrans) are much more likely to be affected than synthetic adhesives. Fungi and bacteria are classified as microorganisms, although the former may consist of forms readily visible to the naked eye (mycelia)(34, 35).

It is known that polyurethane resins based on polyether polyols are moderately to highly resistant to fungal attack, while all polyester urethane resins are highly susceptible to such attack. This susceptibility is related to the number of adjacent unbranched methylene groups in the polymer chain. At least two and preferably three such groups are required for appreciable attack to occur. The presence of side chains on the diol moiety of the polyurethane reduces susceptibility to attack. With the polyethers, attack is dependent on the diol and diisocyanate used. Adipic acid and diethylene glycol, used in making polyester, are able to support mold development. It is not always easy to determine whether deterioration of polyurethane is caused by hydrolytic reversion or by fungal attack. However, a magnifying lens can be used to detect channel-like lesions on the surface of the polyurethane (this is more difficult with adhesives), and below the surface tubular formations branch out in different directions. This network of tunnels is frequently seen to radiate from a single point. The tunnels contain individual mold hyphae or hyphal strands of varying thicknesses. Over a long period, and more rapidly when exposed to high temperature, humidity, and light, the damaged material softens increasingly. Eventually, after several months it becomes a gelatinous mixture of degradation products and fungal hyphae. Of the mold species attacking polyester polyurethane, Stemphylium is one the most active. Biodeterioration can be slowed down by the use of hydrolysis inhibitors (stabilizers) and/or certain fungicides, such as 8-hydroxyquinoline.

15.10.2 Test Methods. ASTM Committee D-14 on Adhesives has four test methods published that are applicable to biological attack. They are as follows:

- o ASTM D1382-64 (1981) Standard Test Method for SUSCEPTIBILITY OF DRY ADHESIVE FILMS TO ATTACK BY ROACHES (see 13.2.25)
- o ASTM D1383-64 (1981) Standard Test Method for SUSCEPTIBILITY OF DRY ADHESIVE FILMS TO ATTACK BY LABORATORY RATS (see 13.2.26).
- o ASTM D4299-84 Standard Test Method for EFFECT OF BACTERIAL CONTAMINATION ON PERMANENCE OF ADHESIVE PREPARATIONS AND ADHESIVES FILMS (see 13.2.17)
- o ASTM D4300-84 Standard Test Methods for EFFECT OF MOLD CONTAMINATION ON PERMANENCE OF ADHESIVE PREPARATIONS AND ADHESIVES FILMS (see 13.2.20)

MIL-HDBK-691B

## REFERENCES

- (15-1) E.M. Petrie, "Plastics and Elastomers as Adhesives", Chapter 10 in HANDBOOK OF PLASTICS AND ELASTOMERS, edited by C.A. Harper, McGraw-Hill, New York, N.Y., 1975.
- (15-2) D.M. Weggemans, "Adhesive Charts", in Appendix, ADHESION AND ADHESIVES, 2nd Edition, Volume 2. "Applications", edited by R. Houwink and G. Salomon, Elsevier Publishing Co., 1967.
- (15-3) N.J. DeLollis, ADHESIVES, ADHERENDS, ADHESION, 2nd Edition (original 1970 edition was ADHESIVES FOR METALS: THEORY AND TECHNOLOGY), Robert E. Krieger Publishing Co., Inc., Huntington, N.Y., 1980.
- (15-4) A.J. Kinloch (Explosives Research and Development Establishment (UK)), "Environmental Failure of Structural Adhesive Joints - A Literature Survey", Technical Note No. 95, August 73. (Unlimited distribution) (AD 784 890).
- (15-5) L.C. May and N.R. Adsit, "The Mechanical Behavior of Adhesive Materials", paper presented at the 20th National SAMPE Symposium and Exhibition San Diego, CA, April 29-May 1, 1975. Published in Proceedings, Vol. 20, pp. 546-553.
- (15-6) D.A. Wangsness. "Sustained Load Durability of Structural Adhesives", Journal of Applied Polymer Science, Applied Polymer Symposia 32, 1977:296-300, based on symposium on "Durability of Adhesive Bonded Structures" held at Picatinny Arsenal, October 27-29, 1976.
- (15-7) J.C. Bolger, "Structural Adhesives for Metal Bonding, Chapter 1, pp. 1-78, in TREATISE ON ADHESION AND ADHESIVES, Vol. 3, edited by R.L. Patrick, Marcel Dekker, Inc., N.Y. 1973.
- (15-8) Union Carbide Corporation, Product Data Bulletin F-43410B 11/77, "UDEL Polysulfone for High-Temperature Structural Adhesive Applications", 4pp. Nov. 1977.
- (15-9) A.H. Landrock, "Properties of Plastics and Related Materials at Cryogenic Temperatures", Plastics Technical Evaluation Center, PLASTEC Rept. 20, July 1965. (AD 469 126).
- (15-10) L.M. Roseland, "Materials for Cryogenic Usage", Proceedings, 21st Annual Meeting, Reinforced Plastics Division, SPI, Chicago, IL, Feb. 8-10, 1966. Section 4C, 6 pp.
- (15-11) R.C. Kausen, "High and Low-Temperature Adhesives- Where Do We Stand?", Proceedings, 7th National SAMPE Symposium on Adhesives and Elastomers for Environmental Extremes, Los Angeles, CA, May 20-22, 1964. Section 1, 51 pp.

## MIL-HDBK-691B

- (15-12) F.R. Williamson and N.A. Olien (Cryogenic Div., Institute for Basic Standards, NBS), "Cryogenic Adhesives and Sealants - Abstracted Publications", NASA SP-3101, prepared for the Aerospace Safety Research and Data Institute, NASA Lewis Research Center, 1977
- (15-13) R.W. Vaughan and C.H. Sheppard (TRW Systems Group), "Cryogenic/High-Temperature Structural Adhesives", NASA CR-134465, prepared for NASA on Contract NAS3-10780, January 1974. 77 pp.
- (15-14) N.J. DeLollis and D. Montoya, "Mode of Failure in Structural Adhesive Bonds", Journal of Applied Polymer Science, 11(6):983-989 (June 1967).
- (15-15) J.D. Minford, "Comparison of Aluminum Adhesive Joint Durability as Influenced by Etching and Anodizing Treatments of Bonded Surfaces", Journal of Applied Polymer Science, Applied Polymer Symposia 32, 1977:91-103, based on symposium on "Durability of Adhesive Bonded Structures" held at Picatinny Arsenal, October 27-29, 1976.
- (15-16) R.F. Wegman, M.J. Bodnar and M.C. Ross, "A New Technique for Assessing Durability of Structural Adhesives", Adhesives Age, 21(7):38-41 (July 1978). Based on a paper presented at 9th National SAMPE Technical Conference, Atlanta, GA. Oct. 4-6, 1977
- (15-17) R.F. Wegman, S.A. Slota and W.C. Tanner, "Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures - Part XIX. Durability of Epoxy Bonds to Aluminum Alloys", Picatinny Arsenal Technical Report 4483, June 1973.
- (15-18) R.F. Wegman, M.C. Ross, S.A. Slota and E.S. Duda, "Evaluation of the Adhesive Bonded Processes Used in Helicopter Manufacture", Part 1. Durability of Adhesive Bonds Obtained as a Result of Processes Used in the UH-1 Helicopter, Picatinny Arsenal Technical Report 4186, Sept. 1971.
- (15-19) R.F. Wegman, S.A. Slota, M.C. Ross, E.A. Garnis and E.S. Duda. "Durability Studies of Adhesive-Bonded Metallic Joints", Picatinny Arsenal Technical Report 4707, Dec. 1974.
- (15-20) R.F. Wegman, S.A. Slota, M.C. Ross, and E.A. Garnis, "The Effect of Environmental Exposure on the Endurance of Bonded Joints in Army Helicopters", Picatinny Arsenal Technical Report 4744, May 1975.
- (15-21) R.F. Wegman, "Durability of Some Newer Structural Adhesives", Journal of Applied Polymer Science. Applied Polymer Symposia 32, 1977:1-10, base on symposium on "Durability of Adhesive Bonded Structures", held at Picatinny Arsenal, October 27-29, 1976.
- (15-22) J.D. Minford, "Durability of Adhesive Bonded Aluminum Joints", Chapter 2, pp. 79-122, in TREATISE ON ADHESION AND ADHESIVES, Vol. 3, edited by R.L. Patrick, Marcel Dekker, Inc., N.Y. 1973

## MIL-HDBK-691B

- (15-23) J.A. Marceau and J.C. McMillan (Boeing Commercial Airplane Co.), "Exploratory Development on Durability of Adhesive Bonded Joints", AFML-TR-76-173, October 1976. Air Force Contract AF 33615-74-C-5065.
- (15-24) W.C. Tanner, "Adhesives and Adhesion in Structural Bonding for Military Materiel", Applied Polymer Symposia, (3):1-25 (1966), based on symposium on "Structural Adhesives Bonding", held at Picatinny Arsenal, Sept. 14-16, 1965.
- (15-25) R.F. Wegman, W.M. Bodnar, E.S. Duda and M.J. Bodnar, "How Weathering and Aging Affect Bonded Aluminum", Adhesives Age, 10(10):22-26 (October 1967)
- (15-26) R.F. Wegman, W.M. Bodnar and M.J. Bodnar, "Effect of Outdoor Aging on Unstressed, Adhesive-Bonded, Aluminum-to-Aluminum Lap Shear-Joints, Three-Year Summary Report", Picatinny Arsenal Technical Report 3689, May 1968.
- (15-27) Hysol Division, Dexter Corporation, "Aerospace Adhesive EA 929", Bulletin A5-129.
- (15-28) A.H. Landrock, "Effects of the Space Environment on Plastics: A Summary with Annotated Bibliography", PLASTEC Report 12, July 1982. AD 288 682.
- (15-29) L.M. Roseland, "Structural Adhesives in Space Applications", Applied Polymer Symposia (3):361-367 (1966), based on symposium on "Structural Adhesive Bonding", held at Picatinny Arsenal, Sept. 14-16, 1965.
- (15-30) R.S. Arlook and D.G. Harvey. "Effect of Nuclear Radiation on Structural Adhesive Bonds", Wright Air Development Center report WADC-TR-46-467, February 1957. (AD 118 063).
- (15-31) M.B. Pearce, "How to Use Anaerobics Successfully", Applied Polymer Symposia (19):207-230 (1972); based on symposium on "Processing for Adhesives Bonded Structures", held at Stevens Institute of Technology, Hoboken, N.J. and sponsored by Picatinny Arsenal.
- (15-32) W.E. Skiens (Battelle Pacific Northwest Laboratories), "Sterilizing Radiation Effects on Selected Polymers", PNL-SA-7640, Conf. 7403108-1. Paper presented at Symposium on "Radiation Sterilization of Plastic Medical Products", 28 March 1979, Cambridge, MA. 18 pp. Available from NTIS as AD D 432 161.
- (15-33) R.M. McCurdy and G.M. Rambosek, "The Effect of Gamma Radiation on Structural Adhesive Joints," Preprint Book, National SAMPE Symposium on "The Effects of Space Environment on Materials" held at St. Louis, MO, May 7-9, 1962.



MIL-HDBK-691B

- (15-34) D.M. Evans and I. Levisohn, "Biodeterioration of Polyester-Based Polyurethane", International Biodeterioration Bulletin, 4(2):89-92 (1968).
- (15-35) R.T. Darby and A.M. Kaplan, "Fungal Susceptibility of Polyurethanes", Applied Microbiology, 16(6):900-905 (June 1968).

(WP# ID-0325m/DISK-0038v. FOR AMTL USE ONLY)

## MIL-HDBK-691B

## CHAPTER 16

## AN OUTLINE FOR A BONDING PROCESS SPECIFICATION

16.1 Introduction Every adhesive-bonding process should have a process specification. This is especially true of a process as critical as that required for structural adhesive bonding. This chapter presents a general outline for a process specification of this type.<sup>(1)</sup>

16.2 An outline for a bonding process specification.

Scope

1. Describe the applicability of the specification.
2. Describe the applicable adhesive.
3. Resolve conflicts with other applicable documents such as engineering drawings, military specifications, other intra-plant documents, etc.

Related specifications. List all applicable documents, engineering drawings, specifications.

Materials Control. Provide description, and source of all materials and equipment used in production, along with batch and lot numbers, as well as dates when produced.

1. Production Materials

These are materials which are incorporated in the product.

- a. Structural adhesives
- b. Sealants
- c. Primers
- d. Paints
- e. Additives such as fillers

2. Non-production Materials and Equipment

These are materials which are not incorporated in the product, and equipment employed in the production process.

- a. Abrasive wheels
- b. Finishing paper
- c. Alumina or silica grit
- d. Chemicals
- e. Parting agents
- f. Solvents
- g. Miscellaneous items

## MIL-HDBK-691B

Facilities Control Describe all facilities completely. List controls for individual areas; materials of construction of processing tanks; rinse water to be used; ovens, presses, autoclaves, etc. available for curing adhesives; testing facilities.

1. Bonding Area Environment
  - a. Humidity control
  - b. Contamination control: Slightly positive pressurized room, restrictions on eating, smoking and using silicone release agents, etc.
  - c. Temperature (between 70°F (21°C) and 85°F (29°C))
2. Compressed Air
  - a. Filter requirements
3. Tooling
4. Processing tanks
5. Facilities for mechanical cleaning of glass-reinforced plastics
6. Facilities for surface preparations and platings

Manufacturing Control

1. Personnel: Certifications, grades, etc.
2. General restrictions
  - a. No markings of surfaces
  - b. No silicone spray on tools
3. Cleaning and surface treatment
  - a. General requirements
    - Work gloves
    - Handling and storing of parts
  - b. Mechanical methods
    - Description of maintenance of abrasives
    - Establish guidelines for operations
  - c. Chemical methods
    - Description of preparation and maintenance of baths
    - Specification of treatment and type of adherend.
    - Time limit set for each step
    - Specify rework procedures

## MIL-HDBK-691B

4. Adhesive preparation
  - a. General
  - b. Liquids, multicomponent
  - c. Tapes, frozen
5. Adhesive application
  - a. General instructions
  - b. Liquid adhesive applications
  - c. Tape or film-adhesive application
  - d. Removal of excess uncured adhesive
6. Curing adhesive bonds
  - a. Description for each system
  - b. Cure pressure
  - c. Cure temperature
  - d. Heat requirements (time periods)
  - e. Special instructions
7. Finishing or post-bonding operations
  - a. Removal of excess cured adhesive
    - Tools
    - Limitations
    - Heat
    - Solvents
    - Strippers
  - b. Machining
  - c. Sealing
  - d. Painting

Quality Control

1. Definitions
2. Procurement controls for adhesives
  - a. Control prior to release to production
  - b. Storage life
  - c. Identification
  - d. Packaging
  - e. Physical properties
  - f. Vendor inspection
  - g. Purchaser inspection
  - h. Description of specimens used and quantity of each specimen

MIL-HDBK-691B

3. Process control

- a. Heat and pressure surveys
- b. Solution controls
- c. Temperature-control charts
- d. Process-control testing of adhesives
- e. Cleaning and surface treatments

Physical appearances as an indicator for inspection

Plating thickness and adherence

Control specimens

Chart frequency of sampling

Data spread

Acceptance criteria

Rejection procedure

Preparation and application of adhesives on specimens to  
accompany production parts

- f. First qualification and periodic requalification tests of  
production facilities including tooling, jigs, treating solutions,  
ovens, presses, etc

First qualification

Periodic requalification

- g. Parts inspection

Bond-line appearance

Nondestructive testing

Records

MIL-HDBK-691B

REFERENCE

- (16-1) Wegman, R.F. et al., "The Effects of Varying Processing Parameters in the Fabrication of Adhesive-Bonded Structures, Part 2. Important Considerations for the Bonding Process," Picatinny Arsenal Technical Report 3999, July 1970. (AD 874 519).

WP# ID-7410A/DISK-0038w FOR MTL USE ONLY.



## MIL-HDBK-691B

## CHAPTER 17

## SPECIFICATIONS

17.1 Organization. This chapter covers the following specifications: ASTM, Federal (including Commercial Item Descriptions), Military, and Aeronautical Materials Specifications (AMS's). A total of 140 specifications are covered, some DOD adopted and some not. There are 18 ASTM Specifications, 34 Federal Specifications and Commercial Item Descriptions, and 23 Aeronautical Materials Specifications. Where DOD approved, the Federal Supply Classification (FSC) is given, along with the code for the Preparing Activity.

17.2 ASTM Specifications (1).

17.2.1 ASTM C557-73 (1985). Standard Specification for ADHESIVES FOR FASTENING GYPSUM WALLBOARD TO WOOD FRAMING, 7 pp., (DOD Adopted) ASTM Committee C-11 on Ceilings and Walls. FSC 8040 YD

This specification covers minimum standards for bonding the back surfaces of gypsum wallboard to wood framing members. It also covers test requirement and test methods for the adhesive used for the application of all thicknesses of gypsum wallboard. Organic adhesives are required.

17.2.2 ASTM F656-80. Standard Specification for PRIMERS FOR USE IN SOLVENT CEMENT JOINTS OF POLY(VINYL CHLORIDE) (PVC) PLASTIC PIPE AND FITTINGS, 2 pp., ASTM Committee F-17 on Plastic Piping Systems.

This specification provides general requirements for primers for use with poly(vinyl chloride) (PVC) pipe and fittings that are to be joined by PVC solvent cements meeting the requirements of Specification D2564. These primers are recommended for use in pressure and nonpressure applications with either plain-end pipe and socket-type fittings or bell-end pipe. The primers shall be organic liquids with water-like viscosities and shall not contain any undissolved particles. The solvent system to be used is not specified.

17.2.3 ASTM E865-82. Standard Specification for STRUCTURAL FILM ADHESIVES FOR HONEYCOMB SANDWICH PANELS, 6 pp., (DOD Adopted) Committee E-6 on Performance of Building Construction.

This specification covers film adhesives for bonding of honeycomb sandwich panels used in tactical shelters. The adhesives may be used for new production or depot repair. The adhesives should be suitable for forming bonds that can withstand long exposures to temperatures from 67 to 200°F (-55 to 93°C) and also withstand the combinations of stress, temperature, and relative humidity expected to be encountered in service. The adhesives are for use in bonding aluminum alloy facing to non-metallic core, inserts, edge attachments and other components of a sandwich panel. The adhesive covers thermosetting films only.

## MIL-HDBK-691B

17.2.4 ASTM E866-82. Standard Specification for CORROSION-INHIBITING ADHESIVE PRIMER FOR ALUMINUM ALLOYS TO BE ADHESIVELY BONDED IN HONEYCOMB SHELTER PANELS, 6 pp., (DOD Adopted) Committee E-6 on Performance of Building Construction.

This specification covers sprayable, pigmented liquid primers for use on aluminum alloys that are to be adhesively bonded in the fabrication of honeycomb sandwich panels for tactical shelters. When applied to a properly cleaned surface of aluminum alloy, the primer imparts corrosive resistance and forms a surface suitable for structural bonding using adhesives complying with Specification E865 and for coating with shelter paint finishes. The primer is a pigmented liquid composed of a modified epoxy resin system, compounded so that it can be spray-applied to produce a continuous uniform coating without addition of solvent.

17.2.5 ASTM D1580-60 (1984). Standard Specification for LIQUID ADHESIVES FOR AUTOMATIC MACHINE LABELING OF GLASS BOTTLES, 2 pp.

This specification covers starch, dextrin, casein, animal gelatin, and other liquid adhesives (except pressure-sensitive types) used for applying paper labels to glass bottles. It includes provisions for adhesive selection based on satisfactory machining characteristics on specific labeling equipment, and adequate adhesion under specified storage conditions. It also provides for the control of uniformity between lots of an adhesive selected on the above bases by limiting variations in nonvolatile content and viscosity.

17.2.6 ASTM D1779-65 (1983). Standard Specification for ADHESIVE FOR ACOUSTICAL MATERIALS, 3 pp., (DOD Adopted) (ANSI Approved). FSC 8040 YD

This specification covers an adhesive for bonding prefabricated acoustical materials to the inside walls and ceilings of rooms in buildings. The adhesive must maintain a specific tensile adhesion (bond strength) for a long period of time under the temperature and moisture conditions likely to be encountered, and to maintain sufficient plasticity to allow for movement of parts of the building as it ages.

17.2.7 ASTM D1874-62 (1981). Standard Specification for WATER- OR SOLVENT-SOLUBLE LIQUID ADHESIVES FOR AUTOMATIC MACHINE SEALING OF TOP FLAPS OF FIBERBOARD SHIPPING CASES, 2 pp.

This specification covers starch, dextrin, casein, resin-base, and other liquid adhesives (except pressure-sensitive types) used for sealing the top flaps of fiberboard shipping cases. It includes provisions for adhesive selection based on: (1) satisfactory machining characteristics on specific equipment, and (2) adequate adhesion under specified storage conditions. It also provides for the control of uniformity between lots of an adhesive.

17.2.8 ASTM D2235-81. Standard Specification for SOLVENT CEMENT FOR ACRYLONITRILE-BUTADIENE-STYRENE (ABS) PLASTIC PIPE AND FITTINGS, 5 pp., (ANSI Approved) ASTM Committee F-17 on Plastic Piping Systems

## MIL-HDBK-691B

This specification provides general requirements for solvent cement for use in assembling acrylonitrile-butadiene-styrene (ABS) plastic pipe and socket-type fittings. The cement is intended for application by brush or other suitable applicator. Recommended procedures for using the cement covered in this specification to obtain satisfactory joints with ABS pipe and fittings are given in an Appendix. The ABS cement shall be a solution of ABS in methyl ethyl ketone (MEK).

17.2.9 ASTM D2559-84. Standard Specification for ADHESIVES FOR STRUCTURAL LAMINATED WOOD PRODUCTS FOR USE UNDER EXTERIOR (WET USE) EXPOSURE CONDITIONS, 7 pp.

This specification covers adhesives suitable for bonding of wood, including treated wood, into structural laminated wood products for general construction, for marine use, or for other uses where a high-strength, waterproof adhesive bond is required. The adhesive shall be classified by the manufacturer as to general type, such as resorcinol, phenol-resorcinol, phenol, and melamine.

17.2.10 ASTM D2560-80. Standard Specification for SOLVENT CEMENTS FOR CELLULOSE ACETATE BUTYRATE (CAB) PLASTIC PIPE, TUBING, AND FITTINGS, 5 pp., ASTM Committee F-17 on Plastic Piping Systems (ANSI Approved)

This specification provides the general requirements for cellulose acetate butyrate (CAB) solvent cements to be used in joining cellulose acetate butyrate pipe, tubing, and fittings. A recommended procedure for joining CAB pipe, tubing, and fittings with the solvent cements specified is given in an Appendix.

17.2.11 ASTM D2564-84. Standard Specification for SOLVENT CEMENTS FOR POLY(VINYL CHLORIDE) (PVC) PLASTIC PIPE AND FITTINGS, 5 pp., Committee F-17 on Plastic Piping Systems (Supersedes MIL-A-22010A)

This specification provides general requirements for poly(vinyl chloride) (PVC) solvent cements to be used in joining poly(vinyl chloride) pipe and socket-type fittings. An appendix on PVC solvent cement selection is included.

17.2.12 ASTM D2851-70 (1981). Standard Specification for LIQUID OPTICAL ADHESIVE, 3 pp.

This specification covers liquid optical adhesive for use in bonding glass to glass or other transparent adherends. The adhesive must be liquid and free from solvent. Each component must be completely reactive (without residual volatile products). The adhesive may be heat-, catalyst-, or radiation-cured.

17.2.13 ASTM D3024-84.<sup>e</sup> Standard Specification for PROTEIN-BASE ADHESIVES FOR STRUCTURAL LAMINATED WOOD PRODUCTS FOR USE UNDER INTERIOR (DRY USE) EXPOSURE CONDITIONS 5 pp.

This specification covers powder-form adhesives suitable for the bonding of wood into structural laminates where the use environment will not produce in the wood an equilibrium moisture content in excess of 16%. The specification covers vegetable or animal protein, such as isolated soy protein and casein. The adhesive must be mold- and water-resistant.

## MIL-HDBK-691B

17.2.14 ASTM D3110-82. Standard Specification for ADHESIVES USED IN NONSTRUCTURAL GLUED LUMBER PRODUCTS, 14 pp.

This specification establishes acceptable performance levels for glues or adhesives to be used in nonstructural glued lumber products, including interior and exterior moldings, window and door stock, and glued lumber panels. The specification is used to evaluate only the adhesives, not the glued wood product made with the adhesives. Two types of joints are covered - laminate joints and finger joints. Two basic types of exposure conditions are prescribed - wet use and dry use.

17.2.15 ASTM D3122-80. (1985) Standard Specification for SOLVENT CEMENTS FOR STYRENE-RUBBER (SR) PLASTIC PIPE AND FITTINGS, 5 pp., (ANSI Approved) Committee F-17 on Plastic Piping Systems.

This specification provides general requirements for styrene-rubber solvent cements to be used in joining styrene-rubber (SR) plastic pipe and fittings. A recommended procedure for joining styrene-rubber pipe and fittings is given in the Appendix. The solvent shall be methyl ethyl ketone or toluene. The rubber shall be of the polybutadiene or butadiene-styrene type.

17.2.16 ASTM D3138-83. Standard Specification for SOLVENT CEMENTS FOR TRANSITION JOINTS BETWEEN ACRYLONITRILE-BUTADIENE-STYRENE (ABS) AND POLY(VINYL CHLORIDE) (PVC) NON-PRESSURE PIPING COMPONENTS, 5 pp., Committee F17 on Plastic Piping Systems

This specification provides general requirements for solvent cements used in joining acrylonitrile-butadiene-styrene (ABS) plastic pipe or fittings to poly(vinyl chloride) (PVC) plastic pipe or fittings. These cements are intended for use in cementing transition joints between ABS and PVC materials in non-pressure applications only (170 kPa or 25 psi or less). The intended application is for joining ABS building drain to a PVC sewer-pipe system. A recommended procedure for joining ABS to PVC pipe and fittings for non-pressure applications is given in the Appendix.

17.2.17 ASTM D3498-76 (1981). Standard Specification for ADHESIVES FOR FIELD-GLUING PLYWOOD TO LUMBER FRAMING FOR FLOOR SYSTEMS, 13 pp.

This specification covers minimum performance standards and test requirements for gap-filling construction adhesives for bonding plywood to lumber framing, particularly floor joists, at the construction site. The specification provides a basis for ensuring the quality of the adhesives and is not intended as an application specification. The adhesive must be gap-filling and must set at temperatures as low as 40°F (4.4°C).

17.2.18 ASTM D3930-85. Standard Specification for ADHESIVES FOR WOOD-BASED MATERIALS FOR CONSTRUCTION OF MANUFACTURED HOMES, 23 pp.

This very lengthy specification provides a standard for measuring and evaluating the performance of adhesives that will be used in joints of wood-based materials in constructing manufactured homes. The wood, as used here, includes lumber, plywood, particle board, gypsum board, and all materials having wood-based surfaces at the bondline. The adhesives are

## MIL-HDBK-691B

classified into types and groups. Classifications are based on: (1) resistance to deformation, (2) resistance to water and water vapor, and (3) gap-filling ability. Group A is structural and Group B is semi-structural. There are 3 types, based on specific applications.

17.3 General Services Administration. Federal Specifications and Commercial Item Descriptions (7).

17.3.1 MMM-A-100D, February 7, 1978. ADHESIVE, ANIMAL GLUE, 15 pp.  
FSC 8040 GSA-FSS

This specification covers animal glues for use in woodworking. There are two types, as follows:

Type I - Dry form (flake, ground, or powdered, as specified)

Grade J1 - lower viscosity and jelly strength

Grade J2 - higher viscosity and jelly strength

Type II - Liquid Form

Type I, grades J1 and J2 adhesive, is intended for use for edge joints in furniture, etc. Type II liquid form is intended for use in edge joints, veneering and doweling in furniture. It may also be used when short assembly periods or high fabricating temperatures are involved.

17.3.2 MMM-A-105, June 23, 1967. ADHESIVE AND SEALING COMPOUNDS, CELLULOSE NITRATE BASE, SOLVENT TYPE, 10 pp. FSC 8040 AR

This specification establishes the requirements for cellulose nitrate-based adhesive and sealing compounds dissolved or dispersed in organic solvents. There are two types, as follows:

Type I - Label adhesive

Type II - Adhesive and sealer, general-purpose

Type I is for use in attaching printed paper labels to shipping containers. Application of additional compound to the top surface of the label will make it water-resistant. Type II compound is for use in repairing and mending many materials, including glass, metals, leather, textiles, paper, china, and some types of plastics, as well as in anchoring glass, metal and some plastic laboratory equipment.

17.3.3 MMM-A-110B, INT AMD-2, January 12, 1976. ADHESIVE, ASPHALT, CUT-BACK TYPE (FOR ASPHALT AND VINYL ASBESTOS TILES), 6 pp and 2 pp amendment. FSC 8040 MR

This specification covers one cut-back type of asphalt adhesive suitable for the installation of asphalt and vinyl-asbestos tiles. The adhesive consists of an asphaltic base material, a volatile solvent, and an asbestos fiber or other mineral filler modified to meet the requirements of this specification. The adhesive is intended for adhering asphalt tile and vinyl-asbestos tile to



## MIL-HDBK-691B

primed and unprimed concrete subfloors, either suspended, on grade, or below grade. It may also be used for bonding these floor coverings to steel or other metal subfloors and suspended plywood or hardwood subfloors that have been properly primed.

The basic specification spells out authorized combinations of solvents permissible, and the amendment modifies this list for temporary use to meet emission requirements.

17.3.4 MMM-A-115C, August 6, 1979. ADHESIVE, ASPHALT, WATER EMULSION TYPE (FOR ASPHALT AND VINYL ASBESTON TILE), 5 pp. FSC 8040 YD

This specification covers a clay-dispersed water-emulsion type of asphalt adhesive suitable for the installation of asphalt and vinyl-asbestos tiles. The adhesive is intended for adhering asphalt tile and vinyl-asbestos tile to concrete subfloors, either suspended, on grade, or below grade. It may also be used for bonding these floor coverings to steel or other metal subfloors and suspended plywood or hardwood subfloors.

17.3.5 MMM-A-121, December 16, 1966. ADHESIVE, BONDING VULCANIZED SYNTHETIC RUBBER TO STEEL, 10 pp. FSC 8040 SH

This specification covers nonstructural adhesives for bonding vulcanized synthetic-rubber gaskets, matting and similar items to steel. Bond strengths are low (about 5 pounds per inch of width). This is a performance specification. Material type is not specified. A Qualified Products List (QPL) is available.

17.3.6 MMM-A-122C, October 30, 1978. ADHESIVE, BUTADIENE-ACRYLONITRILE BASE, MEDIUM SOLIDS, GENERAL PURPOSE, 6 pp. FSC 8040 MR

This specification covers a high-strength general-purpose adhesive specifically for use where resistance to oil, gasoline, and aromatic fuel is essential. The adhesive is a butadiene-acrylonitrile base material. Permissible solvents, including percentages, are specified to meet emission requirements. The adhesive is intended for high-strength bonding of a wide variety of materials, including metal, glass, plastics, and synthetic rubber, particularly the nitrile types. It may also be used as a primer for other adhesives.

17.3.7 MMM-A-125C, March 18, 1969. ADHESIVE, CASEIN-TYPE, WATER AND MOLD RESISTANT, 10 pp. FSC 8040 MR

This specification covers casein types of adhesives for adhering wood surfaces. The adhesive must be in the form of a dry, uncaked powder, and in such condition that it can be mixed with water. There are two types, as follows:

- Type I - Water-resistant
- Type II - Water- and mold-resistant

Type I is for use primarily in the woodworking industry, while Type II is used primarily for lumber laminating. Requirements include plywood shear tests (dry shear and wet shear), block-shear test, working life, setting properties, and mold resistance.



## MIL-HDBK-691B

17.3.8 MMM-A-130B, INT AMD-3, April 7, 1976. ADHESIVE, CONTACT. FSC 8040 ME

This specification covers two types of flexible adhesive for contact bonding of plastic decorative laminates to clean, dry, and smooth wood and metal surfaces. The adhesives will firmly bond such materials as leather, wood, fabrics, unglazed ceramics, wallboards, and carpet to themselves and to each other. The adhesive may be used to install cove-base corners and roll-edge counter-top material. There are two types as follows:

- Type I - Volatile-organic-solvent type
- Type II - Water-dispersion type

The adhesive is composed of polychloroprene (neoprene) rubber and synthetic resins. Permitted solvent formulations are given, including percentages, for Type I.

17.3.9 MMM-A-131A, January 6, 1966. ADHESIVE, GLASS-TO-METAL (FOR BONDING OF OPTICAL ELEMENTS), 9 pp. FSC 8040 AR

This specification covers solvent-type, synthetic-resin adhesives in a two-part liquid form and in dry-film classes suitable for bonding glass to metal, using heat and pressure. Applications include glass prisms and other optical glass elements for bonding to metal supports in optical fire-control instruments. The classification is as follows:

Type I - Liquid adhesive (two-part thermosetting resin)

- Class 1 - Phenolic-neoprene
- Class 2 - Phenolic-polyamide

Type II - Dry-film adhesive

- Class 1 - Fiberglass (loosely woven) carrier supporting phenolic neoprene fabric
- Class 2 - Polyamide (nylon) carrier supporting phenolic polyamide

A Qualified Products List (QPL) is available.

17.3.10 MMM-A-132A (3), April 12, 1984. ADHESIVES, HEAT RESISTANT, AIRFRAME STRUCTURAL, METAL-TO-METAL, 26 pp plus a 2-pp amendment. FSC 8040 AS

This specification covers heat-resistant adhesives for use in bonding primary and secondary structural and external metallic airframe parts which will be exposed to temperatures within the range of -67° to 500°F (-55° to 260°C). The following types and classes, all for long-term exposure, except as noted, are specified:

Type I - for -67° to 180°F (-55° to 82°C)

- Class 1 - High T-peel and blister detection
- Class 2 - Normal T-peel and blister detection
- Class 3 - No T-peel and no blister detection

## MIL-HDBK-691B

Type II - for -67° to 300°F (-55° to 149°C)

Type III - for -67° to 300°F (-55° to 149°C) and for short-term exposures to 300° to 500°F (149° to 260°C)

Type IV - For -67° to 500°F (-55° to 260°C)

Form F - film

Form P - paste

The adhesive must be thermosetting, but there are no restrictions as to the chemical nature of the adhesive. Curing agents must be supplied, or must be incorporated into the adhesive. Fillers, high-moisture and corrosion-resistant, are permitted. Primers may be furnished with the adhesive. A Qualified Products List (QPL) is available.

17.3.11 MMM-A-134, August 17, 1970. ADHESIVE, EPOXY RESIN, METAL-TO-METAL STRUCTURAL BONDING, 29 pp. FSC 8040 AS

This specification covers epoxy resin adhesives for structural bonding, such as in the fabrication and repair of airframe parts, components, and other applications requiring bonding of a similar quality. There are three types, as follows:

Type I (two-part) - Room-temperature setting

Type II (two-part) - Intermediate-temperature setting

Type III (one-part, film or wet form) - High-temperature setting

These adhesives are primarily for use in clad aluminum alloys. A Qualified Products List (QPL) is available.

17.3.12 MMM-A-137D, August 4, 1976. ADHESIVE, RESILIENT FLOORING (WATER SOLUBLE), 9 pp. FSC 8040 MR

This specification covers two classes of adhesive for securing resilient flooring to above-grade floors. It is intended for use in the installation of opaque or translucent vinyl-surface floor coverings with backing, and linoleum and other resilient floorings. It is not recommended for installation of coverings on steel or other metal subfloors. There are two classes as follows:

Class 1 - High viscosity, for trowel application (80,000 - 250,000 cP)

Class 2 - Low viscosity, for spray application (40,000 - 120,000 cP)

The adhesive consists of a binder in a water-base suspension, intimately mixed with inorganic filler and other desirable additives to control odor and prohibit mold growth.

17.3.13 MMM-A-138A(1), June 19, 1975. ADHESIVE, METAL TO WOOD, STRUCTURAL, 12 pp plus 1-p amendment. FSC 8040 AS

This specification covers synthetic-resin adhesives for the structural bonding of clad aluminum alloy to wood. There are two types as follows:

Type I - Single-adhesive system

Type II - Two-adhesive system

## MIL-HDBK-691B

Condition A - Primary adhesive with RT 75 - 90°F (24-32°C) setting secondary adhesive  
 Condition B - Primary adhesive with intermediate-temperature 90 - 180°F (32 - 82°C) setting secondary adhesive.

The adhesive consists of a resin or resins furnished in liquid or jelly form, with or without hardener, or in solid form, as stick, powder, or film. The chemical nature of the adhesive is not specified. The Type-I adhesive is intended primarily for use in the structural bonding of aluminum alloy to wood. It is not to be used for structural bonding. The Type-II adhesive is intended primarily for use in fabricating aluminum-wood-aluminum structural sandwich panel constructions, especially where low-density wood cores are used, as well as for the structural bonding of aluminum-to-wood attachments not of sandwich-type construction. Type II, Condition A adhesive is for applications where small areas are involved, or where heat cannot be used in the final assembly. Type II, Condition B adhesive is for use in cases where the fabrication of large items necessitates a final assembly time exceeding that permissible with Condition A adhesive. Requirements include working life of adhesives in liquid or jelly form, film form composition, accelerator or hardener or modifier, solubility, application, curing conditions, storage life, and shear strength (initial, after high-temperature exposure, immersion in salt water, immersion in fresh water, and immersion in hydrocarbon test fluid), and pH value. A Qualified Products List (QPL) is available.

17.3.14 MMM-A-139A(1), January 31, 1977. ADHESIVE, NATURAL OR SYNTHETIC-NATURAL RUBBER, 17 pp plus 2 pp amendment. FSC 8040 AS

This specification covers natural or synthetic-natural-rubber adhesives, primarily for the manufacture and repair of articles made of materials cured with natural or synthetic natural rubber. The classification is as follows:

- Class 1 - Heat cure for manufacture
- Class 2 - Room-temperature cure for manufacture
- Class 3 - Room-temperature cure for repair

There is currently only one form - a two-part system consisting of the base compound and separate accelerator. These adhesives are intended for adhering natural or synthetic-natural rubber, and in particular, for the manufacture and repair of articles fabricated from natural-rubber-coated fabrics. They must not be used for bonding nylon. Class-3 adhesive is for use only in bonding natural-rubber items in the repair of life-saving equipment. A Qualified Products List (QPL) is available for this class only.

17.3.15 MMM-A-00150B (GSA-FSS), April 29, 1976. ADHESIVE FOR ACOUSTICAL MATERIALS, 9 pp. FSC 8040 GSA-FSS

This interim specification covers one type of adhesive for bonding prefabricated acoustical materials to the inside walls and ceilings of rooms in buildings. The adhesive is not recommended as the sole means of bonding acoustical materials weighing more than 2 1/2 pounds per square foot to ceiling surfaces. The adhesive consists of a resin in a volatile solvent. Requirements on solvent composition are given to meet emission control requirements.

## MIL-HDBK-691B

17.3.16 MMM-A-179B, August 18, 1982. ADHESIVE: PAPER LABEL, 16 pp.  
FSC 8040 MR

This specification supersedes MMM-A-178A, Adhesive, Paper Label, Water Resistant, as well as MMM-A-179A. It covers the requirements for water-resistant, water-emulsion adhesives suitable for adhering printed paper labels to various substrates, such as soft wood, solid fiberboard, hot-rolled low-carbon steel with a black iron oxide coating ("black iron"), glass, tin-coated steel, and enamel-painted metal. There are two types, as follows:

- Type I - Water resistant
- Type II - Water resistant, water emulsion

Latitude is permitted in the selection of raw materials for these adhesives.

17.3.17 MMM-A-180C, August 6, 1979. ADHESIVE, POLYVINYL ACETATE EMULSION, 5 pp. FSC 8040 AS

This specification covers two types of polyvinyl acetate emulsion adhesives, as follows:

- Class A - General purpose adhesive
- Class B - Wood adhesive

The Class A adhesive is for bonding leather to such materials as metal, wood, cloth, paper, etc. and for the general bookbinding in hand operations. The Class B adhesive is for assembly gluing of wood items which are placed or stored in normal indoor-temperature service conditions where the RH is not high and does not fluctuate excessively. It is intended for such joints as dowel, mortise-tenon, lock, and finger in the assembly wood patterns and models. It is not suitable for edge gluing and laminating for furniture parts.

17.3.18 MMM-A-181D, January 23, 1980. ADHESIVES, PHENOL, RESORCINOL, OR MELAMINE BASE, 13 pp. FSC 8040 MR

This specification covers general-purpose, two-part adhesives, or optionally, a one-part adhesive for Type III, for wood assembly gluing. The adhesives are for use in the manufacture of laminated members and other wooden articles where a high-strength, durable adhesive is required. The classification is as follows:

Type I - Room-temperature-setting (75 to 95°F) (24 to 35°C) glue-line temperature

- Grade A - Two years storage life
- Grade B - Six months storage life

Type II - Intermediate-temperature-setting (95 to 190°F) (35 to 88°C) glue-line temperature

Grade C - Six months storage life

- Class 1 - Liquid<sup>1</sup>
- Class 2 - Powder<sup>1</sup>

## MIL-HDBK-691B

Type III - High-temperature-setting (190 to 300°F) (88 to 149°C)  
glue-line temperature

Class 1 - Liquid<sup>1</sup>

Class 2 - Powder<sup>1</sup>

The material shall be furnished as a liquid with a separate hardener, or, when specified, as a powder with a separate hardener. The hardener for the Type III adhesive may be incorporated as a component part of the resin. Only resins based on phenol, melamine or resorcinol may be used. These three resins are formulated with formaldehyde, and the D revision contains a cautionary note on the health hazards of formaldehyde compounds.

17.3.19 MMM-A-182A, October 6, 1967. ADHESIVE, RUBBER, 6 pp. FSC 8040 EA

This specification covers a cold-bonding rubber adhesive for use with natural or synthetic rubber. It is commercially known as rubber cement for cold patching. There are two types as follows:

Type I - Adhesive with a minimum of 6% rubber

Type II - Adhesive with a minimum of 10-12% rubber

The rubber used in making the adhesive shall be first-quality smoked sheet, pale crepe, or fine Para. It shall be plasticized only enough to provide good brushing qualities. Modifying resins may be added to permit the requirements of the specification to be met. The solvent used is naphtha. The Type I adhesive is for use in cold patching of tire inner tubes and similar rubber items. The Type II adhesive is primarily for bonding of components of natural rubber in the assembly of protective masks.

17.3.20 MMM-A-185, Int Amd 2, April 16, 1975. ADHESIVE (FOR PAPER BONDING) 8 pp plus 1p int ammendment. FSC 8040 AS

This specification covers one type of rubber adhesive, commonly known as rubber cement, suitable for mounting photographic prints, maps, drawings and charts, and for general paper-to-paper bonding. The adhesive is crepe natural rubber or synthetic-rubber-base material modified to meet the requirements of this specification. Permissible solvents, including percentages, are specified to meet emission requirements. Application to only one surface will provide only temporary joining. If more permanent joining is desired, both surfaces should be coated liberally with the adhesive, allowed to dry, and then brought together under firm pressure.

17.3.21 MMM-A-187B, September 11, 1974. ADHESIVE, EPOXY RESIN BASE, LOW AND INTERMEDIATE STRENGTH, GENERAL PURPOSE, 7 pp. FSC 8040 AS

This specification covers two types of epoxy-resin-based adhesive for general-purpose application:

Type I - Low-strength, paste form

Type II - Intermediate-strength, paste or liquid form

<sup>1</sup>Unless otherwise specified, Class 1 will be supplied.



## MIL-HDBK-691B

This adhesive is a two-part system consisting of a base polymer of the epoxy type and a suitable accelerator. The two parts are furnished in a kit. In Type I (paste form) the resin and curing agent are of different colors to aid in determining when mixing is complete. Equal parts of resin and curing agent are to be used. In Type II (paste form) the requirement is similar, except that equal parts are not required. The adhesive specified is intended for use in the repair operations, or in the bonding of metals, porcelain, ceramic materials, leather, wood, and various porous and nonporous materials to themselves and to each other.

17.3.22 MMM-A-188C, January 2, 1975. ADHESIVE, UREA-RESIN-TYPE (LIQUID AND POWDER), 6 pp. FSC 8040 AS

This specification covers a urea-formaldehyde thermosetting resin adhesive for the assembly gluing of wood items and the bonding of plastic laminate sheets to plywood. The adhesive is intended for use where moderate water resistance is required. It is not a fully waterproof adhesive. The types are:

- Type I - Powder (with separate curing agent)
- Type II - Powder (with incorporated curing agent)
- Type III - Liquid (with separate curing agent)

17.3.23 MMM-A-189B, November 12, 1975. ADHESIVE, SYNTHETIC RUBBER, THERMOPLASTIC, GENERAL PURPOSE, 17 pp. FSC 8040 MR

This specification covers organic-solvent-base synthetic rubber thermoplastic adhesives for general-purpose use. The classes are as follows:

- Class 1 - 20% nonvolatile content
- Class 2 - 30% nonvolatile content

The adhesive is dissolved in an organic solvent or blend of solvents. Permissible solvents, including percentages, are specified to meet emission requirements. Since these adhesives are thermoplastic, they are not recommended for applications where they will be subject to either continuous high stress, or stress at an elevated temperature. The Class 2 adhesive, with its higher solids content, forms heavier films with controlled penetration and is used for porous surfaces.

17.3.24 MMM-A-250C(1), August 12, 1976. ADHESIVE, WATER-RESISTANT (FOR CLOSURE OF FIBERBOARD BOXES), 10 pp plus 1 p amendment. FSC 8040 MR

This specification covers water-resistant adhesives intended for closure of fiberboard boxes, cartons, and cases. The adhesives are of the following types:

- Type I - For application by automatic box-closing equipment
- Type II - For hand application, by brushing
- Type III - For hand application, from pressurized container (aerosol)

The adhesive must not contain toxic materials, including poly-chlorinated biphenyls (PCB's).



## MIL-HDBK-691B

17.3.25 MMM-A-260B, May 10, 1984. ADHESIVE, WATER-RESISTANT (FOR SEALING WATERPROOFED PAPER), 15 pp FSC 8040 MR

This specification covers water-resistant adhesive intended for application to the seams in the manufacture and closure of waterproofed paper bags, wrappers, and case liners. It may also cover other applications. The following types, grades, and classes are specified:

Type I - For application by machine  
Type II - For hand application, by brushing

Grade A - For subsistence items  
Grade B - For other than subsistence items

Class 1 - Solvent-base adhesive  
Class 2 - Water-emulsion adhesive  
Class 3 - Hot-melt adhesive

This specification supersedes MIL-A-140A (November 23, 1951) and O-A-166 (GSA-FSS) (January 18, 1962).

17.3.26 A-A-342A, January 8, 1980. ADHESIVE, SEMI-SOLID, STICK FORM, WITH DISPENSERS, 1 p FSC 8030 GSA-FSS

This is a Commercial Item Description (CID). GSA has authorized its use in lieu of Interim Federal Specification MMM-A-002015, described below.

The adhesive is a nontoxic, mold-resistant, even-spreading material housed in an impact-resistant container with a cap. It must have a pleasant odor and a smooth uniform consistency. The container must have a mechanism which allows the adhesive stick to be mechanically advanced or retracted without making contact with the adhesive. There are a few simple requirements for nonvolatile content, adhesion, freeze-thaw, and workmanship. The CID is complete on one page.

17.3.27 A-A-529, September 25, 1979. ADHESIVE AND SEALING COMPOUND, CELULOSE NITRATE BASE, SOLVENT TYPE, 1 p. FSC 8040 GSA-FSS

This is a CID. GSA has authorized its use in lieu of Federal Specification MMM-A-105, described above.

The CID covers a cellulose nitrate-base adhesive and sealing compound intended for use in attaching paper labels, waterproofing, and as a general-purpose adhesive.

17.3.28 MMM-A-1058A, Int AMD 1, January 26, 1978. ADHESIVE, RUBBER BASE (IN PRESSURIZED DISPENSERS), 7 pp plus 3 pp amendment. FSC 8040 AS

This interim amendment covers one type of rubber-base adhesive, a regular (high-solids) type, which is relatively colorless, fast-drying, and packaged in an aerosol dispenser. No chlorofluorocarbons or vinyl chloride may be used in the aerosol propellant. The adhesive is intended to provide a quick, convenient method for bonding a wide variety of adherends such as paper,

## MIL-HDBK-691B

glass, cardboard, cloth, wood, plastic film, metal, and foam rubber to themselves, to one another, or to other materials. It is not intended for structural use, or for bonding certain equipment components where such critical properties as high-pressure or dielectric strength may be required.

17.3.29 MMM-A-1617(2), June 18, 1981. ADHESIVE, RUBBER BASE, GENERAL PURPOSE, 14 pp, plus 2-pp amendment. FSC 8040 AS

This specification covers natural- and synthetic-rubber-base adhesives intended for noncritical uses in applications where the unit stress on the adhesive is not appreciable. The adhesive must not be used for structural purposes, or for life rafts, inflatable boots, radome covers, pontoons, deicer boot manufacture, or repair. These adhesives will bond duck, leather, felt, cork, and similar relatively porous materials to themselves or to each other, or to relatively nonporous materials, such as wood, aluminum, steel, rubber, and plastics. The following types are specified:

- Type I - Natural-rubber base, synthetic natural (polyisoprene), styrene butadiene (SBR), reclaim, or combinations thereof; non-oil resistant
- Type II - Polychloroprene rubber-base, oil-resistant
- Type III - Butadiene acrylonitrile (nitrile) rubber-base; fuel-resistant

A QPL is available.

17.3.30 MMM-A-1754, July 1, 1973. ADHESIVE AND SEALING COMPOUND, EPOXY, METAL FILLED, 7 pp. FSC 8040 AS

This specification establishes the requirements for one type of metal-filled, room-temperature-curing, two-part epoxy adhesive and sealing compound. The metal-filler particles may be aluminum, steel, or both. Other fillers may be used as needed. The activator shall be of the polyamide type. The base polymer must be a paste, while the activator may be paste or liquid. The colors of the two components must be different, resulting in a neutral gray when uniformly mixed.

This adhesive can be used as an edge sealing or molding compound for both general-purpose and structural applications, such as on fairing surfaces. The cured adhesive can be sanded, filed, or machined with conventional tools. The adhesive will bond to steel, iron, aluminum, glass (not Pyrex), concrete, ceramics, porcelain, tile, marble, wood, and thermosetting plastics such as phenolic, polyester, or epoxy. It will bond with less strength to brass, copper, and lead. It is not recommended for nickel, tin, zinc, or thermoplastics, such as polyethylene.

17.3.31 MMM-A-1931, September 19, 1975. ADHESIVE, EPOXY, SILVER FILLED, CONDUCTIVE, 7 pp. FSC 8040 AS

This specification covers the requirements for two types of silver-filled, conductive, two-part, room-temperature-curing adhesives. These materials are used primarily to install static discharger bases to exterior aircraft surfaces. They are also suited for applications such as conductive paths on circuit boards, or grounding and bonding metal components without welding,

## MIL-HDBK-691B

brazing, or soldering. The adhesives may be used where hot soldering is not practical, such as to nichrome wire or conductive plastics, or in locations which cannot be subjected to high temperatures. The adhesives may be used in preparing electrodes on specimens used to measure capacitance and loss characteristics. The types are as follows:

- Type I - Volume resistivity 0.010 ohm/cm
- Type II - Volume resistivity 0.003 ohm/cm

The base polymer, in paste form, contains the silver particles, but must not contain copper or other metals, and shall contain no fillers or extenders. The curing agent shall contain no metals, extenders, or fillers. The curing agent may be paste or liquid.

17.3.32 MMM-A-001993(GSA-FSS), February 28, 1978. ADHESIVE, EPOXY, FLEXIBLE, FILLED (FOR BINDING, SEALING, AND GROUTING), 6 pp. FSC 8040 AS

This Interim Federal Specification covers a two- or three-component, mineral-filled, flexible-epoxy-resin-base adhesive to be used in binding, sealing, and grouting concrete. These adhesives are intended to be used to repair spalls and other defects in portland cement pavements. In many cases, 40-mesh sand should be added to the adhesive in a proportion that achieves an optimum balance between performance characteristics, heat of mixing, and cost. The types are as follows:

- Type I - A two-component system, with mineral filler pre-mixed into each component
- Type II - A three-component system, including the epoxy resin, curing agent, and mineral filler

The inert filler is a finely divided quartz silica flour or feldspathic aluminum silicate flour.

17.3.33 MMM-A-002015(GSA-FSS), April 6, 1977. ADHESIVE, SEMI-SOLID, STICK FORM, WITH DISPENSERS, 7 pp. FSC 8040 GSA-FSS

This Interim Federal Specification covers a convenience-type, quick-setting office adhesive in stick form, suitable for bonding paper, photographs, and fabrics. It is intended for mounting photographic prints, maps, drawings, and charts. It is also suitable for bonding fabrics in cases where high strength is not required. (See A-A-342A for a Commercial Item Description (CID) which may be used to specify this material).

17.3.34 MMM-A-002408(GSA-FSS), April 1, 1978. ADHESIVE, FIRE-RESISTANT, THERMAL INSULATION. FSC 8040 GSA-FSS

This interim Federal Specification covers fire-resistant adhesive for securing cloth and tape to certain thermal insulations and for securing certain thermal insulations to metal surfaces. There are three classes as follows:

- Class 1 - For bonding fibrous-glass cloth to unfaced fibrous glass insulation

## MIL-HDBK-691B

For bonding cotton brattice cloth to faced and unfaced fibrous-glass insulation board

For sealing the edges of, and bonding fibrous-glass tape to the joints of fibrous-glass board

For bonding lagging cloth to thermal insulation

Class 2 - For attaching fibrous-glass insulation to metal surfaces

Class 3 - For attaching cork and fibrous-glass insulation to metal surfaces

#### 17.4 Department of Defense (DOD). Military Specifications (7).

##### 17.4.1 MIL-G-413B, October 9, 1963. GLUE, MARINE AND AVIATION MARINE (WATERPROOF), 5 pp. FSC 8040 SH

This specification covers material for fastening sheeting between inner and outer wood skins of floats and flying-boat hulls and for faying wooden seams of ship decks. There are two classes, as follows:

Class 1 - Aviation marine glue for fastening sheeting in built-up skins of floats, flying-boat hulls, and double-plank construction on wood boats

Class 2 - Marine glue for faying wooden seams of ship decks

The Class 1 glue shall contain rosin, pine tar, denatured alcohol, and a drying oil. The drying oil shall be tung oil, rosin oil, or linseed oil. The Class 2 glue shall contain no materials of coal tar origin.

##### 17.4.2 MIL-C-2399B(2), December 10, 1975. CEMENT, LIQUID, TENT PATCHING, 11 pp. plus 3-pp amendment. FSC 8040 GL

This specification covers a liquid, synthetic-rubber-base cement for use in patching tentage. The adhesive is based on copolymers of butadiene and acrylonitrile in a solvent blend of petroleum naphtha, toluol, xylol, acetone, methyl ethyl ketone, or methyl isobutyl ketone. Solvent formulations, with allowable percentages are specified to meet emission requirements.

##### 17.4.3 MIL-A-3167A(OS), January 5, 1976. ADHESIVES (FOR PLASTIC INHIBITORS), 11 pp. FSC 8040 OS

This limited-coordination Navy specification covers adhesives for use with ethyl cellulose or cellulose acetate molded plastic inhibitors. These adhesives are intended for use in adhering web and end plastic inhibitors to cruciform-shape double-base-powder grains. The classification is as follows:

Type I - Cellulose nitrate, 2 classes

Type II - Cellulose acetate, 4 classes

Type III - Solvent adhesive, 2 classes

The Type I, classes 1 and 2 adhesives are for use in adhering ethyl cellulose inhibitors, as specified in MIL-I-3166. The Type I, class 2 adhesives may be diluted with up to 30% by weight of butyl acetate. All the Type II adhesive classes are for use in adhering cellulose acetate inhibitors, as specified in MIL-I-3166. Class 1 may be diluted up to 20% by weight with

## MIL-HDBK-691B

acetone. Type III, class 1 adhesive may be used to adhere either ethyl cellulose or cellulose acetate inhibitors, as specified in MIL-I-3166. The Type III, class 2 adhesive is intended for cementing ethyl cellulose plastic to propellant powder, or to other ethyl cellulose plastic.

The composition of the various types and classes is given in a table. Another table gives the requirements for non-volatile content, viscosity, and specific gravity of the adhesives.

17.4.4 MIL-A-3316B(6), October 22, 1979. ADHESIVES, FIRE-RESISTANT, THERMAL INSULATION, 14 pp. plus 4 pp amendment FSC 8040 SH.

This specification covers fire-resistant adhesives for securing cloth and tape to certain thermal insulations and for securing certain thermal insulations to metal surfaces. The classification is as follows:

Class 1 - (for brush application)

For bonding fibrous-glass cloth to unfaced fibrous-glass cloth insulation

For sealing the edges of, and bonding fibrous-glass tape to the joints of fibrous-glass board

For bonding lagging cloth to thermal insulation

Grade A - Pigmented white

Grade B - Pigmented Red (sealer coating to identify asbestos-free system)

Class 2 - For attaching fibrous-glass insulation to metal surfaces

Grade A - Pigmented white

Class 3 - For attaching cork and fibrous-glass insulation board to metal surfaces

The adhesives specified must be effective for the purpose intended without heating or the addition of other ingredients. A QPL is available.

17.4.5 MIL-A-3562B, October 2, 1959. ASHESIVE, SEALING (FOR FILTERS), 4 pp. FSC 8040 EA

This specification covers a thermosetting liquid resin adhesive for bonding optical elements for use in military optical instruments. The specification replaces MIL-C-3469, Canada Balsam. There is no restriction on the chemical type. If necessary, an activator may be used to cure the adhesive.

17.4.6 MIL-A-5540B(2), December 28, 1973. ADHESIVE, POLYCHLOROPRENE, 16 pp plus 2 pp amendment. FSC 8040 AS

This specification covers neoprene adhesives for joining neoprene-coated fabric to itself and to nylon. The adhesive is for use where adherence to polychloroprene-coated fabric is required, such as in the manufacture and repair of life vests, decoy targets, and pontoons (Note: polychloroprene is sold commercially as neoprene). The classes are as follows:



## MIL-HDBK-691B

- Class 1 - Heat cure for manufacture (coating-to-coating, heat stable to 140°F (60°C))
- Class 2 - Room-temperature-cure for manufacture (coating-to-coating, heat stable to 140°F (60°C))
- Class 3 - Room-temperature-cure for repair (coating-to-coating, heat stable to 140°F (60°C))
- Class 4 - Heat cure for manufacture (coating-to-nylon)
- Class 5 - Room-temperature-cure for repair (coating-to-nylon)

All five classes must be furnished as Form A or B:

Form A - One-part adhesive

Form B - Two-part adhesive

A QPL is available.

17.4.7 MIL-A-8576(2), August 12, 1969. ADHESIVE, ACRYLIC BASE, FOR ACRYLIC PLASTIC, 14 pp. plus 4 pp amendment. FSC 8040 AS

This specification covers acrylic-monomer-base adhesives intended for use in bonding acrylic plastics. There are three types, as follows:

- Type I - Solvent type
- Type II - Non-solvent, high viscosity
- Type III - Non-solvent, medium viscosity

A catalyst is to be furnished as a separate ingredient with each container of adhesive. The base resin must contain an inhibitor to retard polymerization until ready for use. Type I is intended for use in bonding acrylic plastic conforming to MIL-P-5425 and may be used with suitable precautions in bonding other acrylics. It should not be used for bonding material conforming to MIL-P-8184. Type I adhesive shall contain methylene chloride as solvent. Type II shall contain a promoter in a separate container. The promoter is to be added to the resin, followed by the catalyst, to aid in polymerization initiation.

17.4.8 MIL-A-9117D, April 19, 1971. ADHESIVE, SEALING, FOR AROMATIC FUEL CELLS AND GENERAL REPAIR, 4 pp. FSC 8040 84

This specification covers a one-part synthetic elastomeric adhesive for fuel cell repair and for other general repair work where resistance to aromatic fuel is required. The classification is as follows:

- Class G - For use under normal circumstances
- Class L - For use where Air Pollution Regulations are enforced

Both classes must have a nonvolatile content in the range of 14-30%.

17.4.9 MIL-A-13374D, August 8, 1975. ADHESIVE, DEXTRIN, FOR USE IN AMMUNITION CONTAINERS, 10 pp. FSC 8040 MR



## MIL-HDBK-691B

This specification covers four classes of vegetable dextrin adhesives produced from starch and intended for use in the manufacture of spirally wound containers, and in the fabrication of chipboard spacers to be used in such containers, for use in packing ammunition and components. The classes are as follows:

- Class 1 - A liquid adhesive in prepared form
- Class 2 - A cold-water-soluble type which must be mixed with water before use
- Class 3 - A prepared dry adhesive which must first be cooked with water before use
- Class 4 - Dextrin base in dry form to which additional optional chemical ingredients may be added during preparation with water before use.

Optional ingredients in four groups may be added as follows:

- Group A - Alkaline chemicals
- Group B - Fillers
- Group C - Preservatives
- Group D - Defoamers

17.4.10 MIL-A-14064C, May 5, 1980. ADHESIVE: GRINDING DISK, 7 pp. FSC 8040 MR

This specification covers one grade of grinding disk adhesive intended for use for the bonding of abrasive disks to metal disks. Latitude is allowed in the materials to be used, since this is a performance specification.

17.4.11 MIL-A-17682E, March 11, 1982. ADHESIVE, STARCH, 9 pp. FSC 8040 MC

This specification covers requirements for one type of adhesive used for mounting paper or cloth targets. The adhesive may contain reclaimed materials. The base material for the adhesive must be pure wheat, in fine powder form, conforming to Federal Specification N-F-481, containing sufficient preservatives to prevent decomposition, weevil and mold growth in the package, and fermentation after mixing with water.

17.4.12 MIL-A-21016E, January 26, 1967. ADHESIVE, RESILIENT DECK COVERING, 6 pp. FSC 8040 SH

This specification covers adhesives for securing resilient coverings to decks. The adhesive is a water-base latex, free of all ingredients which may affect the serviceability, or have a deleterious effect on metal or resilient covering. The adhesive must be trowelable. A QPL is available.

17.4.13 MIL-A-21366A(SHIPS), February 16, 1966. ADHESIVE, FOR BONDING PLASTIC TABLE TOP MATERIAL, 10 pp. FSC 8040 SH

This limited-coordination Navy specification covers a one-part flexible adhesive for bonding thermosetting plastic table top material conforming to MIL-T-171 to aluminum at room temperature with only nominal pressure. It may be a neoprene resin or other combination of ingredients.

## MIL-HDBK-691B

17.4.14 MIL-A-22397, INT AMD 1(SHIPS), June 12, 1964. ADHESIVE, PHENOL AND RESORCINOL RESIN (FOR MARINE SERVICE USE), 12 pp. plus 5 pp amendment.  
FSC 8040 SH

This specification covers adhesives for bonding wood where an adhesive bond with high strength, resistance to salt water, extreme shrinking and swelling resistance, and long-time durability is required. These adhesives are particularly suitable for use in fabricating wood laminates for ship and boat use and for other severe exterior service. Use of these adhesives in laminating various species of wood is covered by separate laminate specifications. There are two grades, as follows:

- Grade A - One-year storage life
- Grade B - Two-month storage life (immediate use)

The resins used in making the adhesive must be based on phenol, resorcinol, or a combination of both. The hardener shall be provided in either powder or liquid form. When in powder form, it may be combined with part or all of the filler. The filler, when used, must be an inert, insoluble powder. It may be combined with the resin or supplied separately. Amylaceous fillers, such as flour or starch, and protein fillers are not permitted. A QPL is available.

17.4.15 MIL-A-22434A(WEP), March 7, 1961. ADHESIVE, POLYESTER, THIXOTROPIC, 13 pp. FSC 8040 OS

This limited-coordination Navy specification covers a thixotropic polyester adhesive for use in bonding glass-cloth epoxy resin laminate rings to metal components of warhead assemblies, where special application and assembly techniques are involved. The adhesive must bridge voids up to 0.020 inches when applied to vertical and horizontal surfaces. The adhesive is a homogeneous compound prepared by combining colloidal silica with a liquid unsaturated alkyd-styrene type thermosetting resin. Methyl ethyl ketone peroxide is used as the catalyst and cobalt naphthenate as the accelerator to polymerize the resin. Suggested sources of the specified ingredients are given.

17.4.16 MIL-S-22473E, April 12, 1983. SEALING, LOCKING AND RETAINING COMPOUNDS: (SINGLE COMPONENT), 22 pp. FSC 8030 MR

This specification for anaerobic sealants covers single-component compounds and their primers suitable for sealing, locking, and retaining metal parts. The components are normally liquid and are converted to an infusible, insoluble state when confined between closely fitting metal surfaces. The compounds are intended for use in sealing threaded fasteners, plugs, and other threaded fittings against fluid pressure, for locking such threaded assemblies against working loose under shock and vibration (threaded fasteners), and for retaining existing or replacement ball bearings in worn housings, thereby obviating the need for establishing a press fit. Thirteen examples of end-use applications of these materials are given. Fifteen grades are specified, each with varying viscosity and locking torque. Different colors are used to distinguish these grades, although there is duplication of colors. Each compound must be visible under ultraviolet light when tested as specified.

## MIL-HDBK-691B

17.4.17 MIL-A-22895(1)(SHIPS), June 25, 1962. ADHESIVE, METAL IDENTIFICATION PLATE, 6 pp. plus 2 pp amendment. FSC 8040 SH

This limited-coordination Navy specification covers adhesives for use in bonding, without heat or pressure, of metal identification plates to painted or unpainted surfaces. The adhesive is used in place of mechanical attachment and must be resistant to severe-use conditions of interior or exterior exposure to vibration and shock. There are two classes, as follows:

Class A - Two-component liquid polysulfide adhesive, characteristically non-solvent, gap-filling, and completely reactive, for knife application to metal identification plates up to 0.048 inch thick. The service temperature range is up to 250°F, (121°C) but must withstand 400°F (205°C) for short-time emergency conditions.

Class B - Single-component, neoprene or nitrile rubber adhesive in a volatile solvent for brush application to metal identification plates not exceeding 0.030 inch thickness. This adhesive requires smooth surfaces and has a service range up to 200°F (93°C). The solvent must not exceed 65% by weight.

17.4.18 MIL-C-23092B(SHIPS), February 26, 1976. CEMENT, NATURAL RUBBER, MAGNETIC MINESWEEPING CABLE REPAIR, 6 pp. FSC 8040 SH

This limited-coordination Navy specification covers a natural-rubber cement for making vulcanized and unvulcanized bonds of natural or synthetic rubber for the repair of magnetic minesweeping cable. The cement is dissolved in a solvent. No reclaimed rubber is permitted.

17.4.19 MIL-A-23940(1)(AS), September 1, 1966. ADHESIVE, SILICONE RUBBER, 6 pp plus 2 pp amendment. FSC 1336 AS

This limited-coordination Navy specification establishes the minimum requirements for a general-purpose room-temperature-vulcanizing silicone rubber adhesive for use in rocket-motor igniters.

17.4.20 MIL-A-23941A(AS), September 1, 1966. ADHESIVE, EPOXY TYPE, TWO PART, 7 pp. FSC 1336 AS

This limited-coordination Navy specification establishes the requirements for a two-part epoxy adhesive. No other restrictions are established on the chemical or physical nature of the adhesive.

17.4.21 MIL-A-24179A(SHIPS), May 12, 1980. ADHESIVE, FLEXIBLE UNICELLULAR-PLASTIC THERMAL INSULATION, 11 pp plus 2-pp amendment. FSC 8040 SH

This limited-coordination Navy specification covers high initial strength, heat- and water-resistant, contact-type adhesives for bonding flexible unicellular plastic thermal insulation to itself and to metal surfaces. The types and classes are as follows:

## MIL-HDBK-691B

- Type I - Dispersed in water
- Type II - Dispersed in nonhalogenated organic solvent

- Class 1 - Low flash point
- Class 2 - Intermediate flash point

- Type III - Dispersed in nonflammable organic solvent

A QPL is available.

17.4.22 MIL-A-24456(3)(SHIPS), June 15, 1979. ADHESIVE FOR PLASTIC VIBRATION-DAMPING TILES, 10 pp. plus 2 pp amendment. FSC 8040 SH

This limited-coordination Navy specification covers a two-part epoxy adhesive for bonding plastic vibration damping tiles to metal structures on board ships. The vibration-damping tiles are of the type specified in MIL-P-23653. The material shall be supplied in the form of a two-part epoxy system. A QPL is available.

17.4.23 MIL-A-25463B, March 31, 1982. ADHESIVE, FILM FORM, METALLIC STRUCTURAL SANDWICH CONSTRUCTION, 15 pp. FSC 8040 AS

This specification covers the requirements for adhesives in film form for bonding metal facings to metal cores and to metal components of sandwich panels intended for use in primary and secondary structural airframe parts that may be exposed to temperatures up to 500°F (260°C). Included in this specification is the bonding of metal facings to metal components within the sandwich panels which must be cured under the same conditions as the sandwich panel. Fabrication and inspection must be in accordance with MIL-A-83377.

Adhesives covered by this specification can be used for sandwich construction other than metal-to-metal (such as plastic-to-metal), provided testing proves such use is possible. Classification is as follows:

- Type I - For long-time exposure to temperatures from -67° to 180°F (-55° to 82°C)
- Type II - For long-time exposure to temperatures from -67° to 300°F (-55° to 149°C)
- Type III - For long-time exposure to temperatures from -67° to 300°F (-55° to 149°C) and short-time exposure from 300° to 500°F (149° to 260°C)
- Type IV - For long-time exposure from -67° to 500°F (-55° to 260°C)

- Class 1 - For bonding metal facings to metal cores only
- Class 2 - For bonding metal facings to metal cores, inserts, edge attachments, and other components of completed sandwich structures

Cure temperature groups are as follows:

- Group 1 - 100°F (38°C) or less
- Group 2 - Over 100°F (38°C) to 200°F (93°C)
- Group 3 - Over 200°F (93°C) to 300°F (149°)
- Group 4 - Over 300°F (149°C)

## MIL-HDBK-691B

The adhesives must be thermosetting and must not have a deleterious effect on the metal surfaces being bonded over the range of temperatures at which it will be used. There are no ingredient restrictions other than those posed by the technical requirements. Class 2 adhesives must meet the requirements of MMM-A-132, as applicable to the type, plus the requirements specified. The adhesive shall be in film form and shall consist either entirely of adhesive, or of a carrier impregnated with adhesive. A liquid primer may be furnished for use with the adhesive. A QPL is available.

17.4.24 MIL-A-43316A(1)(GL), December 29, 1969. ADHESIVE, PATCHING FOR CHLOROPRENE COATED OR CHLOROSULPHONATED FABRICS, 11 pp. plus 2-pp amendment. FSC 8040 GL

This limited-coordination Army specification covers requirements for one type of solvent adhesive for patching coated fabrics. It is intended for use in repair and patching of inflated dual-wall shelters and other items that are also made of chloroprene-base-coated, chlorosulphonated polyethylene top-coated synthetic fabric. The adhesive is required to effect repairs in a wide temperature range, including -40°F (-40°C), when applied in the specified manner. The adhesive is based on an oil resistant elastomer in a solvent blend of petroleum naphtha, toluol, xylol, or ketones.

17.4.25 MIL-A-45059C, December 2, 1983. ADHESIVE FOR BONDING CHIPBOARD TO TERNEPLATE, TINPLATE, AND ZINCPLATE, 8 pp. FSC 8040 MR

This specification covers a one-part, ready-to-use brushable adhesive for use in bonding chipboard to terneplate, tinplate, and zincplate in the manufacture of fiber ammunition containers and similar applications where resistance to water, oil, mold, etc., is not required. The adhesive is intended primarily to provide a bond between chipboard and the metal between time of manufacture and loading of the ammunition into the fiber containers.

17.4.26 MIL-G-46030D(MR), September 28, 1978. GLUE, ANIMAL (PROTECTIVE COLLOID), 9 pp. FSC 8040 MR

This limited-coordination Army specification covers one type of animal glue for use as a protective colloid in the manufacture of propellants. The glue must be made from raw materials of animal origin. It is intended for use in the hardening operations in ball propellant manufacture. The glue is in granular or pelletized form and must meet a sieve requirement.

17.4.27 MIL-A-46050C(2), February 3, 1983. ADHESIVES, CYANOACRYLATE, RAPID ROOM TEMPERATURE CURING, SOLVENTLESS, 13 pp plus 1 p amendment. FSC 8040 MR

This specification covers solventless, room-temperature-curing cyanoacrylate adhesives for use with or without an activator, when speed of curing is a primary consideration. It also covers the activator, which may be used to provide still faster curing and to enable the adhesives to bond to otherwise inhibiting surfaces. These adhesives are used for nonstructural applications requiring one-component bonding of small, well-mated surfaces where heat and/or pressure cannot be applied.



## MIL-HDBK-691B

Cyanoacrylate adhesives are normally used to adhere plastics, elastomers, metals, and combinations of these. Generally, Type I is preferred for metal-to metal applications, and Type II for rubber, plastics, and rubber/plastics-to-metal applications. The material is not to be used for adhesive bonds in aerospace vehicles for primary or secondary structures where the adhesive is expected to perform a structural function. Setting time is viscosity-related. Lower viscosities will set more rapidly than higher viscosities. Class 1 will set more rapidly than Class 2 or 3. Not all types may be commercially available in all classes.

The types and classes are as follows:

Type I - Methyl-2-cyanoacrylate  
 Type II - Ethyl-2-cyanoacrylate  
 Type III - Isobutyl-2-cyanoacrylate  
 Type IV - n-Butyl-2-cyanoacrylate  
 Type V - Allyl-2-cyanoacrylate

Class 1 - Low viscosity  
 Class 2 - Medium viscosity  
 Class 3 - Medium-high viscosity  
 Class 4 - High viscosity

The surface activators shall be of the following types as specified:

Type IA - for use with Type I  
 Type IIA - for use with Type II  
 Type IIIA - for use with Type III  
 Type IVA - for use with Type IV  
 (Note: Type VA is not listed)

17.4.28 MIL-A-46091B, July 22, 1981. ADHESIVE, BRAKE LINING TO METAL, 10 pp. FSC 8040 MR

This specification covers one type of thermosetting, one-component adhesive for use in bonding brake linings and clutch facings to steel and aluminum. There are two forms, as follows:

Form I - Liquid  
 Form II - Film

The material must be a one-component, heat-curing material. There are no restrictions on the chemical type or physical nature of the materials. The film form shall consist of unsupported film, protected by a liner. The film thickness range is specified. If a solvent is required as a separate thinner or activator, it must be furnished by the adhesive manufacturer.

17.4.29 MIL-A-46106A(2), February 11, 1974. ADHESIVE-SEALANTS, SILICONE, RTV, GENERAL-PURPOSE, 24 pp. plus 2 pp amendment. FSC 8040 MR



## MIL-HDBK-691B

This specification covers two types of one-part, room-temperature-vulcanizing (RTV), nonfuel-resistant silicone compounds which cure to durable rubber sealants and adhesives upon contact with moisture in the air. The specification also covers primers. These compounds are available as thixotropic pastes, or as self-leveling liquids, and so they can be used for a variety of application techniques. They can be used in the automotive, marine-appliance, metal working, aerospace, aircraft, building construction, communication, computer, electrical/electronic and other industries. The specification suggests a large number of typical uses. The compounds are not resistant to many types of fluids, such as fuel and hydraulic fluid. When cured in contact with certain metals such as copper and other sensitive metals, a slight corrosion may result. Primers are recommended for optimum results when the silicone compounds will be exposed to water, high humidity, and elevated-temperature conditions. Two types of silicone compounds are specified:

Type I - Soft spreadable thixotropic paste

Type II - Self-leveling liquid

(The primer, if required, shall also be Type I or II)

17.4.30 MIL-A-46146A(2), Novemer 25, 1981. ADHESIVE-SEALANTS, SILICONE. RTV, NONCORROSIVE (FOR USE WITH SENSITIVE METALS AND EQUIPMENT), 24 pp. plus 2 pp amendment. FSC 8040 MR

This specification covers three types of one-part, room-temperature vulcanizing, non-fuel resistant silicone compounds which cure to durable rubber sealants and adhesives upon contact with moisture in the air. It also covers primers for use with the silicone compounds.

Since these compounds are available as thixotropic pastes or as self-leveling liquids, they lend themselves to a variety of application techniques which are easily adapted to specialty uses, as well as to production-line methods. These materials are noncorrosive to copper and other sensitive metals and are therefore gaining wide acceptance as preferred adhesives and sealants where delicate electronic devices are involved. They are used in sealing electronic devices, as terminal sealants, for potting electronic components, and as high-temperature sealants. There are three types, as follows:

Type I - Soft, spreadable thixotropic paste

Type II - Self-leveling liquid

Type III - High-strength, noncorrosive

The primer, if required, shall be Type I or II, as recommended by the manufacturer of the silicone compound. The silicone compound must vulcanize at room temperature to produce a rubbery compound. The primer must be an air-drying liquid.

17.4.31 MIL-A-46864A(MI), December 20, 1983. ADHESIVE, EPOXY, MODIFIED, FLEXIBLE, TWO COMPONENT, 14 pp. FSC 8040 MI

## MIL-HDBK-691B

This limited-coordination Army specification covers a two-component modified-epoxy adhesive system capable of curing at room temperature. The adhesive is intended primarily for use as a room-temperature-curing, flexible adhesive and sealant system for heat-shrinkable sleeving and molded components. This two-part system may also be employed in areas where bonding to rubber, metals, plastic, or combinations thereof, is required. Curing conditions for laboratory preparation and for field use are given separately.

17.4.32 MIL-A-47040(1)(MI), October 4, 1976. ADHESIVE-SEALANT, RTV HIGH TEMPERATURE, 18 pp. plus 2 pp amendment. FSC 8040 MI

This limited-coordination Army specification covers one type of single-package, high-strength thixotropic vulcanizing silicone rubber for use in the -85°F (-65°C) to 600°F (315°C) range. This adhesive is for use in the aerospace industry. The adhesive must vulcanize at room temperature to produce a rubber compound to meet the physical and electrical requirements of the specification. This compound is not resistant to many types of fluids, such as fuel and hydraulic fluid. When cured in contact with certain metals, such as copper and other sensitive metals, a slight corrosion may occur. Material meeting this specification utilizes atmospheric moisture and liberates acetic acid during cure, which may result in corrosion. This type material can also cause fracture of stressed high-strength steel when applied at high relative humidity. Particular care should be taken if this material is to be used in electrical equipment, especially when in close proximity to small-gauge wire and electrical contacts.

17.4.33 MIL-C-47072(MI), May 10, 1974. CURING AGENT, EPOXY RESIN, 8 pp. FSC 8040 MI

This limited-coordination Army specification covers the requirements for a room-temperature-curing agent for epoxy resins conforming to ASTM D1763, Type I, Grade 2. The curing agent must be a liquid formulation capable of curing epoxy resin compounds at room temperature.

17.4.34 MIL-A-47074A(MI), March 2, 1983. ADHESIVE SYSTEM, EPOXY, FOR DISSIMILAR METAL BONDING, 11 pp. FSC 8040 MI

This limited-coordination Army specification covers two types of epoxy resin adhesive systems for bonding of dissimilar metals, or similar metals, and where dimensional stability is required. There are two types and two classes, as follows:

Type I - Flowable<sup>1</sup>

Type II - Nonflowable

Class 1 - High peel strength<sup>2</sup>

Class 2 - No peel strength required

The materials for both Type I and Type II shall consist of nitrile-phenolic primer and a thixotropic epoxy-based adhesive compound. The adhesive shall be a two-part epoxy-resin-based 100%-solids system, consisting of Part A, which contains epichlorohydrin-bisphenol A-type resin plus iron oxide filler, and Part B, which contains a polyamide resin plus titanium dioxide. In the case of Type II compound, a colloidal silica filler is added to increase viscosity.

## MIL-HDBK-691B

17.4.35 MIL-A-47089(MI), May 1, 1984. ADHESIVE, METAL FILLED, CONDUCTIVE, ELECTRICAL AND THERMAL, 11 pp. FSC 8040 MI

This limited-coordination Army specification covers one type of electrically conductive metal-filled adhesive. The adhesive is intended to be used in making electrical connections when hot soldering is impractical, and in filling voids where electrical conductivity must be maintained. The adhesive is a silver-filled epoxy-type resin with a separate hardener. Cure is effected by catalytic action and does not depend on evaporation.

17.4.36 MIL-P-47125(1)(MI), May 7, 1976. PRIMER FOR SILICONE RUBBER INSULATING MATERIAL, 6 pp. plus 1-p amendment. FSC 8040 MI

This limited coordination Army specification prescribes the requirements for one type of primer used to promote adhesion of the silicone insulating material specified in MIL-I-47096 (Note: This specification is no longer in use) to nonsilicone substrates. The primer shall be room-temperature-drying and capable of accepting an accelerated cure by heating, along with a minimum of 30% RH, and shall be compatible with the material specified in MIL-I-47096. It may be applied by dipping, brushing, spraying, or rolling.

17.4.37 MIL-A-47126(MI), May 24, 1974. ADHESIVE (VISCIOUS), EPOXY RESIN, METAL-TO-METAL BONDING AND SEALING, 6 pp. FSC 8040 MI

This limited-coordination Army specification covers a viscous bonding material composed of an epoxy resin and activator. It is intended for bonding metal-to-metal parts in manufacturing to produce high-strength parts. The adhesive is two-part and the ratio of activator to resin is 4.50 pbw: 100 pbw.

<sup>1</sup>Unless otherwise specified, Type II shall be furnished.

<sup>2</sup>Unless otherwise specified, class 2 shall be used.

17.4.38 MIL-P-47170(1)(MI), August 17, 1976. PRIMER, SILICONE RUBBER SEALANT, 5 pp, plus 1-p amendment. FSC 8040 MI

This limited-coordination Army specification covers a room-temperature-drying silicone rubber sealant primer. The primer may be used to promote adhesion of the sealant covered by MIL-S-47162 (Note: This specification is no longer in use) and similar hard-to-bond surfaces (such as MIL-A-46106, Type I.) The primer may be applied by dipping, brushing, or spraying. The primer and sealant, used as a system, shall be manufactured by the same company.

17.4.39 MIL-L-47274(1)(MI), November 1, 1976. LIQUID IMINE CURING AGENT, 11 pp, plus 2-p amendment. FSC 8040 MI

This limited coordination Army specification covers two types of liquid imine curing agent. It is intended for use as a catalyst for flexible ablative insulating compounds and as a catalyst for insulating adhesive for bonding in rocket motors. The types are as follows:

- Type I - Low functionality
- Type II - High functionality

## MIL-HDBK-691B

17.4.40 MIL-P-47275(1)(MI), June 15, 1977. PRIMER, SILICONE, 7 pp, plus 2 pp amendment. FSC 8040 MI

This limited-coordination Army specification covers one type of silicone primer system used to insure adhesion of silicone rubber to surfaces after vulcanization. It is intended for use as the primer system to insure adhesion of a silicone-rubber-gasket seal that is vulcanized to aluminum alloy. For best results bonding operations should be completed in the 24 hours following primer application. The primer must be suitable for service temperatures between -180° to 400°F (-100° to 204°C). The primer shall be supplied as a one-component system. The diluent shall be methanol or ethanol (one-part primer and up to five parts of diluent.)

17.4.41 MIL-P-47276(1)(MI), August 17, 1976. PRIMER, BONDING, 11 pp. plus 2-pp amendment. FSC 8040 MI

This limited-coordination Army specification covers one type of liquid organic nitrile-phenolic resin primer. It is intended for use with an adhesive tape which will be pressed between two metal surfaces primed as specified.

17.4.42 MIL-P-47279(1)(MI), June 17, 1977. PRIMER, SILICONE ADHESIVE, 6 pp, plus 2-pp amendment. FSC 8040 MI

This limited-coordination Army specification covers the requirements for a room-temperature-drying silicone adhesive primer. It is intended for use in obtaining maximum adhesion when adhesive conforming to MIL-A-25457, (Note: This specification is no longer in use) is applied to metal, glass, ceramics and plastics. The primer may be applied by dipping, brushing, or spraying. The primer and silicone adhesive used as a system should be manufactured by the same company.

17.4.43 MIL-A-47280(MI), August 9, 1974. ADHESIVES, EPOXY, 11 pp. FSC 8040 AR

This limited-coordination Army specification covers two types of room-temperature-curing epoxy adhesive intended for use in bonding metal-to-metal, metal-to-plastics, plastics-to-plastics, and electronic components to boards or metal surfaces where excellent physical and electrical properties are required. There are two types, as follows:

- Type I - High viscosity
- Type II - Low viscosity

The adhesive shall consist of an epoxy resin and an activator. The curing time is specified for 77°F (25°C), 149°F (65°C) and 212°F (100°C.)

17.4.44 MIL-A-47284(1)(MI), November 1, 1976. ADHESIVE, EPOXY RESIN BASE, 7 pp, plus 2 pp amendment. FSC 8040 MI

## MIL-HDBK-691B

This limited-coordination Army specification covers one type of adhesive consisting of an epoxy-resin base and an amine-type curing agent. The epoxy resin contains an inorganic filler. The adhesive is intended for bonding metal-to-metal. Other constructions, such as metal-to-plastic, or plastic-to-plastic, may be bonded, provided the use of the adhesive is substantiated by testing.

17.4.45 MIL-A-48611A(2), April 14, 1983. ADHESIVE SYSTEM, EPOXY-ELASTOMERIC, FOR GLASS TO METAL, 12 pp, plus 1-p amendment. FSC 8040 AR

This specification covers elastomer-modified-epoxy resin adhesive bonding systems for the structural joining of optical glass prisms to metal, the sealing of glass and metal components, and other applications requiring bonding of a similar nature. The materials to be bonded include glass prisms and other optical elements which are bonded to their metal supports in optical fire-control instruments. For maximum reliability and environmental resistance, especially to humid conditions, the Type I adhesive system is recommended. Both Types I and II adhesive systems may be used for general-purpose bonding of materials such as aluminum, stainless steel, brass, bronze, plastics, glass etc., to themselves or in dissimilar combinations. Various bond-line thicknesses may be used for bonded assemblies. However, for the structural bonding of glass prisms to metal mounts, a bond-line thickness of 0.036 to 0.41 cm is recommended. The adhesive is also used for mirror assemblies.

The types are as follows:

Type I - System composed of an epoxy primer component and an epoxy adhesive component

Type II - System composed of an epoxy adhesive component

The adhesive must be a thermosetting resin based on epichlorohydrin bisphenol A-type epoxy resin, modified with acrylonitrile-butadiene rubber. Various additives, modifiers, or fillers may be included. The primer is a two-component room-temperature-curing liquid epoxy. Recommended procedures such as surface preparation, component mixing and application, and work-area environment stabilization to be followed during the use of bonding systems conforming to this specification are contained in MIL-B-48612. The adhesive system described in this specification should be used in place of that covered by MMM-A-131 for military applications.

17.4.46 MIL-B-48612(MU), January 27, 1977. BONDING WITH EPOXY-ELASTOMERIC ADHESIVE SYSTEM, GLASS TO METAL, 9 pp. FSC 12GP AR

This limited-coordination Army specification covers the bonding of glass optical components to metal mounts for use in military instruments. Bonding thicknesses of 0.014 to 0.016 inch are recommended for most bonds, especially where aluminum is the metal mounting material. Other bondline thicknesses may be used, however. The bonding of mirrors and similar components by this specification is not recommended without confirmatory tests for optical quality. There are two types, as follows:



## MIL-HDBK-691B

Type I - Bond with Type I adhesive, MIL-A-48611

Type II - Bond with Type II adhesive, MIL-A-48611

The quality of a bonded assembly shall be of the following two grades:

Grade A - Bonds for prism assemblies or similar components on optical instruments where high quality is mandatory

Grade B - Bonds for noncritical bonded assemblies (Grade A shall apply to all bonded prism assemblies where grade quality is not specified.)

This is a process specification. Topics covered, include assembling components, cleaning, primer preparation, primer application, adhesive preparation, adhesive application, bond fixture, adhesive curing, performance requirements, and bond life requirements.

17.4.47 MIL-A-50926A(PA), June 10, 1975. ADHESIVE MR-23 (FOR USE IN AMMUNITION), 7 pp. FSC 1376 AR

This limited-coordination Army specification covers one type of adhesive, MR-23, for use as an adhesive in nonmetallic cartridge cases. The adhesive, MR-23, is intended for use in the 152-mm ammunition system. The adhesive is a uniform mixture of nitrocellulose and nitroglycerine in acetone and nitromethane.

17.4.48 MIL-A-52194A(MR), January 16, 1967. ADHESIVE, EPOXY (FOR BONDING GLASS REINFORCED POLYESTER), 10 pp. FSC 8040 MR

This limited-coordination Army specification covers the requirements for a two-part epoxy-based adhesive suitable for bonding glass-reinforced polyester where no peel or cleavage is anticipated. Both the resin and the hardener must be in paste form. This specification was prepared to cover material for bonding the two halves of plastic gunstocks. The adhesive is intended for use in applications where its paste consistency is necessary (1) to prevent adhesive drain-off during cure, or (2) to bond adherend surfaces that are not plane. The adhesive is not intended for use where service temperatures exceed 200°F (93°C).

17.4.49 MIL-A-52685, May 11, 1970. ADHESIVE: BONDING, CHLOROPRENE, AIR FIELD MEMBRANE SURFACING, 9 pp. FSC 5610 ME

This specification covers one type of adhesive for bonding chloroprene-coated fabrics. It is intended to be used for the joining, by bonding, of airfield surfacing membranes. The adhesive is a rubber-based adhesive of noncuring-polychloroprene type, modified with a cyclic unsaturated hydrocarbon resin, usable without heating or additives.

17.4.50 MIL-A-60091(1)(AR), April 29, 1981. ADHESIVE FOR BONDING DEMOLITION CHARGES TO STRUCTURAL SURFACES, 7 pp, plus 5-pp amendment. FSC 1375 AR



## MIL-HDBK-691B

This limited-coordination Army specification covers a one-part, ready-to-use adhesive suitable for use in bonding demolition charges to dry, wet, and underwater surfaces of structural materials under all weather conditions. It may also be used in other bonding applications. The adhesive is a synthetic elastomer solvent-type material, with required pigment (olive drab). Its consistency is such that it can be dispensed readily from its collapsible metal tube container by being squeezed by hand. It must be spreadable by means of a wooden tongue depressor.

17.4.51 MIL-A-81236(2)(OS), September 9, 1968. ADHESIVE: EPOXY RESIN WITH POLYAMIDE CURING AGENT, 7 pp 4 pp amendment. FSC 8030 OS

This limited-coordination Navy specification covers one type of adhesive consisting of an epoxy resin and a polyamide curing agent for general use under normal circumstances. It provides for an additional type of material for use under Air Pollution Regulations. The classification is as follows:

- Type I - For general use under normal circumstances
- Type II - For use where Air Pollution Regulations are enforced

The material is a two-part thermosetting epoxy adhesive with a polyamide curing agent. The solvent in Type I shall be of the type normally used when the finished product is for general use under normal circumstances. For Type II adhesive the solvent shall be of a nonphotochemically reactive solvent.

17.4.52 MIL-C-81247(WP), March 1, 1965. CURING AGENT, BICYCLO ANHYDRIDE TYPE, 7 pp. FSC 8040 OS

This limited-coordination Navy specification covers one type of bicyclo anhydride curing agent intended for use in epoxy resin systems using amine accelerators. The material must conform to the infrared spectrum given in the specification, exhibiting minimum transmittance bands only at the same wavelength.

17.4.53 MIL-A-81253(1)(OS), November 16, 1966. ADHESIVE, MODIFIED EPOXY RESIN WITH POLYAMINE CURING AGENT, 6 pp, plus 1 p amendment. FSC 8040 OS

This limited-coordination Navy specification covers one kind of low viscosity, modified-epoxy-resin adhesive. The material is intended for use as an adhesive in rocket motor systems. It includes a triethylenetetramine curing agent.

17.4.54 MIL-A-81270(1)(OS), September 9, 1968. ADHESIVE, SYNTHETIC RUBBER 5 pp. plus 2 pp amendment. FSC 8040 OS

This limited-coordination Navy specification covers one type of general-purpose nitrile-phenolic synthetic-rubber adhesive for general use under normal circumstances.

It provides for an additional type of material suitable for use under Air Pollution Regulations. It is intended for use in rocket motors. The classification is as follows:

## MIL-HDBK-691B

Type I - For general use under normal circumstances

Type II - For use where Air Pollution Regulations are enforced

The solvent content of Type I adhesive shall be of the type normally used when the finished product is for general use under normal circumstances. For Type II adhesive a nonphotochemically reactive solvent shall be used.

17.4.55 MIL-A-81786/11(AS), April 20, 1972. ADHESIVE, EPOXY, FLEXIBLE, 1 p. FSC 4940 AS

This a Military Specification Sheet. The complete requirements for procuring the adhesive described consist of this document and the issue in effect of MIL-K-81786(AS) (described below). The whole text is as follows:

"The adhesive shall be a two part flexible epoxy type which conforms to the requirements of NAVSHIPS Procurement Specifications 0967-221-1010 (Appendix H) and shall be packaged in containers which separate the two components. Each container shall weigh 2.8 grams."

17.4.56 MIL-K-81786A, Supp. 1(AS), August 2, 1973. KIT, MAINTENANCE, ELECTRICAL-ELECTRONIC, CABLE AND CABLE HARNESS, 35 pp. plus 2 pp supplement. FSC 4940 AS

This limited-coordination Navy specification covers an electrical-electronic maintenance kit containing consumable components, tools, and equipment designed for use by shore based and shipboard personnel to maintain, modify and repair electronic cables and cable harnesses. MIL-K-81786/11(AS) described above describes an adhesive required for this kit.

17.4.57 MIL-A-82484, June 13, 1967. ADHESIVE AND SEALING COMPOUNDS, CELLULOSE NITRATE BASE, SOLVENT TYPE (FOR ORDNANCE USE), 11 pp. FSC 8040 OS

This specification covers cellulose nitrate-based adhesive and sealing compounds suitable for ordnance use. The classification is as follows:

Type I - Adhesive, Ordnance (38 to 42% solids)

Type II - Adhesive, Ordnance (low-viscosity)

Type III - Sealing compound, Ordnance (clear or colored by dye)

Types I and II are intended for general ordnance use in ammunition. General use does not imply that the compounds are to be used as all-purpose adhesives; they are not recommended for use with concrete, wood, rubber, ceramics, or paper. Types I and II may be used to provide good bonds for glass, leather, metals, textiles, and some types of thermoplastics. Type III compound is intended for use as a sealing compound in the manufacture of ammunition.

The compositions of Types I and II adhesive are given in a table of 5 ingredients with percentages specified. Type III material must be a uniform solution or homogeneous dispersion of cellulose nitrate of different viscosities and organic plasticizers in relatively low-boiling organic solvent mixtures, so formulated as to meet all the applicable requirements of this specification. Color may be specified for Type III. No benzene or chlorinated solvent shall be permitted in any type.

## MIL-HDBK-691B

17.4.58 MIL-A-82569(OS), January 12, 1969. ADHESIVE, NEOPRENE BASE, MEDIUM VISCOSITY, 6pp. FSC 1336 OS

This limited-coordination Navy specification covers one type of medium viscosity neoprene-base adhesive, using aromatic solvents as the vehicle. The adhesive is intended for use in rocket motors.

17.4.59 MIL-A-82636(OS), December 23, 1984. ADHESIVE, BUTYL, TWO-COMPONENT, 5pp. FSC 8040 OS

This limited-coordination Navy specification covers a two-component butyl adhesive intended for use in bonded-seam construction of chemical-agent protective clothing. The product shall be a solvent-dispersed material suitable for application by paint brush of natural or synthetic fibers. The adhesive shall be capable of being cured in air without heat or pressure.

17.4.60 DOD-A-82720(OS), March 9, 1982. ADHESIVE, MODIFIED EPOXY, FLEXIBLE, TWO-PART (METRIC), 10 pp. FSC 8040 OS

This limited-coordination Navy specification covers one type of room-temperature-curing, two-part, flexible, modified-epoxy adhesive intended for use in assembly of the aft closure of the MK 56 DTRM used on the standard (MR) surface-to-air missile. The material shall be a structural, thermosetting, flexible, modified-epoxy adhesive capable of being used at 59° to 95°F, (15° to 35°C.) The adhesive shall consist of two liquid components, an accelerator hardener or curative designated as Component A, and a base resin designated as Component B, furnished in a kit. The two components must be completely miscible.

17.4.61 MIL-A-83376A(USAF), June 28, 1978. ADHESIVE BONDED METAL FACED SANDWICH STRUCTURES, ACCEPTANCE CRITERIA, 12 pp. FSC 8040 20

This limited-coordination Navy specification covers adhesive bonded sandwich structures, including the metal-to-metal bonding found in these structures. The specification is intended to define acceptance criteria of bonded-metal-faced sandwich assemblies used in aerospace structures. Two types are classified as follows:

- Type I - Components which are fracture- or fatigue-critical, as defined in MIL-I-6870 components, the single failure of which would cause significant danger to operating personnel, or would result in an operational penalty. This includes loss of major components, loss of control, unintentional release, inability to release armament stores, or failure of weapon installation components.
- Type II - All components not classified as Type I. Defects covered in this specification are defined.

17.4.62 MIL-A-83377B, October 6, 1978. ADHESIVE BONDING (STRUCTURAL) FOR AEROSPACE AND OTHER SYSTEMS, REQUIREMENTS FOR, 15 pp. FSC 8040 20

## MIL-HDBK-691B

This document covers requirements applicable to structural-adhesive bonding of metal, composite and core material in any combination. It and the earlier revisions replaced MIL-A-9062. It is intended that the requirements of this document be mandatory for use by contractors to assure the reliability of adhesive-bonded structural components used in aerospace and other systems.

The classification is as follows:

- Type I - Primary structure. Components which are fracture- or fatigue-critical, as defined in MIL-I-6870, components the single failure of which would cause significant danger to operating personnel, or would result in an operational penalty. This includes loss of major components, loss of control, unintentional release, inability to release armament stores, or failure of weapon installation components.
- Type II - Secondary structure. All components not classified as Type I. This is a process-type document to be used as a guide in preparing a process specification. Definitions of terms covered are given.

17.4.63 MIL-S-83432(USAF), January 7, 1974. SEALING COMPOUNDS, ADHESIVE BONDED STRUCTURE, 13pp. FSC 8030 20

This limited-coordination Air Force specification covers sealing compounds that are suitable for sealing and moisture-proofing adhesive bonded structures. These compounds are to be used to prevent the entry of moisture into adhesive-bonded structures. They are suitable for use in a service temperature range from -67° to 300°F (-55° to 149°C). Classification is as follows:

- Type I - Spray application
- Type II - Brush application
- Type III - Gun or spatula application

The sealing compounds shall be two-part epoxy polysulfide materials capable of being cured at specified conditions.

17.4.64 MIL-A-87134(USAF), June 20, 1978. ADHESIVE, CONTACT, FOR CUSTOM FIT HELMET LINERS, 10 pp. FSC 8040 20

This limited-coordination Air Force specification covers a flexible adhesive in a volatile organic solvent for contact bonding of leather to polyurethane foam custom-fit liners in pilots' helmets. It will also bond other materials, such as plastic decorative laminates, fabrics and wood. The foam is covered by MIL-P-83379. The requirements of this specification are equivalent to those of MMM-A-130, except that the ketones and other solvents which attack polyurethane foam are prohibited. The material shall consist of polychloroprene (neoprene) rubber and synthetic resin. The solvents must not attack polyether-based, Freon-blown, rigid polyurethane foam. Ketones, halogenated compounds, and benzene may not be used.

17.4.65 MIL-A-87135(USAF), February 16, 1979. ADHESIVE, NONCONDUCTIVE, FOR ELECTRONICS APPLICATION, 7 pp. FSC 8040 20

## MIL-HDBK-691B

This limited-coordination Air Force specification establishes the requirements for a moderately fast-curing adhesive used for bonding components to printed wiring assemblies to prevent vibration damage. The adhesive materials must have no adverse effect on the materials used in the substrate or components attached thereon, and shall be formulated from resins, elastomers, plasticizers, catalysts, and other ingredients which meet the requirements of this specification.

17.5. Society of Automotive Engineers (SAE) (6).

17.5.1 Aerospace Materials Specifications (AMS).

17.5.1.1 AMS 2491C, October 1, 1981. SURFACE TREATMENT OF POLYTETRAFLUOROETHYLENE, 5 pp (DOD Adopted). FSC MFFP MR

This specification, which is really a process specification, covers the engineering requirements for preparing surfaces of polytetrafluoroethylene (PTFE) for bonding. It also covers the properties resulting from the treatment. The bonding preparation described may adversely affect the electrical properties of the PTFE. A solution of sodium or other alkali metal in anhydrous liquid ammonia or tetrahydrofuran naphthalene or other suitable solvent is used under prescribed conditions. Test requirements are given for use of the preparation with a specific epoxy adhesive type on aluminum. These tests cover tensile strength and shear strength.

17.5.1.2 AMS 3106A, April 1, 1983. PRIMER, ADHESIVE, CORROSION-INHIBITING, -67° to +200°F (-55° to 95°C), 1 p. (DOD Adopted). FSC 8040 AS

The requirements of this specification are embodied in the latest issue of AMS 3107 (see below).

17.5.1.3 AMS 3107, April 1, 1983. PRIMER, ADHESIVE, CORROSION-INHIBITING, FOR HIGH DURABILITY STRUCTURAL ADHESIVE BONDING, 14 pp (DOD Adopted). FSC 8040 AS

This specification supersedes AMS 3106A, dated March 1, 1974. The specification and its four supplementary detail specifications cover corrosion-inhibiting, modified-epoxy primers in the form of ready-to-use sprayable liquids. The adhesive primers are for use primarily in metal surfaces in preparation for high-durability structural adhesive bonding of sandwich panels and metal-to-metal attachments. They may also be used as primers in preparation for final paint-type finishing. The primer should be a sprayable liquid composed of a resin or resin mixture, pigmented and compounded to be compatible with epoxy-base film or paste adhesives. The primer must impart corrosion resistance and contribute to the adhesive properties of the primer and adhesive system.

The primer is useful over the temperature range specified in the applicable detail specification following. Requirements for the uncured primer include: color, solids content, inhibitor content, weight per volume, viscosity, sprayability, and pot life. Requirements for the cured film applied to panels include: adhesion, flexibility, impact resistance, hardness, fluid resistance, corrosion resistance, heat resistance, low-temperature shock, compatibility with sealant, and compatibility with top coat. Requirements for the cured primer used with the adhesive specified in the applicable detail specification include: room-temperature lap shear and metal-to-metal peel.



## MIL-HDBK-691B

17.5.1.4 AMS 3107/1, April 1, 1983. PRIMER, ADHESIVE, CORROSION INHIBITING, HIGH DURABILITY EPOXY, -65° to +200°F (-55° to +95°C), 4 pp (DOD Adopted). FSC 8040 AS

This material must meet the requirements of the basic specification, AMS 3107, above. It must also be compatible with the AMS 3695/1 epoxy film adhesive (see below) and MIL-C-83286 polyurethane coating. Detailed requirements are given for a large number of properties (19, with some subdivisions).

17.5.1.5 AMS 3107/2, April 1, 1983. PRIMER, ADHESIVE, CORROSION-INHIBITING, HIGH DURABILITY EPOXY, -65° to +250°F (-55° to +120°C), 4 pp (DOD Adopted). FSC 8040 AS

This material must meet the requirements of the basic specification, AMS 3107, above. It must also be compatible with the AMS 3695/2 epoxy film adhesive (see below) and MIL-C-83286 polyurethane coating. Detailed requirements are given for a large number of properties (19, with some subdivisions).

17.5.1.6 AMS 3107/3, April 1, 1983. PRIMER, ADHESIVE, CORROSION-INHIBITING, HIGH DURABILITY EPOXY, -65° to +350°F (-55° to +175°C), 5pp (DOD Adopted). FSC 8040 AS

This material must meet the requirements of the basic specification, AMS 3107, above. It must also be compatible with the AMS 3695/3 epoxy film adhesive (see below), and silicone-resin-based top coat. Detailed requirements are given for a large number of properties (19, with some subdivisions).

17.5.1.7 AMS 3107/4, April 1, 1983. PRIMER, ADHESIVE, CORROSION-INHIBITING, HIGH DURABILITY EPOXY, -65° to +420°F (-55° to +215°C), 4 pp (DOD Adopted). FSC 8040 AS

This material must meet the requirements of the basic specification, AMS 3107, above. It must also be compatible with the AMS 3695/4 epoxy film adhesive (see below), and silicone-resin-based top coat. Detailed requirements are given for a large number of properties (19, with some subdivisions).

17.5.1.8 AMS 3681B, July 1, 1983. ADHESIVE, ELECTRICALLY CONDUCTIVE, SILVER-ORGANIC BASE, 6 pp.

This specification covers an electrically conductive adhesive supplied in two components: a paste of silver-filled epoxy-base adhesive, and a separate curing agent which may be paste or liquid. The adhesive is to be used primarily to provide an electrically conductive bond between metallic, thermosetting plastic, and ceramic surfaces, and as an electrically conductive sealing compound. The silver may be in the form of powder, flakes, or balls. The curing agent shall be an amine-type material. Shelf life must be at least 6 months. Requirements are given for the mixed adhesive for pot life, corrosive or noxious vapors, and consistency. Requirements for the cured adhesive are lap-shear strength (aluminum specimens), volume resistivity, salt-spray resistance, fungus resistance, and corrosivity.



## MIL-HDBK-691B

17.5.1.9 AMS 3685A, December 1, 1951. ADHESIVE, SYNTHETIC RUBBER, BUNA N TYPE, 3 pp.

This specification covers a Buna N synthetic rubber-base stock dispersed or dissolved in suitable solvents to form a homogeneous product, ready for use without additions other than solvents for thinning with no more than 7.4% by volume of solvent. Requirements are given for brushing characteristics, weathering, corrosion, skinning, package stability, and toxicity. Requirements also cover: adhesion strength in tension, adhesion strength in shear (aluminum to synthetic rubber) adhesion strength in shear (aluminum to cotton webbing), adhesion strength (stripping method), bonding range, aromatic fuel resistance, water resistance, lubricating-oil resistance, cold flow, and softening point.

17.5.1.10 AMS 3686, September 15, 1975. ADHESIVE, POLYIMIDE RESIN, FILM AND PASTE, HIGH TEMPERATURE RESISTANT, 600°F or 315°C 8 pp (DOD Adopted). FSC 8040 AS

This specification covers a high-temperature, electrical-grade, polyimide resin adhesive in the form of film or paste. The adhesive is used primarily for bonding polyimide-laminate-faced sandwich structures for use as radar-transparent assemblies. It is useful over the temperature range of -67° to 600°F (-55° to 315°C.) The adhesive is a polyimide resin system supplied in sheets, rolls of film or in paste form. It must be suitable for use in electrical applications and shall contain no metal fillers or other inorganic additives, except for anti-oxidants and thixotropic agents of not more than 35% by weight, total, based on cured-resin solids. When in film form, the carrier shall be "E" glass cloth. Storage life must be at least 6 months. Requirements for the uncured adhesive cover: solids content of paste adhesive, volatile content of film adhesive, and weight of film adhesive. Requirements for the cured adhesive include: tensile shear at six different exposure conditions, and flatwise tensile at three different exposure conditions.

17.5.1.11 AMS 3687, March 1, 1974. ADHESIVE FILM HUMIDITY-RESISTANT, FOR SANDWICH PANELS, -67° to 203°F (-55° to 95°C).

This specification covers a high-humidity resistant, modified-epoxy adhesive in the form of film. It is used primarily for bonding aluminum-faced sandwich panels in the construction of lightweight portable shelters. The adhesive is useful in the temperature range specified in the title. The adhesive is a modified-epoxy film supplied in sheets or rolls, consisting entirely of adhesive material, or of a carrier impregnated with adhesive, with a suitable nonadhering separator film on both surfaces. The adhesive must possess high humidity resistance, be compatible with AMS 3106 corrosion-inhibiting primer (now superseded by AMS 3107 primer), and must not have a deleterious effect on the surfaces or materials being bonded. The storage life must be at least 6 months. Requirements for the uncured adhesive include tack, volatile content, and color. Requirements for the cured adhesive (2 hour maximum cure at 347°F (175°C) and 20 psi pressure) include tensile shear (5 tests at various conditions), fatigue strength, creep rupture (2 tests at various conditions), blister detection, tensile shear, sandwich peel (3 tests at

## MIL-HDBK-691B

various conditions), flatwise-tensile strength (4 tests at various conditions), flexural strength (total load) (4 tests at various conditions, creep deflection in flexure (2 tests at various conditions), with a total of 21 tests. The humidity requirement is for 95% to 100% RH at 203°F (95°C).

17.5.1.12 AMS 3688A, October 1, 1981. ADHESIVE, FOAMING, HONEYCOMB CORE SPLICE, STRUCTURAL, -67° to +180°F (-55° to +80°C), 11 pp (DOD Adopted). FSC 8040 AS

This specification covers a foaming-type, heat-curing, resin-base adhesive in the form of a paste or sheet. It is used primarily in splicing aluminum alloy or nonmetallic honeycomb core, and for providing a shear tie between core edges and inserts or edge members in honeycomb assemblies for use over the temperature range specified in the title. It is useful for filling gaps between core faces which are inserted into channels or similar areas where bonding pressure cannot be obtained. The adhesive is a heat-curing, nominally 250°F (120°C), resin system containing fillers and foaming agents as necessary to meet the requirements specified. The adhesive must have low sagging properties to ensure complete filling of core splice gaps when splices are cured in a vertical position. The adhesive must be suitable for splicing nonperforated honeycomb core without damage to core node bonds located adjacent to the splice. When supplied as a sheet, the sheet shall be unsupported and be provided with a suitable nonadhering separator film on both surfaces. When in paste form the paste shall be a thixotropic, single component, or two-part system suitable for extrusion from a disposable cartridge or caulking gun. The uncured adhesive, when supplied as a single component, shall have a storage life of at least 3 months at 0°F (-18°C.) When supplied as a two-part paste system, the storage life at the time and temperature specified by the manufacturer, shall be at least 3 months. Requirements are also given for working life. Requirements for the cured adhesive are given for sagging, expansion ratio, peak exotherm, density, and beam shear at -67°F (-55°C), 75°F (24°C), and 180°F (82°C).

17.5.1.13 AMS 3689A, October 1, 1981. ADHESIVE, FOAMING, HONEYCOMB CORE SPLICE, STRUCTURAL, -67° to +350°F (-55° to +175°C), 11 pp (DOD Adopted). FSC 8040 AS

This specification is similar in all respects to AMS 3688A above, except for the curing temperature of 350°F (175°C), and the range of usefulness.

17.5.1.14 AMS 3690, January 15, 1960. ADHESIVE COMPOUND, EPOXY, ROOM TEMPERATURE CURING, 3 pp.

This specification calls for an epoxy-resin adhesive consisting of two components, an epoxy resin and a hardener. Fillers and modifiers may be included in either component. The adhesive is for general-purpose use for nonstructural bonding of aluminum, corrosion-resistant steel, brass, and many thermosetting plastics to themselves and to each other. It is primarily intended as an adhesive for electrical components and devices operating at temperatures no higher than 185°F (85°C). Requirements cover curing, pot life, corrosivity, tensile-shear strength at various conditions, including temperature extremes and thermal cycling, and fluid resistance.

## MIL-HDBK-691B

17.5.1.15 AMS 3691, January 15, 1960. ADHESIVE COMPOUND EPOXY, MEDIUM TEMPERATURE APPLICATION, 3 pp.

This specification is similar to AMS 3691 above, except for the maximum-use temperature of 250°F (120°C) and curing conditions which call for testing cures carried out at no higher than 250°F (120°C) with less than 10 psi pressure.

17.5.1.16 AMS 3692, January 15, 1960. ADHESIVE COMPOUND, EPOXY, HIGH TEMPERATURE APPLICATION 3 pp.

This specification is similar to AMS 3690 above, except for the maximum-use temperature of 500°F (260°C) and curing conditions which call for cure carried out according to the manufacturer's recommendations, with less than 10 psi pressure.

17.5.1.17 AMS 3693B, July 1, 1983. ADHESIVE MODIFIED EPOXY, MODERATE HEAT RESISTANT,, 250°F (120°C) CURING, FILM TYPE, 7 pp. (This specification is similar to Federal Specification MMM-A-132, Type 1, Class 2 and Military Specification MIL-A-25463, Type 1, Class 2, which are described below.)

This specification covers a modified epoxy adhesive in the form of supported film supplied in rolls or sheets. It is intended primarily for structural bonding of metallic alloys and rigid nonmetallic surfaces to themselves and to each other, and for bonding of internal and external structural honeycomb components operating in the range of -65° to +180°F (-55° to +80°C). A liquid primer suitable for spray or brush application may be required for use with the adhesive. The material consists of a supported-film adhesive with protective liners. Uniformly dispersed fillers may be included in the film. The resin shall conform to MMM-A-132, Type 1, Class 2, and MIL-A-25463, Type 1, Class 2. Shelf life must be at least 6 months at 0°F (-18°C). Cured-product requirements cover tensile shear strength at three different temperatures up to 180°F (80°C), and after salt-spray exposure, humidity exposure, and fuel immersion, flatwise tensile strength and flexural strength at various temperatures, T-peel strength at 75°F (24°C), sandwich-peel strength at three different temperature conditions up to 180°F (80°C), creep deformation and corrosivity. The adhesive film in each roll or sheet must be protected on one or both sides by nonadhering separator film.

17.5.1.18 AMS 3695, April 1, 1983. ADHESIVE FILM, EPOXY-BASE FOR HIGH DURABILITY STRUCTURAL ADHESIVE BONDING, 14 pp.

This specification and its supplementary detail specifications cover film adhesives compounded from modified-epoxy resins in the form of ready to use sheet, supplied in rolls, either supported by mat or by woven monofilaments, or unsupported. It is intended primarily for bonding metal to metal or aluminum honeycomb sandwich assemblies for service usage over the temperature range specified in the applicable detail specifications following. The adhesive shall be a modified-epoxy film in sheets or rolls, consisting entirely of adhesive material, or of a carrier impregnated with adhesive, with a suitable nonadhering separator film on both surfaces. The adhesive shall be used with AMS 3107 corrosion-inhibiting primer and cured in accordance with

## MIL-HDBK-691B

the applicable detail specification to form an adhesive-primer system. The adhesive must not have a deleterious effect on the surface of materials being bonded.

Requirements for the uncured adhesive cover color, solids content, weight, thickness and working life. Requirements for the cured adhesive for metal-to-metal applications cover tensile shear (dry, and after exposure to humidity, salt spray, aromatic fuel, JP-4 fuel, phosphate ester fluid, hydraulic fluid, anti-icing fluid, diester lubricating oil, and polyol ester), fatigue, creep-rupture deformation, climbing peel (dry, after humidity exposure, and after salt-spray exposure), crack extension test (2-edge test), and sustained stress loading. Requirements for the cured adhesive for metals to-honeycomb application cover climbing peel (dry) and flatwise-tensile strength.

17.5.1.19 AMS 3695/1, April 1, 1983. ADHESIVE FILM EPOXY BASE, HIGH DURABILITY, FOR 200°F (95°C) Service, 9 pp.

This adhesive is intended for use with the AMS 3107/1 corrosion-inhibiting primer (above) to form an adhesive/primer system meeting the requirements specified in the basic specification, AMS 3695 (above). Detailed requirements are given for a large number of properties (15, with subdivisions).

17.5.1.20 AMS 3695/2, April 1, 1983. ADHESIVE FILM, EPOXY-BASE, HIGH DURABILITY, FOR 250°F (120°C) Service, 9 pp.

This adhesive is intended for use with the AMS 3107/2 corrosion-inhibiting primer (above) to form an adhesive/primer system meeting the requirements specified in the basic specification, AMS 3695 (above). Detailed requirements are given for a large number of properties (15 with subdivisions).

17.5.1.21 AMS 3695/3, April 1, 1983. ADHESIVE FILM, EPOXY-BASE, HIGH DURABILITY, FOR 350°F (175°C) Service, 10 pp.

This adhesive is intended for use with the AMS 3107/3 corrosion-inhibiting primer (above) to form an adhesive/primer system meeting the requirements specified in the basic specification, AMS 3695 (above). Detailed requirements are given for a large number of properties (15, with many subdivisions).

17.5.1.22 AMS 3695/4, April 1, 1983. ADHESIVE FILM, EPOXY-BASE HIGH DURABILITY, FOR 420°F (215°C) Service, 10 pp

This adhesive is intended for use with the AMS 3107/4 corrosion-inhibiting primer (above) to form an adhesive/primer system meeting the requirements specified in the basic specification, AMS 3695 (above). Detailed requirements are given for a large number of properties (15, with many subdivisions).

17.5.1.23 AMS 3698, October 15, 1979. ADHESIVE FILM, HOT-MELT, ADDITION-TYPE POLYIMIDE, FOR FOAM SANDWICH STRUCTURE, -67° to +450°F (-55° to +230°C), 11 pp.

## MIL-HDBK-691B

This specification covers one type of hot-melt, polyimide adhesive in the form of supported film furnished in rolls or cut sheets. It is intended primarily for structural-adhesive bonding of foam sandwich and glass fiber, honeycomb-core sandwich assemblies requiring high strength, excellent electrical properties, and heat resistance up to 450°F (230°C). The material must be a bis-maleimide, hot-melt, addition-type, polyimide adhesive compounded to meet the requirements specified, and supplied in film form with an E-glass scrim carrier, such as Style 112, coupling with AMS 3824, in rolls or as cut sheet, with a suitable nonadhering separator film on both surfaces.

Requirements are given for storage life and working life of the uncured adhesive. The adhesive must be compatible with, and capable of being co-cured with, the hot-melt, addition-type polyimide-resin-impregnated cloth conforming to AMS 3844 or AMS 3849. Requirements for the cured adhesive cover co-cured facings and precured facings separately. The following properties are covered for the uncured adhesive: color, solids content, weight, thickness, tack, and drape. For the co-cured and precured facings there are requirements for flatwise-tensile strength at three different temperatures up to 450°F (232°C). Honeycomb climbing-peel tests are required for the precured facings at two different temperatures and tensile-shear (lap) tests are required for aluminum-alloy facings. The adhesive film in each roll or sheet must be protected on both sides by nonadhering separator film.



MIL-HDBK-691B

REFERENCES

1. Landrock, A. H., Chapter 11, "Commercial and Government Specifications and Standards," in Handbook of Plastics and Elastomers. (C. A. Harper, editor-in-chief), McGraw-Hill, NY, 1975.
2. Landrock, A. H., "Standards and Specs: Are They Really Indigestible?" Plastics Design Forum, 2(6): 81-88 (November/December 1977).
3. Landrock, A. H., Introduction, pp 2-3 "Specifications for Adhesives," desk top data bank<sup>R</sup>, the International Plastics Selector, Inc., San Diego, CA, 1979.
4. ASTM Standards can be found in the latest issue of the Annual Book of ASTM Standards. Most of the standards listed, whether test methods, practices, or specifications, are included in Volume 15.06 - Adhesives, which can be obtained from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. Separate copies of each standard may also be purchased from ASTM.
5. Acknowledgment is made for some of this material taken from discussions of ASTM Tests in "Adhesives," edition 3, desk top data bank<sup>R</sup>, the International Plastic Selector, Inc., San Diego, CA, 1980.
6. SAE Standards (ARP's and AMS's) are available from the Society of Automotive Engineers, Inc., 400 Commonwealth Avenue, Warrendale, PA 15096. A catalog listing all current standards is also available.
7. Military and Federal specifications and standards can be obtained at no charge from the Naval Publications and Forms Center, 5801 Tabor Avenue, Philadelphia, PA 19120.



## MIL-HDBK-691B

## APPENDIX

## GLOSSARY OF TERMS

The definitions given in this Appendix are taken from a number of sources, which have been cited. They include the latest ASTM Committee D-14 and ISO TC 61 definitions. In some cases several definitions are given. A few definitions found in literature sources have been used to supplement or replace more complicated definitions from glossaries.

A-Stage. An early stage in the reaction of certain thermosetting resins in which the material is fusible and still soluble in certain liquids. Sometimes referred to as Resol. (See also B-stage and C-stage) (1)

abhesive. A material which is adhesive-resistant and applicable as a nonsticking surface coating; release agent. (2)

adhere, v. To cause two surfaces to be held together by adhesion (q.v.). (1)

adherence. The state in which two surfaces are held together by interfacial forces. (3)

adherend. A body which is held to another body by an adhesive (a narrower term than substrate, q.v.). (1)

adhesion. The state in which two surfaces are held together by chemical, or physical forces, or both, with the aid of an adhesive. (3)

adhesive. A substance capable of holding materials together by surface attachment. Adhesive is the general term and includes, among other, cement, glue, mucilage, and paste (q.v.). All of these terms are used interchangeably.

adhesive, anaerobic. An adhesive that cures spontaneously in the absence of oxygen, the curing being inhibited by the presence of oxygen and catalysed by metallic ions. (3)

adhesive, cold-setting. An adhesive that sets at temperatures below 68°F (20°C). (1)

adhesive, contact. An adhesive that is apparently dry to the touch and which will adhere to itself instantaneously upon contact; also called contact-bond adhesive. (1) An adhesive that is applied to both adherends and allowed to become dry and then develops a bond when the adherends are brought together without sustained pressure. (3)

adhesive, dispersion (or emulsion). A two-phase system with one phase (the adhesive material) in a liquid suspension. (3)

adhesive, encapsulated. An adhesive in which the particles or droplets of one of the reactive components are enclosed in a protective film (microcapsules) to prevent cure until the film is destroyed by suitable means. (3)

## MIL-HDBK-691B

adhesive, film. An adhesive in film form, with or without a carrier, usually set by means of heat and pressure. (3) The main advantage is uniformity of glueline thickness.

adhesive, gap-filling. An adhesive subject to low shrinkage in setting, employed as a sealant. (2)

adhesive, heat-activated. A dry adhesive that is rendered tacky or fluid by application of heat, or heat and pressure, to the assembly (1)(3)

adhesive, heat-sealing. A thermoplastic film adhesive which is melted between the adherend surfaces by heat application to one or both of the adjacent adherend surfaces. (2)

adhesive, hot-melt. A thermoplastic adhesive that is applied in a molten state and forms a bond on cooling to a solid state.

adhesive, hot-setting. An adhesive that sets at temperatures above 68°F (20°C). (1)

adhesive, intermediate-temperature setting. An adhesive that sets in the temperature range from 87° to 211°F (31° to 99°C). (1)

adhesive, latex. An emulsion of rubber or thermoplastic rubber to water. (2)

adhesive, one-component. An adhesive material incorporating a latent hardener or catalyst activated by heat. Usually refers to thermosetting materials, but also describes anaerobic, hot-melt adhesive, or those dependent on solvent loss for adherence. (2) Thermosetting one-component adhesives require heat to cure.

adhesive, pressure-sensitive. An adhesive which, in the dry state, is aggressively and permanently tacky at room temperature and firmly adheres to a variety of dissimilar surfaces upon contact without the need for more than finger or hand pressure.

adhesive, room-temperature setting. An adhesive that sets in the temperature range from 68° to 86°F (20° to 30°C).

adhesive, solvent. An adhesive having a volatile organic liquid as a vehicle. This term excludes water-based adhesives. (1)

adhesive, solvent activated. A dry adhesive or adherend that is rendered tacky just prior to use by application of a solvent (3).

adhesive, structural. An adhesive of proven reliability in engineering structural applications in which the bond can be stressed to a high proportion of its maximum failing load for long periods without failure. (3)

adhesive, two-component. An adhesive supplied in two parts which are mixed before application. (2) Such adhesives usually cure at room temperature.

adhesive, warm-setting. A term that is sometimes used as a synonym for intermediate-temperature-setting adhesive (q.v.). (1)

## MIL-HDBK-691B

amylaceous, adj. - Pertaining to, or of, the nature of starch; starchy. (1)

assembly. (for adhesive). A group of materials or parts, including adhesive, which has been placed together for bonding, or which has been bonded together. (1)(3)

autoclave. A closed container which provides controlled heat and pressure conditions. (2)

B-stage. An intermediate stage in the reaction of certain thermosetting resins in which the material softens when heated to a rubbery state and swells when in contact with certain liquids, but may not entirely fuse or dissolve in some of the solvents which will dissolve resins in the A-stage. The resin in an uncured thermosetting adhesive is usually in this stage. Sometimes referred to as Resitol. (1)(2)

backing. The flexible supporting material for an adhesive. Pressure-sensitive adhesives are commonly backed with paper, plastic films, fabric, or metal foil; heat-curing thermosetting adhesives are often supported on glass-cloth backing.

bag molding (blanket molding). A method of molding or bonding involving the application of fluid pressure, usually by means of air, steam, water or vacuum, to a flexible cover which, sometimes, in conjunction with the rigid die, completely encloses the material to be bonded.(1)

bag, vacuum. A flexible bag by which pressure may be applied to an assembly inside the bag by means of evacuation of the bag. (3)

binder. A component of an adhesive composition that is primarily responsible for the adhesive forces which hold two bodies together.

bite, n. The penetration or dissolution of adherend surfaces by an adhesive. (2)

body. The consistency of an adhesive which is a function of viscosity, plasticity, and rheological factors. (2)

bond, v. The union or joining of materials by adhesives. (1, modified)

bond line. See glue line.

bond strength. The unit load (force) supplied in tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly, with failure occurring in or near the plane of the bond (the interface). The term adherence (q.v.) is frequently used in place of bond strength. (1, modified)

bond, structural. See structural bond.

## MIL-HDBK-691B

C-stage. The final stage in the reaction of certain thermosetting resins in which the material is relatively insoluble and infusible. Certain thermosetting resins in a fully cured adhesive layer are in this stage. Sometimes referred to as Resite. (1)

catalyst. A substance that markedly speeds up the cure of an adhesive when added in minor quantity, as compared to the amounts of the primary reactants.  
(1) Material which promotes cross linking in a polymer or accelerates drying.  
(2)

cement, n. (See adhesive and solvent cement). A synonym for adhesive.

cement, v. To bond with a cement.

cohesion. The state in which the particles of a single substance are held together by primary- or secondary-valence forces. In adhesives, cohesion is the state in which the particles of the adhesive or adherend are held together. (1)

collagen. The protein derived from bone and skin used to prepare animal glue and gelatin. (2)

colophony. The resin obtained from various species of pine trees. (2)

contact bonding. The deposition of cohesive materials on both adherend surfaces and their assembly under pressure. (2)

copolymer. See polymer.

copolymerization. See polymerization.

core. The honeycomb structure used in sandwich-panel construction.

corrosion. The chemical reaction between the adhesive or contamination and the adherend surfaces, due to reactive components in the adhesive film, leading to deterioration of the bond strength. (2)

coverage. The spreading power of an adhesive over the surface area of the adherend. (2, modified)

cross-linking (crosslinking). The union of adjacent molecules of uncured adhesive (often existing as long polymer chains) by catalytic or curing agents. (2)

cure, v. To change the physical properties of an adhesive, usually by chemical reaction, which may be condensation, polymerization, vulcanization, or crosslinking. Such change is usually accomplished by the action of heat and catalyst, alone or in combination, with or without pressure. (1, modified)

cure (curing) temperature. The temperature to which an adhesive or an assembly is subjected to cure the adhesive. (2)

## MIL-HDBK-691B

cure (curing) time. The period of time necessary for an adhesive or an assembly to cure under specified conditions of temperature, or pressure, or both. (2)

curing agent (hardener). A substance or mixture of substances added to an adhesive to promote or control the curing reaction. An agent which does not enter into the reaction is known as a catalytic hardener or catalyst. A reactive curing agent or hardener is generally used in much greater amounts than a catalyst, and actually enters into the reaction. (5)

degrease. To remove oil and grease from adherend surfaces. (2)

dextrine. A water-based product derived from the acidification and/or roasting of starch. (2)

dielectric curing. The use of a high-frequency electric field through a joint to cure a synthetic thermosetting adhesive. A curing process for wood and other nonconductive joint materials.

diluent. A liquid additive whose sole function is to reduce the concentration of solids and the viscosity of an adhesive composition.

diluent, reactive. A low-viscosity liquid added to a high-viscosity solvent-free thermosetting adhesive which reacts chemically with the adhesive during curing. The advantage of lowered viscosity is gained with minimum loss of other properties. (3)

doctor roll. A roller mechanism that revolves at a different surface speed, in a direction opposite to that of the spreader roll, resulting in a wiping action to control the amount of adhesive supplied to the spreader roll. (1)(2)

dry, v. To change the physical state of an adhesive or an adherend by the loss of solvent constituents by evaporation, or absorption, or both. (1)

elasticity, modulus of. The ratio of stress to strain in elastically deformed material. (2)

elastomer. A macromolecular material which, at room temperature, is capable of recovering substantially in size and shape after removal of deforming force. (1)

extender. A substance, generally having some adhesive action, added to an adhesive to reduce the amount of the primary binder required per unit area. (1)

failure, adherend. Joint failure by cohesive failure of the adherend. (2)

failure, adhesive. Rupture of an adhesive bond at the interface between the adhesive and adherend. (1, modified)

failure, cohesive. Rupture of an adhesive bond in such a way that the separation appears to be within the adhesive. (1, modified)

## MIL-HDBK-691B

failure, contact. The failure of an adhesive joint as a result of incomplete contact during assembly, between adherend and adhesive surfaces or between adhesive surfaces. (2)

faying surface. The surface of an adherend which makes contact with another adherend. (2)

feathering. The tapering of an adherend on one side to form a wedge section, as used in a scarf joint. (2)

filler. A relatively nonadhesive substance added to an adhesive to improve the working properties, permanence, strength, or other qualities. (1)

fillet. That portion of an adhesive which fills the corner or angle formed where two adherends are joined. (1) The term for junction of the outer skin and inner core in honeycomb assemblies. (2)

glue, n. Originally a hard gelatin obtained from hides, tendons, cartilage, bones, etc. of animals. Also, an adhesive prepared from this substance by heating with water. Through general use the term is now synonymous with the term "adhesive." (1) The term is most commonly used for wood adhesives, however.

glue line (bond line). The layer of adhesive which attaches two adherends. (1) The interface between an adhesive and an adherend. (3)

green strength. The ability of an adhesive to hold two surfaces together when brought into contact and before the adhesive develops its ultimate bond properties when fully cured. (6)

gum. Any of a class of colloidal substances exuded by, or prepared from plants. Sticky when moist, composed of complex carbohydrates and organic acids which are soluble or swell in water. (1)

hardener. A substance or mixture of substances added to an adhesive to promote or control the curing reaction by taking part in it by catalysis or crosslinking.

heat reactivation. The use of heat to effect adhesive activity, e.g., hot-melt adhesive; completion of the curing process of a B-staged resin. (2)

honeycomb core. A sheet material, which may be metal, foamed into cells (usually hexagonal) and used for sandwich construction in structural assemblies, especially in aircraft construction. (2, modified)

inhibitor. A substance that slows down chemical reaction. Inhibitors are sometimes used in certain adhesives to prolong storage or working life. (1)

interface. The contact area between adherend and adhesive surfaces. (2)

jig. A former used to hold a bonded assembly until the adhesive has cured.



## MIL-HDBK-691B

joint. The location at which two adherends are held together with a layer of adhesive. (1)

joint, butt. A joint made by bonding two surfaces that are perpendicular to the main surface of the adherends. (3)

joint, lap. A joint made by placing one adherend partly over another and bonding together the portions of the adherends. Double-lap joints involve the overlapping by opposing faces of one adherend. (2)

joint, scarf. A joint made by cutting away similar segments of two adherends at an angle less than 45 degrees to the major axis of two adherends and bonding the adherends with the cut areas fitted together to be coplanar. (1) (3)

joint, starved. A joint that has an insufficient amount of adhesive to produce a satisfactory bond. This condition may result from too thin a spread to fill the gap between the adherends, excessive penetration of the adhesive into the adherend (when porous), too short an assembly time, or the use of excessive pressure. (1, modified)

laminate, n. A product made by bonding together two or more layers of material or materials. (1)

laminate, v. To unite layers of material with adhesive. (1)

laminate, cross, n. A laminate in which some of the layers of material are oriented at right angles to the remaining layers with respect to the grain or strongest direction in tension. (1, modified)

laminate, parallel, n. A laminate in which the grain of all layers of material are oriented approximately parallel to each other. (2)

legging. The drawing of filaments or strings when adhesive bonded substrates are separated. (1)

matrix. The part of an adhesive which surrounds or engulfs embedded filler or reinforcing particles and filaments. (1)

modifier. Any chemically inert ingredient added to an adhesive formulation that changes its properties. (1)

modulus. See elasticity, modulus of.

monomer. A relatively simple compound which can react to form a polymer. (1)

mucilage. An adhesive prepared from a gum and water. Also, in a more general sense, a liquid adhesive which has a low order of bonding strength. (1)

Newtonian fluid. A fluid in which the shearing rate is directly proportional to the applied torque. (2)

novalak. A phenolic-aldehydic resin that, unless a source of methylene groups is added, remains permanently thermoplastic. (1)

## MIL-HDBK-691B

open time. See open assembly time under time, assembly.

paste, n. An adhesive composition having a characteristic plastic-type consistency, that is, a high order of yield value, such as that of an adhesive prepared by heating mixture of starch and water and subsequently cooling the hydrolyzed product. (1, modified)

penetration. The passage of an adhesive into an adherend. (2)

permanence. The resistance of an adhesive bond to deteriorating influences. (1)

plasticity. A property of adhesives that allows the material to be deformed continuously and permanently without rupture upon the application of a force that exceeds the yield value of the material. (1)

plasticizer. A material, such as a high-boiling-point organic solvent, incorporated in an adhesive to increase its flexibility, workability, or distensibility. (1)

polymer. A compound formed by the reaction of simple molecules having functional groups which permit their combination to proceed to higher molecular weights under suitable conditions. (1)

polymerization. A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that in the original substance. When two or more monomers are involved, the process is called copolymerization or heteropolymerization. (1)

porosity. The ability of an adherend to absorb an adhesive. (2)

post cure, v. To expose an adhesive assembly to an additional cure, following the initial cure, for the purpose of modifying specific properties. (1)

post-vulcanization bonding. Conventional adhesive bonding of previously vulcanized elastomeric adherends.

pot life (working life). The period of time during which an adhesive or resin prepared for application after mixing with catalyst, solvent, or other compounding ingredients, remains usable. (1)(3)

prebond treatment. See surface preparation.

pressure-sensitive adhesives (PSA's). Adhesive materials which bond to adherend surfaces at room temperature immediately as low pressure is applied. (3)

primer. A coating applied to a surface of an adherend prior to the application of an adhesive to improve adhesion and/or durability of the bond. (3)

## MIL-HDBK-691B

release agent. An adhesive material which prevents bond formation. (2)

resite. An alternative term for C-stage (q.v.). (1)

resitol. An alternative term for B-stage (q.v.). (1)

resol. An alternative term for A-stage (q.v.). (1)

sagging. Run or flow-off of adhesive from an adherend surface due to application of excess or low viscosity material. (2)

sandwich panel. An assembly composed of metal skins (facings) bonded to both sides of a lightweight core. (2)

sealant. A gap-filling material to prevent excessive absorption of adhesive, or penetration of liquid or gaseous substances. (2)

self-vulcanizing, adj. Pertaining to an adhesive that undergoes vulcanization without the application of heat. (1)

service conditions. The environmental conditions to which a bonded structure is exposed, e.g., heat, cold, humidity, radiation, vibration, etc. (2)

set, v. To convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile constituents. (1) The term is usually used for thermoplastic adhesives, unless a chemical process, such as polymerization, is involved. (7)

shear, tensile. The apparent stress applied to an adhesive in a lap joint. (2)

shelf life. See storage life.

shrinkage. The volume reduction occurring during adhesive curing, sometimes expressed as a percentage volume or linear shrinkage; size reduction of adhesive layer due to solvent loss or catalytic reaction. (2)

slippage. The movement of adherends with respect to each other during the bonding process. (1)

solids content. The percentage by weight of the nonvolatile matter in an adhesive. (1)

solvent bonding. See solvent welding.

solvent cement. An adhesive utilizing an organic solvent as the means of depositing the adhesive constituent. (2)

solvent cementing. See solvent welding.

## MIL-HDBK-691B

solvent reactivation. The application of solvent to a dry adhesive layer to regenerate its wetting properties. (2)

solvent welding (solvent bonding) (solvent cementing). The process of joining articles made of thermoplastic resins by applying a solvent capable of softening the surfaces to be joined, and pressing the softened surfaces together. Adhesion is attained by means of evaporation of the solvent, absorption of the solvent into adjacent material and/or polymerization of the solvent cement. (5)

squeeze-out. Excess adhesive pressed out at the bond line due to pressure applied in the adherends. (1, modified)

stabilizer. An adhesive additive which prevents or minimizes change in properties, e.g., by adherend absorption, demulsification, or rapid chemical reaction.

storage life. The period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use. Sometimes call shelf life. (1) Refrigerated storage often extends storage life considerably.

strength, cleavage. The tensile load expressed in force per unit of width of bond required to cause cleavage separation of a test specimen of unit length. (2)

strength, fatigue. The maximum load that a joint will sustain when subjected to repeated stress application after drying, or after a conditioning period under specified conditions. (2)

strength, impact. Ability of an adhesive material to resist shock by a sudden physical blow directed against it. Impact shock is the transmission of stress to an adhesive interface by sudden vibration or jarring blow of the assembly, measured in work units per unit area. (2)

strength, longitudinal-shear (lap-joint strength). The force necessary to rupture an adhesive joint by means of stress applied parallel to the plane of the bond. (3)

strength, peel. The force per unit width necessary to bring an adhesive to the point of failure and/or to maintain a specified rate of failure by means of a stress applied in a peeling mode. (2)

strength, shear. The resistance of an adhesive joint to shearing stresses; the force per unit area sheared, at failure. (2)

strength, tensile. The resistance of an adhesive joint to tensile stress; the force per unit area under tension at failure. (2)

structural adhesive. See adhesive, structural and structural bond

## MIL-HDBK-691B

structural bond. A bond which stresses the adherend to the yield point, thereby taking full advantage of the strength of the adherend. On the basis of this definition, a dextrin adhesive used with paper (e.g., postage stamps, envelopes, etc.) and which causes failure of the paper, forms a structural bond. The stronger the adherend, the greater the demands placed on the adhesive. Thus, few adhesives qualify as "structural" for metals. A further requirement for a structural adhesive is that it be able to stress the adherend to its yield point after exposure to its intended environment. (8)

substrate. A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend, q.v. (1)

surface preparation (surface treatment). A physical, or chemical preparation, or both, of an adherend to render it suitable for adhesive joining. (1) The term prebond treatment is sometimes used, but is deprecated. (2)

tack. The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure. (1)

tack, aggressive. See tack, dry.

tack dry, n. The property of certain adhesives, particularly nonvulcanizing rubber adhesives, to adhere on contact to themselves at some stage in the evaporation of volatile constituents, even though they seem dry to the touch. Sometimes called aggressive tack. (1) (3).

tack-dry (tacky-dry), adj. The state of an adhesive which has lost sufficient volatiles (by evaporation or absorption into the adherend) to leave it in the required sticky (tacky) condition. (3)

tackifier. An additive intended to improve the stickiness of a cast adhesive film; usually a constituent of rubber based and synthetic-resin adhesives. (2)

tack range (tack stage). The period of time in which an adhesive will remain in the tacky-dry condition after application to an adherend under specified conditions of temperature and humidity. (1) (2)

tape. A film form of adhesive which may be supported on carrier material. (2)

temperature, curing. The temperature to which an adhesive or an assembly is subjected to cure the adhesive. The temperature attained by the adhesive in the process of curing it (adhesive curing temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly curing temperature). (1)

## MIL-HDBK-691B

temperature, drying. The temperature to which an adhesive on an adherend, or in an assembly, or the assembly itself, is subjected to dry the adhesive. The temperature attained by the adhesive in the process of drying it (adhesive drying temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly drying temperature). (1)

temperature, setting. The temperature to which an adhesive assembly is subjected to set the adhesive. The temperature attained by the adhesive in the process of setting it (adhesive setting temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly setting temperature). (1)

tests, destructive. Tests involving the destruction of assemblies in order to evaluate the maximum performance of the adhesive bond. (2)

tests, nondestructive. Inspection tests for the evaluation of bond quality without damaging the assembly, e.g., ultrasonics, visual inspection, etc. (2)

thermoplastic, adj. Capable of being repeatedly softened by heat and hardened by cooling. (1)

thermoset (thermosetting), adj. Having the property of undergoing a chemical reaction by the action of heat, catalysis, ultraviolet light, etc. leading to a relatively infusible state. (1, modified)

thinner, n. A volatile liquid added to an adhesive to modify the consistency or other properties. (1) (also called diluent)

thixotropic, adj. A term applied to materials having the property of thixotropy (q.v.).

thixotropy. A property of materials which display a reduction in viscosity when a shearing action is applied. Some adhesive systems become thinner in consistency on agitation and thicker again when left undisturbed. (2)

time, assembly. The time interval between the spreading of the adhesive on the adherend and the application of pressure or heat, or both, to the assembly. For assemblies involving multiple layers or parts, the assembly time begins with the spreading of the adhesive on the first adherend. Assembly time is the sum of the open and closed assembly times. Open assembly time is the time interval between the spreading of the adhesive on the adherend and the completion of the assembly of the parts for bonding. During this period the adhesive-coated surfaces are exposed to the air before being brought into contact. Closed assembly time is the time interval between completion of assembly of the parts for bonding and the application of pressure or heat, or both, to cure or set the adhesive. (1, modified) (3)

time, curing. The period of time during which an assembly is subjected to heat or pressure, or both, to cure the adhesive. Further cure may take place after removal of the assembly from the conditions of heat, or pressure, or both. (1)



## MIL-HDBK-691B

time, drying. The period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat, or pressure, or both. (1)

time, joint-conditioning. The time interval between the removal of the joint from the conditions of heat, or pressure, or both, used to accomplish bonding and the attainment of approximately maximum bond strength. Sometimes called joint aging time. (1)

time, setting. The period of time during which an assembly is subjected to heat, or pressure, or both, to set the adhesive. (1)

vehicle. The carrier medium (liquid) for an adhesive material which improves its ease of application to adherends; solvent component of an adhesive. (2)

viscosity. A measure of the resistance to flow of a liquid. For Newtonian liquids, the shear rate is proportional to the shear stress between laminae of moving fluid; for non-Newtonian liquids it is not proportional. (2)

vulcanization. A chemical reaction in which the physical properties of a rubber are changed in the direction of decreased plastic flow, less surface tackiness, and increased tensile strength by reacting it with sulfur or other suitable agents. (1)

weldbonding. A process in which a joint is formed by spot welding through an uncured adhesive bond line, or by flowing an adhesive into a spot-welded joint. (4)

wetting. A surface is said to be completely wet by a liquid if the contact angle is zero, and incompletely wet if it is a finite angle. Surfaces are commonly regarded as unwettable if the angle exceeds 90 degrees. (2)

working life. See pot life.

## MIL-HDBK-691B

## REFERENCES

1. American Society for Testing and Materials (ASTM), ASTM D907-82, "Standard Definitions of Terms Relating to Adhesives", 1982, published in volume 15.06 (Adhesives), 1984 Annual Book of ASTM Standards.
2. Shields, J., ADHESIVES HANDBOOK, 2nd Edition, Newnes-Butterworth, London, 1976 (available from Butterworths, Woburn, MA 01801).
3. International Organization for Standardization (ISO), International Standard (IS) 6354, "Adhesives - Vocabulary", First Edition, 1982. Available from American National Standards Institute (ANSI), 1430 Broadway, NYC, NY 10018.
4. Rodgson, M. E., Chapter 13, "Pressure Sensitive Adhesives and Their Applications", ADHESION 3, (K.W. Allen, Ed.), Applied Science Publishers, Ltd. Available from the International Ideas, Inc., Philadelphia, PA.
5. Whittington, L.R., WHITTINGTON'S DICTIONARY OF PLASTICS, 2nd Edition, Technomic Publishing Co., Westport, CT, 1978. (sponsored by the Society of Plastics Engineers)
6. Synthetic Surfaces, Inc., Scotch Plains, NJ, "The Importance of Green Strength in Adhesive Selection", Tech Sheet 472A, 1982.
7. Rayner, C.A.A., Chapter 4, "Synthetic Organic Adhesives", ADHESION AND ADHESIVES, 2nd Edition, Vol. 1 - Adhesives, (R. Houwink and G. Salomon, eds.), Elsevier Publishing Co., 1965.
8. DeLollis, NJ, ADHESIVES, ADHERENDS, ADHESION, Robert E. Krieger Publishing Co., Huntington, NY, 1980.
9. Bolger, J.C., "Single-Component Epoxy Adhesives for Sheet Steel and Aluminum Bonding", pp 369-387 in APPLIED POLYMER SYMPOSIA No. 32, Durability of Adhesive Bonded Structures, 1977, (M.J. Bodnar, Ed.). Paper presented at Symposium at Picatinny Arsenal, Dover, NJ, Oct 27-29, 1976.

MIL-HDBK-691B

NOTES

Subject term (key word) listing

Adherends  
Adhesives  
Adhesive Bonding  
Durability  
Handbook  
Joint Design  
Specifications  
Surface Preparation  
Test Methods

Custodians:

Army -- MR  
Navy -- AS  
Air Force -- 99

Preparing activity:

Army -- MR  
Project No. 8040-0347

Review activities:

Army -- ME, GL, MI  
Navy -- AS, SH  
Air Force -- 20

User activities:

Army -- AT, MR  
Navy -- YD

(WP# ID-7411A/DISC-0038w. FOR MTL USE ONLY)