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MIL-HDBK-132A

9 May 1984

SUPERSEDING

MIL-HDBK-132(MR)

31 October 1960

MILITARY HANDBOOK

PROTECTIVE FINISHES
FOR METAL AND WOOD SURFACES



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MIL-HDBK-132A

DEPARTMENT OF DEFENSE
WASHINGTON, DC 20301

Protective Finishes for Metal and Wood Surfaces

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PREFACE

The primary object of this handbook is to provide a working knowledge of protective finishes, both inorganic and organic, as used by the Department of Defense for equipment and ordnance. The handbook is not intended to be an exhaustive treatise on the subject, but rather to furnish detailed information on the protective finish system and procedures that have proved satisfactory in service. It is intended to supplement, but not replace, various specifications and standards for protective finishes used by the military. The subject matter is about equally divided between inorganic and organic finishes. The words "paint" and "painting" are used broadly in the handbook to include varnishes, lacquers and sealers. It is hoped that the information contained herein will aid the material conservation program by promoting the use of less critical materials protected with suitable finishes.

In the preparation of the handbook, the following sources were freely consulted:

"Definition of Terms Relating to Paint, Varnish, Lacquer and Related Materials" and various product specifications, American Society for Testing and Materials

"Painting of Naval Ordnance Equipments", Bureau of Ordnance

"Paint Manual - New Construction and Equipment", Corps of Engineers

"Organic Coatings, Properties, Selection, Use", Building Science Series 7, U.S. Department of Commerce

"Paint Manual", Bureau of Reclamation

"Steel Structures Painting Manual", Steel Structures Painting Council

"Phosphating Materials and Process", Technical Report 54-2906, Rock Island Arsenal Laboratory

"Cleaning and Black Finishing of Ferrous Metals", TM9-1861, Department of the Army

"Phosphatizing and Black Oxide Coating of Ferrous Metals", MIL-HDBK-205, Department of Defense

Various Military and Federal Specifications and Standards

"Paints and Protective Coatings"

Departments of the Army, the Navy, and the Air Force
(Army TM-5-618, NAVFAC MO-110, Air Force AFM 85-3)

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GENERAL REFERENCES

Federal and Military specifications and standards are government publications and are available from the Naval Publication and Forms Center, 5801 Tabor Avenue, Philadelphia, PA 19120.

Aerospace Material Specifications are available from the Society of Automotive Engineers, Inc., 400 Commonwealth Drive, Warrendale, PA 15096.

ASTM specifications and standards may be obtained from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

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1. INTRODUCTION

1.1 The usual metals of construction and most of their alloys are subject to corrosion when exposed to the atmosphere. Clean surfaces of such metals react chemically with the oxygen of the air, especially under moist or humid conditions. The properties of the corrosion products vary according to inherent characteristics of the metals from which they are formed.

1.2 The noble metals such as gold and platinum do not react with atmospheric elements and present a non-corroding surface resistant to even more highly corrosive media. Only the more active acids and alkalies are of any appreciable consequence in attacking these metals. However, silver, one of the noble metals, does tarnish in the presence of hydrogen sulfide and moisture.

1.3 Oxide coatings formed on the corrosion resistant metals and alloys, such as the stainless steels, titanium, chromium, aluminum, nickel, copper, bronze and tin, are little, or not at all, changed by exposure to moisture. Such coatings tend to protect underlying metal because of their chemical stability and continuity, the latter being of importance in excluding air from the metal.

1.4 Metals, such as most ferrous alloys, magnesium, cadmium and zinc, form less stable compounds upon atmospheric exposure. Rust (on ferrous metals) is chemically unstable and, upon continued exposure, affords no protection to the piece on which it forms. Magnesium, cadmium and zinc protect the underlying metal for appreciable periods if the coating is continuous and undamaged. If a naturally formed coating becomes damaged, the exposed area again corrodes. Repeated removal of the products of corrosion is followed by renewed corrosion, which continues until the metal has been consumed.

1.5 All metals possess different electric potentials, a circumstance that promotes attack on one metal by the other when dissimilar metal couples are exposed. The reaction is called galvanic corrosion. Elementary facts related thereto are generally well known. Lack of attention, however, to obvious ones costs huge sums in replacement of corroded metals.

1.6 Production of metallic articles is accompanied by huge and mounting costs of mining, transportation, refining and fabrication of basic forms. As all but special alloys and the noble metals are subject to some form of corrosive attack, it becomes increasingly important in view of dwindling natural resources to conserve present supplies by adequate means. Protection may be obtained with paint and electrodeposited metal coatings.

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1.7 Petroleum oils and greases, when applied to clean metallic surfaces, serve as temporary barriers to the atmosphere as long as they are unchanged by chemical reactions often occurring between them and underlying metals or minute amounts of corrosion products. Oils and greases are usually applied to provide protection during storage and shipping. Because of their lack of durability and their incompatibility with more durable coatings, oily coatings are seldom, if ever, employed as final protective coatings and must be removed prior to application of the latter. A supplementary rust-preventing oil is sometimes the final coating, such as in the case of conversion coatings for iron and steel (see 4.4.1). MIL-C-16173 specifies this type of corrosion preventive compound and is intended for use in extended undercover and outdoor protection of machinery, instruments, bearings and other corrodible surfaces. Such a coating may be considered an exception to the above lack of durability statement afforded to oily coatings.

1.8 Heavy phosphate coatings on steel, with a supplementary coating of oil, may also be considered an exception to the above statement. Such coatings, however, lack the durability of the more costly metallic or paint type coatings. Phosphate coatings on ferrous metals (and corresponding coatings and other treatments on other metals) tend to protect the underlying metal. Chromate conversion coatings are produced on various metals and their alloys such as aluminum, cadmium, copper, magnesium, silver and zinc. This treatment is intended for use as a final finish for the metal surface to inhibit corrosion and retard the formation of corrosion products. The films can be modified from thin, clear-bright and blue-bright to the thicker, yellow iridescent, to the heaviest brown, olive drab and black films. The darker colored films usually give better corrosion protection. With the exception of anodic coatings on aluminum, most treatments do not supply adequate protection for long exposure unless given supplementary coatings such as oil or paint.

1.9 Usually, the corrosion resistance imparted by a "system" consisting of a phosphate or similar treatment, plus a supplementary coating, far exceeds the sum of protection given by treatment or coating independently. For example, in salt spray tests, a phosphate treatment alone protected clean steel for four hours. A prime and finish coat of paint protected clean untreated steel from salt spray for 200 hours. Combining the phosphate treatment with the same paint system protected the steel for 536 hours. This synergistic effect varies to some extent with the metal, its rate of corrosion, the quality of the bond of the phosphate coating with the underlying metal, compatibility of treatment with the paint and quality of the paint.

1.10 Physical and mechanical performances of usual metals of construction are quite well defined. A reasonable amount of reliance may be placed on them, as long as they remain free from corrosion and retain original contours or dimensions. Unfortunately, corrosion disturbs physical and mechanical performances, usually reducing their value. In view of this basic fact, every effort must be exerted to protect original dimensions to assure operations within design limits. Basic design, all-important in building of equipment, becomes of little value for long-term use when protective measures are ignored or neglected.

1.11 The foregoing brief discussion emphasizes the necessity for application of adequate protective measures to preserve structural materials and equipment in original shapes and forms free from variables introduced by corrosion.

2. CLEANING MATERIALS AND PROCESSES

2.1 Rust and corrosion removal. Corrosion is described basically as the destruction of the metallic state of a metal or, more commonly, the conversion of a metal into an oxide or a hydrated form of the oxide. Iron and steel are the most common metals used in industry today for structural purposes. The high pollutant content of many atmospheres directly affects the performance of these metals. It is well known that the rate of rusting varies according to the degree of pollutants (namely sulfur dioxide) present in the air. The processes occurring in the corrosion reaction can thus be represented in the following way: The iron absorbs sulfur dioxide from the dissolved state in the atmosphere and reacts with it to form ferrous sulfate. Both substances are then oxidized by the air to form ferric oxide (Fe_2O_3) and sulfuric acid. Next, the free sulfuric acid attacks the iron to form ferrous sulfate which, with the oxygen in the air, forms rust and free sulfuric acid. In this way, the presence of sulfur and its oxides in an atmosphere of pollutants aids in a regenerative process of ferrous sulfate and sulfuric acid formation as a catalyst in a continuous rusting action.

Three distinct groups of reactions are involved in the corrosion process, where sulfur oxides and water are present as catalysts. Initially, rust will appear on the surface of the iron or steel above a certain relative humidity. The oxides of sulfur are then absorbed by the rusty iron. In the second stage, the oxides of sulfur, iron and oxygen combine to form the ferrous sulfate. The third stage is the actual rusting, which involves the conversion of ferrous sulfate into hydrated iron oxide with the liberation of free sulfuric acid and regeneration of ferrous sulfate.

In most instances, corrosion attack starts prior to cleaning or removal of soils and other contaminants. Rust and corrosion is removed by the following mechanical methods: hand tools such as sanders, flame cleaning and sand blasting. Solvent cleaning is accomplished by hand wiping with aliphatic solvents and vapor degreasing. Corrosion products can further be removed by soaking parts in hot alkaline cleaning solutions, electrocleaning, spray washing and chemical acid pickles.

2.1.1 General cleaning. Adequate cleaning of metals is the first step in preparing them for all finishing operations. All foreign substances, regardless of origin or nature, must be removed to a degree where the metal surfaces are substantially bare and free from substances tending to interfere with subsequent treatments or operations. Most metals go through one or more of a variety of fabrication or processing operations such as heat treating, forging, casting, rolling, stamping, extruding, polishing and buffing, etc. During these operations the metals pick up such soils as oil, grease, rust, heat-scale, smut, buffing compounds, drawing compounds, embedded particles, fingermarks and shop dirt. These foreign materials must be removed before application of a finish or coating. If not removed, a defective or non-uniform coating or one that adheres poorly to the surface may result.

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2.2 Foreign material classification. Dirt that accumulates on a surface may be placed in three classes: greasy soils, foreign particles and basis metal compounds or scale.

2.2.1 Greasy soils. Greasy soils include rust preventive compounds, mineral and fatty cutting oils. These greasy soils are further subdivided into those that are saponifiable (react with alkalies to form soaps) and those that are unsaponifiable.

2.2.2 Foreign particles. Foreign particles include abrasives in polishing compounds (aluminum oxide, silica, carborundum, etc.), salts, graphite and embedded sand and steel from air blasting operations.

2.2.3 Basis metal compounds or scale. Basis metal compounds or scale are usually oxides left on the surface as a result of casting, forging, rolling or heat treatment. Chlorides, sulfides and sulfates of the basis metal also fall into this category.

2.3 Clean surface. A clean metal surface means that the bare, basis metal is not only free from dirt, but also has not been changed by controlled treatments into oxides, phosphates or other compounds. In the finishing field, the cleanliness of a surface may be described as generally clean, grease free, mechanically clean and chemically clean.

2.3.1 Generally clean surface. A generally clean surface has had the major portion of its dirt removed, but a trace may still remain. This degree of cleanliness is obtained by mechanical cleaning and by pickling.

2.3.2 Grease free surface. A grease free surface is one that is free from oil and grease, but retains scale, rust and foreign matter. This degree of cleanliness is obtained with the aid of organic solvents.

2.3.3 Mechanically clean surface. A mechanically clean surface is one which is free from stressed, torn, smeared or disturbed metal. This degree of cleanliness is achieved by mechanical grinding or abrasion, chemical pickling or polishing and electropolishing.

2.3.4 Chemically clean surface. A chemically clean surface is free of every type of foreign matter and is the cleanest of all four types. This degree of cleanliness is obtained by a series of cleaning operations and rinses, which usually include use of alkaline compounds, wetting agents and acids. Treatments involve simple immersion in solutions or electrochemical action.

Selecting a cleaning process for a surface requires consideration of the following factors: (a) nature and type of surface dirt; (b) type of base metal (some metals may be attacked by the cleaning agents); (c) size and shape and strength or fragility of the part and simplicity or intricacy of surface; (d) operations to be performed after cleaning; (e) special precautions such as those to preserve dimensional tolerances; and (f) cost.

2.4 Cleaning methods. The following paragraphs discuss methods that are commonly used by the military. These methods have been broken down into mechanical, chemical and electrochemical.

2.5 Mechanical cleaning methods. These methods include grinding, brushing, abrasive blasting, steam or flame jet cleaning, tumbling, polishing and buffing. A brief description of each method follows.

2.5.1 Grinding. Grinding cleans by abrading away the dirt, usually taking part of the basis metal with it. This method is commonly used to smooth metallic surfaces, but is rarely used solely for cleaning purposes because of its relatively high cost. Besides removing coarse irregularities and leveling of welds, etc., abrasive action is extensively used for gross metal removal in the machining of surfaces or parts to desired shapes. Abrasive action is also employed in polishing, buffing and honing operations. Several different types of grinding machines have been developed for handling different surface contours. These units include surface, cylindrical, external, internal and form grinders.

Grinding is done with power driven wheels, disks or belts; units can be stationary or portable. Wheels consist of abrasive particles bonded together in various shapes such as disks, cones or balls. The reproducibility of manufactured aluminum oxide (Al_2O_3) and silicon carbide (SiC) and their good performance makes them the most commonly used abrasive materials. Other frequently used abrasives include: corundum, emery, silica, diamond, boron nitride and metallic materials. The most commonly used bonding materials are vitrified ceramics (glass or porcelain), phenolic resins, rubber, sodium silicate and shellac. Aluminum oxide wheels can be used for grinding most metals and many nonmetals; they are especially suited for grinding the high strength materials, such as steels of all types. Silicon-carbide wheels are used generally for grinding lower strength materials such as cast iron, nonferrous metals (brass, aluminum) and nonmetals.

Abrasive belts consist of a flexible backing to which abrasive particles are bonded with an adhesive. The backing may be paper, cloth, vulcanized fibers or a combination of these materials. The abrasives most commonly used are aluminum oxide, silicon carbide, flint and emery. Hide glue, phenolic resins and synthetic varnish are the most commonly used adhesives. Abrasive belts are generally used for lighter work than are grinding wheels.

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2.5.2 Brushing. Brushing (sometimes called wire brushing), power brushing or scratch brushing is an abrasive operation performed with power driven wire or nonmetallic fiberfilled rotary brushes. Power driven brushes are extensively used for cleaning, deburring, edge blending and surface finishing of metals. The brush fill material is generally arranged in radial (both narrow and wide faced) or cup-like designs. The fill material can be straight wire, twisted wire, crimped wire or natural or synthetic fibers. By using different types of brushes and various kinds, length and gages of wire, fibers or hair, a wide range of abrasive action is possible. Steel wire is generally used for coarse finishing operations requiring heavy abrasion. Moderate abrasion is achieved with soft, fine wire made of brass or nickel-silver alloy. Mild abrasive action needed for fine finishing usually requires the use of nonmetallic brushes, such as Tampico (hemp) fiber, horse hair or other bristles.

Dry wire brushing is used for the removal of rust, scale, oxide films, excess weld metal, paint and other contaminants from metal surfaces. Wire brushing is particularly suited for removing tenacious scale, dirt, embedded sand and paint from surfaces where difficulty in removal might be encountered with chemical methods. With abrasive or polishing compounds applied to either wires or fibers, power brushing can be employed for polishing surfaces, as well as removing burrs and rounding edges on metal parts.

Almost any part that can be easily handled by the operator and does not have precise dimensions may be wire brushed. However, some skill on the part of an operator is required, as uneven removal of metal may easily ruin the part. Wire brushing may be used on most types of steel or iron. With stainless steel, wire particles that may become embedded in the surface may later corrode, giving the effect of surface staining or the appearance of poor corrosion resistance. Stainless steel brushes avoid this problem. These remarks apply as well to aluminum. When wire brushes are used on magnesium, close control of dust is necessary because of the explosive nature of magnesium dust. Also pickup of metal from the brush may cause galvanic corrosion. For best results, a Tampico fiber or stainless steel brush should be used on magnesium parts.

2.5.3 Abrasive blasting. Abrasive blast cleaning involves the forceful direction of abrasive particles at high velocity against metal surfaces to remove contaminants or to condition the surfaces for subsequent finishing. Abrasive blasting is performed to remove dirt, rust, oxide scales or burrs or to roughen the surface in preparation for subsequent paint or other coatings. The abrasive materials may consist of cast iron or steel grit, cast iron or steel shot, cut wire, aluminum oxide, silicon carbide, sand, ground quartz, glass beads, walnut shells, corn cobs or rice hulls. The particles may be propelled against the workpiece by entrainment in a stream of air or liquid or by centrifugal force. The effects of abrasive blasting on surface finishes depend on the type and hardness of the abrasive, particle size of the abrasive, velocity at impact and angle of impact with the part surface.

There are two basic types of dry blasting, namely: (1) mechanical (or airless) blasting in which the abrasive particles are propelled by means of a power driven, rapidly rotating, bladed wheel; and (2) air blasting in which the abrasive is propelled through a nozzle by compressed air. Of the two methods, mechanical blasting is more widely used because of the generally more rapid removal of surface contaminants and lower overall operating costs. For wet blasting, finer (relative to dry blasting) abrasive particles are suspended in chemically treated water to form a slurry. This slurry, which is continually agitated to prevent settling, is forced by compressed air through one or more nozzles, which are directed against the workpiece to remove surface contaminants. Blast cleaning is conducted in enclosures which contain the abrasive propelling device, tables or other means of holding or manipulating the workpieces and provisions for collection and recycle of the abrasive and control of dusts. Blast cleaning can be done on a piece, batch or continuous basis with manual, semiautomatic or automatic processing and control.

Iron or steel shot or grit are used widely for blast cleaning castings, forgings, stampings, welds and heat treated parts of all shapes and sizes. Blasting with iron or steel abrasive is extensively used on cast iron, carbon and alloy steels and nickel and titanium alloys. To avoid contamination with embedded ferrous particles, nonmetallic abrasives are frequently used on parts of stainless steel, copper, brass, zinc, aluminum, tin or lead. Embedded ferrous particles (if used) may be removed by pickling in acid, but embedment of heavy steel shot in the softer metals may be so deep that excessive pickling would be required to dislodge them.

Although blasting can replace some chemical cleaning methods because the blasted surface is mechanically clean and, in some respects, chemically clean as well, it is not very effective for the removal of viscous and resilient soils such as grease, oil or tar. In addition, these soils will coat the abrasive particles and equipment and eventually disrupt the overall blasting operation. For these reasons, parts coated with grease or other viscous soils should be thoroughly degreased or scrubbed and dried prior to dry blasting operations. Blasting should be avoided for cleaning parts where close dimensional tolerances must be maintained. Thus, blasting has limited use on complex, curved surfaces and on parts with deep crevices, threads or machined surfaces.

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2.5.3.1 Shot peening. Shot peening is a cold working operation accomplished by pelting the metal surface with round metallic shot thrown at a relatively high velocity and under controlled conditions. Although shot peening cleans the surface, it differs from blasting in that the cleaning action is incidental to peening's primary purpose of increasing fatigue strength of parts. Shot peening produces a compressive stress in the outer surface layer of the metal. This compressively stressed layer promotes greater fatigue strength in parts that are subject to repeated bending or twisting forces.

Equipment for shot peening is similar to that used for blast cleaning except for some auxiliary equipment required for providing the better process control needed for shot peening. Cast-steel shot and cast-iron shot are the most widely used media for peening most metals. Glass beads are generally used for peening stainless steels, aluminum, titanium, magnesium and other metals that might be contaminated by steel or iron shot. The glass beads can be used in either dry or wet peening processes. Besides increasing the fatigue strength of parts, shot peening is used to form, straighten or correct the shape of slender parts; to improve the resistance to stress corrosion of metals such as aluminum, brass, stainless steel and magnesium; to overcome porosity; and to workharden surfaces.

Surface cleaning by abrasive blasting is covered by TT-C-490, method I; additional remarks on the process are presented in section 10. Shot peening is covered by MIL-S-13165.

2.5.4 Steam or flame jet cleaning. Cleaning with jets of steam or flames is a suitable method for use on parts too large, heavy or unwieldy to be handled by conventional procedures. In steam cleaning a jet of high pressure steam is directed at the surface to physically remove scale and other contaminants from the metal surface. Oily and greasy soils can be removed more readily by adding chemical detergents to the jet stream. With suitable caustic detergent additions to the stream, old paint as well as grease, dirt, soot, etc., can be removed. See section 9 for applicable compounds.

Oxyacetylene flames are directed over localized areas of the metal surface during flame cleaning. The intense heat produced at the surface causes the scale or rust to break away from the basis metal because of different rates of expansion between the scale or rust and the metal. In addition, vaporization of moisture entrapped within the layers of scale and between the scale and metal also helps loosen and remove scale. Flame jets also can be used to remove old paint prior to refinishing. As flame cleaning is only moderately effective in removing oil and grease, it would be better if these soils were removed by some other cleaning method before flame cleaning.

Although jet cleaning is quite expensive, it is an economical method for the removal of the major portion of scale from large unwieldy parts. Properly shaped jets or flame beads can reach crevices or portions of surfaces that are inaccessible to other mechanical cleaning methods. On the other hand, thin sections may warp or buckle and patches of tenacious scale may remain on parts, making further treatment necessary.

2.5.5 Barrel and vibratory finishing. Barrel and vibratory finishing (also sometimes referred to as tumbling or mass finishing operations) involve the rolling or tumbling of parts in rotating barrels or agitated containers for cleaning or conditioning part surfaces. Barrel and vibratory finishing provide controlled methods for processing small or large quantities of parts to polish or improve surface finishes; to remove heat treatment scale, burrs, sharp edges and flash; and to form radii on edges. The barrel and vibratory finishing processes can reduce costs significantly, especially where large numbers of production parts (particularly large numbers of small components) require hand deburring, smoothing or other surface finishing.

The barrel finishing operation involves the controlled rotation of a barrel containing the parts, usually with a lubricating (cushioning) liquid and sometimes with abrasives. Cleaning, deburring, abrading or burnishing (or combinations of these actions) take place, depending on the type of barrel and the media. The important action in tumbling or barrel finishing, i.e., the load sliding on itself or against the abrasive media, is controlled by the speed of rotation and the tilt of the barrel. Finishing barrels are mounted on shafts driven by variable speed motors. The barrels are usually round (with inside baffles), hexagonal or octagonal. The sides are either tapered or parallel. The axis of rotation of the barrels is usually horizontal or at a small angle to the horizontal. Media used in barrel and vibratory finishing operations are: (1) manufactured abrasives (metallic and nonmetallic products); and (2) natural stone and agricultural materials. Typical media include: aluminum oxide, silicon carbide, limestone, silica, hard and soft steel shapes, zinc balls, nylon, ground corn cobs and walnut shells. The lubricants may be water or aqueous solutions containing alkaline detergents, soap-based compounds or acids.

The main advantage of barrel finishing (also vibratory finishing) is low operating costs. Large volumes of small parts can be handled readily and several treatments and rinses can be carried out in the same barrel, thus avoiding transfer of components from one piece of equipment to another. On the other hand, the process has some drawbacks. It rounds sharp edges. Threads may be damaged unless small size media are used. Inside surfaces of small holes and tubing are inaccessible unless small size media are used. Parts with crevices or narrow dimensions may be damaged by the tumbling action in the barrel. Barrel finishing is suitable for most metals; however, close control is required to prevent excessive abrading of nonferrous metals.

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In vibratory finishing, the entire load, including parts, lubricating liquid and abrasive media, is subjected to an oscillating motion or gyrating vibration in specially designed equipment. Some units use combined rotary-vibratory motion. The continuous motion produces a constant scouring or scrubbing action that operates on all portions of the work load simultaneously. The time cycles are shorter and the work loads per unit volume are greater in vibratory finishing than in conventional barrel finishing. For these reasons, vibratory finishing has, during the past 10 to 15 years, replaced conventional barrel finishing operations for many small parts.

2.5.6 Abrasives for polishing. Polishing is the abrading operation which frequently follows grinding and precedes buffing. Both polishing and buffing employ abrasive particles either glued or impregnated in a flexible wheel or belt. Neither of the processes can be considered a true cleaning operation, because removal of contamination is not their primary objective. The purpose of polishing is to remove or smooth out grinding lines, scratches, pits, mold marks, parting lines, tool marks and other surface defects that adversely affect part appearance or performance. In most instances, polishing is used to produce an intermediate smoothing of the surface preparatory to more refined finishing methods. Buffing, which generally follows polishing, further smooths the surface to improve its appearance, but removes very little metal in comparison to polishing. Because there is some resiliency or deformation of the media used for polishing or buffing, neither can be considered a precision machining process, such as grinding.

Polishing wheels vary greatly in diameter, thickness and material depending upon the part that is being processed and the finish and metal removal rate desired. Most wheels are made of woven cotton fabric, canvas, felt or leather disks glued or sewn together or a combination of glued or sewn disks. Cotton fabric wheels are the most commonly used medium for general purpose polishing because of their versatility and their relatively moderate cost. Felt wheels are used for fine finishing of contoured shapes. Leather wheels are employed where fine finishes are desired. Wood wheels covered with leather are normally used for flat surfaces. Abrasives are usually applied to wheels with synthetic adhesives or cements, which have generally replaced the hide glue formerly used. The common abrasives include fused aluminum oxide, silicon carbide and emery. Woven cloth abrasive belts, moving over various types of contact wheels, provide polishing action similar to that achieved with wheels. Part configuration usually dictates whether wheel or belt polishing is employed. Tallow, grease, oil and other lubricants (available for application in stick, paste, liquid or spray forms) are used to extend wheel or belt life, minimize frictional heat and improve surface finishes. The advantage of polishing is chiefly the appearance obtained by smoothing of a surface prior to further finishing.

The limitations of polishing with motorized wheels are: inaccessibility of inside corners, dulling of edges, limited adaptability to changes of surface contour, tendency of polishing wheels to work around projections on a surface (thus not polishing these projections thoroughly), high cost and difficulty of accurately describing a finish (aside from specifying the final abrasive grain size used). Some of these limitations have been overcome by contour fitting polishing heads and automatic techniques. These usually apply to high volume production of a standard item. It is seldom possible to obtain a high polish on cast iron. Warping and discoloration can result from the use of polishing techniques. Stainless steels, being very hard and abrasion resistant, are easily overheated. Greased polishing wheels prevent overheating and possible damage of aluminum. Embedded particles of abrasive may cause trouble in subsequent finishing. Precautions must be taken with magnesium because of the explosive nature of fine magnesium dust. Care must be taken not to wear through thin electroplated deposits.

Buffing operations can be divided into four categories, each category corresponding to a specific final finish. The buffing categories are: satin finishing (satin or brushed surfaces), cut-down buffing (preliminary smoothing), cut and color buffing (smoothing to intermediate luster) and color buffing (high gloss mirror finish). The different actions which take place during buffing are indicative of finishes obtained. These actions are:

- (1) Cutting: abrasion of the metal surface.
- (2) Burnishing: flowing of the metal to fill irregularities in the surface produced by pressure, wheel speed and process heat.
- (3) Chemical action: aided by heat, the reaction of fatty acids (present in some greasy buffing compounds) to form metallic soaps, which aid buffing of certain metals.

Buffing wheels are normally more resilient and softer than those used for polishing. Wheels made of muslin are used most widely for buffing; other materials include wool, flannel and sheepskin. Buffing procedures utilize a wide variety of abrasives including: aluminum oxide, silicon carbide, tripoli, lime, rouge and pumice. For example, aluminum oxide and silicon carbide buffing compositions are used to produce satin finishes on aluminum, steel, stainless steel and brass. Tripoli compositions are used to buff brass, copper, aluminum, zinc, nickel, precious metals and nonmetals. Lime compositions produce a high luster on nickel, copper, brass and plastic when applied in color buffing. Chromium oxide is used for coloring stainless steel and chromium plated parts. Rouge is employed to achieve a high luster on precious metals and glass.

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Buffing compounds are available and extensively used in liquid, paste and bar forms. Buffing compounds in liquid form (suspensions in various emulsions) are sprayed or allowed to flow continuously onto the rotating wheel or belt. Liquid compounds are especially suited for use on semiautomatic or automatic buffing machines. One advantage of liquid compounds over bar or paste compounds is that a constant supply of abrasive is maintained on the wheel, which results in better surface finishes at lower cost.

Buffing enhances the appearance of metals that can be used without a protective finish: for example, stainless steel, chromium and nickel plate and precious metals. For better appearance or added protection, or both, a clear lacquer is sometimes applied to buffed metal. Buffing is a relatively expensive operation.

2.6 Chemical cleaning methods. Chemical cleaning may be subdivided into solvent cleaning, vapor degreasing, alkaline cleaning, acid cleaning, pickling, molten-salt descaling and paint stripping. These general methods are discussed in the paragraphs that follow. For cleaning specific metals see methods discussed in sections 10-14.

2.6.1 Solvent cleaning. Solvent cleaning is one of the oldest and most widely used methods of cleaning metal surfaces. The process removes oil, grease, loose metal chips and other contaminants by use of organic solvents, such as petroleum hydrocarbons, chlorinated hydrocarbons, petroleum-chlorinated hydrocarbon blends, alcohols and coal-tar hydrocarbons. Typical aliphatic petroleum solvents are kerosene, naphtha, Stoddard solvent (colorless refined petroleum product) and mineral spirits. Trichloroethylene, 1,1,1-trichloroethane and perchloroethylene are representative of chlorinated hydrocarbon solvents. Other solvent materials include ethanol, methanol, acetone and toluol. The alcohol, cold-tar and petroleum solvents constitute a serious fire hazard so that they must be stored and used with great care. The chlorinated hydrocarbons are excellent solvents and are nonflammable, but are more toxic and more expensive than the aliphatic petroleums. Mineral spirits and Stoddard solvent are probably the most widely used solvents because of their low cost and their relatively high flash points. Solvents may be used straight, as a diphase mixture or as an emulsion. Wetting agents are often added to the solvent systems to enhance their cleaning performance. The chlorinated solvents have been used in industrial vapor degreasing operations and specialized cleaning applications. The choice of solvent and cleaning method depends on a careful evaluation of the cleaning jobs to be done, the equipment required and the cost per unit cleaned. Solvent choice may be further limited by air pollution control restrictions. Their toxic properties and the methods for handling them safely are well established. Excessive inhalation of solvent vapor and excessive skin contact can easily be avoided by keeping degreasing equipment in good condition, providing adequate ventilation and by using protective clothing and equipment. Leading degreasing solvent manufacturers maintain highly trained technical staffs and complete laboratory facilities to help solvent users maximize solvent service life and plant safety.

Diphase cleaning employs two immiscible liquid phases. One phase consists of water plus water soluble wetting agents, while the second phase (heavier) consists of an organic solvent. Diphase cleaning works by combining the solvent and emulsifying properties of both phases. Emulsion cleaning, which also uses a two phase medium, differs from diphase cleaning in that one phase is dispersed in the other. The two phases consist of water and an organic solvent with suitable emulsifiers added to form an oil-in-water or water-in-oil emulsion.

Straight solvent and diphase treatments are usually carried out at room or slightly above room temperature, while emulsion cleaning is usually done at temperatures ranging from about 140 to 180°F (60 to 82°C). Parts are cleaned by immersion in a tank of the solvent medium, with or without agitation, or by spraying with solvent media. Supplemental hand wiping with a brush or rag may be necessary for removal of tenacious soils from some parts. After solvent cleaning, most parts are dried. The parts are dried at room temperature or by the use of external heat, centrifuging or an absorptive medium.

Ultrasonic action is sometimes used in conjunction with solvent cleaning to promote loosening and removal of tightly adherent soils. The ultrasonic action is especially useful for speeding up and promoting the effective removal of minute particles of insoluble soils, greases, oils and metals from crevices, deep recesses and other difficult to reach areas.

Although solvent cleaning is sometimes used as the final cleaning step, it is more frequently used as a precleaning operation to prepare the metal surfaces for additional processing. For example, emulsion cleaning may be used for precleaning buffed metals, such as zinc-alloy die castings, copper and brass before electroplating. Emulsion cleaning is generally followed by alkaline soak, spray or electrolytic cleaning in the overall electroplating cycle. This is done to remove all traces of the organic solvent and other cleaning by-products from the parts and also to minimize contamination of the electroplating baths.

Solvent cleaning is an effective, safe and economical method for cleaning most metals. Solvents do not normally attack the metal surfaces unless they become contaminated with acids or alkalis. Proprietary stabilizer compounds are added to inhibit the hydrolysis of chlorinated hydrocarbons to prevent the formation of free hydrochloric acid, which may occur in the presence of water. Parts dry readily after solvent cleaning and thus are in good condition for storage or further cleaning or processing. On the other hand, solvent cleaning has the following limitations:

- (1) Solid soils, saponifiable greases and metallic soaps are often not effectively removed.
- (2) A residual oil film may be left on surfaces.

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- (3) With chlorinated hydrocarbons, the presence of zinc, magnesium, or aluminum dust must be avoided as these materials tend to break down the chlorinated solvents with the formation of hydrochloric acid.
- (4) Flammability and toxicity hazards exist with some of the solvents.
- (5) Material costs are higher than those for alkaline cleaning.

An applicable specification for solvent cleaning is TT-C-490, method II. Also see section 9 for other applicable specifications.

2.6.2 Vapor degreasing. Vapor degreasing is a specialized form of solvent cleaning carried out at an elevated temperature with solvent vapors. Equipment includes a metal tank, a heating device for vaporizing the solvent and cooling coils to condense the solvent for return to a boiling sump. Nonflammable hydrocarbons, such as trichloroethylene, perchloroethylene, methylene chloride and 1,1,1-trichloroethane are common solvents for vapor degreasing. Work to be cleaned is lowered or conveyed into the vapor zone. Because the work is cold relative to the solvent vapor, solvent condenses on work surfaces and then runs off and drops back to the bottom of the tank, carrying the dissolved oil, grease and dirt with it. When the work reaches the temperature of the vapors, condensation stops. The cleaned and dried work is then removed from the unit and is ready for the next processing step. Condensed solvent returned to the sump is again heated to boiling to produce distilled vapors to clean more work. The entrained soils in the spent solvent are concentrated in the boiling sump.

The vapor degreasing action of the condensing solvent can be augmented, if necessary, to remove heavy greases or oils and stubborn soils by immersion of the parts in the boiling solvent or by spraying the parts with liquid solvent within the vapor zone. The final step after either of these treatments is vapor phase degreasing.

When very high standards of cleanliness are required and are not attainable with the above mentioned methods of straight vapor degreasing, immersion vapor degreasing or spray vapor degreasing, ultrasonic cleaning is often employed. In most instances, the work is precleaned with one of the above methods and then subjected to ultrasonic treatment in a solvent bath. The high frequency sound waves pass through the solvent and produce rapid agitation and cavitation on the work surface. The ultrasonically produced cavitation promotes rapid removal of strongly adhering soils, as well as the removal of soils from crevices and hard to reach areas of intricately shaped parts.

With use, the concentration of oils, etc., in the solvent boiling sump builds up so that periodic cleanouts of the degreaser unit are necessary. The interval between cleanouts (e.g., weekly, biweekly, monthly, etc.) is governed by the volume of work processed and the amount of soil removed. Where auxiliary distillation is employed, the degreaser cleanout interval can be prolonged several-fold. If no auxiliary still is available, solvent is recovered, using the degreaser boiling sump, by diverting the distilled solvent to a separate tank for temporary storage. The maximum grease or oil concentration that can be achieved with this method is generally about 50-50 oil-solvent mixture by volume. Such a mixture is usually picked up by a scavenger (vendor) for further solvent recovery and disposal of the residual material. By use of an auxiliary still and steam stripping, an oil-solvent mixture containing about 95% oil can be obtained. Such a mixture usually can be disposed of readily to a scavenger handling oily wastes. Because of the substantial savings resulting from reduced degreaser downtime, greater solvent recovery and lower waste volumes, an auxiliary still is advocated in plants processing significant amounts of work (i.e., use more than five or six drums of solvent per month) in their degreasing operations. The same still can service more than one degreaser.

Because of its versatility, vapor degreasing is extensively used in the metal working, electronics and aerospace industries. Properly used, it is considered an economical and safe cleaning method for most metals and alloys. Solvent cleaning using vapor degreasing techniques is covered by TT-C-490, method II.

2.6.3 Alkaline cleaning. Alkaline cleaning, in all of its forms, is the most widely used cleaning method. Alkaline compounds in aqueous solution are very effective for removing organic and water soluble soils, vegetable and animal greases and solid particulates from metal surfaces. Alkaline cleaning is relatively free of operating problems and is considered to be the most economical cleaning method for high production use in electroplating and other metal coating operations.

A good alkaline soak cleaner must be soluble in water; wet the surface of the metal workpieces; wet and penetrate soil; saponify or dissolve soils and greases or emulsify or suspend insoluble or nonsaponifiable oils and greases; prevent formation of calcium and magnesium deposits from hard water; prevent tarnish and corrosion of basis metals; minimize foam; and rinse freely.

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The alkaline baths are usually operated at elevated temperatures ranging from about 150 to 212°F (66 to 100°C) with lower temperatures being employed for cleaning nonferrous alloys. Soak cleaning is sometimes accelerated by installing mechanical or ultrasonic devices in the tanks. More frequently, pressure sprays are adopted when significant speeding up of the alkaline cleaning is required. Electrolytic alkaline cleaning which is often used to supplement soak or spray cleaning is covered in paragraph 2.7.2. To eliminate traces of alkali, the cleaned surface must be thoroughly rinsed or neutralized prior to most subsequent finishing operations. Poor rinsing can cause poor results in subsequent plating or coating operations.

An applicable specification for alkaline cleaning is TT-C-490, method III and method V. The strong alkaline materials such as MIL-C-14460 and MIL-C-46156 are used for light derusting as well as cleaning. MIL-C-14460 materials can also be used as electrolytic alkaline cleaners (see 2.7.2).

2.6.4 Acid cleaning. Acid cleaning is used mostly to remove light organic and inorganic soils from metal surfaces and differs from acid pickling, which uses stronger acids to remove relatively thick scale or oxide. Only relatively light dissolution of basis metal is involved with acid cleaning. Removal of oils and greases depends on organic solvents in the acid cleaning solutions. Acid cleaners are usually composed of mineral or organic acids along with water-miscible solvents, organic wetting agents and detergents. Typical acids include phosphoric, chromic, acetic, citric and tartaric. Representative solvents include ethylene glycol and monobutyl ether. Soils are removed by wetting, emulsification, solubilization and by oxide or metal dissolution. A slight etch is often left on acid cleaned surfaces.

Acid cleaning is performed, either hot or cold, in soak tanks and spray systems. Acid cleaning is not suitable for removing heavy coats of grease, oil, scale and dirt, as a deep etch would result from the long immersion times necessary for thorough cleaning. Acid cleaning is primarily used on ferrous, copper and aluminum alloys. It is seldom used on nickel, magnesium, lead or tin. An applicable specification for acid cleaning is TT-C-490, method VI.

2.6.5 Pickling. The term "pickling" generally refers to the chemical dissolution or removal of scale and oxides from metal surfaces by immersion in acid solutions. Pickling achieves one or more of the following:

- (1) Complete removal of scale by acid treatment alone or after the scale has been conditioned in a molten salt bath or by mechanical treatment.
- (2) Removal of contaminated or damaged surface metal.
- (3) Removal of oxide films.
- (4) Activation of the metal surface for plating or other coating operations by removal of invisible oxide or passivating films.
- (5) Passivation of the metal or alloy surface to provide greater corrosion resistance.

The choice of the pickling acid composition and operating temperature depends on the metal to be pickled, the type of scale to be removed, the type of surface desired after pickling and operating costs. Pickling is readily carried out on sheet, strip, wire, tubing, forgings, castings and fabricated parts. Before pickling, oily and greasy soils should be removed by solvent or alkali cleaning.

Sulfuric and hydrochloric are the two acids most widely used in industry for pickling iron and steel materials. Acid pickling baths may contain inhibitors designed to retard the attack on the basis metal while not significantly decreasing the rate of oxide or scale dissolution. Sulfuric acid solutions are generally heated [e.g., 150 to 212°F (66 to 100°C)] to speed up the pickling rate. Hydrochloric acid solutions, which have significantly higher pickling rates than sulfuric baths for comparable strength solutions, are suitable for use at room temperature as well as at higher temperatures. Phosphoric acid, which is slower than either sulfuric or hydrochloric acid, is used where it is important to obtain a steel surface free from carbonaceous smut. Nitric acid is used in pickling the stainless steels. Hydrofluoric acid is frequently added in small amounts to other acid baths to accelerate the pickling rate, particularly for stainless steels, titanium and nickel alloys; it is also used to remove embedded sand from castings.

Sulfuric acid solutions (alone or with additives such as dichromates) are widely used for removal of scale or oxide from copper and its alloys. These solutions are used because they readily dissolve scale or oxide with little or no attack of the basis metal. Sulfuric acid solutions, in conjunction with an oxidizing agent such as chromic acid, nitric acid or sodium dichromate, are used for tarnish removal or bright dipping of copper alloys. For other nonferrous metals, particularly aluminum and magnesium, many combinations of acids are used. Some of these are chromic, nitric and hydrofluoric, together with certain inorganic salts (see sections on surface preparation for plating, coating or painting of specific metals).

During the past decade, hydrochloric acid has been replacing sulfuric acid pickling at an increasing rate. Some reasons for this change include: (1) hydrochloric acid's faster pickling speed, which lends itself more readily to continuous pickling operations; (2) the lighter and smut free surfaces produced with hydrochloric acid pickling of high carbon steels; (3) the greater availability of relatively low cost, by-product hydrochloric acid from chlorination processes in the chemical industry; and (4) the greater ease with which spent HCl pickle liquors can be disposed of or regenerated.

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A properly controlled pickling bath is generally more efficient for scale, oxide and rust removal than mechanical abrasion because the solution is in contact with all surfaces, regardless of contour. Pickling increases corrosion resistance of metals and alloys by removing contaminants from the surfaces. On the other hand, improperly controlled or prolonged pickling may result in uneven surface attack, pitting or loss of dimensional tolerances on parts. Thin sections and corners of parts are particularly vulnerable to excessive localized metal removal. The smuts formed during pickling of some metals require additional treatment for their removal. Because subsequent seepage of entrapped pickling solutions in holes or crevices of complex shapes can adversely affect plating or other coating operations, it is important that thorough neutralization and rinsing be accomplished on such parts.

Pickling of ferrous metals, particularly high strength steels, can cause hydrogen embrittlement. With parts subject to fluctuating stresses this may lead to performance failure unless adequate measures are taken to provide embrittlement relief (section 7). Accordingly, where metals or alloys are susceptible to hydrogen embrittlement, pickling should be eliminated where possible or held to a minimum. For these metals, mechanical methods of scale or oxide removal should be considered, as they can eliminate or minimize the amount of acid pickling needed. The use of molten-salt descaling baths can greatly reduce the acid pickling requirements and thus also minimize the danger of hydrogen embrittlement.

2.6.6 Molten-salt descaling. During casting, hot rolling, heat treating, forging and other processing or fabricating operations, metals and alloys acquire scale or oxide coatings as well as other contamination. The scales and oxides on refractory metals, titanium alloys, high alloy and stainless steels are generally difficult to remove using acid pickling alone. Accordingly, a molten-bath descaling operation followed by an acid dip is usually employed to clean up these metals and alloys. Molten-bath descaling generally involves the removal of heavy scale or oxide films without appreciable basis metal removal. On the other hand pickling, as indicated earlier, refers to the removal of scale or oxide along with some basis metal dissolution. For the most part, descaling involves the use of caustic (plus other ingredients) in a molten bath to alter, condition, loosen or remove scale. The three principal methods of descaling are: (1) reducing (sodium hydride) process; (2) oxidizing salt process; and (3) electrolytic (oxidizing/reducing) process.

The sodium hydride descaling bath consists of molten sodium hydroxide containing about 1.0 to 2.5% of sodium hydride; the bath is usually operated at temperatures of 700 to 750°F (371 to 399°C). The sodium hydride chemically reduces the scale or oxides to metal or to a lower oxide state. The sodium hydride concentration is maintained within the desired range by reacting metallic sodium with hydrogen or cracked ammonia in a special compartment of the descaling tank. The work to be descaled is immersed in the bath for periods of about 1 to 20 minutes or until the reducing reaction stops. The work is then removed from the bath, allowed to drain for a brief time and then, while still hot, quenched in water. The steam generated during quenching blasts off or mechanically loosens and removes the reduced scale. After quenching, a short acid dip in a sulfuric acid or nitric/hydrofluoric acid solution followed by water rinsing might be required to produce a clean, bright surface. One advantage of the sodium hydride bath over the customary oxidizing salt baths is that it can be used for descaling metals that undergo a change of properties at higher temperatures. Because embrittlement is a potentially serious problem with titanium and its alloys, a modified sodium hydride bath had been developed to decrease hydrogen pickup. The modified bath is basically similar to the conventional bath, except that it is saturated with TiO_2 and contains about 20% sodium carbonate to minimize hydrogen pickup. The modified bath is operated at about 700°F (371°C) with a sodium hydride content of about 0.5 to 1.0%.

When oxidized metal is immersed in the salt bath, the metal and scale are heated rapidly to the bath temperature, thereby enabling the metal oxide to react with the oxidizing salt, forming more readily soluble compounds. When the metal is then water quenched, the thermal shock and formation of steam cause the insoluble constituents of the scale to be loosened and partially spalled off, while solubilized constituents dissolve in water. Oxidizing salt baths, used in conjunction with acid pickling, are extensively employed for descaling refractory metals, stainless steels and other metals. The major constituent of the baths is usually sodium hydroxide with oxidizing salts (e.g., sodium nitrate) and other ingredients added to enhance the descaling action. The purpose of the baths is to alter or condition the scale so that, as in the case of titanium oxide, sodium titanate will be formed. If scale constituents are converted sufficiently by the salt, then the new compounds formed will be more soluble and attacked more readily in sulfuric or nitric acid pickling solutions. Most of the descaling bath compositions in common usage are proprietary.

The operating temperatures for the oxidizing salt bath generally range from about 800 to 1000°F (427 to 538°C) and the part immersion times are usually 1 to 15 minutes. The unequal expansion of the basis metal and the scale that occurs when the part is heated up in the bath causes the scale to crack. The salt can then penetrate the cracks and react with the scale to form oxides or salts that change the physical and chemical nature of the scale, so that it is mechanically loosened or conditioned favorably for subsequent removal in the acid pickling bath.

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The treated parts are allowed to drain for a short time and then, while still hot, are quenched. The steam produced during quenching further removes, loosens or conditions the parts for the acid pickling operations. In some instances with tough scales, it may be necessary to repeat the descaling/pickling cycle one or more times to achieve the degree of surface cleanliness required. During the past few years, proprietary low temperature oxidizing salt descaling baths that operate at about 375 to 425°F (191 to 218°C) have been developed. These baths, originally developed to descale precipitation hardening titanium alloys, have proved useful in descaling other metal parts that could not withstand treatment in the higher temperature baths.

The electrolytic salt descaling baths operate at about 900°F (482°C) and consist mainly of sodium hydroxide, plus smaller amounts of salts such as sodium chloride, sodium fluoride and sodium carbonate. The advantage of the electrolytic descaling bath is that the workpiece can be given either a reducing or oxidizing treatment or both, depending on the polarity imparted to the workpiece. The process can be carried out batchwise in a single tank or on a continuous basis using two separate tanks. The continuous process is widely used for descaling hot rolled and annealed stainless steel strip. A special electrical grid system is employed to provide cathodic polarity to the strip in one tank and anodic polarity in the other. In addition to the reducing and oxidizing action of the gases on the scale, the evolution of hydrogen or oxygen on the workpiece surface helps to physically loosen or dislodge the scale from the workpiece. After completion of the electrolytic descaling cycle, the parts are quenched in water and acid dipped as described above for the other molten-salt descaling operations.

The principal advantages of molten-salt descaling/pickling over acid pickling are that it minimizes metal loss and hydrogen embrittlement and generally produces cleaner and smoother surfaces on many ferrous and nonferrous metals. On the other hand, the high temperatures used in descaling not only require special heating and handling equipment, but also preclude treatment of metals whose properties might be adversely affected by exposure to the elevated temperature. Descaling is not suited for processing metals with low melting points and those that are attacked by caustic soda, such as aluminum, magnesium, zinc, tin and lead.

2.6.7 Paint stripping. Stripping of old paint finishes is often necessary before application of new ones. Most paint removal is accomplished by use of a combination of chemical stripping and mechanical action. The type of stripper is governed by the paint film to be removed and basis metal.

The two basic methods of chemical removal of paint are (1) hot stripping and (2) cold stripping. Hot stripping is generally carried out using strong aqueous alkali solutions which are effective for paints based on drying oils and polymerized resins. Paint is usually removed by immersing the part in the boiling or hot alkali stripping solution or by applying the solution as hot spray from steam guns. Cold stripping generally involves the use of organic solvents; however, it is also carried out using a mixture of alkalies, solvents and wetting agents. Tank immersion, spraying and brushing techniques are used in cold stripping. Solvents such as ketones, esters, etc., are effective on lacquer films, while solvents such as methylene chloride and other chlorinated hydrocarbons are effective for many synthetic and oleoresinous films.

Practically all paint stripping requires some sort of mechanical assistance (usually brushing) to remove the loosened material. Even after thorough rinsing, the stripped metal surfaces may require one or more supplementary cleaning procedures before repainting. Chemical stripping is usually a quick acting method of removing old paint from surfaces; however, in some instances long periods of time (e.g., 4 hours or more) are required to attain best results.

Because of the reactivity, toxicity or flammability of stripper materials, they should be handled and used with adequate ventilation and care to protect operator health and safety.

More detailed data and information on paint stripping materials and techniques and the applicable specifications for paint stripping are presented in section 9.

2.7 Electrochemical cleaning methods.

2.7.1 Electropolishing. Electropolishing is an electrochemical process for smoothing metal surfaces by controlled anodic dissolution of metal in concentrated acid or alkaline solutions. The process has been widely adopted for the industrial finishing of metals and alloys for decorative and engineering applications. Metal parts are electropolished to achieve one or more of the following objectives:

- (1) Smooth the surface to improve appearance and reflectivity.
- (2) Remove damaged or disturbed surface metal produced by mechanical machining or abrasion.
- (3) Improve corrosion resistance.
- (4) Remove burrs from locations inaccessible to mechanical methods of deburring.
- (5) Provide a good surface for receiving sound adherent coatings.

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Viscous liquid gas films formed on metal surfaces during electropolishing promote relatively rapid dissolution of metal on the elevated spots on a rough finish and a slower attack at depressed areas. The smoothing and rounding off of high spots results in surfaces with a glossy or lustrous appearance.

In electropolishing, the work is connected to the positive (anodic) lead of a direct current source. The cathode is connected to the negative terminal and may be any metal (or carbon) that is chemically resistant to the electrolyte. Cathode materials often used include carbon, stainless steel, copper and lead. Anode current densities range from about 100 to 1000 A/ft² (11 to 110 A/dm²), with the more typical current densities falling in the range of about 200 to 600 A/ft² (22 to 65 A/dm²). Equipment layout, handling of work as to racking or holding, etc., are similar to those for electroplating operations. Individual cathodes suitably placed relative to the work are always preferred in order to improve the distribution of current. Suitable uniformity is seldom provided if the tank is used as cathode. Electropolishing baths are not generally used for removal of scale or oxide, as the baths are specially compounded to dissolve metal, not scale. Removal of scale is nonuniform in electropolishing baths and pitting results at metal sites exposed first, while scale remains at other sites. For these reasons scale should be removed before electropolishing by molten-salt descaling, pickling, barrel tumbling or by wet or dry abrasive blasting. Analogously, oily and greasy soils should be removed by solvent or vapor degreasing, alkaline soak cleaning or electrocleaning prior to electropolishing. Good rinsing after soak or electrocleaning minimizes dragout into the electropolishing baths of alkaline compounds, wetting agents and other contaminants.

Although perchloric-acetic acid baths have the widest applicability to electropolishing of different metals and alloys, they are not recommended for use in the typical metal finishing shop because of the explosive hazard. Several disastrous explosions involving these baths have occurred in the U. S. and Europe. The baths most widely used in industrial electropolishing are based on mixtures of phosphoric and chromic acids or phosphoric and sulfuric acids. To these basic acid systems, organic acids (such as citric, glycolic and tartaric) and alcohols (such as ethanol and butanol) are sometimes added.

Sulfuric-phosphoric acid electrolytes are used for electropolishing 300 and 400 stainless steels, high strength steels and nickel base alloys. Phosphoric-chromic acid mixtures are suitable for polishing stainless steels, copper, brass and steel. Aluminum, copper alloys, stainless steels and high strength steels are satisfactorily electropolished in sulfuric-phosphoric-chromic acid mixtures. For electropolishing precious metals, alkaline cyanide baths are used. Proprietary electropolishing methods are extensively used in industry, because they have desirable features of low cost, easy operation and excellent results.

Electropolishing is applicable to many metals and alloys. An important advantage of the process is its ability to polish simultaneously multiples of thin sectioned or intricately shaped parts that present problems for mechanical wheel finishing. Electropolishing is widely used on stainless steel parts because it is more costly to polish them using mechanical polishing/buffing methods. Some disadvantages or limitations of electropolishing are (1) surface defects such as seams, inclusions and voids are revealed and not removed without excessive metal removal; (2) metals and alloys that tend to pit cannot be electropolished satisfactorily; and (3) electropolishing is more expensive than barrel or vibratory finishing methods.

2.7.2 Electrolytic alkaline cleaning. Electrolytic alkaline cleaning, although slightly more costly, is generally considered to be superior to conventional alkaline cleaning (i.e., soak or spray). The cleaner surfaces produced with the electrolytic method are considered suitable to meet the most exacting requirements for plating or other coating processes. In electrocleaning, the usual detergent and emulsifying actions of the alkaline cleaning solution on soils are augmented by the scrubbing action produced by the generation of large quantities of gas on the surfaces being cleaned.

In electrolytic cleaning, the alkaline solution is the electrolyte, the metal part(s) to be cleaned is one electrode and the tank or a steel plate is the other electrode. Small parts are readily handled in rotating barrels. When current is passed, the water in the electrolyte decomposes to form oxygen at the anode and hydrogen at the cathode. The gas bubbles break up the film of soil rapidly. The metal to be cleaned may be either the anode or cathode. The evolution of twice as much gas at the cathode favors making the metal the cathode. One disadvantage of cathodic cleaning is that positively charged metallic ions, soaps and other colloidal materials are attracted to and deposited as loose smut on parts being cleaned. Another drawback is that the hydrogen evolved on the parts may be diffused into high strength steel parts, causing embrittlement. Conversely, during anodic cleaning some oxide or tarnish may form on the parts. There is also the possibility of etching or pitting of nonferrous metals if anodic cleaning time is prolonged in an uninhibited bath. Alloys of lead, nickel and silver should not be anodically cleaned. Lead alloys are attacked rapidly, while nickel and silver surfaces are passivated. Because zinc, aluminum, brass, lead, tin, solders, etc., are attacked by strong alkaline cleaners, specially inhibited cleaners are required for these metals.

To reduce smut deposition with cathodic cleaning and oxide formation or metal attack during anodic cleaning, periodic reversal of current may be employed. Periodic reverse cleaning usually accelerates cleaning action, provides better smut removal and yields a more active surface for subsequent plating or coating operations. To prevent deposition of loose metallic smut, the work should be removed from the electrocleaner during the anodic part of the cycle.

Material conforming to MIL-C-14460 may be used in electrolytic cleaning. Refer to section 9 for other applicable specifications.

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2.7.3 Electrolytic pickling. The advantage of applying an electric current to pickling is similar to that for alkaline cleaning: The liberation of gas mechanically loosens scale and other soils and speeds up the process. In electrolytic pickling, the baths are usually acidic. The work may be made either the cathode or anode. Cathodic pickling is the more aggressive treatment. For example, mild steel and 400 series stainless steel can be electrolytically pickled using sulfuric acid solutions (containing 8 to 15% H_2SO_4 by volume). Typical electrolytes for pickling 300 series stainless steels are 8 to 10% HNO_3 or 8 to 10% HNO_3 plus 3 to 5% HF (acid contents are % by volume). Anodic pickling, in an electrolyte such as 30% (by weight) sulfuric acid solution, is often employed to produce a mildly etched surface suitable for subsequent electroplating. Anodic pickling is also employed on high strength metals where hydrogen embrittlement must be avoided. In some instances a combination of anodic and cathodic pickling is employed; alternating current can also be employed for pickling. Electrolytic pickling is more rapid than chemical pickling, requiring in most instances from one half to 3 minutes for completion, as compared with 5 to 15 minutes for chemical pickling.

The electrolytic pickling process has certain limitations in that the temperature and acid concentration must be more closely controlled than for chemical pickling. The costs for equipment and its maintenance are much higher for electrolytic than for chemical pickling.

3. ELECTROPLATED FINISHES

3.1 General. Electroplating is the most widely used method for the commercial production of protective metal coatings. It entails the electrodeposition of a sound adherent metallic coating upon an electrode to produce a surface with characteristics or dimensions different from those of the basis metal. Electroplated coatings generally impart one or more of the following benefits to the surface of the plated objects: improved corrosion resistance; improved resistance to wear and abrasion; improved appearance (including color and brightness); improved frictional and nongalling characteristics; solderability; electrical conductivity; heat and light reflectivity; and other special properties. Thick electrodeposits are often used to salvage parts by building up dimensions on worn or mismachined undersize components.

The following are some of the desirable features of electroplating which make it, for many applications, more attractive or economical than other methods for applying metal coatings:

- (1) Ability to plate a large number of metals and alloys on a large variety of sizes and shapes of parts made of different materials.
- (2) Ability to apply and closely control deposit thickness. Plating thicknesses cover a wide range usually in the range of 0.00001 to 0.0015 in (0.25 to 38 μm).
- (3) Ability to plate articles at relatively low temperatures, usually at temperatures ranging from about 60 to 200°F (16 to 93°C), as opposed to other metal coating processes requiring elevated temperatures which can adversely affect basic metal properties.
- (4) Ability to produce smooth, uniform coatings of high purity and quality at relatively low cost.

Not all metals can be electrodeposited easily and economically. For example, high temperature fused salt baths are required for electrodeposition of refractory metals.

The complete electroplating process includes cleaning, surface conditioning or activating, plating, rinsing and drying. The cleaning and surface activating operations consist of two or more steps that are required for removing grease, oil, soil and oxide films from the basis metal. Frequently, parts are solvent cleaned or vapor degreased prior to loading on the electroplating line. Sequential treatments in an alkaline cleaning solution and an acid activating solution with intermediate rinsing are the minimum requirements customary for these purposes. Specific cleaning and surface conditioning procedures are employed to prepare various basis metal substrates for electroplating with different metals in order to achieve sound adherent coatings.

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During electroplating, metal ions in either acid, alkaline or neutral electrolytes (usually aqueous) are reduced and deposited onto the cathode surfaces (the workpieces being plated) by the passage of direct current. The metal ions in solution are usually replenished by dissolution of metal anodes in bar form or in small pieces or balls contained in inert wire or expanded metal baskets or holders. However, replenishment with metal salts or metal oxides is sometimes practiced, especially for chromium plating. In such cases, an inert (insoluble) material must be employed as the anode; e.g., lead-antimony (6-8% Sb) alloy is frequently used in a sulfate type chromium plating bath. Hundreds of different electroplating solutions have been used commercially, but generally only about two or three types are employed widely for a single metal or alloy. For example, cyanide solutions are extensively used for electroplating copper, zinc, silver and cadmium. However, noncyanide alkaline solutions containing sodium or potassium pyrophosphate or another chelating agent have been adopted recently for zinc and copper plating, particularly in plants where it is desired to lessen or eliminate cyanides in their rinse waters and plant effluents. Acid sulfate solutions are also used to plate zinc and copper, especially for electroplating relatively simple shapes. The choice of the particular electrolyte to use is governed by items such as: plate quality; reagent costs; electroplating rates; relative ease of bath maintenance and control; operating temperature; waste treatment costs of associated rinse waters; sludge removal; and disposal, etc.

Parts are usually electroplated in still tanks, barrels and in a variety of automatic equipment. Barrels are used mostly for plating large numbers of small parts that tumble freely in slowly rotating barrels. Racks are generally used for larger parts that cannot be tumbled because of surface impingement damage to coatings or distortion of part shape. Perforated plastic barrels range in diameter from about 6 to 30 in (15.2 to 76.2 cm), depending on part size and shape. Direct current loads up to several hundred amperes are distributed to the parts being plated in horizontal barrels, through dangles suspended from a current carrying bar located at the longitudinal axis. In oblique barrels, a conductive button at the bottom transmits the current.

In rack plating, the parts are attached to plastic coated copper frames designed to carry current equitably to a few hundred small parts, several medium sized shapes or just a few large products through spring-like rack tips affixed to the rack splines. Racks fabricated for manual transfer from cleaning, plating and rinsing tanks generally hold 5 to 15 lbs (2.3 to 6.8 kg) of parts having a surface area of about 5 to 10 sq ft (0.46 to 0.93 sq m). Larger racks for holding heavier parts and loads are constructed for use with mechanical hoist or transfer systems. Mechanized transfer systems for both barrels and racks are utilized for high volume production involving six to twenty or more sequential operations. In some systems, dwell time and transfer periods are programmed on magnetic tape or cards for complete automation of the electroplating line.

Properties of electroplated coatings vary considerably with the type and composition of the plating solution, current density, bath or workpiece agitation, solution pH and temperature. Small amounts of addition agents and brighteners can exert a significant influence on plate properties and coating appearance. Excellent coverage of the properties of a large variety of electrodeposited metals and alloys is provided in the book Modern Electroplating, edited by Lowenheim, which is cited in the Selected Bibliography at the end of this handbook. Most of the electrodeposited coatings used by the military are described below with greater emphasis placed on the more widely used coatings namely: nickel, chromium, cadmium, copper, zinc and tin. Brush or selective plating is covered in the last part of the section.

The specific metal or alloy plates, that are discussed are listed below in the order in which they are presented:

- Nickel
- Black nickel
- Chromium
- Black chromium
- Cadmium
- Zinc
- Copper
- Lead
- Silver
- Tin
- Cobalt
- Brass
- Copper-tin-alloy
- Copper-tin-zinc alloy
- Tin-zinc alloy
- Tin-nickel alloy
- Lead-tin alloy
- Nickel-cobalt alloy
- Indium
- Rhodium
- Gold

Military Specification MIL-S-5002 covers the requirements for cleaning, surface treatments and inorganic coatings for metallic surfaces of weapon systems parts.

ASTM Standard B 322 covers recommended practice for cleaning of metals prior to electroplating.

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3.2 Nickel plate. Nickel is one of the most important metal coatings applied by electroplating for protective and decorative purposes. With the exception of electrolytic tin, nickel consumption for electroplating purposes is greater than that of any other metal. The wide usage is attributed to nickel's good combination of physical and chemical properties. In addition to possessing good strength, hardness and ductility, nickel plates exhibit high resistance to corrosion in rural, marine and industrial environments as well as in natural waters, seawater, and neutral and alkaline salt solutions. The main limitation of nickel as a coating metal is in its electropotential relationship to iron and steel in most environments. This condition makes necessary the use of relatively pore-free nickel coatings for satisfactory protection of the substrate metal. Fortunately, as the thickness of the nickel plate increases, the deposit tends to close pores and corrosion protection is improved. Plates of the order of 0.001 in (25 μm) usually provide good protection.

Nickel plate, with or without an underlying strike plate, is primarily employed as a bright coating underneath a comparatively thin chromium electroplate to provide a decorative and corrosion protective coating for parts of steel, zinc, brass and other basis metals. Nickel, by itself, is electrodeposited on steels and other basis metals to provide corrosion resistant finishes. On aluminum and magnesium, nickel plates are usually applied over a two layer coating consisting of a zinc immersion coating and a copper strike. Heavier nickel deposits are frequently employed to build up worn parts or provide wear resistant surfaces. Nickel electrodeposition is also extensively used for the electroforming of intricately shaped objects, which would be difficult or expensive to fabricate using conventional metalworking or machining methods. The thinner nickel coatings used to decorate and protect steel, copper and zinc alloys against corrosive attack in rural, industrial or marine atmospheres generally range from 0.0002 to 0.0015 in (5 to 38 μm) in thickness. Typical copper underplates for zinc alloys generally range from a minimum of 0.0002-0.0003 in (5-8 μm) up to about 0.001 in (25 μm). The thicker coatings, used for engineering applications (such as providing surfaces with good wear and abrasion resistance, buildup of worn parts and protection against severe chemical corrosion) can range from about 0.002 to 0.020 in (50 to 500 μm). Where greater tarnish resistance or reflectivity is desired, cover the nickel coating with approximately 0.00002 in (0.5 μm) chromium plate thickness.

Nickel is generally electroplated from Watts (sulfate-chloride-boric acid), sulfamate, fluoborate or chloride baths. Each type of solution usually consists of the corresponding nickel salt, a buffer such as boric acid and a small concentration of a wetting agent. A small amount of another organic chemical may be added to brighten the deposits or control some other property. Many proprietary versions of the above bath types are in commercial use. In many instances proprietary brightener, leveller and additive formulations (or combinations thereof) for use with standard type baths are marketed. By proper selection of nickel bath compositions and addition agents and by control of electroplating conditions, nickel deposits with dull, satin, semibright or fully bright surfaces and a wide range of properties can be produced.

As an undercoat for chromium, which is probably the most important use of nickel plating, minimum thickness for outdoor service is about 0.0012 in (30 μ m), applied either in one or two layers. The use of double layer (duplex) nickel is now widespread because it offers better corrosion protection. In double layer nickel deposition, the nickel immediately under the chromium top coat is a bright nickel containing sulfur while the bottom layer under that is a semibright nickel essentially free of sulfur. In any galvanic electrolytic cell set up between these coatings, the bright nickel reacts anodically to the purer semibright nickel. If microscopic corrosion in the top coat material penetrates the bright nickel layer, galvanic action causes the microscopic pits to spread laterally in the outer nickel layer. The net effect is to retard penetration toward the base metal and lengthen the useful life of the coating.

Nickel sulfamate baths are widely used for engineering applications because the deposits produced are low in stress and frequently contain fewer inclusions than those produced in other nickel baths. The sulfamate coating is often used to provide moderate corrosion and oxidation resistance where low tensile stress in the deposit is required to avoid marked reduction in fatigue strength. AMS Specification 2424 covers low stress nickel plating in a sulfamic acid bath.

Federal Specification QQ-N-290 covers the requirements for electrodeposited nickel plating on steel, copper and copper alloys and zinc and zinc alloys. This specification requires that all steel parts having a hardness of Rockwell C 40 or higher be baked at a minimum of $375 \pm 250^{\circ}\text{F}$ ($191 \pm 140^{\circ}\text{C}$) for 3 hours or more, within 4 hours after plating to provide relief from hydrogen embrittlement. Plated springs or other parts subject to flexure are not to be flexed prior to the baking treatment. The Specification further indicates that for high strength materials (Rockwell C 40 and above) it may be beneficial to extend the baking time to 23 hours to insure complete hydrogen embrittlement relief.

Special approval of the procuring authority is required for nickel plating of steel parts having an ultimate tensile strength greater than 240,000 psi (1655 MPa). A stress relief treatment at a minimum of $375 \pm 250^{\circ}\text{F}$ ($191 \pm 140^{\circ}\text{C}$) for 3 hours or more, prior to cleaning and plating, is called for (unless otherwise specified) on steel parts which have been machined, ground, cold formed or cold straightened. This treatment provides for the relief of damaging residual tensile stresses.

Military Specification MIL-STD-868 (USAF) deals with a low embrittlement process adopted by the Air Force for nickel plating high strength steels. This specification spells out cleaning procedures as well as bath compositions and operating conditions for plating nickel from either a Watts-type or sulfamic acid bath. Baking within 4 hours after plating for 23 hours at a temperature of $375 \pm 250^{\circ}\text{F}$ ($191 \pm 140^{\circ}\text{C}$) is called for. Plating qualification procedures require that specimens undergo sustained load tests at 75% of ultimate notched tensile strength. To pass, the specimen must endure the sustained load test for 200 hours without failing or cracking.

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Other documents dealing with various facets of nickel electroplating are as follows:

- ASTM Standard Specification B 456 - Electrodeposited Coatings of Nickel Plus Chromium
- AMS Specification 2403 - General Purpose Nickel Plating
- AMS Specification 2423 - Nickel Plating (Hard Deposit)
- AMS Specification 2424 - Nickel Plating (Low Stressed Deposit)

3.3 Black nickel plate. Electrodeposition of black nickel coatings is carried out primarily to provide a dark, nonreflecting, decorative finish on steel and copper alloy parts. It produces lustrous black coatings on smooth surfaces and dull black films on matte surfaces. It is a good candidate for coating solar energy collection devices. Typical applications include cameras, military instruments, optical equipment, typewriters and costume jewelry. The coating by itself offers little protection against corrosion. On ferrous metals, an undercoating of zinc, nickel, copper or brass is usually applied prior to black nickel plating to provide corrosion protection.

Black nickel deposits are produced in either a sulfate or chloride bath. The aqueous sulfate bath contains nickel sulfate, zinc sulfate, ammonium sulfate and sodium thiocyanate. The chloride bath is an aqueous solution containing nickel chloride, zinc chloride, ammonium chloride and sodium thiocyanate. The exact composition of the black nickel deposits is not known, but probably consists of nickel, zinc, sulfides and oxides of nickel and zinc, plus occlusions of other compounds. The deposits are hard and brittle; they readily chip or flake on bending or impact. For that reason, the black nickel coatings are generally not allowed to exceed 0.00004 to 0.00006 in (1.0 to 1.5 μm) in thickness.

Military Specification MIL-P-18317 covers the use of electrodeposited black nickel for blackening brass, bronze or steel surfaces.

3.4 Chromium plate. There are two principal types of chromium plating, i.e., decorative and hard. In decorative plating, a thin chromium coating serves as a protective, nontarnishing durable surface finish. Usually, decorative chromium is applied over coatings of copper plus nickel (or nickel alone) on all basis metals. Because it is difficult to obtain dense, pore-free chromium deposits, the parts to be chromium plated are first plated with a pore-free undercoat of copper-nickel or nickel, which has greater ductility and good corrosion resistance. Typical decorative chromium plate thicknesses over copper-nickel or nickel undercoats generally range from 0.00001 to 0.000025 in (0.25 to 0.64 μm). In hard (also known as "industrial" or "engineering") chromium plating, thicker coatings are used to take advantage of the special properties of chromium, including good resistance to wear, abrasion, friction, heat and corrosion. Unlike decorative chromium plating, hard chromium is generally applied to the basis metal without an intermediate coating. Hard chromium is normally deposited in thicknesses ranging from about 0.0001 to 0.020 in (2.5 to 500 μm).

By itself, chromium electroplate has excellent corrosion resistance. Chromium plate is resistant to tarnishing and oxidation at temperatures above 572°F (300°C). A thin, self-healing transparent oxide film that forms enables chromium to resist corrosion and maintain its good appearance. This passive oxide film prevents further oxidation of the underlying chromium metal. However, the thin decorative chromium plates are very porous and corrosion of the basis metal occurs at the pore sites. For that reason, an intermediate coat of nickel is used to protect the base metal, while the very thin layer of chromium over the nickel keeps the latter tarnish free. Because it is applied in greater thicknesses, hard chromium plate is usually less porous and more impervious to chemicals or water which normally penetrate the more porous thin chromium plates. Microcracks usually are present in the hard chromium electroplates, but they tend to become plugged during initial exposure to corrosive conditions and prevent further corrosion. The two most important physical properties that make hard chromium plate valuable for engineering applications are its wear resistance and low coefficient of friction. For many applications involving wear, abrasion and erosion, chromium is unsurpassed. The chromium plated surface has very little tendency to seize, gall or weld to another metal surface when the two are rubbed together under pressure.

Typical parts coated with decorative chromium include: exterior and interior automotive parts, boat hardware, plumbing fixtures, appliances, cabinet hardware, etc. Representative applications for hard chromium plating include: restoration of original dimensions of worn, mismachined or undersized parts; coating of tools, dies, rolls, gauges and other parts to minimize wear and abrasion and to reduce galling, friction and corrosion; and coating of gun barrel bores, pump shafts and hydraulic rams.

Chromium plating solutions generally contain chromic acid and a small amount of sulfuric acid and fluosilicate or fluoride ions. The ratio of the concentration of the chromic acid to the catalyst acid radicals or anions ranges from about 50:1 to 250:1 and, preferably, should be about 100:1. Insoluble lead alloy anodes are almost always used in chromium plating from chromic acid baths. For conventional sulfate baths, lead-antimony (6-8% Sb) alloy is preferred, while for fluoride-containing baths, lead-tin (4 to 7% Sn) alloy is recommended. Cathode current efficiencies for deposition of chromium are low and generally range from about 8 to 15%. Chromium baths have poor throwing power. For plating irregular shapes, it is necessary to place anodes carefully around the surface of the item. Special conforming anodes are built for some shapes. "Thieves" are also used to prevent excessive plate buildup at high current density areas. Small parts, such as screws or bolts, can be barrel plated in small batches, but the operation must be carefully controlled.

The use of microporous or microcracked chromium (or an outer layer of microporous or microcracked chromium in a duplex chromium plate) has resulted in plates providing improved corrosion protection of nickel plated parts. The multitude of small openings in microporous or microcracked plate improves overall corrosion resistance by reducing the corrosion current density at each exposed nickel site.

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3.4.1 Porous chromium plate. Porous chromium plate refers to a modified form of engineering chromium containing intentionally produced pores or cracks for holding lubricants on surfaces such as cylinder liners. The porous structure is useful on such items as cylinder walls and piston rings, where the pores retain miniature pools of lubricating oil and thus overcome the nonwetting property of chromium plate. Mechanical, electrochemical or chemical techniques are employed to produce porous chromium plates. Mechanical methods entail either grit blasting the surface to be plated or roughening it with a fine knurling tool. The roughened surface is then chromium plated; final finishing to size is achieved by grinding, boring or polishing. Channel type (an etched network surrounding small, flat plateaus), pin-point type (essentially many coarse pits) and other types of porous chromium deposits are produced by electrochemically or chemically etching the chromium plate. The type of porosity obtained depends on careful control and regulation of plating conditions and the subsequent etching conditions.

Military Specification MIL-C-20218 covers porous electrodeposited chromium plating applied to cylinder liners of internal combustion engines. Military Specification MIL-C-7460 describes the requirements for porous (channel type) chromium plating of bores of aircraft engine cylinders. AMS Specification 2407 deals with the use of porous chromium plating to improve the load carrying and lubricating characteristics of ferrous parts.

Federal Specification QQ-C-320 covers the requirements for electrodeposited chromium plating; class 1 relates to corrosion protective plating while class 2 deals with engineering plating. This specification requires that all coated steel parts having a hardness of Rockwell C 40 or higher be baked at a minimum of $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) for 3 hours or more, within 4 hours after plating to provide embrittlement relief. Plated springs or other parts subject to flexure are not to be flexed prior to the hydrogen embrittlement relief treatment. The specification further states that it may be beneficial to extend the baking time to 23 hours to insure complete hydrogen embrittlement relief. Special approval of the procuring authority is required for chromium plating steel parts having an ultimate strength greater than 240,000 psi (1655 MPa). All steel parts having an ultimate tensile strength of 150,000 psi (1034 MPa) and above, which are machined, ground, cold formed or cold straightened, are to be baked at a minimum of $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) for 3 hours or more prior to cleaning and plating for the relief of damaging residual tensile stresses.

The endurance limit of high strength steels may be reduced about 30 to 65% when chromium plated in either a conventional sulfate or fluoride bath. Shot peening before plating, by imparting compressive stresses to the basis metal surfaces, generally lowers the extent of fatigue strength loss produced by electroplating. Shot peening of steels prior to plating is covered in Military Specifications MIL-S-13165 and MIL-R-81841 and, also, Federal Specification QQ-C-320. This latter specification states that plated parts below Rockwell C 40 hardness, which are subjected to static loads or designed for limited life under dynamic loads or combinations thereof, need not be peened prior to plating.

High crack count chromium plate, deposited under appropriate conditions in a chromic-sulfuric-fluosilicate solution to promote a compressive stress, has little or no harmful effect on fatigue strength of steel.

Military Standard MIL-STD-1501(USAF) covers the process for low embrittlement chromium plating of high strength steels. Bath compositions and operating conditions for chromium plating the steel parts in a chromic acid-sulfuric acid type bath are specified. The baking treatment and the qualifying tests employing sustained load specimens are similar to those described earlier for low embrittlement nickel plating.

ASTM Specification B 456 deals with electrodeposited coatings of nickel plus chromium on steel, copper and other metals and alloys. ASTM Specification B 177 covers chromium plating on steel for engineering use. AMS Specification 2406 relates to electrodeposition of hard chromium coatings.

3.5 Black chromium plate. Black chromium deposits are hard, adherent, heat resistant and have a low reflective index. The color of the plate is dark gray approaching a dull black; the plate may be waxed or oiled to darken the surface. Typical military applications, where a non-reflecting black coating is desirable, include: (1) rocket launcher rails; (2) interior surfaces of optical parts; and (3) small arms applications. Black chromium coatings have a high absorption of solar energy. The black chromium coating provides limited corrosion protection, but added protection can be obtained by use of a corrosion resistant underplate such as nickel. Although black chromium plate is generally applied to steels, it may also be used as a coating for other metals such as brass, copper, iron and chromium. The black coating is sometimes applied over bright chromium plate, but requires special activation for good adhesion. Black chromium deposits generally involve only a slight dimensional change of 0.000005 to 0.0002 in (0.13 to 5 μ m).

Black chromium can be plated from an aqueous solution containing chromic acid and acetic acid, with a minor amount of barium carbonate or barium acetate. Typical operating conditions are:

Current density - 40 to 90 amp/ft² (4.3 to 9.7 amp/dm²)
 Temperature - Room to 110°F (43°C)
 Plating time - 30 to 45 minutes

Mild steel anodes are generally preferred to carbon anodes because of the attrition of carbon anodes. Parts with deeply recessed areas may require auxiliary iron wire or platinum anodes as the throwing power of the black chromium bath is not appreciably greater than that of the ordinary chromium solutions. The processing operations require careful control and proper maintenance of the solution to assure satisfactory plating results.

Military Specification MIL-C-14538 covers the electrodeposition of black chromium plates. The hydrogen embrittlement relief treatment after plating and the stress relief treatment prior to cleaning and plating, required for steels having a hardness of Rockwell C 40 and higher, are similar to those cited earlier (Federal Specification QQ-C-320) for regular chromium plating in paragraph 3.4.

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3.6 Cadmium plate. Cadmium plating is used primarily to provide an attractive corrosion protective coating over various basis metals, in particular, steel and cast iron. Cadmium has a silvery-white luster, not as bright as chromium, but more satiny. Cadmium is anodic to iron and steel and provides sacrificial protection to these basis metals even when the cadmium coating is nicked or scratched. The cadmium must corrode before the ferrous base itself is attacked. The protective value of cadmium is directly proportional to the thickness of plate because of this sacrificial feature. Cadmium, like zinc, forms a white, loosely adhering powder when it corrodes. The cadmium corrosion product is less bulky than that of zinc and does not form as fast at high humidity. The corrosion of cadmium plate can be significantly retarded by applying one of many chromate treatments.

Due to the relatively high cost of cadmium, its application is generally restricted to thin deposits. Coatings are usually less than 0.001 in (25 μ m) thick and the most widely used thickness for parts used indoors or sheltered outdoor locations are in the range of 0.0002 to 0.0005 in (5 to 13 μ m). Nevertheless, use of cadmium plates for aircraft, marine and military outdoor applications is common. Cadmium is frequently employed to coat parts or assemblies made up of dissimilar metals to minimize corrosion. Cadmium's excellent solderability and low contact resistance makes it attractive for use in electrical fixtures.

Because cadmium is a highly toxic substance, we should not use this metal when an alternate process meets the performance requirements and is considered satisfactory for use on the item under consideration.

Most cadmium plating is carried out using aqueous cyanide solutions formulated with cadmium oxide, sodium cyanide and sodium hydroxide. Upon dissolution of the cadmium oxide, a cadmium cyanide complex $[\text{Na}_2\text{Cd}(\text{CN})_4]$ is formed.

Cadmium may be plated bright, semibright or matte, depending on the addition agents and operating conditions employed. Cyanide baths are generally employed for cadmium plating because of their ability to produce good, dense, fine grained deposits with excellent covering power and good plate distribution over complex shapes. Cyanide baths are suitable for still, automatic and barrel plating operations. Both soluble and insoluble anodes are used in the cyanide baths, with the soluble anodes being the more widely used. Ball shaped cadmium anodes in a spiral cage holder of bare steel are usually employed. Insoluble anodes generally consist of low carbon steel strips.

Acid cadmium baths are generally inferior in throwing and covering power, compared to alkaline cyanide baths. Without brightener additions, the acid cadmium deposits tend to be coarse grained and rough. However, acid cadmium fluoborate baths, containing proprietary additives, are useful for avoiding or minimizing hydrogen embrittlement of steel. The fluoborate baths with proprietary addition agents produce fine grained deposits considered comparable to those obtained in the alkaline cyanide baths in protective quality and appearance. The aqueous fluoborate bath usually contains cadmium fluoborate, ammonium fluoborate and boric acid, plus small amounts of addition agents.

Many investigations have been carried out on new or modified cadmium solutions (both acid and alkaline) in order to avoid or minimize hydrogen embrittlement of high strength steels or to come up with plated coatings that are more amenable to embrittlement relief by baking. To date, the success achieved has been only limited. With some steels, especially those in the strength range of 240,000 psi (1655 MPa) or above, complete embrittlement relief is not always obtained, even with prolonged baking treatments at $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) of 23 hours or longer. For such parts, vacuum deposited cadmium or organic coatings are often employed.

Except for special plating applications, such as those involving low hydrogen embrittlement, in which fluoborate and other solutions are employed, the cyanide bath is almost always used for cadmium plating.

The main purpose of chromate conversion finishes on electroplated cadmium coatings is to retard or prevent the formation of white corrosion products on surfaces exposed to stagnant water, high humidity atmospheres, salt water, marine atmospheres or cyclic condensation. Most of the chromate coatings also provide a good base for paint. Phosphate finishes on electroplated cadmium coatings serve primarily as a paint base. Detailed information on chromating of cadmium and zinc surfaces, along with temperature limitations in service of such chromated parts, are given in section 4 of this handbook.

Cadmium plate has several advantages. For example, it is especially suitable where close tolerance allows only a small build up of 0.0001 to 0.0002 in (2.5 to 5.1 μm). The reasons are: a thin plate, although porous, provides good protection; cadmium build up is easier to control than that of other electroplates; for threaded parts (bolts, nuts, screws and washers) cadmium protects against galvanic corrosion, particularly between aluminum or magnesium and steel or copper. Cadmium plate is ductile and withstands deformation. Cadmium plate reduces the tendency of copper plated electrical contacts to oxidize and does not increase contact resistance.

Cadmium plate has a number of disadvantages. It is inferior to zinc of the same thickness in outdoor industrial atmospheres. Paint does not adhere well to a bare cadmium surface. However, painting is successful if the cadmium is first given a phosphate or a chromate treatment. (This also applies to zinc plate.) Cadmium plate is susceptible to corrosion by fumes of organic materials, especially in warm stagnant atmospheres. These materials include paint drying oils, electrical insulation, impregnated paper, wooden packing crates and certain resins. Good ventilation in their presence is required. Although used commercially in electrical assemblies, their use in some military electrical, electronic, hydraulic and optical assemblies may be prohibited. Because military materiel may be exposed to more severe conditions, the corrosion product of cadmium may become objectionable. It has been found that cadmium, among other metals, under certain conditions will grow into filaments or "whiskers" of metal that may interfere in the normal functioning of electronic components. Cadmium plate is soft. If buffing or polishing is required, it is likely to be removed with resultant exposure of base metal.

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Cadmium, because of its toxicity, should not be used as a plating for any object intended for use as a food container or cooking utensil or for any object likely to come in contact with food. Cadmium plated sheets and any structural shapes that may be subjected to heat from welding, brazing or soldering operations, should be suitably labelled because of the danger from poisonous vapors during such operations.

Because of its toxicity and high cost (about 6 to 8 times that of zinc) efforts are being made to develop substitute coatings for cadmium. One that is already finding considerable commercial use is an electroplated tin-zinc alloy, which will be discussed later under "Alloy Plate".

Federal Specification QQ-P-416 covers the requirements for electrodeposited cadmium plating. This specification requires (unless otherwise stated) that all steel parts having a hardness of Rockwell C 40 or higher be baked at a minimum of $375 \pm 25^{\circ}\text{F}$ ($191 \pm 14^{\circ}\text{C}$) for 3 hours or more, within 4 hours after plating to provide hydrogen embrittlement relief. Plated springs or other parts subject to flexure are not to be flexed prior to baking. It may be beneficial to extend the baking period to 23 hours to assure complete hydrogen embrittlement relief. Cadmium plating of steel parts having an ultimate tensile strength greater than 240,000 psi (1655 MPa) is not recommended and must have the specific approval of the procuring activity. All steel parts having an ultimate tensile strength of 150,000 psi (1034 MPa) and above, which are machined, ground, cold formed or straightened after heat treatment, are to be baked at a minimum of $375 \pm 25^{\circ}\text{F}$ ($191 \pm 14^{\circ}\text{C}$) for 3 hours or more, prior to cleaning and plating for stress relief. On ferrous parts heat treated or having an ultimate tensile strength between 180,000 to 240,000 psi (1241 to 1655 MPa) and approximately Rockwell C 40 to C 49, care should be taken prior to cadmium deposition by using processes for cleaning and plating that result in little or no hydrogen embrittlement. Details of the sustained-load tests that are used to evaluate the effectiveness of the embrittlement relief for different types of parts are given in the specification.

Cadmium plating should not be used on parts for space applications or on parts which in service reach a temperature of 450°F (232°C) or higher or come in contact with other parts which reach these temperatures.

Military Specification MIL-S-5002 contains an additional warning, indicating where cadmium plating shall not be used for weapon systems application.

Cadmium plated parts, which have been given a hydrogen embrittlement relief treatment, usually acquire a passive film during the baking operation. This film interferes with the application of a chromate conversion coating. Reactivation of the cadmium surfaces is achieved by a brief immersion (5 to 15 sec) in a dilute sulfuric acid or hydrochloric acid solution (1 vol % conc. acid and 99 vol % water). The surfaces should be reactivated as soon as possible following the baking operation. Chromate treatments should not be used on cadmium plated parts that will not be painted and which will be continuously exposed to temperatures of approximately 300°F (149°C) or more.

The following are two military standards formulated by the USAF covering low embrittlement processes for cadmium plating of high strength steels:

- (1) MIL-STD-870 - Cadmium Plating, Low Embrittlement, Electrodeposition
- (2) MIL-STD-1500 - Cadmium-Titanium Plating, Low Embrittlement, Electrodeposition

The first standard spells out procedures for: cleaning, plating, baking and sustained-load testing of cadmium-plated steel parts and specimens. Plating is carried out in a cadmium cyanide bath. The baking and sustained-load test requirements are similar to those described earlier for low embrittlement nickel and chromium plates on high strength steels. The second standard covers the electrodeposition of a cadmium-titanium coating (Ti content between 0.07 and 0.05%) on high strength steel parts. Plating is carried out with a cadmium cyanide bath containing 40 to 80 ppm titanium. The baking treatment called for is a minimum of 12 hours at $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$). Test specimens are required to pass sustained-load tests at 75% of ultimate notched tensile strength for 200 hours without failing or cracking.

Other documents dealing with various aspects of cadmium plating are as follows:

- (1) ASTM Standard Specification A 167 - Electrodeposited Coatings of Cadmium on Steel
- (2) AMS Specification 2400 - Cadmium Plating
- (3) AMS Specification 2401 - Cadmium Plating (Low Hydrogen Content Deposit)
- (4) AMS Specification 2419 - Cadmium-Titanium Alloy Plating

3.7 Zinc plate. Electroplated zinc is one of the most widely used coatings for protection of iron and steel against corrosion. Zinc, being anodic to iron and steel, offers less costly and more complete protection when applied in thin films than similar thicknesses of nickel and other cathodic coatings. Plate thicknesses usually range from 0.0002 to 0.001 in (5 to 25 μm) and more, depending upon the anticipated applications and environments. Because zinc is relatively inexpensive and readily applied in tank, barrel or continuous plating facilities, it is frequently the preferred coating for most ferrous parts to protect them against atmospheric and indoor corrosion. Electrodeposited zinc is used widely for coating small articles (e.g., screws, nuts, bolts, washers, etc.), formed parts, castings, metal screening, wire and strip.

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Zinc plate does not have high wear or abrasion resistance and is not suitable where gouging or binding is a factor. Thus, it is not suitable on grounding contacts where increased electrical resistance of zinc plated surfaces is objectionable. Zinc plate with supplementary chromate treatment is a poor electrical conductor. On the other hand, electrodeposited zinc coatings are essentially pure and, unlike coatings made by Sheradizing or hot dipping, contain no layers of alloyed iron. Electrodeposited zinc coatings are generally ductile and withstand severe bending and other mechanical deformation better than other types of zinc coatings of similar thickness.

The main disadvantage of zinc plate is that when it corrodes, it forms a loose, bulky, white corrosion product, usually a basic zinc carbonate. In most environments, this "bloom" or "white rust" does not form a continuous film capable of slowing down further corrosion. Furthermore, the voluminous corrosion products often foul optical, electrical, electronic and hydraulic equipment. This is particularly so in warm and humid locations where condensation or absorption of moisture frequently occurs. As with cadmium, a supplemental chromate treatment is employed primarily to retard the formation of white corrosion products on zinc plated surfaces exposed to stagnant water, high humidity atmosphere, salt water, marine atmospheres or to cyclic condensation and drying. As the chromating treatment dissolves some of the zinc plate, it is recommended that the zinc plate be greater than 0.0002 in (5.1 μ m) in thickness, whenever a supplemental chromate coating is applied. The chromated zinc surfaces are also good paint bases. Supplemental chromate treatments (except when followed by painting) are not to be used on zinc plated parts that will be exposed continuously to temperatures over 150°F (66°C) or, intermittently for short periods, to temperatures of approximately 300°F (149°C) or more.

Phosphate coatings are another prepaint and corrosion inhibitive chemical treatment for electroplated or hot dipped zinc surfaces. The phosphate film preconditions the surface to receive and retain paint and protects the surface against under-paint corrosion. The primary purpose of phosphate finishes on zinc plated surfaces is to prolong the useful life of the paint finish.

The bulk of fabricated steel parts that are zinc electroplated are coated in cyanide baths. The use of acidic chloride, sulfate and fluoborate baths is largely restricted to the plating of mill products, such as wire, strip, sheet and conduit. The throwing power of the acid baths is generally inferior to that of the cyanide baths, but for plating relatively flat products this is not a significant drawback. The aqueous zinc cyanide baths are formulated using either zinc cyanide or zinc oxide and appropriate amounts of sodium cyanide, sodium hydroxide and sodium carbonate. The plates produced in the cyanide bath may be matte, or, with appropriate addition agents, fully bright. Soluble zinc anodes are normally used in general purpose plating and in wire and strip plating.

During the past five years, the use of noncyanide alkaline solutions, prepared with zinc pyrophosphate or another chelating agent (such as tetrasodium phosphate, sodium citrate or the sodium salt of ethylene diamine tetraacetic acid) has increased considerably in some facilities to minimize or avoid the treatment of cyanide wastes. Similarly, the recent greater use of low cyanide baths has been spurred by the desire to minimize the amount of cyanide that has to be treated in the rinse waters, spills, etc., from the zinc plating operations.

Hydrogen embrittlement is more apt to occur in cyanide zinc plating than in the plating of most other common metals, including cadmium. For critical steel spring tempered parts, it may be preferable to employ cadmium instead of zinc plating.

Extensive exposure tests have been conducted in different areas of several countries on coatings on steel. Some of the results are as follows:

- (1) Zinc and cadmium coatings fail more rapidly in industrial than in rural areas and the cadmium fails faster than zinc.
- (2) In marine or rural areas, thin coatings of zinc or cadmium furnish better corrosion protection than coatings of nickel or chromium of equal thickness. In marine exposures, cadmium is superior to zinc.
- (3) Different plating processes for zinc and cadmium have little effect on the protective value of the coatings, but may affect the mechanical properties (forming operations).
- (4) Electroplated zinc coatings furnish about the same protection as hot dipped (galvanized) zinc coatings of equal thickness.

Zinc plating has many advantages. The cost is low and it is readily available. A comparatively thin coat of zinc will protect plain carbon steel even if the base metal is exposed. With proper supplementary treatment, it can be painted to form a system with extremely high corrosion resistance. It is widely used to eliminate galvanic couples for magnesium or its alloys, commercially pure aluminum, steel or copper. Cadmium is recommended for copper bearing and aluminum alloys.

Electroplating of zinc has some advantages over hot dipping (galvanizing). Tempered and high carbon steels can be electroplated from an acid zinc bath. It reveals defects on the steel surface. A heavier zinc coat can be applied. The thickness and uniformity of the coat can be more accurately controlled.

Zinc plating also has some limitations. Zinc plate is known to cause intergranular disintegration of steel on parts that reach a temperature of 700°F (371°C) or higher.

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The nature and aggressiveness of the environment determine to a large extent the degree of two-metal corrosion. Usually the metal with lesser resistance to the given environment becomes the anodic member of the couple, but sometimes the potential reverses for a given couple in different environments. Usually both steel and zinc corrode by themselves, but when they are coupled, the zinc corrodes and the steel is protected. In an exceptional case, such as some domestic waters at temperatures over 180°F (82°C), the couple reverses and the steel becomes anodic. Apparently the corrosion products on the zinc, in this case, make it act as a surface noble to steel.

Zinc plating should not be used on parts which, in service, reach a temperature of 500°F (260°C) or higher or come in contact with other parts which reach those temperatures.

Federal Specification QQ-Z-325 covers the requirements for electrodeposited zinc coatings. In general, the requirements for stress relief prior to cleaning and plating, embrittlement relief after plating and reactivation of baked zinc surfaces for chromating, are similar to those described earlier for cadmium (Federal Specification QQ-P-416).

ASTM Standard Specification A 164 deals with electrodeposited coatings of zinc on steel and AMS Specification 2402 also covers zinc plating.

3.8 Copper plate. Copper electrodeposits are most widely used as undercoatings in multiplate coating systems. Although copper is relatively corrosion resistant, it is rarely used alone as a final plate where a durable and attractive surface is required, because it tends to tarnish and stain rapidly when exposed directly to the atmosphere. Plating of zinc and steel parts with copper before nickel and chromium plating is carried out on a large scale in industry. Cyanide copper plating of zinc die castings provides a suitable undercoat for reliable plating of these items with nickel and chromium. The copper undercoating improves the nickel bond and thus promotes better adhesion.

Since copper plate is cathodic to most base metals, its protective value depends on the degree to which it envelops the basis metal. Copper less than 0.0005 in (13 μ m) thick gives very little protection because of its porosity. If applied thin over less noble metals (nickel, iron or zinc) there is strong galvanic action if the base metal is exposed by a pinhole or scratch.

Where copper plate is employed by itself, it is generally to take advantage of some specific characteristic such as electrical or thermal conductivity (e.g., cookware) or as a temporary coating for metal treatment operations. As an undercoat for other plates, copper plate provides two main functions: *adhesion and smooth surface*. It adheres well to base metals such as steel or zinc and succeeding plates, in turn, adhere well to it. Copper plate is easily buffed or can be plated bright and smooth to provide a base for a mirror finish top plate. Copper plates varying in thickness from 0.001 to 0.005 in (25 to 125 μm) are used as a heat treatment stopoff to prevent case hardening of steel on selected areas of the part. Copper deposits, about 0.0002 in (5.1 μm) in thickness, are used to prevent basis metal migration into tin overlayers to poison solderability. For plating printed circuit through holes, plate thickness is generally about 0.001 in (25 μm). As an undercoating for nickel and other metals, plate thickness usually ranges from 0.0002 to 0.001 in (5.1 to 25 μm). Copper strike plates may range from 0.00001 to 0.00002 in (0.25 to 0.50 μm). When used for decorative applications, such as housewares, architectural trim, etc., the plate thickness may go up to 0.010 in (250 μm) or more. For such applications, a clear organic coating is generally applied to prevent tarnishing.

Copper can be electrodeposited from numerous solutions. However, four main types (i.e., alkaline cyanide, alkaline pyrophosphate, acid sulfate and acid fluoborate) account for most of the commercial plating. The primary constituent of each bath is the corresponding copper salt. All four bath types are also apt to contain small amounts of organic additives for refining the grain or brightening the plate. Even though the areas of application for the four types of copper plating solutions overlap, each bath has some fairly well defined areas of usefulness. For example, acid baths cannot be used to plate copper directly on bare steel or zinc, because a poorly adherent copper deposit is formed by immersion. The usual procedure is to deposit an initial copper strike plate on zinc and steel parts in a cyanide bath and then transfer them to an acid bath to build up the deposit at a faster rate. A nickel strike may be used instead of the copper strike on steel parts.

There are three principal types of cyanide baths: (1) regular copper cyanide - relatively low efficiency (10 to 50%); (2) Rochelle copper cyanide - intermediate efficiency (30 to 60%); and (3) high efficiency (99+%) copper cyanide with high metal content. The regular cyanide bath contains cuprous cyanide, sodium cyanide, sodium hydroxide and sodium carbonate. Strike versions of the bath are less concentrated. The Rochelle bath is similar to the regular cyanide bath, but additions of Rochelle salt (sodium potassium tartrate) permit operation at higher current densities and higher current efficiencies. The higher efficiency bath contains a substantially higher metal and salt content than the other two baths; frequently, more conductive potassium salts are used in place of some or all of the sodium salts. Regular and Rochelle baths have good throwing and covering power and can deposit good adherent copper plates on zinc and steel. A cyanide strike plate must first be applied to steel or zinc before plating in the high efficiency bath. Much higher plating rates and ability to produce thicker deposits are features of the high efficiency baths.

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The pyrophosphate bath has characteristics similar to the high efficiency cyanide bath; the plating rates are high, current efficiencies are 99+%, and thick deposits are possible. The bath has good throwing power, is noncorrosive and nontoxic. A strike plate is needed for plating on zinc and steels. Pyrophosphate baths are widely used in the plating of printed circuits. The use of pyrophosphate baths has grown because their freedom from cyanide makes treatment and disposal of the pyrophosphate bath effluents less of a problem.

The acid copper sulfate bath is widely used because it plates rapidly, is low in cost and is readily controlled. The acid fluoborate bath produces good plates at high deposition rates; its main drawback is its high initial cost. The acid baths are used extensively for coating wire, electroforming and many other engineering applications.

Military Specification MIL-C-14550 covers electrodeposited copper coatings on metal surfaces. The requirements for stress relief and hydrogen embrittlement relief for copper plating of high strength steel parts are generally similar to those described earlier for cadmium (Federal Specification QQ-P-416). Copper plating is also covered in AMS Specification 2418.

3.9 Lead plate. The appearance of electroplated lead, together with its physical and chemical properties, limits its commercial use primarily to corrosion protection and bearing applications. Because lead can be so readily applied by hot dipping, such coatings are more frequently used than electroplates. However, electroplated lead coatings for comparable thicknesses are less porous and more ductile than hot dipped coatings and are used where these characteristics are important. Typical uses for electroplated lead include: (1) protection of metals from corrosive liquids such as dilute sulfuric acid and hydrofluoric acid; (2) linings of brine refrigerator tanks and chemical tanks; (3) linings of pipes, pumps and other equipment used in the manufacture and storage of chemicals; (4) coatings for storage battery hardware (nuts and bolts); and (5) linings for bearings. Deposit thicknesses for these applications generally range from 0.0005 to 0.010 in (13 to 254 μ m). Frequently, for bearings, a lead-tin alloy plate is employed.

Unlike zinc or cadmium, lead is cathodic to iron and, if the plate is pitted or broken, the base metal will corrode. Some tests show that pores in lead plate tend to be self healing and resist undercutting of the plate. Lead is soft and buffing further improves corrosion resistance by flowing the metal and closing up pinholes. It furnishes a high degree of corrosion protection in industrial atmospheres, particularly those with a high content of sulfur gases. The formation of surface films of sulfate and oxide helps retard corrosion. It resists the action of sulfuric acid and for this reason is plated on hardware used with lead storage batteries. In rural and marine environments lead plate offers only fair protection and is easily pitted. It is too soft to resist wear by abrasion, which makes it unsuitable as a general finish. This softness, which enables it to take particles away from a bearing surface by absorption, together with its low friction resistance, makes it valuable as an anti-friction surface for bearings. A comparatively thin coat of plated lead gives engine bearings long life under severe conditions. Lead coatings also facilitate soldering of parts.

Although lead can be electroplated from a variety of solutions, only the fluoborate, fluosilicate and sulfamate baths are of commercial importance. The fluoborate baths yield fine grained and dense deposits and are the most widely used of the three types of baths. The fluoborate baths are less susceptible to decomposition and easier to control than the fluosilicate and sulfamate baths. Lead can be deposited directly on steel from the fluoborate bath, but not from the fluosilicate. However, a thin copper undercoat is often employed to enhance adhesion of the lead plate from the fluoborate bath. A typical fluoborate bath contains lead fluoborate, free fluoboric acid, excess boric acid and a small amount of animal glue, peptone or resorcinol to promote a smooth deposit.

Military Specification MIL-L-13808 covers electrodeposited lead plating on iron and steel, copper and copper-rich alloy surfaces. The requirements regarding stress relief and hydrogen embrittlement relief for lead plating high strength steel parts are generally similar to those described earlier for cadmium (Federal Specification QQ-P-416).

ASTM Standard Specification B 200 deals with electrodeposited coatings of lead and lead-tin alloys on steel and ferrous alloys. AMS Specification 2414 covers lead plating for preventing galling of metal parts and for improving the performance of bearings.

AMS Specification 2415 describes the electrodeposition of lead and indium plates for producing an alloy coating by diffusion of the indium into lead.

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3.10 Silver plate. Electroplated silver coatings are lustrous, soft, ductile and malleable. Silver is used to provide decorative, protective and engineering coatings. Prior to World War II, the major uses of silver plating were for decorative and protective coatings on holloware, flatware, cutlery, jewelry, surgical and musical instruments, etc. Because of silver's good chemical resistance, high electrical and thermal conductivities, good resistance to high temperature oxidation and good bearing properties, the use of silver electroplating for industrial and engineering applications has increased greatly from that earlier period. The increase was especially marked in the electronics and related industries and for bearing applications. Coating thicknesses for most applications generally range from about 0.0001 to 0.002 in (2.5 to 50 μ m). For example, deposits for tableware and holloware are usually 0.001 to 0.002 in (2.5 to 50 μ m) in thickness. For bearings, the thickness generally ranges from 0.004 to 0.020 in (100 to 500 μ m) and may go up to 0.060 in (1500 μ m) for special applications.

Because silver is cathodic to steel, it is necessary that silver coatings (if used alone) be pore-free, if they are to provide protection to steel. Freedom from porosity generally requires silver plates 0.001 in (25 μ m) or more in thickness. However, thinner coatings of silver will provide protection to steel if used over an undercoat of copper, nickel or copper-nickel; such systems are usually employed to conserve silver and cut costs. Military Specification QQ-S-365 calls for a minimum plating thickness of 0.0005 in (13 μ m) on all surfaces in which silver is functionally necessary (for example: appearance, wear, corrosion protection or conductivity). On ferrous surfaces the total plated thickness should not be less than 0.001 in (25 μ m). This must be comprised of at least 0.0005 in (13 μ m) or more of silver plate over 0.0005 in (13 μ m) or less of nickel or copper or any combination of nickel or copper; the copper is to be deposited first over the steel surface.

The following are typical thicknesses of silver coatings for various applications:

Thickness		Use
in	μ m	
0.0003	(7.6)	For articles such as terminals which are soldered.
0.0005	(13)	For corrosion protection of nonferrous basis metals.
0.0005	(13	For electrical contacts, depending on pressure, friction, and electrical load.
to	to	
0.010	250)	
0.0005	(13)	For increasing the electrical conductivity of basis metals.

Silver is usually electroplated from alkaline cyanide solutions. The conventional solutions contain potassium silver cyanide, potassium cyanide, potassium carbonate, plus small amounts of addition agents for grain refining and brightening. The high speed silver baths are more concentrated versions of the conventional baths, which also contain potassium nitrate and potassium hydroxide. The high speed baths are operated at higher temperatures and are used for plating thicker coatings (e.g., on bearings) at higher rates.

Silver plating is usually carried out in two or three stages. One or more strike plates are first applied in dilute strike baths (solutions of low silver and high cyanide content) according to the nature of the basis metal, in order to obtain good adhesion of the final silver plate. Steel, for example, is often plated in two different strike baths prior to transfer to the regular silver plating bath. One strike plate is generally employed over nickel, copper, lead, zinc and their alloys. Copper, copper alloys and steel are sometimes plated with nickel before striking with silver.

Silver plate has high electrical conductivity and fair solderability and, for bearings, a high seizure resistance and resistance to corrosion by oxidized oils. During storage, silver tarnishes rapidly in sulfur-bearing atmospheres. Ordinary cardboard and paper often contain sufficient sulfur compounds to cause tarnish; therefore, sulfur-free packing materials should be employed. For electrical parts, tarnish (silver sulfide) is still a good conductor. Under high potentials and a humid atmosphere, silver may migrate across insulators and cause shorts.

Supplemental chromate treatments may be used to increase the tarnish resistance of the silver plate for some applications.

Military Specification QQ-S-365 covers the general requirements for electrodeposited silver plate. The requirements regarding stress relief and hydrogen embrittlement relief for silver plating high strength steel parts are generally similar to those described earlier for cadmium (Federal Specification QQ-P-416).

Other documents covering various aspects of silver plating are as follows:

AMS Specification 2410 - Silver Plating (Nickel Strike, High Bake)

AMS Specification 2411 - Silver Plating (For High Temperature Applications)

AMS Specification 2412 - Silver Plating (Copper Strike, Low Bake)

AMS Specification 2413 - Silver and Rhodium Plating.

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3.11 Tin plate. Desirable characteristics of electrodeposited tin are its resistance to corrosion and tarnish, its nontoxic nature, its solderability and its ductility and softness. The largest single use of electrodeposited tin coatings is in the production of electrotinned sheet steel for cans. The electrolytic process has largely replaced hot dipping and now accounts for almost all tin plate production, especially in the United States. The electrolytic process is more economical and provides better control of plate thickness, greater uniformity and a substantial reduction in the amount of tin required to give satisfactory corrosion resistance. Electroplated tin is also employed extensively as a coating on refrigerator parts, dairy and other food handling equipment, washing machine parts, kitchenware, automotive pistons and piston rings, electronic components, electrical lugs and connectors and copper wire.

Electrolytic tin has many desirable features. It can be applied as a thin and uniform coating and is resistant to atmospheric corrosive attack and to aqueous solutions in the absence of oxygen. Electroplated coatings can be applied as thin as 0.000015 in (0.38 μm) for tin can stock and generally need be only about 1 to 2 mils (25 to 50 μm) thick for other applications. By electrodepositing from an alkaline bath over hot dipped tin plate, the number of pores has been reduced 5 to 10% of those in hot dipped coatings of equal total thickness.

As a coating on steel, tin is more noble than the basis metal and thus does not provide sacrificial protection and will, in fact, promote corrosion of the basis metal at discontinuity (pore) sites. This fact is important with electroplated tin, because extremely thin coats generally contain many discontinuities which extend through to the basis metal. Tin should be cathodic to iron, but the potential reverses in most sealed cans containing food products and the tin acts as a sacrificial coating, thus protecting the steel. Complex ion formation apparently causes this reversal. Tin is relatively inert, but in the presence of oxygen or other oxidizing agents, it is attacked. Thus, for most food and beverage products in which the steel base is anodic to tin, the inner surfaces of the tin cans are coated with organic finishes such as lacquers and enamels.

Typical tin plate thicknesses for various applications are shown below:

Use	Plate thickness	
	in	μm
Soldering	0.0002 to 0.0005	(5 to 13)
Resist atmospheric corrosion	0.0005 to 0.0015	(13 to 38)
Prevent galling and seizing	0.0002 to 0.0004	(5 to 10)
Prevent case during nitriding	0.0002 to 0.0006	(5 to 15)
Resist abrasion, corrosion	0.002	(50)

Tin is electroplated mostly from alkaline stannate (potassium or sodium stannate plus potassium or sodium hydroxide) and acid (tin sulfate/sulfuric acid or tin fluoborate/fluoboric acid) baths. The stannate baths have greater throwing power, are easier to control and are more adaptable to varied types of work. On the other hand, the acid processes have higher plating rates and substantially lower power requirements. This is because the deposition valence is two, rather than four, current efficiency higher and cell voltage lower. The choice of bath will be governed greatly by the type of work to be plated. Electroplated tin is usually dull or matte in appearance. The coatings of almost all electrolytic tin plate and many tin plated items are brightened by heating the parts up to about 450°F (232°C) either in hot oil or by electrical induction. At this temperature the plate is reflowed, resulting in a coating with a smoother surface and smaller or fewer pores. Recently, bright tin deposits for decorative applications have been produced in acid sulfate plating solutions using proprietary additives.

Tin plate readily accepts solder, but the acceptance decreases with long storage. It can be used on surfaces to prevent galling or seizing. Tin plate on steel forms a good paint base.

Military Specification MIL-T-10727 covers the electrolytic plating and hot dipping of ferrous and nonferrous metals with tin. Electrodeposited tin, type I, of MIL-T-10727, has been replaced with the industry standard ASTM B 545, Electrodeposited Coatings of Tin. Federal Specification QQ-T-425 deals with electrolytic tinplate produced from low carbon-reduced steel. AMS Specification 2408, Tin Plating, is another document dealing with tin plating.

3.12 Cobalt plate. The properties of electrodeposited cobalt are similar to those of nickel in many respects. Cobalt coatings are bluish white, are generally similar to iron and nickel in hardness and resemble nickel in their microstructure. Cobalt's resistance to atmospheric corrosion is generally comparable to that of nickel. Cobalt coatings offer excellent resistance to wear and abrasion.

Until about 1969, the price of cobalt was substantially higher than that for nickel. This price relationship, coupled with the limited technology on plating bright, corrosion protective coatings and the relatively high internal stress of cobalt deposits, discouraged widespread applications of cobalt plating. Since 1969, uses for cobalt and nickel-cobalt have been increasing.

Cobalt can be plated from solutions that are similar to nickel plating electrolytes, with the nickel salts replaced by the corresponding cobalt salts. Cobalt is usually plated from chloride, sulfate or sulfamate baths. Because of their magnetic properties, cobalt coatings are widely used for electronic applications, such as memory drums, disks and tapes.

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3.13 Alloy plate. Alloy plating is simultaneous codeposition of two or more metals. Some alloy coatings are better than single metal deposits in appearance or engineering properties. Alloy plates are often denser and harder, tougher and stronger and less porous. Some alloys have good corrosion and wear resistance. Others have unique magnetic or antifrictional characteristics. The metals most commonly used in depositing alloys are tin, nickel, lead, zinc and copper. Using suitable solution formulations, it is possible to produce a wide range of alloy electroplates.

In general, electrodeposited alloys have properties resembling those of metallurgically produced alloys, but there are many exceptions. Although many alloy plating processes have been developed, comparatively few have merited extensive commercial use. This is because alloy plating must be justified by some significant advantage, since it is usually more difficult to control than plating a single metal.

Changes in concentration, degree of acidity or alkalinity, temperature and addition agents affect the ratio of the metals deposited. There is no simple relation between the ratios of the two metals in the bath and that deposited from the bath. For example, to deposit a nontarnishing alloy of 90% silver and 10% cadmium, the bath should contain 40% silver and 60% cadmium. A cobalt-nickel alloy containing 75 to 95% cobalt is deposited from a sulfate solution containing equal amounts of cobalt and nickel. Anodes must be controlled to dissolve in the bath in the same ratio as that being deposited from the bath. In general, because of variations in current density, the composition of an alloy will vary on different parts of an irregularly shaped article. However, by careful control of bath composition, temperature, pH, addition agents, anode composition and other operating conditions, it is generally possible to achieve sound deposits of the desired alloy composition. Some of the more widely used alloy plating processes (including brass, bronze, tin-zinc and others) are described below.

3.13.1 Brass plate. Brass is one of the more widely used alloy plates. Electrodeposited brass coatings are applied mainly for decorative purposes to a variety of steel products, principally hardware and electrical fittings, to simulate the appearance of solid brass. Deposits in the composition range of 70-80% copper and 20-30% zinc are among the more widely plated brass alloys. Brass coatings are generally plated from alkaline cyanide baths containing mainly copper cyanide, zinc cyanide and sodium cyanide, with or without other reagents. Coating thicknesses are generally in the range of 0.00005 to 0.0003 in (1.3 to 7.6 μm). Brass can be plated directly on steel. Cast iron is usually strike plated with copper, tin, zinc or nickel, prior to brass plating. Aluminum surfaces are given a zincate treatment before applying the brass. An important engineering use of brass plate is to provide a good surface for bonding rubber to steel or other metal products.

Brass deposits of 0.0002 in (5 μm) provide very little corrosion protection and are therefore frequently covered with a clear protective lacquer.

3.13.2 Copper-tin alloy plate. Copper and tin can be codeposited in all proportions from aqueous copper, cyanide-tin stannate solutions. Many proprietary processes are also available. Of principal commercial importance are the alloys in the range of 8 to 15% tin, balance copper; these alloys are generally referred to as bronzes. Decorative and protective coatings on cabinet hardware made of steel, or zinc or lead die-cast alloys constitute one important use. Bronze plate is also used for coating radio and television chassis, steel wire products and as a stopoff coating in the nitriding of steel parts. Alloy deposits containing 5 to 10% tin are deposited on steel and aluminum bearings. During times of nickel shortages, it was substituted with some success for nickel plate as the undercoating for decorative chromium. Copper-tin alloy plate is more expensive than copper but it is superior in corrosion resistance, hardness and rate of plating. The corrosion protection of bronze plates can be improved by the application of protective lacquer coatings.

A 40 to 45% tin alloy (speculum) was developed and commercialized in England, but used only to a limited extent in the United States. Speculum has a silvery appearance and is employed for decorative applications for indoor use, such as tableware and bathroom fixtures.

3.13.3 Copper-tin-zinc alloy plate. The Cu-Sn-Zn ternary alloy, which may be called a form of "white brass", is known by various trade names, as most processes for plating it are proprietary. The ternary alloy is deposited from a bath containing copper and zinc cyanides, sodium stannate and a brightening agent. The deposit is blue-white, relatively hard (Rockwell C 50), wear resistant, tarnish resistant, nonmagnetic and easily soldered. These alloys are used to replace tin for many applications because of brightness, good throwing power and protective value.

3.13.4 Tin-zinc alloy plate. The use of tin-zinc alloy plate as a substitute for cadmium plating on many applications is steadily increasing. Part of the growth increase can be attributed to the fact that use of tin-zinc alloy as a replacement for cadmium lessens the waste treatment problem associated with adequate removal of toxic cadmium from plant effluents. The alloys of greatest interest are those in the range of 80 ± 5% tin, balance zinc. The 80Sn-20Zn alloy possesses, to a greater extent than other materials, the desirable combination of corrosion resistance and solderability which accounts for the principal uses of cadmium. The value of the 80Sn-20Zn alloy plate (with respect to corrosion protection), as compared to zinc, cadmium and tin, depends on the type of exposure, but on the whole is generally comparable and in some instances better. Where tin-zinc alloy can be substituted for either cadmium or tin plates, substantial savings in cost result.

Tin-zinc plate has a whitish appearance. The hardness of the coating is less than that of zinc, but considerably greater than that of tin. The tin-zinc alloy plate does not flake on impact and also has useful antifrictional properties. The tin-zinc coating is used because it : (1) protects the underlying steel at pores and at locally damaged points; (2) provides a high intrinsic resistance to corrosive attack; (3) solders and welds easily; (4) protects both steel and aluminum where steel bolts are used in aluminum structures; and (5) provides an excellent surface for paint and lacquers.

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The modern tin-zinc alloy plating process was developed by the Tin Research Institute, Greenford, Middlesex, England, and is entirely free from patent or other restrictions. The tin-zinc alloy is usually plated from an aqueous bath containing potassium stannate, zinc cyanide, potassium cyanide and potassium hydroxide; the corresponding sodium salts may be used instead of potassium. The throwing power of the bath is excellent with respect to metal distribution and the composition of the deposit. Tin-zinc coatings are generally applied directly to the basis metal without the need for any undercoats.

The tin-zinc coating process is used in the production of: (1) radio chassis and other electronic equipment; (2) steel components for aircraft, including undercarriages, oil filters and hydraulic systems; (3) evaporator units for refrigerators; (4) switchgear; (5) nuts and bolts; and (6) steel, copper and brass parts for electrical installations.

3.13.5 Tin-nickel alloy plate. The alloy plate of primary commercial interest is that containing 65% tin and 35% nickel, ± 2 to 3% either way. The tin-nickel deposit is semibright, fairly hard and solderable. It has excellent resistance to most common chemical reagents, as well as excellent resistance to most atmospheric environments, including industrial. Its main uses have been in printed circuit manufacture and in the electronics field. The alloy is usually plated from an aqueous solution containing stannous chloride, nickel chloride, ammonium bifluoride and ammonium hydroxide. ASTM Specification B 605 covers the tin-nickel alloy electrodeposited coating.

To provide serviceability, the coating must be deposited in a stress free condition. In addition, it is generally inadvisable to specify tin-nickel finishes for parts subject to deformation in service. Tin-nickel can be deposited directly on steel, copper and copper-base alloys; however, on steel, an undercoat of copper 0.00016 in (4 μ m) is essential for severe service conditions; and on copper-zinc alloys, a similar undercoating is essential to prevent zinc diffusion for all service conditions. Zinc-base alloy must always be coated first with copper. Lack of copper coverage on zinc-alloy parts will cause reaction of substrate with the tin-nickel electrolyte and contaminate the bath with zinc.

3.13.6 Lead-tin alloy plate. Lead-tin alloy plates can be deposited over a wide range of compositions. The lead-tin alloy plates are more widely used than pure lead plates. Lead-tin and lead-tin-copper alloy electrodeposits have useful bearing properties. Codeposits of 6 to 15% tin with lead and 1 to 3% Cu or 10% Sn with lead are used on bearings in thicknesses of about 0.001 in (0.025 mm) or more. Alloy plates in the 50 Pb - 50 Sn range are applied for solderability purposes, especially in the printed circuit field. The protection against salt spray corrosion of lead plates is enhanced by codepositing tin. The plating baths for lead-tin alloy are generally similar to those for lead plating, but with tin salts added. Lead-tin coatings are covered by:

MIL-L-46064, Lead Tin Alloy Coating (Electrodeposited), 93% Pb - 7% Sn
 MIL-P-81728, Plating, Tin-Lead (Electrodeposited), 50-70% Sn -- 50-30% Pb
 ASTM B 579, Electrodeposited Coatings of Tin-Lead Alloy (Solder Plate)
 50-70% Sn

3.13.7 Nickel-cobalt alloy plate. Nickel-cobalt deposits containing 17 to 18% cobalt are finer grained and brighter than nickel plates produced without brighteners. During the nickel shortage, nickel-cobalt alloy plates containing 30 to 50% cobalt were used as substitutes for nickel coatings under chromium and are finding use for wear and erosion resistant coatings on dies for extruding plastics or casting metals. Nickel-cobalt alloy plates possess desirable magnetic properties which make them useful for memory drums, disks, tapes, etc. Nickel-cobalt alloy deposits are plated from nickel solutions to which appropriate amounts of cobalt salts have been added.

3.14 Indium plate. Electrodeposited indium is soft, ductile, tarnish resistant and has a silver-white, satiny appearance. Indium melts at 311°F (155°C). Electroplates are usually thin [0.0001 in (2.5 μm)] over an initial coating of silver, lead, cadmium, zinc, copper or tin and later heat diffused into the underlying layer. When alloyed with other metals, it imparts greater hardness, increased tensile strength, lower friction, better wear resistance and increased corrosion resistance. Important uses of indium electroplates include aircraft and automotive bearings, where it provides good wear resistance and natural lubricating qualities. Electroplated indium is used for coating silverware and other decorative consumer items and also for coating electronic parts.

Indium can be plated from cyanide, sulfamate, sulfate and fluoborate baths. The cyanide baths are the most widely used for general purpose electroplating.

AMS Specification 2415 covers the electrodeposition of lead and indium and the subsequent diffusion of indium into the lead to alloy it and improve the performance and prevent corrosion of bearings or other parts. Diffusion of indium into the lead is accomplished by heating the coated parts in an oil bath at 340 to 350°F (171 to 177°C) for 2 hours or more. The indium content of the coating usually ranges from 5.5 to 8.0 wt.%. The diffused coating thickness is generally 0.001 in (25 μm) or more.

3.15 Rhodium plate. Rhodium can be electroplated as a bright whitish coating, which is not tarnished appreciably in the air and has excellent resistance to acids, halogens and both marine and industrial atmospheres. Rhodium plate prevents galling of sliding electrical contacts, furnishes a highly decorative finish and provides a mirror surface that is highly reflective and nontarnishing. Typical plate thickness for rhodium generally ranges from 0.000002 to 0.001 in (0.05 to 25 μm). Reflectors for search lights and motion picture projectors are plated with about a 0.00001 in (0.25 μm) thick rhodium coating. Plates up to 0.001 in (25 μm) thick are applied over nickel for wear resistance and plates 0.00002 to 0.0001 in (0.5 to 2.5 μm) in thickness are applied over silver and gold for electrical contact surfaces.

Rhodium is usually electroplated from sulfate-sulfuric acid or phosphate-phosphoric acid baths. The rhodium is usually supplied as sulfate or phosphate concentrates. To avoid immersion deposits, metals other than nickel, silver, gold or platinum are plated with nickel prior to rhodium plating. Nickel underplates are also employed prior to rhodium plating of corrosion and heat resistant steels.

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Military Specification MIL-R-46085 covers the requirements for the electrodeposition of rhodium over metallic surfaces. The specification spells out the requirements for rhodium plating of high strength steels, which are generally similar to those described earlier for cadmium plating (Federal Specification QQ-P-416).

3.16 Gold plate. Gold plating can be divided into two engineering and decorative applications. Electroplated gold coatings are fine grained and dense in structure. Engineering uses are mainly in the fields of electrical equipment, electronic controls and communication equipment. Desirable features of gold plate that make it especially suited for such applications include: (1) excellent resistance to tarnish and corrosion by most chemicals; (2) good resistance to high temperature oxidation; (3) low electrical contact resistance; and (4) good solderability even after prolonged storage periods. Typical applications for gold plate include: printed circuitry, electric contacts, electronic components, infrared heat reflectors, waveguides and associated equipment. Decorative gold coatings are applied to jewelry, watches, novelty items and general trim. In spite of gold's high cost, electroplated coatings are not very expensive because they are generally used in relatively thin layers. Representative plate thicknesses for gold generally range from 0.00002 to 0.0015 in (0.5 to 38 μ m). The thinnest gold plate that approaches freedom from pores is a minimum of 0.0001 in (2.5 μ m) in thickness, depending on the character and smoothness of the substrate. Generally, for electrical contact surfaces, deposits of about 0.00005 to 0.0002 in (1.3 to 5 μ m) are employed.

Gold is mostly plated from (1) alkaline cyanide baths; (2) mildly acid cyanide baths containing citrates; and (3) neutral baths containing phosphates. The latter two baths have supplanted the older alkaline cyanide baths for many applications, partly because the newer baths are easier to control and partly because they produce plates with fewer pores. Most of the baths used industrially are based on proprietary formulations developed to produce deposits meeting the requirements of one or more general uses. Proprietary cyanide free and low cyanide baths are now in use to a limited extent, especially in plants wanting to eliminate or minimize the amount of cyanide in their effluents. Alloying elements used to control the color and physical properties of the plates include: nickel, cobalt, indium, antimony, tin, copper and silver. In most cases, the alloyed gold plates are harder, brighter and less ductile than pure gold deposits. Small concentrations of nickel or cobalt are added to gold baths to increase the hardness and wearability of alloyed deposits applied to electrical contact surfaces; the amount of codeposited cobalt or nickel is customarily only 0.2 to 0.3%, but may range up to 25%. Silver is alloyed with gold to provide electrodeposited surfaces with increased hardness and brightness. Generally, a copper, nickel, copper plus nickel, or copper plus silver strike or underplate is used on steel and many nonferrous metals prior to gold plating.

Military Specification MIL-G-45204 covers electroplated gold coatings on metallic surfaces. This specification describes the requirements for stress relief and hydrogen embrittlement relief for gold plating of high strength steels. These requirements are generally similar to those described earlier for cadmium plating (Federal Specification QQ-P-416).

Other documents dealing with gold plating are:

- (1) ASTM Specification B 488 - Electrodeposited Gold for Engineering Uses
- (2) AMS Specification 2422 - Gold Plating for Electronic Applications
- (3) AMS Specification 2425 - Gold Plating for Thermal Control

3.17 Palladium plate. Palladium plating is used for electrical applications requiring freedom from oxidation. The excellence of palladium as a contact material, coupled with its relatively low cost, accounts for the attractiveness of palladium as a coating. Palladium has a moderately high melting point and is an effective diffusion barrier. Palladium can be electroplated from several types of electrolytes, such as solutions containing the following as the primary ingredients:

- (1) Palladium amino nitrate $[Pd(NH_3)_4(NO_3)_2]$
- (2) Palladium amino bromide $[Pd(NH_3)_4Br_2]$
- (3) Palladium chloride-ammonium chloride

Salts and other reagents are added to the above materials to provide increased solution conductivity and the proper pH. The palladium plates can be bright or semibright, depending on bath composition and operating conditions.

Military Specification MIL-P-45209 covers the requirements for electrode position of palladium on metal surfaces. The specification spells out the requirements for stress relief and hydrogen embrittlement relief for palladium plating of high strength steels. These requirements are generally similar to those described earlier for cadmium plating (Federal Specification QQ-P-416).

3.18 Brush plating. Brush plating is a special electroplating procedure for coating parts or selected areas of parts without the use of immersion tanks. Metals are deposited by this process directly onto conductive cathode surfaces from highly concentrated solutions that are held in an absorbent material wrapped or attached to an inert anode. Electroplating is carried out by brushing or swabbing the part (cathode) with the electrolyte-bearing absorbent material (e.g., absorbent cotton, surgical gauze, etc.) encasing the anode.

The Dalic brush plating process was originally developed by Laboratories Dalic, Paris, France, in the 1940's. Since the most popular and advanced versions of the brush plating process are proprietary, it is often referred to as Dalic (SIFCO Metachemical, Division of SIFCO Industries, Inc., Cleveland, Ohio) or Selectron (Selectrons, Ltd., New York, NY) plating. The term "selective plating" is also used to describe the brush plating process.

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Although regular or concentrated versions of conventional plating solutions can be used for brush plating, special proprietary formulations are generally employed because of the faster deposition rates and better quality plates achieved with their use. The brush plating solutions contain highly complexed metallo-organic compounds, wetting agents and other materials such as alcohols, etc., to enhance their performance. The metal contents of brush plating solutions are generally about 5 to 50 times as concentrated as conventional tank electroplating solutions. These concentrated electrolytes, coupled with the relatively close spacing between the electrodes, permits the use of high current densities, which, for brush plating, range from about 500 to 6,000 A/ft² (55 to 650 A/dm²). These high current densities permit high deposition rates, which generally are about 30 to 60 times faster than those with conventional bath plating for most metals.

Brush plated deposits serve the same functions that conventional bath electroplates do. For example, brush electroplates are used to provide:

- (1) Corrosion protection.
- (2) Wear resistance.
- (3) Improved solderability.
- (4) Low electrical contact resistance.
- (5) Salvage of worn or mismatched parts.

Brush plating offers some unique features or advantages which make it particularly suitable for:

- (1) On-site plating in the field, since equipment and solutions are readily portable and the process is relatively simple to operate.
- (2) Repair of localized defective areas of electroplates.
- (3) Rapid plating of small areas of large parts.
- (4) Coating components or assemblies too large for existing conventional plating facilities.
- (5) Coating parts needing considerable masking before bath plating, thereby reducing masking costs.
- (6) Plating parts in place without requiring costly disassembly and handling; this can reduce machine downtime and production delays.
- (7) Plating ultra high strength steels with minimal hydrogen embrittlement.
- (8) Providing, in many cases, good plate adhesion to aluminum, stainless steels and refractory metals.
- (9) Selective plating or repair of printed circuit boards.

Brush plating is generally too costly and should not be used when areas to be plated are relatively large or conventional bath immersion electroplating techniques can be employed.

Proprietary solutions are available for brush plating most of the common metals including copper, cadmium, chromium, cobalt, iron, lead, nickel, tin and zinc. Solutions are also available for plating the following precious metals: silver, gold, indium, platinum, rhenium, rhodium and palladium. Two or more appropriate solutions can often be mixed to formulate alloy plating baths, e.g., mixing lead and tin solutions for bearing alloys, solder, etc.

The basic equipment required for brush plating is a rectifier, flexible cable electrode leads and clamps, brush plating tools or fixtures (styli) and a plating solution container. The rectifier should be capable of providing up to 24 or more volts and have sufficient dc ampere capacity to handle the anticipated plating work; it should also be equipped with a voltmeter, ammeter and ampere-hour meter. Brush plating requires an assortment of hand styli in a range of sizes and contoured shapes to fit the parts to be plated. A stylus consists of a conductive metal core, cooling fins for heat dissipation, an insulated handle and shaped anode of graphite or platinum. Graphite anodes are used for most applications, while the platinum anodes are used mostly for small hole plating and other fine plating operations. The anode is wrapped with an absorbent cotton batting and covered with Dacron or cotton sleeving, which serves as the source and reservoir for the plating solution. The absorbent pad is impregnated with electrolyte by periodically dipping the pad in the solution or by pumping or gravity feeding solution to the pad. Relative movement between the anode and cathode is needed during plating. Either the anode is rubbed against the surface to be treated or vice-versa. For example, the anode may be held against a round part which revolves in a lathe or drill press. Rubbing or swabbing is continued until the ampere-hour meter reading indicates that the desired thickness of plate has been deposited. The relative speed of movement and the applied voltage required for achieving good coating results vary for different substrates and plating solutions. Such data are provided with the proprietary solutions.

Special abrasives, masking materials and purified solutions, generally comparable to those used in high quality tank electroplating, are used for abrasive and chemical cleaning, masking, deoxidizing and activation of workpiece surfaces prior to plating. Specific proprietary cleaning and activating solutions are generally used for each metal. Reverse current cleaning, in which the part is made the anode instead of the cathode, is accomplished by switching leads or by use of switching controls on rectifiers specifically designed for brush plating. The special brush plating rectifiers are usually equipped with safety features, including fast acting short circuit protection. Recommended operating conditions for carrying out the cleaning and surface activation treatments on different basis metals using the proprietary solutions are provided.

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Military Standard MIL-STD-865(USAF) provides specific instructions on cleaning and other processing steps for brush plating various metals on: (1) aluminum and aluminum base alloys; (2) copper and copper base alloys; (3) 300 series and 400 series stainless steels, alloys containing chromium, high nickel ferrous alloys, cobalt base alloys; (4) low carbon steels; (5) cast iron and high carbon steels; (6) ultra high strength steels; and (7) dissimilar metals. This standard defines high strength steel as steel heat treated to 180,000 psi (1241 MPa) and above. These high strength steel parts are to be baked for 4 hours at $375 \pm 25^{\circ}\text{F}$ ($191 \pm 14^{\circ}\text{C}$) within 4 hours of plating with either nickel, chromium, gold or cadmium. Parts plated with DALIC Cadmium Code 2022, DALIC Cadmium Code 2023 "No Bake" or Selectron Cadmium LHE Code SPS 5070 can be used on these high strength steels and do not require a post bake plate.

4. CHEMICAL TREATMENTS AND PRETREATMENTS

4.1 General. The chemical conversion or "surface conversion" treatments for metals, described in this section, result in organic films produced by chemical modification of the surface by treatment with suitable reagents. The films formed are primarily metal oxides, chromates and phosphates, which are chemically bonded to the substrate. These coatings are formed readily and inexpensively on the metal surface by immersing the parts in a solution or by spraying, brushing or swabbing the parts with solution. Some of the coatings can be sealed or impregnated with oil, wax or other lubricants and most of them provide a good bond for paint or other organic coatings. By controlling operating conditions, a wide variety of coating properties can be obtained. Besides providing a good bonding surface, conversion coatings enhance surface appearance, resist staining and provide corrosion protection.

4.2 Chromate treatments. Chromate treatments are used primarily to retard corrosion, to improve paint bonding and, secondarily, for coloring. During chromating, a thin layer of metal substrate is converted to a film by reaction with aqueous solutions containing hexavalent chromium and other active organic and inorganic compounds. Chromate coatings are most frequently applied on zinc, cadmium, aluminum and magnesium and, to a lesser extent, on copper, brass, bronze and silver (processes for chromating magnesium are discussed under individual treatment names; see paragraphs 4.5 to 4.5.6).

The chromating solution is usually acidic and contains chromic acid or sodium or potassium chromate, plus other organic or inorganic compounds as activators, accelerators or catalysts. These latter agents include acetate, formate, fluoride, nitrate, phosphate and sulfamate ions.

When first formed, most chromate films are soft, gelatinous and easily removed by abrasion. Following a water rinse and subsequent exposure to air and drying, the coating becomes harder, less soluble, more adherent and abrasion resistant and more protective against corrosion. Chemically, the coating appears to be a complex mixture consisting of basic chromium chromate and hydrous oxides of both chromium and the basis metal. Chromate coatings will start to lose corrosion resistance properties if exposed to temperatures of 140°F (60°C) or above during drying, curing and subsequent fabrication or service. Baking at paint curing temperatures, after an organic finish has been applied, is normal practice and does not appear to affect the properties of the chromate film.

Although chromate conversion coatings can be applied by chemical or electrochemical action, the bulk of the coatings are applied by a chemical immersion, spray or brush treatment. The immersion time periods generally range from about 5 to 60 seconds, although a longer time might be necessary for some of the darker or heavier coatings. Many chromate treatments used in industry employ proprietary solution formulations. With these processes, a wide variety of protective and decorative films, ranging from colorless to iridescent yellow, brass, bronze and olive drab can be produced. The appearance and properties of the coatings depend on the basis metal and the processing procedures employed. Additional coloring of the coatings can usually be achieved by dipping the parts in organic dye baths to impart red, green, black, blue and other colors.

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The chromate conversion film has relatively poor abrasion resistance, but this is mostly compensated for by its inhibitive, self-healing feature. Should the chromate film be scratched, the exposed metal is protected by the bleeding of soluble chromate from the area adjoining the scratch. Because chromate films are thin, chromating produces no appreciable dimensional changes on parts. Although the chromate film itself is a poor electrical conductor, its use for electrical conductors is not precluded because electrical connections usually penetrate the thin film.

4.2.1 Chromating of aluminum. Chromate coatings are used extensively on aluminum for aircraft, electronics and other applications. Being lower in cost than anodizing, the process is generally employed where the greater abrasion resistance or highly decorative colors obtainable with anodized aluminum are not required. The chromate coatings have good bonding properties for subsequent organic coatings, offer good resistance to corrosion (especially in chloride environments) and range from clear to yellow in color. The coating color and properties depend on immersion time, solution composition, solution pH and, to some extent, on the aluminum alloy composition. The depth of color is a guide to the thickness of the chromate film which, under normal circumstances, is proportional to the protective value.

Conventional cleaning procedures involving solvent cleaners or vapor degreasing are used routinely on aluminum for removal of grease or other organic contaminants prior to chromating. The removal of soil from aluminum is most frequently achieved by using alkaline cleaners that function by dissolving or dispersing soils and, sometimes, augmented by etching of the metal. An etching type cleaner may be used when a matte or nonspecular surface is desired. Inhibited nonetching cleaners are employed when dissolution or roughening of the aluminum surface is undesirable. Aluminum alloys containing copper, manganese or silicon are especially susceptible to smut formation on their surfaces during alkaline cleaning. The smut generally consists of loosely adherent, finely divided particles of the undissolved aluminum alloy metals or their oxides. Typical aqueous deoxidizing and desmutting solutions for aluminum alloys are:

- 1) 10 to 50% by volume nitric acid solution (HNO_3) - This solution is prepared by diluting concentrated nitric acid (sp gr 1.42) with water.
- 2) Nitric-hydrofluoric acid solution ($\text{HNO}_3\text{-HF}$) - A 75% by volume nitric to 25% by volume hydrofluoric acid solution is prepared by diluting three volumes of concentrated nitric acid (sp gr 1.42) with one volume of hydrofluoric acid (48% by weight).
- 3) Phosphoric-chromic acid solution ($\text{H}_3\text{PO}_4\text{-CrO}_3$). Solution contains 20 g/L CrO_3 , 35 mL/L concentrated phosphoric acid (85% by weight, sp gr 1.69) and water.

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Chromating zinc and cadmium electroplates removes some of the metal coating. To allow for this loss, the minimum plate thickness should be at least 0.00015 in (3.8 μ m). For zinc and cadmium surfaces, the olive drab coating is the most protective of all chromate coatings. The coating is generally heavier and more resistant to abrasion than other colored coatings; this makes the olive drab coating well suited for many military applications.

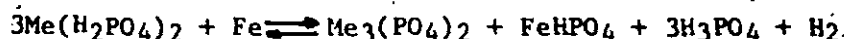
Applicable military specifications on chromate treatments for zinc and cadmium surfaces are MIL-T-12879 and MIL-C-17711. Other pertinent documents are ASTM Standard B 201 and D 2092.

4.2.3 Chromating of copper, brass and silver. Bright chromate dip treatments have advantages over conventional acid bright dips for copper alloys because they make a passive film, while producing a surface with a high luster. The chromate film provides good protection against corrosion and sulfide tarnishing on unplated parts. The film also provides a good paint base. Chromate coatings are applied to silver electroplates to prevent sulfide tarnishing. Pretreatment and chromating procedures for copper, copper alloys and silver are generally similar to those described for aluminum, zinc and cadmium.

4.3 Phosphate treatments. Phosphate treatments of one form or another are among the most widely used protective treatments for iron and steel surfaces and, to a lesser extent, for zinc, aluminum and cadmium surfaces. Phosphate coatings are relatively inexpensive and easy to produce. The treatments are readily adaptable to mass production. Phosphating is the treatment of iron, steel, zinc plated steel and other metals by immersion in a dilute solution of phosphoric acid, plus other reagents, to produce an integral conversion coating on the surface. Phosphate coatings are used to: (1) provide a good base for paints and other organic coatings; (2) condition the surface for cold forming operations by providing a base for drawing compounds and lubricants; and (3) impart corrosion resistance to the surface by the coating itself or by providing a suitable base for rust preventative oils and waxes.

Amorphous aluminum phosphate films are extensively used as a base for organic coatings. Crystalline aluminum phosphate coatings are used chiefly for bonding paint to aluminum and also to provide lubrication for cold forming.

Commercial phosphating solutions are generally proprietary and usually consist of metal phosphates dissolved in phosphoric acid solutions containing accelerators and other special agents to improve bath performance. Commonly used accelerators include nitrites, nitrates, chlorates and peroxides. A simplified overall equation for phosphating steel is as follows:



where:

Me = Zn, Mn or Fe.

The metal is provided by the basis material or the phosphating solution.

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The nitric acid solutions are the general purpose reagents for removal of smut from aluminum. The nitric acid - hydrofluoric acid solution is especially effective for removing smut formed on high silicon (5% or more) alloys. Phosphoric acid - chromic acid solutions are generally used for the selective removal of oxides without significant attack of the aluminum surface. Proprietary deoxidizing and desmutting solutions are extensively used.

The chromating solutions for aluminum often contain hexavalent chromium, a fluoride and an accelerator (such as ferrocyanide or ferricyanide). The pH range is usually 1.0 to 2.5. Nitric acid often is added as an acidifying agent. The fluoride, in the acidified solution, is the active reagent; it dissolves the existing oxide film and reacts with the aluminum. During the coating process, some of the hexavalent chromium is reduced to the trivalent state and a thin film of complex chromium gel is formed; the gel is composed of salts or oxides of hexavalent and trivalent chromium and aluminum. With drying and aging, the chromate film hardens and becomes more insoluble and abrasion resistant. For many applications, rinsing and drying complete the overall chromating operation.

The military specification for chromate treatments for aluminum and aluminum alloys is MIL-C-5541. MIL-C-81706 covers the chemicals used in producing the chromate coatings. Other pertinent documents for chromating aluminum are ASTM Standard B 449 and AMS Specifications 2473 and 2474.

4.2.2 Chromating of zinc and cadmium. Zinc and cadmium surfaces are chromated to provide tarnish and corrosion protective films which may be (1) bright or colored on zinc and cadmium electrodeposits or (2) colored on zinc die castings. Some chromate treatments brighten zinc or cadmium surfaces. The chromate coatings on zinc and cadmium retard the formation of white corrosion products upon exposure to stagnant water, moist atmospheres or stagnant environments containing organic vapors.

The chromate coatings are frequently applied to zinc or cadmium plated parts immediately after electrodeposition. No special preparation besides the rinse after plating is necessary. In some instances, a baking operation to eliminate hydrogen from the plated part is carried out following electrodeposition. When this happens, alkaline cleaning and acid dipping are customary before chromating.

Alkaline cleaning of zinc die castings is usually carried out in a proprietary solution or a solution containing sodium carbonate, sodium hydroxide and a wetting agent. The cleaned work is thoroughly rinsed and then dipped in 1 to 2% sulfuric or phosphoric acid for 15 to 30 seconds at room temperature to assure neutralization of any remaining alkaline films. After another thorough rinse, the work is then chromated. Hot dipped zinc coatings are cleaned in a manner similar to that used for die castings.

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Prephosphating cleaning of iron or steel parts is generally accomplished by alkaline cleaning or solvent degreasing. Pickling in phosphoric acid or other mineral acid solutions is used for removal of rust or other corrosion products. Rinsing in water, or in special activating solutions, generally completes the pretreatment. In some instances (e.g., with iron phosphating) cleaning and phosphating are carried out simultaneously in the same solution. The pretreatment procedures for phosphating aluminum alloys include alkaline cleaning and, sometimes, acid or caustic etching, deoxidizing or desmutting dips, along with the attendant rinses.

The method of applying phosphate coatings is generally governed by the size and shape of the part to be coated. Immersion and spray techniques are the most frequently used methods, but coatings are occasionally applied by brushing and rolling. Small parts, such as nuts, bolts, screws, stampings, etc., are coated in tumbling barrels immersed in the phosphating bath. With the immersion method, phosphate coatings are produced on surfaces by submerging properly cleaned articles in baths at temperatures of about 120-210°F (49 to 99°C) for periods ranging from a few minutes (e.g., 2 to 5 min) to over an hour, depending on the type of coating and the coating weight desired. With spray techniques, the phosphating times are shorter and generally range from about 0.2 to 2.0 minutes; the range of solution operating temperatures is 110 to 160°F (43 to 71°C).

After phosphating, the parts are thoroughly rinsed. The final rinse after phosphating of iron, steel and zinc is usually carried out in a hot [150 to 200°F (66 to 93°C)], dilute chromic acid or chromic acid-phosphoric solution (pH 2 to 4) for a minimum of 1 minute. The rinse removes unreacted chemicals and improves corrosion resistance of the phosphated surface. Following the acid rinse, the parts are thoroughly dried before the application of a supplementary treatment, such as painting, or a dip in a suitable oil, wax or lubricant. When the phosphate coating is applied primarily to serve as a basis for oils and lubricants to lower friction or to assist in cold extrusion or forming operations, the chromic acid rinse is usually omitted.

The crystalline phosphate coating acts as a mechanical bond for paint, greatly improving adherence of the paint film. The life of an organic finish is much longer over a phosphated surface than over bare steel. A phosphate coating under paint prevents the spread of rust or corrosion beyond the area of the actual scratch or exposed metal surfaces.

4.3.1 Types of phosphate coatings. The three principal types of phosphate coatings in general use are zinc, iron and manganese. Aluminum phosphate coatings represent a fourth type, which is less extensively used. These coatings, together with their uses, are described in paragraphs 4.3.1.1 to 4.3.1.4.

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4.3.1.1 Zinc base phosphate. The zinc phosphate coatings are extensively used because they provide the best corrosion resistance when applied under organic coatings. Zinc phosphate coatings are crystalline and vary from light gray to gray-black in color; they provide an excellent surface for paint adhesion. The zinc phosphate coatings are applied mostly to iron and steel and, to a lesser extent, on zinc, cadmium or aluminum surfaces, using immersion and spray techniques.

Spray coatings on steel surfaces generally range from 100 to 1000 mg/ft² (1.1 to 11 g/m²) while immersion coatings range from 150 to 4000 mg/ft² (1.6 to 43 g/m²). As a prepaint coating, zinc phosphate is normally applied in the weight range of 150 to 300 mg/ft² (1.6 to 3.2 g/m²), though heavier coatings are often used as a paint base. As an aid in drawing, extrusion or other cold forming of metal, suitable lubricants such as soap, molybdenum disulfide or oil are applied to intermediate phosphate coatings, which generally range from about 200 to 1000 mg/ft² (2.2 to 11 g/m²). Relatively heavy coatings of 1000 to 3000 mg/ft² (11 to 33 g/m²) serve as excellent retainers for oils and rust preventatives to provide good corrosion resistance. The heavy phosphate coatings are used on bearings and moving parts to reduce scouring and friction. Zinc phosphate coatings are rarely used without some supplementary treatment, such as painting or impregnating with oils or other compounds.

Zinc phosphate coatings are suitable for applications where contact with alkaline environments or exposure to temperatures in excess of 200°F (93°C) is not expected. Representative parts utilizing zinc phosphate coatings include nuts, bolts, screws, gear housings, cartridge clips and links and other ordnance hardware.

4.3.1.2 Iron base phosphate. Iron phosphate coatings are relatively thin and consist of very fine (almost amorphous) crystals which are iridescent blue to blue-brown in color. Coating weight is generally in the range of 30 to 100 mg/ft² (0.3 to 1.1 g/m²), which is substantially less than that for zinc or manganese phosphates. Although spray coating techniques are generally employed, the iron phosphate coatings are also applied using immersion methods. Both methods apply coatings that provide an excellent surface for paint adhesion and exhibit good resistance to flaking from flexing and impact. The chief application of iron phosphate coatings is as a prepaint treatment for metals, mostly steels.

4.3.1.3 Manganese base phosphate. The coatings containing manganese are the heaviest of the phosphate coatings and generally range from 1000 to 4000 mg/ft² (11 to 43 g/m²) in weight. Manganese phosphate coatings are usually black or black-brown in color. Because of their coarsely crystalline structure, which is more porous than that of other phosphates, the coatings containing manganese can retain a larger amount of lubricant or rust preventative. For this reason, manganese phosphate coatings are applied extensively to friction or bearing surfaces of ferrous parts to prevent or minimize galling, seizing or scouring. Manganese phosphates also serve as a good base for paint. Manganese coatings are usually applied only by immersion; the coating times generally range from about 5 to 30 minutes.

Although manganese base phosphate coatings are more resistant than zinc base phosphate coatings to alkaline environments, the corrosion resistance of the manganese coatings is less than that of zinc coatings in other surroundings. Manganese coatings, although more resistant to heat than zinc coatings, should not be exposed to temperatures in excess of 250°F (121°C).

4.3.1.4 Aluminum phosphate coating. A typical solution for producing amorphous phosphate coatings on aluminum contains about 9.3 oz/gal (70 g/L) phosphoric acid, plus small amounts of chromates and fluoride. The fluoride removes the oxide film on the surface and attacks the aluminum base metal to provide the ions needed to form aluminum phosphate. The treatment times vary from a few seconds to several minutes at temperatures of 100 to 130°F (38 to 54°C). The coating weights can be varied from 10 to 400 mg/ft² (0.11 to 4.3 g/m²).

Crystalline phosphate coatings on aluminum are produced using solutions containing zinc or manganese acid phosphates, an oxidizing agent such as nitrate and a complex fluoride to serve as the activating agent. Satisfactory coatings can be produced by spraying the solution for 1 to 2 minutes at 130 to 135°F (54 to 57°C) or by immersing for 5 minutes in a solution at 130 to 135°F (54 to 57°C).

4.3.2 Phosphate coating limitations. Some limitations of phosphate coatings, along with some precautions to be observed in the use of phosphate treatments, are cited below. The phosphate process must be properly controlled to prevent the formation of a loose, powdery coating or a coarse, spongy coating. Phosphate treatments other than specific prepaint treatments are not suitable for internal surfaces of optics, because of the possibility of dusting and, if oiled, the deposit of an oil film on the optical elements. Porous castings may trap cleaning solution that may blister paint films. A wear resistant manganese phosphate coating on moving parts will abrade softer metals, such as aluminum; therefore, such contacts should be avoided.

4.3.3 Specifications. Applicable documents for phosphate treatments are as follows:

GOVERNMENT

DOD-P-16232

TT-C-490

OTHER

AMS Specification 2473

AMS Specification 2480

AMS Specification 2481

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4.4 Chemical oxide treatments. Oxide films formed by controlled chemical treatments constitute an important group of conversion coatings. (Anodically produced oxide films on aluminum and magnesium are discussed in section 5.) The oxide conversion coatings are used mostly on iron, steel, stainless steels, copper, aluminum, zinc and cadmium. The coatings are generally thin and are used extensively for decorative or appearance purposes. Black oxide coatings are used extensively on military hardware to reduce light reflection on surfaces where paint would be objectionable because of excessive film thickness, poor electrical conductivity or other reasons. Oxide coatings are also used to provide a paint base and corrosion protection. The coating color and properties are largely governed by the metal or alloy treated, its surface characteristics, the composition and temperature of the bath and time of immersion. The appearance of the coating depends greatly on the surface of the basis metal. Shiny coatings are obtained on highly polished surfaces, while dull matte coatings are produced on etched, brushed or abrasive blasted surfaces.

Most oxide films, by themselves, provide only limited protection against corrosion. To improve corrosion resistance, the oxide films are often coated with oil, wax or clear lacquer. The lacquer finished oxide films are generally more corrosion resistant than oil or wax treated films.

The oxide forming processes vary greatly with the basis metal or alloy. The treatment may require aqueous solutions of alkalis or salts, molten salt baths or even various charcoal and oil treatments. Most of the oxide treatments used commercially are proprietary. The surfaces to be coated should be free of oil, grease, rust or other contaminants that might cause bare spots or other imperfections which would impair the performance of the coating. Satisfactory cleanliness can be achieved using appropriate cleaning methods, as described in section 2. The following descriptions apply to the oxide coating of specific metals and alloys.

4.4.1 Ferrous alloys (plain carbon and low alloy steels). Excluding phosphate coatings, black oxide coatings are the most extensively used conversion coatings for iron and steel. The chemical blackening process is fast and relatively simple to operate. The black oxide coating is readily applicable to wrought iron, cast and malleable irons, carbon and low alloy steels. The coating is applied by immersing the clean ferrous metal parts in a strongly alkaline aqueous solution containing oxidizing agents such as nitrites, nitrates or chlorates. Some baths also contain activators such as cyanides, tartrates and tannates, which chelate dissolved iron in the solution by complex formation. The bath temperatures are maintained at about 290 to 310°F (143 to 154°C) and the immersion time periods generally range from about 5 to 60 minutes. The coated parts are usually given a chromic acid rinse, followed by a final application of oil or wax.

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Coatings formed on iron and steel are largely magnetic oxide (Fe_3O_4) and are in the order of 0.00003 to 0.00007 in (0.76 to 1.8 μm) thick. The black oxide coatings exhibit good resistance to abrasion and chipping and, when oiled or waxed, provide low friction, nongalling surfaces. By itself, the black oxide coating affords very limited corrosion protection, but with an application of rust inhibiting oil, the corrosion resistance is much improved. Because this coating produces little dimensional change, it is particularly useful on precision parts or parts that cannot tolerate a heavier coating.

Another treatment involves heating the steels up to about 650 to 850°F (343 to 454°C) in the presence of charred bone or other carbonaceous materials. The parts are kept at temperature for several hours; after cooling the parts are coated with rust preventing oils. Gun-metal finish is produced in this manner.

Specification MIL-C-13924, class 1 is applicable to black oxide coatings for ferrous (nonstainless steel) metals.

4.4.2 Stainless steel. Black oxide coatings on stainless steel and chromium-iron steels are applied by immersing the clean parts in an aqueous alkaline nitrate-chromate solution at about 285°F (141°C). The solution is prepared by adding sodium dichromate to the alkaline nitrate bath containing sodium hydroxide and sodium nitrate, described in paragraph 4.4.1. After immersion for 30 to 40 minutes, the parts are removed and rinsed first in cold and then in hot water. Surfaces are then thoroughly dried using compressed air or another suitable method and oiled. Although this relatively low temperature dichromate treatment is primarily for stainless steel and chromium-iron alloys, it is also suitable for applying black oxide coatings to cast and malleable iron and to all carbon and low alloy steels.

The alloys which are blackened in this type of bath can be readily processed in the alkaline oxidizing process above (see 4.4.1) according to MIL-C-13924, class 1 or by one of the alternate processes for stainless steel parts, as outlined below in accordance with MIL-C-13924, classes 3 and 4.

Another method for producing a durable black finish on stainless steels involves the immersion of parts for about 30 minutes in a molten dichromate salt bath at temperatures ranging from 700 to 800°F (371 to 427°C). After coating, the work is allowed to drain briefly and then is placed on a cooling fixture for about 10 minutes. The work is then immersed in a tank of boiling or near boiling water, dried and oil dipped. Generally, sodium dichromate mp 608°F (320°C) is preferred to potassium dichromate mp 748°F (398°C) in this process, because of its lower melting point and consequent lower operating temperature. Tempering can be done in conjunction with the blackening at temperatures up to 900°F (483°C) and is applicable to chromium stainless steel with draw temperatures above 900°F (483°C). Although the high temperature dichromate blackening treatment is effective, there are certain limitations. Only parts that have been annealed or tempered at temperatures of above 900°F (483°C) may be treated. Thin sections may warp.

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Several patented processes for blackening stainless steel are marketed and some produce good deposits. Some make use of electrolysis. Their bath compositions are unknown. Some baths do not work equally well on every stainless alloy. The deposits on some alloys may have a gray or even a greenish hue. In addition, some methods depassivate the stainless steel surface, defeating the original purpose of the steel.

Although cast and malleable irons may be effectively treated in class 4 proprietary baths, they have not been included because of the class 4 salt spray requirement.

Specification MIL-C-13924 (classes 3 and 4) is applicable to black oxide coatings for stainless steels.

4.4.3 Copper and copper alloys. Copper oxide coatings can be produced on copper and copper alloys by several methods. In one, which may be called the copper carbonate-ammonia method, a dense brown or black oxide coating can be produced by immersing brass parts in an ammoniacal copper carbonate solution at 175 to 200°F (79 to 93°C) for about 0.5 to 5 minutes. The best black coatings are obtained on 80 Cu/20 Zn alloy; high zinc and high copper alloys tend to form gray and brown coatings.

A smooth, jet black film of cupric oxide needles can be produced on many copper alloys, containing at least 80% copper, by immersing them in solutions based on potassium or sodium chloride and potassium or sodium hydroxide. Most of the solutions used commercially are proprietary and usually contain special addition agents to enhance the overall coating process. The solution operating temperatures are about 210 to 215°F (99 to 102°C) and the immersion times are usually from 5 to 15 minutes. Steel, brass and other metal or alloy parts are frequently electroplated with copper to provide a suitable metal surface for production of the black oxide coating with the chloride process. The cupric oxide coating provides an excellent base for paint, lacquer, rubber or other organic coatings.

A third method, for producing deep matte black coatings on copper and many of its alloys, utilizes aqueous solutions containing ammonium persulfate and sodium hydroxide. The immersion times in boiling solutions generally range from 5 to 10 minutes. In a fourth method, applicable where copper content is over 95%, the copper is anodically oxidized in a hot, aqueous, alkaline electrolyte containing sodium hydroxide, plus a small amount of sodium molybdate or other reagents. Typical treatment times are 3 to 5 minutes for baths at about 185°F (85°C), with anode current densities of 10 to 15 A/ft² (1.1 to 1.6 A/dm²). The electrolytic process requires rigorous control to prevent gray or pale blue coatings and equipment is more expensive than for chemical immersion treatments.

Black chemical finishes for copper alloys are covered by Specification MIL-F-495.

4.4.4 Aluminum. The attractive features of chemical conversion treatments for producing oxide films on aluminum are their speed and economy. Two examples of commercial, chemically produced oxide films are those obtained with the Alrok (Aluminum Company of America) and MBV (Modifizierter Bauer-Vogel) processes. These patented processes date back to the 1930's, are somewhat similar in operation and produce generally similar coatings. The Alrok film is produced by immersion of the part for 20 minutes in a near boiling aqueous solution containing sodium carbonate and potassium dichromate. The MBV process involves immersion of parts for 3 to 5 minutes in solutions containing mainly sodium carbonate and sodium chromate. Both Alrok and MBV films can be sealed or dyed if desired. Sealing of the Alrok film in a hot potassium dichromate solution imparts a yellowish-green to grayish-green color. These colors on aluminum are in contrast to the usual black oxide films on other metals.

Although the aluminum oxide conversion coatings can be used without further treatment, they are mainly employed as an undercoating for organic finishes. The oxide coatings are thinner, softer and more porous than anodized films and are suitable, in many instances, for protection against mild corrosion. However, they cannot compete against anodized coatings in applications where resistance to wear, abrasion or more corrosive environments is required. Dyed oxide coatings are inferior to dyed anodized coatings because of poor color quality and light fastness.

Specification MIL-C-5541 applies to chemical conversion coatings on aluminum and aluminum alloys.

4.4.5 Zinc and cadmium. Zinc surfaces can be blackened by immersion at room temperature in a solution containing copper sulfate and potassium chloride. Immersion in a solution of copper sulfate, potassium chlorate and sodium chloride at 200°F (93°C) produces a black coating on cadmium. A black coating of molybdenum sesquioxide is obtained on zinc and cadmium surfaces by immersing them in an aqueous solution containing ammonium molybdate and ammonium hydroxide. Proprietary oxide coating processes are available for blackening zinc and cadmium surfaces. The black coatings on zinc and cadmium are intended mainly for decorative purposes but can also serve as a paint base.

4.4.6 Specifications. The following specifications are applicable for oxide treatments:

- MIL-C-13924 (black oxide on iron and steel)
- MIL-F-495 (copper alloys)
- MIL-C-5541 (aluminum alloys)

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4.5 Chemical treatments for magnesium. Because of their lightness and good strength-to-weight ratio, magnesium alloys are extensively used in aircraft, automotive, portable equipment and other industries. Bare magnesium generally develops a thin surface film of magnesium oxide and carbonate, which provides moderate corrosion protection against normal inland environments for many parts. However, supplementary protection in the form of coatings is required for marine environments and for many industrial and military applications.

Because magnesium is highly electropositive, it and its alloys are more susceptible to galvanic attack than most metals. Galvanic attack requires the presence of dissimilar metals and moisture. Because it is difficult to control the presence of moisture, the most common methods of protecting magnesium against galvanic corrosion involve separating it from other metals by a film or coating of paint, sealant or electroplated metal. The danger of localized galvanic attack has generally limited the use of metallic coatings to special applications, such as nickel plating, to provide wear and abrasion resistance. Paints adhere poorly to bare magnesium surfaces. Furthermore, the alkaline corrosion products of magnesium often react with the paint, causing peeling or blistering of the paint film. Accordingly, considerable effort has been expended in developing chemical immersion or anodizing methods of treating magnesium surfaces, to produce more protective surface films or films that perform well under paint. Although some of the films can be used with no post treatments, a supplemental protective organic coating is required for most applications.

Several protective treatments for magnesium have been developed. These processes consist of chemical or anodic treatments in solutions that usually contain dichromates or mixtures of dichromates and other oxy-acid salts such as nitrates, phosphates and sulfates. The choice of the particular protective treatment to employ depends on the application and severity of the environment to which the magnesium alloy part is exposed.

A clean surface is needed prior to chemical or electrochemical treatment of magnesium parts to insure adherent and continuous protective films. Accordingly, all surface contaminants such as oil, grease, oxides, dirt, etc., must be removed using one or more of the cleaning methods described in section 2. Typical cleaning cycles for magnesium and its alloys are shown in figure 1. The sequence of operations involved for several chemical and anodic treatments for magnesium are shown in figure 2. The chemical conversion coatings can be generally applied using immersion, spray or brush techniques.

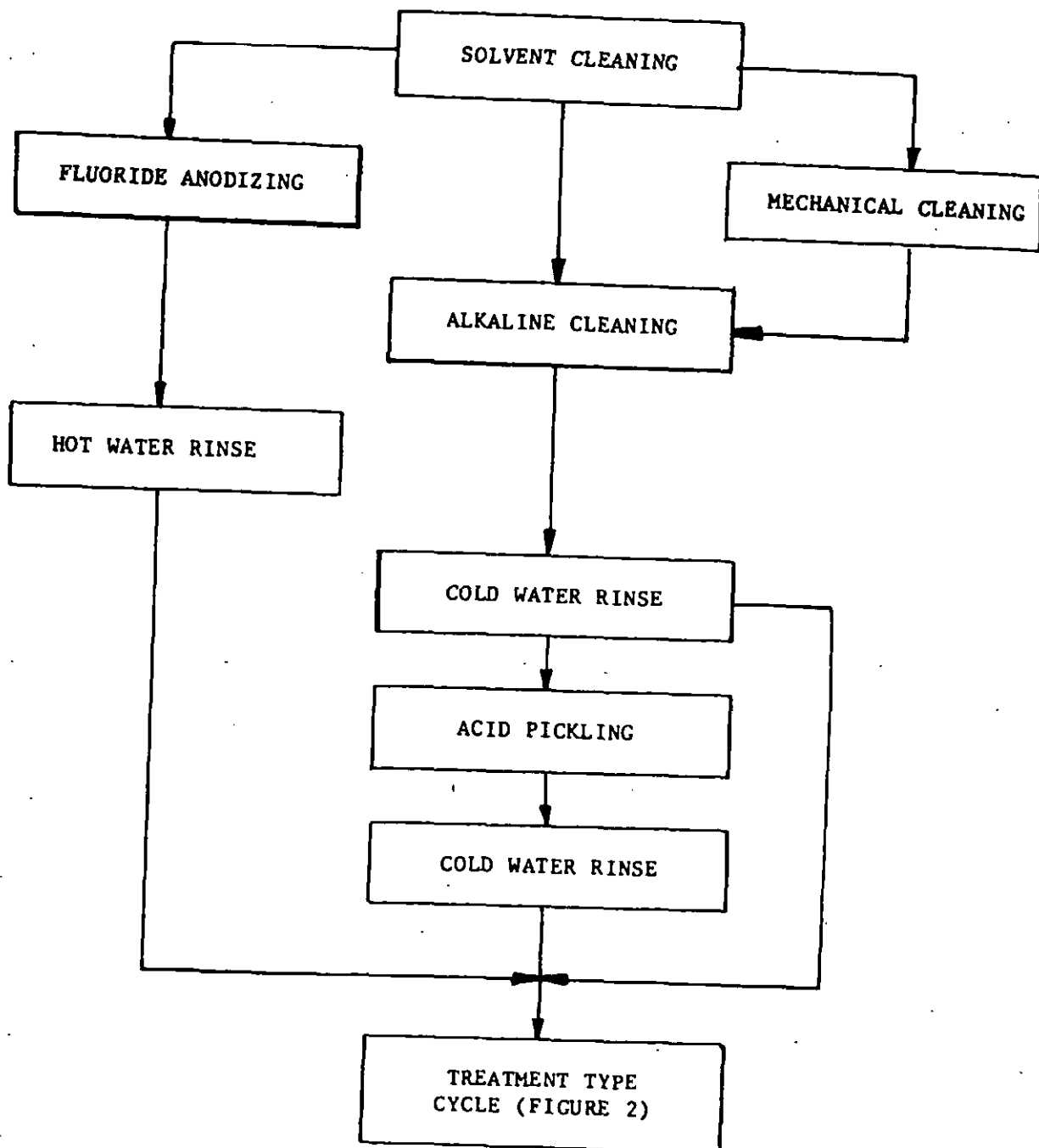
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The commercial designations of chemical and anodic treatments for magnesium, together with the handbook paragraph numbers, are shown in the following tabulation:

<u>Treatment listed in figure 2 from MIL-M-3171</u>	<u>Commercial designation of process</u>	<u>Handbook paragraph</u>
Type I	Dow No. 1	4.5.1
Type III	Dow No. 7	4.5.2
Type IV	Dow No. 9 or Galvanic Anodizing	5.2
Type VI	Dow No. 19	4.5.7
Type VII	Fluoride Anodizing or Magnesium Elecktron	5.5
Type VIII	Iridite 15	4.5.3

The individual chemical treatments shown in figure 2, together with other chemical processes for magnesium, are discussed below. Galvanic anodizing and fluoride anodizing, along with other anodic treatments for magnesium, are covered in section 5.

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FIGURE 1. Flow sheet for cleaning cycles for magnesium.

CLEANING
(FIGURE 1)

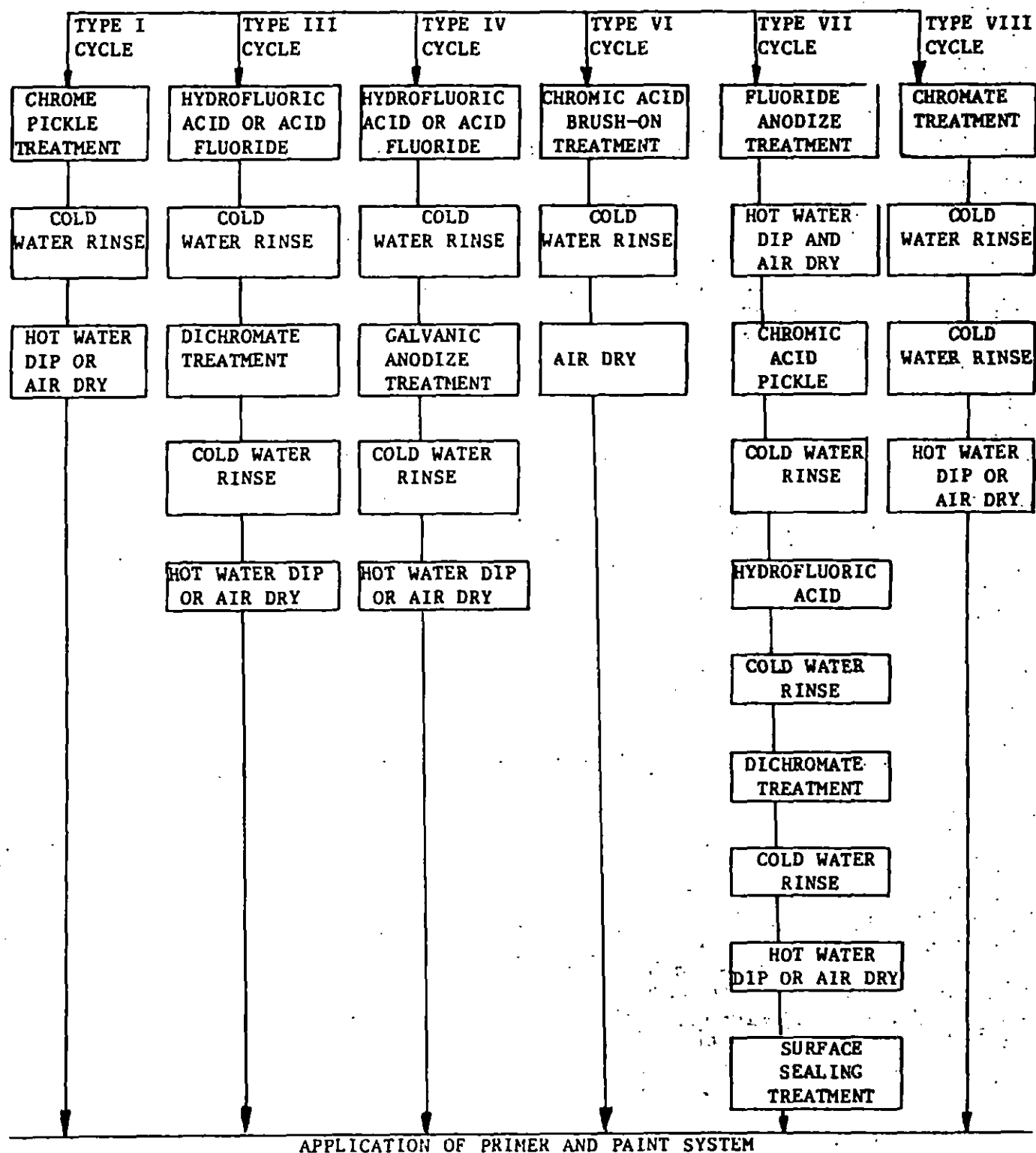


FIGURE 2. Flow sheet for treatment cycles for magnesium.

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4.5.1 Chrome pickle (Dow No. 1) treatment. The chrome pickle treatment is probably the simplest, least expensive and most commonly used of the chemical methods developed for magnesium alloy surfaces. It is one of a series of treatments developed by the Dow Chemical Company and is known as Dow No. 1 or, sometimes, simply Treatment No. 1. The coating is used to protect magnesium parts during shipment and storage, as well as to provide a good base for paints.

Suitably cleaned wrought magnesium parts are coated by immersion and agitation for 0.5 to 2 minutes in an aqueous solution of sodium dichromate and nitric acid at 70 to 110°F (21 to 43°C). Upon withdrawal, the parts are held above the tank for 5 seconds to allow the adhering solution to drain and also to promote a better colored coating. The parts are then rinsed, first in cold water and next in hot water, to facilitate drying. Sand, permanent mold and die castings are treated in a sodium dichromate-nitric acid bath to which a small amount of sodium, potassium or ammonium acid fluoride has been added. The immersion time period is 0.5 to 2 minutes and the operating temperature is 70 to 140°F (21 to 60°C). The withdrawal, rinsing and drying operations for the castings are similar to those for the wrought magnesium alloys.

The color, luster and finish of the coating produced by the chrome pickle treatment varies with the age and condition of the solution and the composition and heat treat condition of the magnesium alloy being processed. The most desirable paint base is a matte gray to yellow-red, iridescent coating, which exhibits a pebbled etch finish when viewed under magnification. Bright, brassy, smooth coatings are unsatisfactory for use as a paint base; however, they are suitable for protection during shipping and storage. This type of coating indicates an excess of nitric acid or a buildup of nitrate salt in the bath.

The chrome pickle treatment can be applied by spraying or brushing techniques. Articles too large to be immersed are processed by carefully brushing their surfaces with a generous amount of fresh pickle solution for at least 1 minute. The parts are then washed off immediately with plenty of cold running water. This coating is less uniform in color and appearance than those produced by immersion or spray methods, but is equally good as a paint base. Powdery coatings are not good as paint bases and indicate poor rinsing or failure to keep the surface wet with solution during the treatment cycle by continuous brushing. Brush application is suitable for repair or touch-up of coatings produced by different treatment solutions or techniques.

Although the chrome pickle treatment is applicable to essentially all magnesium alloys, it must be used with care on parts where close dimensional tolerances are required. The etching action of the chrome pickle baths may remove as much as 0.0006 in (15 μ m) of metal from the surface during treatment. This limits the use of the chrome pickle on close tolerance machined parts unless allowances are made or the amount of surface metal removal can be tolerated. Parts processed by the chrome pickle treatment are not to be subjected to temperatures above 450°F (232°C).

The chrome pickle treatment for magnesium is covered by MIL-M-3171, type I.

4.5.2 Dichromate (Dow No. 7) treatment. The dichromate process (also known as Dow No. 7) is probably the most widely used immersion type chemical treatment on magnesium parts for applications where maximum corrosion protection is required. It provides the best paint base and corrosion protection qualities of all the Dow dip treatments for magnesium and it is exceeded in performance only by some anodized magnesium coatings. The dichromate treatment is applicable to all magnesium alloys except EK30A, EK41A, HM31A, HM21A, HK31A, La141A and M1A; no coatings form on these alloys. The treatment causes no appreciable change in dimensions and is normally applied after finish machining. The coating varies from light to dark brown, depending on the alloy to which it is applied.

Prior to the dichromate treatment, magnesium parts must be suitably degreased, alkaline cleaned and activated, if necessary. The treatment is accomplished in two steps (figure 2, type III cycle). The parts are first pickled in an aqueous hydrofluoric acid solution (12 wt.% HF) at 70 to 90°F (21 to 32°C) for 0.5 to 5 minutes and thoroughly rinsed in cold water. In the second step, parts are immersed for 30 minutes in a boiling 10 to 15% sodium dichromate solution saturated with calcium fluoride or magnesium fluoride. Following this step, the parts are thoroughly rinsed in cold water and then, hot water, at about 160 to 180°F (71 to 82°C) to facilitate rapid drying. After drying, the desired paint coat is applied as soon as possible.

Treatment of certain types of magnesium alloys requires some modification of the hydrofluoric acid pickle or the first stage of the dichromate process. For example, AZ31B magnesium alloy parts are immersed for 30 seconds, while all other wrought alloys and castings are immersed for 5 minutes in the hydrofluoric acid pickle. For parts with aluminum inserts or rivets, the hydrofluoric acid bath is replaced with a solution containing sodium, potassium or ammonium acid fluoride, because aluminum is rapidly attacked by hydrofluoric acid.

Parts processed by the dichromate treatment are not to be subjected to temperatures above 550°F (288°C).

The dichromate treatment for magnesium is covered by MIL-N-3171, type III.

4.5.3 Chromate (Iridite No. 15) treatment. The chromate treatment (also known as the Iridite No. 15 process, Allied-Kelite Products Div., The Richardson Co.) provides a satisfactory paint base and protective coating on all magnesium alloys, in contrast to the somewhat restrictive dichromate (Dow No. 7) treatment (see 4.5.2). The coatings, applied by dip or brush methods, are similar to those of the dichromate treatment, being dark brown to light reddish brown in color. The chromate treatment has the desirable feature of being relatively fast, i.e., the coating step requiring less than 1 minute. Coating performance is generally similar to that of the dichromate (Dow No. 7) treatment. The chromate treatment causes no appreciable dimensional changes and normally is applied after machining.

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After suitable cleaning and acid pickle activation, the magnesium alloy parts are chromated in either of two solutions, depending on the aluminum content of the alloy. Magnesium alloys containing more than 1% aluminum are treated in a solution containing about 5 oz/gal (37.5 g/L) of proprietary chromate salts, 2.9 oz/gal (21.8 g/L) hydrochloric acid, plus a small amount of proprietary wetting agent. The solution used to treat magnesium alloy with less than 1% aluminum contains the same amount of proprietary chromate salts and wetting agent as the above solution, but has a lower hydrochloric acid concentration of 0.8 oz/gal (6.0 g/L) hydrochloric acid. The immersion time periods and solution operating temperatures are the same for both solutions: 15 to 30 seconds and 75 to 100°F (24 to 38°C), respectively. After chromating, the parts are given two cold water rinses, followed by a dip in hot water to facilitate drying (figure 2, type VIII cycle).

Parts processed by the chromate treatment are not to be subjected to temperatures above 550°F (288°C).

This chromate treatment for magnesium alloys is covered by MIL-M-3171, type VIII.

4.5.4 Sealed chrome pickle (Dow No. 10) treatment. The sealed chrome pickle, known as Dow No. 10, is essentially the chrome pickle (Dow No. 1) process followed by sealing for 30 minutes in the boiling solution of the dichromate process (Dow No. 7). The resultant coating is similar to that of the chrome pickle with the added corrosion inhibitive property of chromates absorbed in the film. Although the sealed chrome pickle is most commonly employed on wrought products, it is applicable to all alloys. It was originally developed for M1A alloy, where the dichromate (Dow No. 7) treatment is not applicable. The sealed chrome pickle is used as a substitute for the dichromate process or to obtain more protection than is provided by the chrome pickle treatment. The coating is matte gray to yellow-red iridescent through to brown, depending on the particular magnesium alloy being treated. The corrosion resistance of the coating is comparable to that of the dichromate process.

The steps in the coating process include chrome pickling as described above (para. 4.5.1), followed by cold water rinsing. The parts are then immersed for 30 minutes in a boiling solution containing 10 to 15 wt.% of sodium dichromate, plus a small amount of calcium fluoride or magnesium fluoride. Parts are rinsed in cold water and then in hot water to hasten drying.

For best results the dichromate boil should immediately follow the chrome pickle treatment. Sealing an old chrome pickle film, as supplied by the metal producer as a protective coating for shipping or storage, is not very effective because aging of the film prevents proper sealing.

4.5.5 Alkaline dichromate (Dow No. 8) treatment. The alkaline dichromate treatment (also known as Dow No. 8) produces a coating that varies from dark brown to black in color. The treatment is suitable for all magnesium alloys, (except EK30A, EK41A, HK31, HM21 and M1A) and produces only very slight changes in dimensions. The brown-black finish possesses good light absorbing qualities and is suitable for use on optical instruments. The coating is durable and has good protective and paint base properties. It is somewhat harder and more abrasion resistant than the Dow No. 7, 1 or 10 coatings. For severe exposures, it is better than coatings produced by the chrome alum (Dow No. 4) treatment and comparable to the galvanic anodized coating (Dow No. 9). However, the color is not as reproducible as that from the galvanic treatment, especially on Alloy AZ31A.

The previously cleaned parts are given the alkaline dichromate treatment in two stages. First, the parts are treated in a hydrofluoric acid or acid-fluoride pickle similar to that of Dow No. 7 and then rinsed. The parts then are immersed for 30 to 40 minutes in a boiling 212°F (100°C) aqueous solution containing ammonium sulfate, sodium dichromate and ammonium hydroxide. To obtain a more uniform black coating, either Nigrosine black or Indulin blue dyes are added to the alkaline dichromate bath. After coating, the parts are thoroughly rinsed in cold water and finally in hot water to facilitate drying.

4.5.6 Chrome alum (Dow No. 4) treatment. The chrome alum treatment (Dow No. 4) has relatively low protective value, similar to that of the chrome pickle (Dow No. 1) treatment. The process is used primarily on die castings and produces a black coating. The coating is suitable for mild indoor use, but is not satisfactory for outdoor service unless painted.

Parts to be treated are first suitably precleaned. Any coating from the suppliers' treatment, such as Dow No. 1, is first removed in an alkaline cleaner. The parts are then immersed in a boiling, aqueous solution of potassium chrome alum and sodium dichromate. Immersion time varies from 2 to 15 minutes depending on the condition of the bath. The parts are rinsed thoroughly in cold water and finally in hot water to aid drying.

4.5.7 Chromic acid brush-on (Dow No. 19) treatment. The Dow No. 19 treatment is used for: (1) protecting parts during temporary storage; (2) protective touch-up of previously treated work; and (3) brush application where parts and assemblies are too large to be immersed. The chromic acid brush-on treatment is covered by MIL-M-3171, type VI. The uses of the type VI coatings are generally similar to those of the type I chrome pickle (Dow No. 1) treatment. The type VI treatment is less critical to apply than the type I treatment by brush application. Also, the type VI treatment is relatively inexpensive, not harmful when solution is trapped in faying surfaces and does not present the toxicity hazards of the type I treatment. The type VI treatment can be readily applied to magnesium parts by brushing, dipping or spraying. A dilute chromic acid-calcium sulfate solution at 70 to 90°F (21 to 32°C) is used for the type VI treatment.

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Proper brush application of the type VI treatment requires that the surface of the parts be kept wet with the solution for a sufficiently long time (usually about 1 to 3 minutes) to produce a brown film. The parts are then rinsed in cold running water and dried in an oven or by exposure to a blast of hot air. The paint base properties of the type VI coating are comparable to those of the type I coating.

Type VI processed coatings require painting or sealing before exposure to overnight, outdoor atmospheric conditions. Type VI coatings can vary from brassy iridescence to dark brown, depending upon treatment time. Up to 1 minute of treatment produces a brassy film and from 2 to 3 minutes, a dark brown coating. Prolonged treatments produce loose, powdery coatings. For best paint adhesion, the dark brown coating is preferred.

The type VI (Dow No. 19) treatment is applicable to all magnesium alloys when close dimensional tolerances are not required. Parts processed by this treatment are not to be subjected to temperatures above 450°F (232°C).

4.6 Stannate immersion (Dow No. 23). The stannate immersion (Dow No. 23) treatment was developed by the Dow Chemical Company under an Ordnance Corps contract. The process is available for use under a royalty and a fee-free license from Dow. The process was developed to provide a protective paint base on all magnesium alloys, including shapes that contain inserts and fasteners of other metals such as brass, copper, steel, etc. The treatment deposits a layer of tin on the dissimilar metals and reduces the chance of galvanic corrosion. The high alkalinity of the bath results in an attack on aluminum, so that the treatment should not be employed on parts containing aluminum inserts or fasteners. As a paint base, the stannate coating is comparable to the coatings produced by the dichromate treatment (Dow No. 7) and to the Dow No. 17 anodic treatment. The coating's low electrical resistance makes it especially suitable as a paint base where radio frequency (RF) grounding is required.

The preferred cleaning cycle includes solvent degreasing, when necessary, followed by alkaline cleaning, hydrofluoric acid pickling and rinsing. The stannate coating is produced by immersing the parts in an aqueous solution containing potassium stannate, tetrasodium pyrophosphate, sodium hydroxide and sodium acetate. Parts are treated in the bath at 180°F (82°C) until a minimum coating thickness of 0.00015 in (3.8 μ m) is formed or until bare metal, including inserts, is no longer visible. The recommended 20 minute immersion period normally produces a 0.0002 in (5 μ m) thick coating on magnesium alloys and a slightly heavier coating on steel inserts. A cold water rinse follows the stannate treatment.

If parts are to be painted, the stannate coating is neutralized by immersing the parts in a room temperature solution containing sodium acid fluoride for 30 seconds. The parts are rinsed first in cold water and then hot water to facilitate drying. The use of wash primers is mandatory when painting over the stannate film.

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4.7 Wash primer (pretreatment coating). The wash primer (Formula No. 117-B for metals) represents an interesting departure from standard surface pretreatments in that it combines an organic coating with an etching solution. There is some question whether it should be called a primer or a pretreatment. Probably due to the fact that a conventional primer is always applied over it, the term "pretreatment" is given comparable billing with primer in the title of the military specification governing this treatment. The "wash" description reflects its extremely low consistency, suggestive of solutions for washing. The wash primer coating is for use on clean metal surfaces of all types.

The wash primer was developed to provide a substitute for conventional phosphate treatments. The purpose of the material is to increase the adhesion of the paint system. It is not intended as a permanent protective primer in itself, although some protection is afforded for short periods of time. However, to insure the best results, the pretreatment film should be coated with primer as soon as possible. The wash primer is a mixture of resins, solvents, pigments, water and phosphoric acid. Originally it was (and still usually is) supplied in two parts: the resin (or "base") component and the acid (or "activator") component. These are mixed in the ratio of 4 parts resin component to 1 part acid component and applied to the precleaned metal surface. The base component contains polyvinyl-butylal resin, basic zinc chromate, magnesium silicate, lampblack, butyl alcohol, isopropyl alcohol and water. The acid or diluent component contains phosphoric acid, water and isopropyl alcohol. The acid component is not a thinner, but a necessary activator for the treatment. After the addition of the acid component, the primer must be used within 8 hours.

The wash primer increases adhesion of paint systems to metal. It can be used where phosphate coatings cannot, i.e., on large or unwieldy parts that cannot be dipped or on parts with sections that are masked off. It can be used for treatment or touch-up in the field, where industrial pretreatment equipment is not available. It may be used as a shop coat. It may be used on dissimilar metals that cannot be pretreated together by other processes.

As for limitations: the two package type wash primer must be prepared for use each time by mixing the components and it must be used within 8 hours after mixing. The treatment should be coated with primer within 24 hours after application, since it loses its effectiveness after a short exposure to adverse weather conditions. The protection of aluminum is not quite as good as that given by anodized or Alrok treatments. Tests show that wash primer as a touch-up pretreatment for magnesium surfaces gives corrosion protection over the treated area, but the phosphoric acid should be reduced by 50 to 75%. Wash primer is better than other touch-up materials for magnesium exposed to humid conditions.

The two package wash primer is covered by DoD-P-15328.

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4.8 Passivation treatment. When the bare surface of a common metal or alloy is not attacked by the medium that normally might attack it, the metal or alloy is said to be in the passive state. Passivity is not a constant state or an absolute property, for example, like melting point, but exists only in certain environments or under certain conditions. Some metals remain passive under a broad range of conditions while others lose their passivity with only a slight change in environment. It is widely accepted that resistance to attack or corrosion is not an inherent property but depends on the ability of the metal to form a protective film. Therefore, some authorities define passivity as the tendency or ability of a metal to form a protective film. Aluminum, chromium and stainless steels are examples of metals that meet the film forming concept of passivity. Other authorities believe that passivity is an electronic property, inherent in the metal, and not a surface phenomenon.

The noble metals, such as gold or platinum, do not readily corrode, but for a different reason. Their nobility, which is not to be confused with passivity, depends on their atomic structure and only slight tendency to ionize or pass into solution.

The protective film associated with passive metals is usually an oxide or a hydrate film. It may be very thin and in many cases not visible to the naked eye, but its presence has been established. In order for this film to be protective, it must be continuous and insoluble in the particular environment or medium to which it is exposed. Also the film must be self-healing, i.e., if broken, it will reform when re-exposed to an oxidizing agent. The passivity of certain metals interferes in the application of some of the processes of metal finishing. In such cases, the protective film is removed by some form of dip or electrolytic treatment before the actual coating process begins.

The surface is then receptive to the treatment, i.e., "activated". A disadvantage of this procedure, particularly for stainless steels, is that a major benefit of the alloy is destroyed merely for the purpose of applying a particular finish and one must then be concerned with protecting the basis metal.

Passivity has a greater influence on the corrosion resistance of stainless steels than on that of most other metals. This passivity is often removed locally, where small particles of metal become embedded in the surface as a result of mechanical fabricating or cleaning operations. For example, during forming, machining, abrasive blasting, tumbling, grinding and other processing operations, particles of iron or other metals may be embedded or smeared on the surfaces of stainless steel parts. If not removed, the iron corrodes and produces rust-like spots on the stainless steel. To prevent this condition, semi-finished or finished stainless steel components are given a passivation treatment. The passivation treatment generally consists of immersing the part in an aqueous solution of nitric acid or of nitric acid and oxidizing salts. The passivation treatment dissolves the embedded or smeared iron particles and restores the original corrosion resistant surface to the stainless steel by forming a thin, transparent oxide film. The following solution and operating conditions are suitable for passivating 200 and 300 series stainless steels and chromium grades containing 16% or more Cr:

Composition:

Nitric Acid - 20-50%
Water - Balance

Temperature - 120-160°F (49-71°C)

Immersion time - 10 to 30 min.

This method is not suitable for free machining grades of stainless steel and polished surfaces.

Free machining grades, polished surfaces and 400 series stainless steels containing less than 17% Cr, are passivated in a nitric acid-dichromate solution as shown below:

Composition:

Nitric Acid - 20 to 40%
Sodium dichromate - 2-6 wt.%
Water - Balance

Temperature - 70 to 120°F (21-49°C)

Immersion time - 25 to 40 min.

Both of the above methods may also be employed to remove lead, copper, zinc or cadmium applied to stainless steel wire for cold heading, wire drawing or spring winding.

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Several important points should be kept in mind with regard to prolonging the passivity of bare stainless steels. Stainless steels are normally passive but, when exposed to nonoxidizing corrosive conditions, they become active. Localized corrosion frequently results from the depletion of the oxidizing agent. For example, in sea water, pitting beneath a barnacle is a sample of localized corrosion from depletion of oxygen. The maximum corrosion resistance of stainless steel is obtained from a bare, clean surface, free from grease, oil, dirt, etc. Ordinary air is a passivating agent for clean stainless steel surfaces.

The passivation treatments for stainless steels were previously covered by QQ-P-35. This document is no longer used by the DoD. Used instead is ASTM A 380, Cleaning and Descaling Stainless Steel Parts, Equipment and Systems. This is now the accepted standard for cleaning or passivation treatments for stainless steels.

5. ELECTROCHEMICAL CONVERSION COATINGS (ANODIC COATINGS)

5.1 General. The finishing methods to be described are surface conversion treatments, commonly called anodic treatments, which are applied with the aid of electrolysis to magnesium, aluminum and zinc surfaces. In certain cases, some of the chemical conversion processes may be substituted for anodic treatments.

Because of electric current cost (and also higher equipment and racking costs) anodic treatments are more expensive than chemical conversion treatments. However, anodic coatings are denser, thicker and harder than chemical conversion coatings. They offer maximum protection for magnesium and aluminum against corrosion and wear. The anodic coatings provide excellent paint base surfaces. The protection desired must be weighed against the coating cost when a selection is being made. Specific anodizing processes for magnesium, aluminum and zinc, and their alloys, are presented and discussed in this chapter.

5.2 Galvanic anodize (Dow No. 9) treatment. The galvanic anodize treatment, also known as Dow No. 9, may be applied to all magnesium alloys and forms. The process is particularly useful for those alloys that are not receptive to the dichromate treatment (Dow No. 7). These alloys include EK30A, EK41A, HM31A, HM21A, HK31A and M1A. The process makes use of the relatively high potential difference existing between magnesium workpieces and the steel tank or steel cathodes hung in the tank. Generally, no external current is required, but parts must be racked firmly for proper galvanic action to take place. Monel, stainless steel or phosphor bronze racks are often used. Properly applied coatings are uniformly dark brown to black in color. Time of treatment, condition of bath and composition of the alloy influence the color of the coating. The galvanic anodize treatment produces no appreciable dimensional change and is normally applied after machining. The process is used extensively on optical, electronic and other parts where a nonreflective coating is required. The dark coating provides good corrosion resistance and paint base characteristics similar to those of the Dow No. 7 coating.

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The galvanic anodize treatment is applied in two stages (section 4, figure 2). Properly solvent degreased and alkaline cleaned parts are first pickled in the hydrofluoric acid or acid fluoride bath as in the dichromate (Dow No. 7) treatment and then rinsed. The parts are then galvanically anodized for at least 10 minutes or as long as 30 minutes in an aqueous sodium dichromate solution containing ammonium sulfate and ammonium hydroxide until uniformly covered with a dark brown to black coating. The bath temperature is maintained at 120 to 140°F (49 to 60°C); the bath pH is kept between 5.6 and 6.0 by additions of a solution containing 5% by weight each of chromic acid and sulfuric acid. The magnesium parts must have a good external electrical connection with the tank or cathode plates. The current density should not exceed 10 A/ft² (1.1 A/dm²) of anode area at any time. Ordinarily, 70 to 150 ampere-minutes per square foot of anode is sufficient to produce a uniform coating. When the area of work is large, in respect to tank size, it is important not to allow the anode current density to fall below 2 amp/sq ft (0.2 A/dm²), as poor coatings result. In such instances, it is customary to employ an external current source to maintain the anode current density within the desired range. After anodizing, the parts are thoroughly rinsed in cold water, followed by a hot water rinse to facilitate drying.

Gray and nonuniform coatings indicate that cleaning before treatment is inadequate or that the treating solution was depleted. Nonadherent or poor quality coatings are generally caused by too high a current density, too prolonged a treatment or by too low a bath pH. An increase in time required to secure a uniform coating also indicates a depletion of the solution.

A more pronounced black coating may be obtained by the addition of small amounts of either Nigrosine Black or Indulin Blue dyes to the anodizing solution.

Parts processed by the galvanic anodize method should not be subjected to temperatures above 550°F (288°C). The galvanic anodize treatment is covered by MIL-M-3171, type IV.

5.3 Dow No. 17 anodize treatment. The Dow No. 17 process is probably the most versatile of all the Dow chemical or anodic treatments for magnesium. The process can be used on all forms and alloys of magnesium and uses an aqueous acidic electrolyte containing a combination of fluoride, phosphate and chromate ions. Anodizing can be carried out using either alternating or direct current, but alternating current is more commonly used because of the lower cost of electrical equipment. However, about 30% less time is required for anodizing with direct current for a given current density. The coatings produced are generally similar, regardless of the type of current used. In each case, the voltage is increased to maintain the current density range desired. The Dow No. 17 coatings exhibit excellent corrosion resistance and paint base qualities. They also possess good hardness and abrasion resistance. All machining, drilling or other metal removal should be carried out prior to anodizing. It is also recommended that parts have all edges rounded off before anodizing to avoid subsequent chipping of the coating.

Dow No. 17 coatings usually correspond to one of three specific types, depending on the end or terminal voltage employed and the intended use of the coating. The first type is a very thin, clear coating produced with a terminal voltage of 40 volts; the anodizing time is 1 to 2 minutes. The coating is used as a base for subsequent clear lacquers or paints to produce a final appearance similar to clear anodizing on aluminum. The second type of coating is produced by anodizing to an end voltage of 60 to 75 volts; the time required ranges from 2.5 to 5.0 minutes depending on the alloy and the current density. The thin, light gray-green coating is used in most applications which are to be painted. The coating thickness is about 0.0003 in (7.6 μm) and produces a buildup of about 0.0002 in (5 μm) per surface.

The third type corresponds to a thick, dark green coating produced with an end voltage of 75 to 95 volts; the anodizing times generally range from about 11 to 30 minutes. The coating thickness is about 0.0009 to 0.0012 in (23 to 31 μm); the dimensional increase is about 2/3 of the coating thickness. The thick coatings offer the best combination of abrasion resistance, protective value and paint base characteristics. Allowances must be made for the anodic coating buildup where close dimensional tolerances are involved.

The thick, dark green coating is subject to fracture or spalling from physical abuse such as flexing, but provides some compensation through the corrosion inhibiting effect of the chromate film. The thick, dark green coatings are recommended for castings and extruded sections. The light gray-green coating, being less subject to spalling, is recommended for use on sheet materials.

The Dow No. 17 process is essentially a one step treatment. The properly precleaned parts are immersed in a heated aqueous solution containing ammonium acid fluoride, sodium dichromate and phosphoric acid or ammonium acid fluoride, sodium dichromate and ammonium acid phosphate. The operating temperatures generally range from 160 to 180°F (71 to 82°C); the baths will not operate below 140°F (60°C) but can be operated up to the boiling point. The current densities range from 5 to 50 A/ft² (0.54 to 5.38 A/dm²) or more, with either alternating or direct current.

For direct current operation, a grounded unlined steel tank usually serves as the cathode. Where the tank is lined or made of a nonconductive material, mild steel plates serve as cathodes. With alternating current, the parts are usually divided into two groups with approximately equal surface areas; each group serves as an electrode. Anodizing is preferably carried out using a reasonably constant applied current. Initially, 1 to 30 volts is applied and the voltage is raised continuously to maintain the desired current density as the coating thickness and resistance increase. The treatment times vary mainly with magnesium alloy, end voltage and current density. Complex parts should be agitated while totally immersed in solution to minimize entrapment of air in pockets or blind holes. Periodic repositioning of complex parts is desirable to promote uniform coating of all surfaces.

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After anodizing, the work is rinsed first in cold water and then in hot water to facilitate drying. When the anodized parts are to be left unpainted or painted only in certain areas, they are usually sealed by a 15 minute immersion in an aqueous solution containing sodium silicate at 200 to 212°F (93 to 100°C). The sealed parts are rinsed in cold water and then in hot water to facilitate drying.

The Dow No. 17 treatment is covered by MIL-M-45202, type I, class C for light green coatings and type II, class D for thick, dark green coatings. Other documents dealing with the Dow No. 17 treatment include AMS Specifications 2478 and 2479.

The caustic anodize (Dow No. 12) treatment was superseded by the Dow No. 17 treatment.

5.4 HAE anodic treatment. The HAE anodic finish is an electrolytically applied ceramic coating for magnesium that was developed at the Pitman-Dunn Laboratories, Frankford Arsenal. (Further information on the HAE process is available from Western Sealant Metal Finishing Co., Philadelphia, PA.) The ceramic coatings, which are produced by an anodic treatment in a caustic solution, have excellent corrosion, abrasion and heat resistance. The high voltage HAE coating is probably the hardest currently available for magnesium. The HAE bath has good throwing power and provides a coating which is an excellent paint base. The HAE coating can be sealed and the residual alkali neutralized to improve its corrosion resistance and paint base properties. For maximum corrosion protection, resin sealing or painting over the coating is required.

The HAE process is applicable to all magnesium alloys, after proper allowance has been made for dimensional change, but should not be used on parts which will be flexed in service. All machining, drilling or other metal removal should be performed prior to anodizing. It is also recommended that parts have all sharp edges rounded off before anodizing.

The HAE process deposits a brown ceramic coating ranging from tan for light films to dark brown for the heavy films. The HAE bath is an aqueous solution containing potassium hydroxide, aluminum hydroxide, trisodium phosphate, potassium fluoride and potassium manganate or potassium permanganate. Solvent degreasing and alkaline cleaning are generally employed to prepare parts for HAE anodizing. Three principal types of coatings can be produced using the above electrolyte by varying the operating conditions and processing times. The HAE process uses alternating current because direct current is not satisfactory. The three types of coatings are as follows:

- (1) **Low voltage coating.** The low voltage coating is applied in about 15 to 20 minutes using approximately 9 volts ac at a current density of 40 A/ft² (4.3 A/dm²) and a bath temperature of 140 to 150°F (60 to 66°C). The coating is relatively soft, smooth and olive drab in color.

- (2) High voltage (light coating). The light coating is produced in about 8 minutes using a current density of 18 to 20 A/ft² (1.9 to 2.2 A/dm²); the terminal voltage is 60 volts ac. The bath is operated at room temperature, about 70 to 90°F (21 to 32°C), and cooling is generally required. The coating is relatively soft, smooth and tan in color.
- (3) High voltage (hard coating). The heavy or full hard coating is produced by anodizing to an end voltage of 85 volts ac. The current density ranges from 18 to 25 A/ft² (1.9 to 2.7 A/dm²) and the treatment time is 60 to 75 minutes. Solution cooling is generally required to maintain it at the operating temperature of 70 to 90°F (21 to 32°C). The dark brown coating produced is harder and slightly rougher than that obtained in (1) and (2) above.

The light tan coatings range from about 0.00015 to 0.0003 in (3.8 to 7.6 μ m) in thickness, whereas the heavy coating is usually about 0.001 to 0.0015 in (25 to 38 μ m) in thickness. The dimensional increase associated with the HAE coatings is about 80% of the film thickness.

Equipment and electrode arrangements, similar to those used for the alternating current version of the Dow No. 17 treatment, are suitable for the HAE process. After anodizing, the parts are thoroughly rinsed in cold water and then are usually given one of several post treatments depending on end-use application. One post treatment involves a 1 minute dip at room temperature in a solution containing ammonium bifluoride and sodium dichromate. This post treatment is necessary to neutralize the alkali retained in the coating to allow good paint adhesion; it also improves the protective value of the coating, especially in the unpainted condition. After the dip, the parts are allowed to drain but are not rinsed. The parts are then allowed to dry in air, or to age from 3 to 4 hours or from 6 hours to overnight in a humid environment (85 \pm 5% RH) at approximately 185°F (85°C). Aging improves the protective quality of the coatings.

When light tan coatings are to be dyed, the processing sequence is as follows: (1) anodize; (2) cold water rinse; (3) hot water rinse; (4) dry; (5) dye; (6) rinse; and (7) dry. If specified or desired, the dyed coating can be sprayed lightly with an acrylic ester resin lacquer in order to seal the pores.

The HAE and Dow No. 17 treatments are the most widely used processes for anodizing magnesium alloys. The corrosion protection properties of both coatings are closely comparable, but the high voltage HAE coatings are harder and more abrasion resistant than the Dow No. 17 coatings. Other attractive features of the HAE coatings are its stability at high temperature and good dielectric strength.

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The HAE treatment for magnesium is covered by MIL-N-45202 with classifications as follows:

Type I - Light coating

Class A - Tan coating (HAE)

Grade 1 - Without post treatment (dyed)

Grade 2 - With bifluoride-dichromate post treatment

Type II - Heavy coating

Class A - Hard brown coating (HAE)

Grade 1 - Without post treatment

Grade 3 - With bifluoride-dichromate post treatment

Grade 4 - With bifluoride-dichromate post treatment including moist heat aging

Grade 5 - With double application of bifluoride-dichromate post treatment including moist heat aging

Additional information on the HAE process is provided in AMS Specification 2476.

5.5 Fluoride anodizing process plus corrosion preventive treatment. The fluoride anodizing treatment is essentially a cleaning process involving an anodic treatment followed by a stripping operation to remove the fluoride coating and, lastly, a corrosion preventive treatment of the surface to provide better protection. The fluoride anodize treatment was developed in England by Magnesium Elektron Ltd. The fluoride anodizing process is primarily an anodic cleaning process for use on castings to remove foundry sand. The process is useful as an inspection tool to reveal surface defects in castings. The process can also be used on magnesium-rich wrought alloys to remove surface contamination due to sheet rolling and to remove graphite lubricant used in deep drawing operations. The anodizing and stripping portions of the treatment may be applied to all magnesium alloys and forms. The anodizing portion of the treatment is suitable to take the place of shot or grit blasting as a means of cleaning magnesium alloys of adherent foundry sand and the subsequent pickling operation. The anodizing treatment also removes impurities of active metals at the surface.

The anodizing treatment is usually carried out with alternating current at a constant current density of about 5 A/ft^2 (0.54 A/dm^2) until the voltage reaches 120 volts. The operating temperature of the aqueous ammonium bifluoride bath is from 60 to 86°F (16 to 30°C). The treatment times generally range from 10 to 15 minutes. After anodizing, parts are rinsed in hot water and then dried by exposure to heated air.

The magnesium fluoride film formed is thin, 0.0001 in (2.5 μm) or less, and produces no appreciable dimensional changes. The film is white or pearly gray. In addition to being a good paint base, the magnesium fluoride film provides a considerable amount of corrosion protection. Because the film does not have the property of self healing, improved corrosion protection is obtained by chromating or using the Dow No. 17 or HAE anodic treatments. Stripping of the fluoride film in a boiling chromic acid solution is generally done before application of chromate type treatments such as the Dow No. 7. Stripping of the film is not required for application of the Dow No. 17 or HAE anodic films. Additional corrosion protection of the chromated surfaces (especially castings) is provided by sealing with a resin such as MIL-C-46079, epoxy coating. The sealing operation is often employed even if painting follows.

The fluoride anodizing process plus corrosion preventive treatment is covered by MIL-M-3171, type VII.

5.6 MGZ anodizing process. The MGZ process for anodizing is a recent development of the Doehler Jarvis Castings Division of NL Industries, Toledo, Ohio. The MGZ treatment produces a hard, protective, dark green to dark gray coating for magnesium and its alloys. The MGZ coating is free of nodules and other irregularities and is reported to be more protective than other anodized coatings such as Dow No. 17 and HAE. The processing times for the MGZ process are equal to or less than those required for the HAE or Dow No. 17 processes.

The MGZ process is carried out as follows. After vapor degreasing and alkaline cleaning, the magnesium parts are dipped in a hot aqueous chromic acid solution for 5 minutes and then rinsed. Parts are then anodized using alternating current in an aqueous bath containing chromate, vanadate, phosphate and fluoride ions. The bath is continually cooled to maintain a temperature of about 180°F (82°C). Anodizing is performed at constant current density of 50 to 60 A/ft² (5.4 to 6.5 A/dm²), under progressively increasing potential. The terminal voltage is 340 volts. The treatment time usually ranges from 3 to 8 minutes. Water rinsing completes the operation. No further sealing or other post treatment is required with the MGZ coating.

Data generated by the Doehler Jarvis Casting Division showed that the salt fog resistance of the MGZ coating, without any post treatment, surpassed that provided by sealed or post treated Dow No. 17 or HAE anodized coatings on magnesium AZ31B sheets and AZ91B die cast plates. Modified Taber abrasion tests showed that a 0.001 in (25 μm) MGZ coating was markedly superior in wear resistance to thicker 0.0012 in (30 μm) coatings produced by the Dow No. 17 and the 0.0015 in (38 μm) coatings produced by the HAE processes.

As indicated earlier, the MGZ treatment is a recently developed process which is currently (May, 1976) in pilot plant or limited commercial use.

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5.7 Cr-22 anodic treatment. The Cr-22 process for anodizing magnesium was developed at the Pitman-Dunn Laboratories, Frankford Arsenal. The Cr-22 coating is smooth, moderately hard and has good corrosion resistance. The coating can be used as a base for organic finishes or as a final finish, with or without an inorganic seal. The Cr-22 treatment produces green or black ceramic coating; the color depends on the anodizing bath composition and operating conditions. Coating thicknesses usually range from about 0.0003 to 0.0011 in (7.6 to 28 μ m). Although not as hard as the HAE coating, the Cr-22 coating has good abrasion resistance. It also has high dielectric strength, requiring 500 to 600 volts for dielectric breakdown. The heavier Cr-22 coatings, like those produced by the HAE and Dow No. 17 treatments, will spall under compressive deformation.

Prior to anodizing, the magnesium parts are degreased, alkaline cleaned and acid pickled as required. Anodizing is carried out with alternating current in an aqueous bath containing chromic acid, hydrofluoric acid, phosphoric acid and ammonium hydroxide. The bath temperature is maintained at about 185 to 195°F (85 to 91°C), and current density usually ranges from 15 to 25 A/ft² (1.6 to 2.7 A/dm²) with the terminal voltage at 320 volts. The treatment times are generally 12 to 15 minutes. The parts are then rinsed and dried. If parts are to be used without further organic finishes, they are usually sealed by immersing them in a hot (near boiling or boiling) aqueous sodium silicate solution for 2 minutes. After sealing, which greatly enhances the corrosion resistance of the coating, the parts are dried without rinsing.

The properties of the Cr-22 coatings vary with extended operation of the bath. To maintain coatings quality, particular attention must be given to the replenishment of bath constituents.

Cr-22 coatings for magnesium were originally covered by Military Specifications MIL-M-45202 (Ord) and MIL-M-45202A, type II, class B and class C. In the more recent versions of the specification, the Cr-22 treatments were deleted since this process is not used to any extent.

5.8 Manodyz anodic treatment. The Manodyz process is one of the older (1940's) methods for anodizing magnesium that was patented by Consolidated Vultee Aircraft Corporation. The Manodyz coating is applied in a strongly alkaline bath using either alternating or direct current. The aqueous bath contains sodium hydroxide, sodium silicate and phenol. With alternating current, the coating produced is gray in color and approximately 0.0004 in (10 μ m) thick. With direct current, the coating is light green and up to 0.0008 in (20 μ m) thick. The coating has considerably more resistance to corrosion than the dichromate treatment (Dow No. 7); it is also harder and more wear resistant than most of the chemical conversion coatings for magnesium. The Manodyz coating provides a good base for paint and organic coatings.

After vapor degreasing and alkaline cleaning, parts are pickled in a bath containing chromic acid and calcium nitrate. If the magnesium alloy has a high aluminum content, fluoride is added to the pickle bath. Anodizing is carried out in a hot, 165 to 190°F (74 to 88°C) bath, at a current density of 30 to 40 A/ft² (3.2 to 4.3 A/dm²) dc or 15 to 25 A/ft² (1.6 to 2.7 A/dm²) ac. It generally takes about 25 minutes to obtain the desired coating. After anodizing, the parts are first rinsed in cold water and then neutralized in a weak chromic acid solution for 2 to 5 minutes. When removed, the parts are dried without rinsing in order to retain chromate in the coating and improve its performance as a paint base.

The Manodysz process is not used to any significant extent at the present time.

5.9 Sulfuric acid anodizing of aluminum. Sulfuric acid anodizing is the most widely used and economical process for anodic treatment of aluminum surfaces and chromic acid anodizing is second in both respects. The general characteristics of the anodizing processes, together with a discussion of cleaning and surface preparation operations preceding anodic treatment, which are common to both processes, are presented below, prior to the detailed coverage of the individual processes.

Aluminum and its alloys form a thin, tightly adherent film that constitutes a barrier against corrosive attack. The surface films, developed in a typical outdoor environment, are usually continuous, of low solubility and relatively impervious. However, these natural aluminum oxide coatings are too thin to be of significant value under more severe corrosive conditions.

For maximum protection, thicker oxide coatings produced by anodizing processes are required. Anodizing of aluminum involves the electrochemical conversion of the surface to aluminum oxide, wherein the aluminum serves as the anode in an aqueous electrolyte and the oxygen is provided by the electrolytic dissociation of water. Anodizing of aluminum and its alloys provides corrosion protection, decorative surfaces, wear resistant surfaces, a good base for paints and other coatings and surfaces with special electrical and engineering properties.

The properties of the anodic coatings are significantly influenced by the nature, concentration and temperature of the electrolyte. Other important items affecting the coating properties are the type of current, current density, processing time and the alloy composition. The two most common electrolytes are sulfuric acid and chromic acid; oxalic acid is also used but to a markedly lesser extent. The films produced in these electrolytes differ in color, porosity, flexibility and other characteristics.

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Preparative operations for all aluminum anodizing treatments are essentially the same and can be comparatively simple or extensive, depending on the particular parts being anodized and their intended use. The cleaning and surface preparation procedures prior to anodizing aluminum are generally similar to those used to condition aluminum surfaces for chromating (section 4, figure 1). Solvent cleaning or vapor degreasing is generally used first to remove grease and other organic contaminants from aluminum. Soak cleaning may then be carried out in an inhibited alkaline cleaner, such as sodium carbonate containing phosphate or silicate. A phosphoric acid solution may also function as a cleaner. In many instances, the cleaner is strong enough to etch the aluminum slightly or is followed by an alkaline etching solution containing sodium hydroxide. Alloying elements in the aluminum, particularly copper, may not be dissolved by the etchant and give rise to a smut on the surface. A desmutting bath such as nitric acid is then used to remove the smut. Finally, if a bright or shiny appearance is to be maintained, a bright dip made of concentrated nitric acid and phosphoric acid may be employed.

The most extensively used anodizing process for producing thick anodic coatings on aluminum is that employing sulfuric acid. In addition to yielding coatings having a wide range of desirable properties, sulfuric acid anodizing has the advantages of low cost, rapid coating and comparatively low voltage operation. The low voltage is due to the high conductivity of the sulfuric acid electrolyte and its ability to penetrate the film to the underlying metal. The electrolyte has a solvent action on the film, i.e., part of the film dissolves as new oxide is formed at the basis metal interface. This solvent action influences the film properties. The sulfuric acid process can be categorized according to the two general types of anodic coatings that are produced, i.e., conventional and hard coat. The conventional process is more extensively employed, being used to produce protective and decorative coatings ranging in thickness from about 0.0001 to 0.0012 in (2.5 to 30 μ m). The hard coat sulfuric acid process is used to produce thick, hard, wear resistant anodic coatings ranging in thickness from about 0.0005 to 0.005 in (13 to 127 μ m); the hard coat process is discussed in detail later in this subsection.

Conventional sulfuric acid anodizing is usually carried out at room temperature, 68 to 77°F (20 to 25°C) in an aqueous solution of sulfuric acid (12 to 20 wt.% H_2SO_4) using direct current. A constant current density of about 12 A/ft² (1.3 A/dm²) is usually employed; the voltage required varies with the different alloys and electrolyte conditions, but usually ranges from 10 to 25 volts. In general, the coating hardness may be increased by lowering the temperature, decreasing the acid concentration and increasing the current density, while softer and more porous coatings are produced by the reverse operations. Vigorous agitation of the electrolyte is provided to insure uniform electrolyte temperature, especially adjacent to the work. Clean air is generally employed for bath agitation. Sulfuric acid anodizing is usually carried out in steel tanks lined with plastic or rubber. Cathode area is provided by using lead or removable stainless steel or aluminum strips. Because the anodizing rate varies with different types of aluminum alloys, it is good practice to group "similar" alloy parts on the processing racks. Articles with dissimilar metal inserts (such as those of iron, steel and brass) that are anodically attacked in the bath, are not anodized as assemblies, unless the non-aluminum materials can be effectively masked. After anodizing, the parts are rinsed in water and then are usually either dyed or sealed.

The anodic coating varies from a colorless, clear transparent film to one that is opaque or translucent. Generally, some of the metallic sheen of the base metal remains. The coating color is influenced by the alloy composition, treatment time and bath composition. For example, silicon causes opaque occlusions in the relatively transparent film, resulting in dark gray color. In the as-anodized condition, the coatings formed in sulfuric acid (also chromic and oxalic acid) are very hard and in a highly porous, absorptive state, suitable for dyeing. Once dyed, or if used clear, the anodic coating is given a further treatment to seal the pores and yield a continuous, stain resisting, easily cleaned surface with improved corrosion resistance. The color fastness of dyed coatings is also greatly enhanced by sealing.

Anodic coatings produced by the sulfuric acid process can be sealed by immersing the parts in any one of several solutions. The principal sealing treatments are:

- (1) Hot water sealing. Hot water sealing is the most common sealing treatment. It consists of immersing the parts in hot or boiling water [200 to 212°F (93 to 100°C)] for 10 to 30 minutes, depending on coating thickness. This treatment involves hydration and converts some of the surface aluminum oxide to crystalline alpha alumina monohydrate, which occupies a greater volume than the alumina from which it was formed. This increase in volume closes and effectively seals the pores. Hot water sealing does not affect the color or appearance of the film. It does increase the corrosion resistance of the coating, but not as much as does dichromate sealing. Steam is sometimes employed in place of hot or boiling water to speed up sealing.

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- (2) Dichromate sealing. The part is immersed in a hot [190 to 210°F (88 to 99°C)] aqueous solution containing 5 to 6% by weight of sodium or potassium dichromate for 20 to 30 minutes. This treatment imparts a yellow color to the anodic coating, but at the same time it also provides the best corrosion resistance of any of the sealing treatments. This is due to the absorption of corrosion inhibiting chromate into the pores of the film. Dichromate sealing is very useful as protection against stress corrosion in Duralumin and other high strength alloys, particularly in sections where traces of the corrosive sulfuric acid from the anodizing bath might remain. The dichromate treatment is sometimes used as a second sealer over dyed coatings that had first been sealed in a nickel acetate or cobalt acetate bath. To avoid yellowing of the applied color, the strength of the dichromate sealing bath is reduced to 1% sodium or potassium dichromate by weight. The second seal is used to further improve the corrosion resistance of the coating.
- (3) Nickel or cobalt acetate sealing. Anodic coatings can be sealed by immersing parts in a hot [180 to 210°F (82 to 99°C)] aqueous solution containing 0.5 to 1% weight of nickel acetate or cobalt acetate for 15 to 20 minutes. This treatment is primarily used to seal porous anodic films after they have been colored with organic dyes. The nickel or cobalt salts are absorbed into the coating where they are precipitated as virtually colorless hydroxides, which help stabilize the color. The pores of the film are sealed in the same bath or given a further hot water sealing in a subsequent treatment.

Deionized, distilled or high purity water is recommended for use in sealing bath makeup. Frequent bath replacement is also advised. Sealing generally produces a slight reduction in the hardness and abrasion resistance of the anodized coatings.

Conventional sulfuric acid anodizing is suitable for treating essentially all aluminum alloys. This includes those alloys with a nominal copper content in excess of 5%, or a nominal silicon content in excess of 7% and, also, alloys containing over 7.5% of total alloying elements. Chromic acid anodizing is not suitable for treatment of these highly alloyed materials.

The sulfuric acid anodic treatment for aluminum provides good corrosion resistance and a good paint base for aluminum surfaces, especially when dichromate sealed. For dyeing purposes, the sulfuric acid anodic film has better absorption than the chromic acid anodic film. It is thicker, more porous and has a greater affinity for the dye. The film is heat resistant, even for temperatures approaching the melting point of the basis metal. The anodic film has good dielectric strength [about 200 volts/0.001 in (7.87 volt/ μ m)] and is sometimes used for electrically insulating aluminum.

One disadvantage of the sulfuric acid anodizing process is the danger of acid entrapment at joints, blind holes, pores, crevices or other cavities, with an adverse effect on service life. Accordingly, sulfuric acid anodizing should not be employed on complex castings or assemblies where acid entrapment is apt to occur. For such applications, chromic acid anodizing should be used. Anodizing makes welds conspicuous. Dyeing accents them further unless a black or very dark color is used. In most instances, allowances should be made for dimensional buildup where close tolerances are required, as all fabrication and machining of parts is completed prior to anodizing. The dimensional buildup is about half the anodic coating thickness.

Conventional sulfuric acid anodizing is covered by Military Specification MIL-A-8625; type II. Other pertinent documents covering the process are ASTM Specification B 580 and AMS Specifications 2471 and 2472.

Hard coat anodizing is the other type of anodizing carried out in sulfuric acid electrolytes. Hard coat anodizing is used to produce thick, relatively dense, hard, wear resistant and corrosion resistant coatings that range in thickness from about 0.0005 to 0.005 in (13 to 127 μm). The most frequently applied coatings usually are 0.001 to 0.003 in (25 to 76 μm) in thickness. Many of the commercially used hard coat processes are proprietary.

The hard coat processes differ from the conventional process described above mainly in that lower electrolyte temperatures and higher current densities and voltages are used. The lower temperature is employed to reduce the solvent action of the electrolyte. The reduced solvent action, combined with the high heat generated by use of high current densities, produces thicker cell walls and, consequently, a harder and denser coating than that obtained with conventional anodizing. Hard coating installations must be provided with efficient refrigeration systems. The hard coat baths often contain small amounts of other chemicals or addition agents. For example, one of the Alumilite (Aluminum Company of America) hard coat electrolytes contains 12 wt.% sulfuric acid and 1 wt.% oxalic acid. The Martin (developed by Glenn L. Martin Co. and acquired by Aluminum Company of America) hard coat electrolyte contains 15 wt.% sulfuric acid and is saturated with carbon dioxide. The Hardas (Hard Aluminum Surfaces, Ltd., Scotland) and Sanford (Sanford Process Corporation, Natick, Mass.) processes are among other proprietary methods for hard coating aluminum.

Anodizing conditions for producing hard coatings vary with the specific process and alloy, but generally are within the following ranges: electrolyte temperature: 25 to 50°F (-4 to 10°C); current density: 24 to 36 A/ft² (2.6 to 3.9 A/dm²); and voltage: up to 70 volts and higher. While direct current is generally employed, some processes employ alternating current superimposed on direct current.

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Special care must be exercised in applying the hard coat processes, as not all alloys are receptive to the treatment. For example, hard coating is not normally recommended for aluminum alloys with a copper content in excess of 5.0%, a silicon content in excess of 8.0% or alloys with a combined copper-silicon content in excess of 8.0%. Such alloys require special processing procedures for satisfactory anodizing. Sharp corners and edges on parts should be rounded prior to anodizing, as chipping of the hard coating at such locations would be apt to occur.

The hard coatings are generally darker than conventional sulfuric acid coatings. The colors generally vary from amber to black, depending on alloy composition, anodizing conditions and coating thickness. When hard anodic coatings are to function primarily as abrasion resistant surfaces, they are not sealed, as sealing lowers abrasion resistance. To obtain even greater wear resistance, the hard coat surface can be impregnated with molybdenum disulfide or graphite. For applications where corrosion resistance as well as abrasion resistance is required, the coatings are usually sealed in (1) a 5 to 6 wt.% sodium or potassium dichromate solution; (2) hot or boiling water; or (3) a hot nickel or cobalt acetate solution.

Allowances should be made for the dimensional buildup that occurs with hard coat anodizing. About half of the coating thickness represents buildup; the other half comes from the conversion of the aluminum alloy surfaces. Finish lapping, light grinding or honing of hard anodized components can be carried out. Because anodic coatings, especially those of the hard coat type, often cause reduction in the fatigue properties of components, careful consideration should be given to the use of the process on parts to be highly stressed in service.

The outstanding features of the hard coat anodic coatings are extreme abrasion resistance and hardness, which has been described as "file-hard" and "equal to or better than" cyanide-hardened steel. The film is a nonconductor and has good insulating properties. Hard coated aluminum inserts can be used in place of dissimilar metal inserts in aluminum assemblies where a hard bearing surface is required. They are also good paint bases.

Typical uses of hard coatings include such applications as valves, sliding parts, hinge mechanisms, gears, pinions, cams, pistons, swivel joints, bearing races, blower impellers, rocket nozzles, insulation plates and blast shields.

Hard coat sulfuric acid anodizing is covered by Military Specification MIL-A-8635, type III. Other pertinent documents are ASTM Specification B 580 and AMS Specifications 2468 and 2469.

5.10 Chromic acid anodizing. The chromic acid method is the second most commonly used method for anodizing aluminum. The coatings provide good corrosion protection and also provide excellent surfaces for good adhesion of paint or other organic finishes. Chromic acid anodizing produces coatings that provide better corrosion protection, but at a higher cost, than the chromate chemical conversion systems. The process is mainly applicable to aluminum and aluminum alloys with a copper content lower than 5% or total alloying constituents lower than 7.5%. The high copper and high alloy aluminum materials are anodically coated using the conventional sulfuric acid process.

Chromic acid anodic coatings are thinner, softer and less resistant to abrasion than the sulfuric acid coatings. For most applications the coating thickness is generally about 0.00005 to 0.0002 in (1.3 to 5.1 μm). The chromic acid anodic coating is generally opaque and light gray on the purer aluminum materials and darker gray to black on copper and silicon bearing alloys. Although thin, the anodic coatings are highly protective, presumably partly due to the retention of a small amount of chromic acid in the film. The corrosion inhibitive feature of hexavalent chromium accounts for the chromic acid process being greatly preferred over the sulfuric acid process for anodizing parts subject to stress and also for anodizing intricately shaped assemblies or parts where electrolyte may be entrapped in joints, blind holes and crevices. The thin chromic acid anodic coatings generally have little or no adverse effects on fatigue and other mechanical properties. Chromic acid coatings are more flexible than sulfuric acid coatings and can thus better withstand deformation.

Mild steel tanks are generally used to hold the chromic acid bath and also serve as the cathode during anodizing. The tank is usually partially lined with glass, plastic or other insulation material to lower the cathode-to-anode area relationship to about a 1 to 1 ratio. In nonconducting tanks, lead, steel or stainless steel cathodes are employed. Mechanical or air agitation of the bath is required to keep the electrolyte immediately adjacent to the aluminum parts from overheating. Articles with inserts of steel, brass or other substances, that may be attacked during the anodizing operation or interfere with the uniform formation of anodic coating on the aluminum surfaces, should not be anodized as assemblies, unless these inserts can be effectively masked.

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The cleaning and surface preparation procedures for conditioning aluminum surfaces for chromic acid anodizing are similar to those described earlier for sulfuric acid anodizing. Chromic acid anodizing is usually carried out in an aqueous solution containing 5 to 10 wt.% of chromic acid using direct current. The bath temperature is maintained at 90 to 100°F (32 to 38°C). Starting with an initial voltage of about 5 volts, the voltage is gradually increased during a period of about 5 minutes to 40 volts. The voltage is maintained at 40 volts for 30 to 40 minutes; during this period the current density is generally 1 to 5 A/ft² (0.11 to 0.54 A/dm²). The coating thickness depends mostly on electrolyte concentration, anodizing conditions and treatment time. After anodizing, the parts are usually rinsed in hot water [150 to 185°F (66 to 85°C)] to facilitate drying. Because of its relatively low porosity (as opposed to sulfuric acid anodic coatings) the chromic acid coating is generally not sealed.

For some applications, however, sealing of the chromic acid coating is employed. The sealing treatments (involving immersion of parts in hot water, hot dichromate solutions or hot nickel or cobalt acetate solutions) are similar to those described earlier for sealing sulfuric acid coatings (subsection 5.9). In some cases, the hot water solution may be acidified and kept within the pH range of 4.0 to 6.0 with chromic acid. To provide better corrosion protection, parts are generally allowed to air dry without further rinsing after sealing. If desired, chromic acid coatings can be dyed. After dyeing, the colored film is usually set and sealed in a hot nickel or cobalt acetate solution. This may be followed by a hot water seal. In some instances steam may be used to seal dyes that bleed excessively in hot water.

Chromic acid anodic coatings, because of their thinness, usually produce no significant change in part dimensions. About one half of the coating thickness represents buildup. The chromic acid anodic coating, in addition to having very good corrosion resistance, is also a good paint base. The anodic coating is heat resistant, even for temperatures approaching the melting point of the basis metal. The coating also has good dielectric strength.

Chromic acid anodizing is covered in Military Specification MIL-A-8625, type I. Other pertinent documents dealing with the process are ASTM Specification B 580 and AMS Specification 2470.

5.11 Miscellaneous anodizing processes for aluminum. The sulfuric acid and chromic acid processes account for most of the aluminum anodizing done in this country. Several lesser used processes exist and are briefly discussed below either for informational purposes or because the film formed has a unique property that allows it to be used for a specific application.

5.11.1 Oxalic acid anodizing. The oxalic acid anodizing process was originally developed in Japan and had been used extensively, especially in Germany and Japan. Currently, the use of the process is somewhat limited.

There are several anodizing processes using oxalic acid electrolytes with considerable variation in operating conditions. For example, the current used may be dc, ac or dc with superimposed ac. One oxalic acid process for anodizing aluminum with direct current uses an electrolyte containing 3 to 5 wt.% oxalic acid at about 70 to 85°F (21 to 29°C). The treatment times are from 15 to 60 minutes.

The oxalic acid anodic coatings are usually yellow, gold or bronze in color, depending on the alloy and the anodizing conditions. These colors are often attractive enough so that they are used without dyeing. Oxalic acid coatings are generally harder and more abrasion resistant than conventional sulfuric acid or chromic acid coatings, but are not so hard or abrasion resistant as sulfuric acid hard coat films. The oxalic acid process is often used to produce relatively thick coatings, e.g., 0.001 to 0.002 in (25 to 50 μ m), as this can be readily done without the use of the special techniques required for the hard coat processes. Oxalic acid anodizing processes are more expensive than sulfuric acid processes and have been supplanted by them for many applications.

5.11.2 Sulfo-organic acid anodizing. Proprietary anodizing processes such as Kalcolor (Kaiser Aluminum and Chemicals Corporation) and Duranodic-300 (Aluminum Company of America) produce integrally colored coatings using sulfo-organic acid electrolytes. The aqueous Kalcolor electrolyte contains sulfosalicylic acid plus a small amount of sulfuric acid or a metal sulfate. The Duranodic-300 electrolyte is based on sulfophthalic acid plus a small amount of sulfuric acid. Colors are produced by different alloying elements in the aluminum reacting with the sulfo-organic acid electrolytes. The colors produced depend on the basis metal composition, current density, voltage, film thickness and electrolyte composition. The coatings are harder and denser than those produced by the conventional sulfuric acid process and are generally similar in these properties to hard coat films. The integrally colored films have good corrosion protection properties and are widely used for outdoor decorative applications.

5.11.3 Boric acid anodizing. The boric acid process is used to produce thin barrier type anodic coatings in a hot aqueous boric acid-borax electrolyte. Voltages up to 600 volts and a treatment time of about 30 minutes are used. The anodic coatings have high dielectric properties and are applied primarily to unalloyed aluminum foil for use in electrical capacitors. Barrier type anodic films can also be produced using ammonium tartrate solutions.

5.11.4 Phosphoric acid anodizing. Anodizing in phosphoric acid solutions (30 wt.% phosphoric acid) or in phosphoric acid-sulfuric acid solution (15 wt.% phosphoric acid and 15 wt.% sulfuric acid) has been used to provide a base for polymeric films and for electroplating copper, nickel and chromium or nickel and chromium to protect aluminum in severe environments. The anodic treatment serves as a substitute for the zincate treatment. Special electroplating techniques are needed to achieve adherent electroplates.

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5.11.5 Sulfamic acid anodizing. Sulfamic acid anodizing is carried out using warm [86 to 104°F (30 to 40°C)] aqueous solutions containing 5 to 20 wt.% sulfamic acid ($\text{NH}_2\text{SO}_2\text{OH}$). The current density ranges from about 10 to 20 A/ft² (1.1 to 2.2 A/dm²) and treatment times are about 15 to 40 minutes. The anodic coatings are generally comparable to those produced by conventional sulfuric acid anodizing. The high cost of sulfamic acid makes the process economically noncompetitive with the sulfuric acid process.

5.12 Principal Al and Mg anodizing treatments. Characteristics and uses of the principal processes for anodizing magnesium and aluminum are summarized in table 1.

5.13 Anodizing of zinc and zinc alloys. Anodic coatings are applied to zinc and zinc alloy surfaces to provide high quality finishes with high corrosion resistance plus the decorative advantage of color. The anodic treatment can be applied to wrought or die cast zinc and zinc base alloy parts, as well as those formed from electrodeposited, mechanically deposited and hot dipped zinc on steel or to parts thermal sprayed with zinc. Electrodeposited or mechanically deposited zinc should have a minimum thickness of 0.0007 in (18 µm).

The zinc anodizing treatments are often applied to washer impeller and housing assemblies exposed to detergents, bleach, sand and hot water. Trim and other parts of motor pumps may be coated to prevent corrosion, erosion and cavitation due to road salts and gravel impingement. Bulk gasoline tank closure fittings may be anodized to reduce or prevent corrosion due to pools of rain water, salt, laden snow or sea water. Anodized galvanized steel may be used for items such as electrical fittings, pole-line hardware, containers and storage tanks.

The zinc surfaces must be thoroughly cleaned prior to the anodic treatment. Grease or oil can be removed by vapor degreasing, ultrasonic cleaning, solvent cleaning or by emulsion cleaning. Degreasing or precleaning operations are usually followed by alkaline cleaning. The parts are then thoroughly rinsed with water prior to the application of the anodic coating.

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The recommended operating conditions for applying different types of anodic coatings to zinc surfaces are given in the tabulation below:

Item	Zinc anodizing processes			
	Class 1 APCF	Class 2 SSC	Class 3 SSCV	Class 4 SSCMn
Terminal voltage, volts	200	105	90	105
Current density,				
dc, A/ft ²	125-150	125-150	125-150	125-150
dc, A/dm ²	14-17	14-17	14-17	14-17
ac, A/ft ²	40-50	40-50	40-50	40-50
ac, A/dm ²	4.4-5.5	4.4-5.5	4.4-5.5	4.4-5.5
Minimum operating				
temperature, °F	140	140	176	158
°C	60	60	80	70
Processing time, min	7	9	10	8
Nominal coating				
thickness, inch	0.00125	0.0016	0.0016	0.0015
micrometer	32	41	41	38
Color	Green	Light Gray	Dark Gray	Brown

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TABLE 1. Principal anodic treatments for magnesium and aluminum:

Treatment number or designation	Treatment name or description	Alloys which can be treated	Principal ingredients of aqueous electrolyte	Coating appearance	Uses or remarks
Dow No. 17	Dichromate anodize	All Mg	Ammonium acid fluoride, sodium dichromate, and phosphoric acid	Clear, green, also light to dark brown	Widely used process; provides very good combination of abrasion resistance, protective value, and paint base characteristics
Dow No. 9	Galvanic anodize	All Mg	Sodium dichromate, ammonium sulfate and ammonium hydroxide	Dark brown to black	For alloys not receptive to the chemical dichromate treatment (Dow No. 7); requires galvanic couple for operation; often used where black finish needed
HAE	HAE anodize	All Mg	Potassium hydroxide, aluminum hydroxide, trisodium phosphate, potassium fluoride, and potassium-manganate	Tan, brown, or olive drab	Widely used process; high corrosion and excellent abrasion resistance; hardest of all anodic coatings for magnesium
	Fluoride anodize plus corrosion-preventive	All Mg	Ammonium bifluoride	White or pearly gray	Used as an anodic cleaning process; provides some corrosion protection, but often is followed by chemical dichromate treatment (Dow No. 7)
Cr-22	Cr-22 anodize	All Mg	Chromic acid, hydrofluoric acid, phosphoric acid, and ammonium hydroxide	Green or black	Hard coating with good abrasion and corrosion resistance not as hard as HAE coating
MGZ	MGZ anodize	All Mg	Solution containing chromate, vandate, phosphate, and fluoride ions	Dark green to dark gray	Newly developed process still in pilot plant and limited commercial production; coating properties and uses similar to those of Dow No. 17 and HAE processes

TABLE 1. Principal anodic treatments for magnesium and aluminum - (cont'd)

Treatment number or designation	Treatment name or description	Alloys which can be treated	Principal ingredients of aqueous electrolyte	Coating appearance	Uses or remarks
—	Conventional sulfuric acid anodize	All Al	Sulfuric acid	Clear transparent to dark gray	Most widely used and economical process for anodizing aluminum; coating provides good corrosion resistance and a good paint base
—	Hard coat sulfuric acid anodize	All Al(a)	Sulfuric acid plus minor amounts of other materials	Amber to black	Requires low temperature bath; coatings are thick, relatively dense, and hard; coatings have very good abrasion, wear and corrosion resistance
—	Chromic acid anodize	All Al(b)	Chromic acid	Light gray to dark gray	Coatings are thinner, softer, and less resistant to abrasion than sulfuric acid coatings; used primarily to increase corrosion resistance and provide good paint base; used on stressed and intricately shaped parts.

(a) Special techniques are required for hard coat anodizing of aluminum alloys with high content of copper, silicon or other alloying constituents.

(b) Chromic acid anodizing is not suitable for aluminum alloys with a copper content higher than 5 percent or with total alloying constituents exceeding 7.5 percent.

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For class 1 coatings, the anodizing bath is composed of such materials as ammonium hydroxide, chromic acid, phosphoric acid and hydrofluoric acid or ammonium fluoride. Class 2 coatings are produced using a sodium silicate-chromate solution while class 3 coatings are produced in a sodium silicate-chromate-vanadate solution. A sodium silicate-chromate-manganate electrolyte is employed for class 4 coatings. An externally applied voltage (ac or dc to 200 volts) is used to form the protective anodic coating.

Zinc anodizing produces a film of the barrier layer type, i.e., a porous structure overlaying an initial barrier layer. During the anodizing of zinc, a complex fritted compound (of fused particles) is formed by anodic spark discharge beginning at about 65 to 70 volts. The coating is hard, porous, absorbent and has excellent masking properties. It is thicker, harder and more corrosion resistant than zinc chromate or phosphate conversion coatings. As the anodized coatings are porous and absorbent, they are very receptive as a base for paints, enamels, lacquers, etc.

Unless otherwise specified, the anodic coatings are generally completely sealed to improve corrosion resistance. Sealing is accomplished by immersion in a sealing medium such as hot 10% (by volume) solution of sodium silicate followed by air drying. Sealing (or painting by brush, spray or immersion) with organic finishes, lacquers or enamels is also carried out to enhance abrasion resistance and appearance along with corrosion control. The type of sealing employed is usually specified in the contract or order governing the parts. Anodized coatings that are not sealed may be adversely affected by weak acids or moderately strong bases. These reagents tend to dissolve the anodic coatings and penetrate to and attack the basis metal or substrate, causing lifting of the coating.

Anodic coated articles of zinc and zinc base alloys should not be used for food containers or as an item likely to come in contact with food or beverage. The coating contains chromium ions and zinc and zinc base alloys are soluble in the presence of acid foods.

Anodic coatings for zinc and zinc alloys are covered by MIL-A-81801.

6. MISCELLANEOUS INORGANIC FINISHING METHODS

6.1 Cementation and diffusion methods. Cementation is a method of applying a metallic coating to a metal article without the use of baths or electrolysis and their accompanying rinsing operations.

The cementation process (sometimes called pack cementation, impregnation or diffusion coating) produces an alloy coating by heating the basis metal in intimate contact with a coating metal. The coating metal may be in the form of a finely divided powder or a volatile metal compound (usually a halide) which, at high heat, reacts with the surface of the metal to be coated. In the surface reaction, the volatile halide is dissociated and deposits metal that alloys with the basis metal and slowly diffuses inward. The basis metals to which the cementation process is applied are mostly ferrous, copper and nickel alloys. Use of the process is limited to substrate metals that alloy with the coating metals.

Cementation coatings are generally uniform in thickness irrespective of the geometry of the surfaces being treated. Thus, the process is well suited for forming protective coatings on threaded parts and surfaces of small, intricately shaped articles. The cementation coating consists of an outer layer of pure or highly concentrated coating material, with the remainder comprised of successively changing alloys of the basis metal. The alloy coating is integrally bound to the basis metal.

The coating procedure varies with the type of charge employed. With a powdered metal charge, intimate contact between the basis metal and the coating metal during treatment is maintained either by tumbling the work in a slowly revolving cylinder partially filled with the powdered metal or by packing the work tightly in metal powder in a stationary retort. With the halide compound method, the charge (consisting of the coating metal, a halide compound and an inert carrier) is packed in a retort around the parts to be coated. When the halide method is used, the coating process is often called chemical vapor deposition. During the cementation treatment, the load is heated to an elevated temperature which is maintained from 1 to 24 hours. In some instances, especially where large parts are involved, a layer of slurry material (consisting of the coating metal, a halide, an inert carrier and a binder) is applied to the part to be diffusion coated. The slurry coated parts are then heated in the reaction vessel to promote alloying and diffusion. Zinc, aluminum and chromium are coated commercially on steel and other metals using cementation processes. The three processes described in paragraphs 6.1.1, 6.1.2 and 6.1.3 below deal with the cementation of these three metals with steel.

Cementation requires long time periods, is difficult to operate on a large scale and is generally restricted to small items. These disadvantages limit commercial use.

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6.1.1 Chromium diffusion (chromizing). Chromium cementation or chromizing processes are used to produce a chromium rich layer on iron or steel surfaces. This layer has characteristics resembling those of a straight chromium stainless steel and exhibits good resistance to abrasion and wear. Chromizing is used on parts to enable them to withstand heat and oxidative and corrosive environments. Because the chromium diffuses into the base metal surface, the chromium rich layer is an integral part of the article's surface and will not peel off. Chromizing produces little or no dimensional change on the parts.

With the powder process, the cleaned part(s) to be treated are packed in a mixture containing 55 wt.% chromium powder and 45 wt.% alumina and heated in an inert or hydrogen atmosphere to about 2370 to 2550°F (1300 to 1400°C) for 3 to 4 hours. Three hours at 2370°F (1300°C) produces a coating approximately 0.006 in (150 μ m) in thickness. Lower temperatures and shorter heating times are used when thinner layers are desired. The alumina in the powdered mixture prevents the chromium particles from coalescing. Oxygen and water vapor must be excluded to prevent inactivation of the chromium particles by formation of oxide films.

Because gaseous chromizing is lower in cost and permits use of simpler controls to prevent the deterioration of the chromizing powder, it has supplanted the powder process for many chromizing applications. In gaseous chromizing, the cleaned part(s) to be treated are placed in a hydrogen atmosphere inside a vessel with a powdered mixture containing chromium or ferrochromium, a diluent such as alumina or kaolin and an ammonium halide. At elevated temperatures of 1830 to 2010°F (1000 to 1100°C), gaseous chromium halide is formed, which decomposes on the steel surface to deposit chromium metal. The chromium diffuses into the steel and the halide (which serves as the carrier) recombines with the chromium powder. The depth of penetration at 2010°F (1100°C) is about 0.004 in (100 μ m) in 4 hours and 0.008 in (200 μ m) in 12 hours.

Chromium diffusion saves chromium by enabling chromized, ordinary steel to be used in place of solid stainless steel in those applications where a passive surface is the controlling factor. It may avoid machining difficulties encountered with stainless and high chrome steels. The high temperatures employed in the process may deform certain articles. The process may alter mechanical properties of the metal. The process is suitable for small items. It should be kept in mind that, at best, a chromized surface can be given the corrosion resistance of a straight chromium stainless steel and not that of chromium nickel stainless steel. This makes it somewhat vulnerable to marine exposures.

6.1.2 Zinc diffusion (Sheradizing). Cementation with zinc powder is generally known commercially as "Sheradizing", in recognition of Sherard Cowper-Coles, developer of the process. After cleaning, the articles (generally steel or iron) to be coated are packed in a zinc powder mixture, consisting of zinc dust and inert ingredients, inside a metal drum. The drum is tightly sealed to minimize oxidation of the zinc and rotated slowly, while heated at 660 to 700°F (350 to 370°C) by electricity or gas. A slight tumbling action promotes coating uniformity. The coating thickness is controlled by the treatment time, which usually ranges from 3 to 12 hours. After a 3 hour treatment at 660 to 700°F (350 to 370°C), thickness is about 0.002 in (50 μ m).

Sheradized coatings are hard, have a matte gray appearance and consist of an iron-zinc alloy that is progressively richer in zinc toward the outside surface. The amount of essentially pure zinc on the surface determines the dimensional change. The actual coating buildup varies with the treatment time and generally is about 0.0005 to 0.001 in (13 to 25 μ m).

The zinc diffusion coating has good resistance to outdoor, marine and industrial exposures. The process is particularly useful for threaded parts (such as nuts, bolts, screws, etc.) because the coating is very uniform and does not fill up the threads. Hollow articles or those with deep recesses can be completely coated.

On the other hand, the zinc diffusion process is limited to small items. For purely corrosion resistance purposes, it does not have the protective life of heavier galvanized coatings. The heavier coatings may flake on bending.

6.1.3 Aluminum diffusion (Calorizing). Calorizing is the trade name for the cementation of a metal surface with aluminum. The aluminum cementation or aluminizing process is generally similar to those described above for chromium and zinc, with some variations in conditions to account for differences in the metals. Aluminized coatings may be applied using a rotating drum method, by a pack-diffusion procedure or with a slurry technique. The coatings are applied to carbon steels to improve corrosion or oxidation resistance and to a variety of high alloy steels as well as nickel and cobalt base alloys to improve oxidation resistance. The steel and highly alloyed materials are coated to substantially extend their service life at elevated temperatures. Generally, the depth of penetration of the aluminum is from 0.005 to 0.040 in (130 to 1000 μ m), and the aluminum content in the iron-alloy layer is generally 25 to 35%.

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In the drum process, the parts to be treated are packed in a mixture of powdered aluminum, aluminum oxide and a small amount of ammonium chloride. The drum is rotated slowly and heated to 1560 to 1740°F (850 to 950°C), while an inert or hydrogen atmosphere is maintained within it. Employing this treatment for 4 to 6 hours produces an iron-aluminum alloy layer about 0.001 to 0.006 in (25 to 150 μ m) in thickness containing about 60% aluminum. In this condition, the coating has poor protective qualities, so it is given an additional heat treatment in air at 1500 to 1800°F (815 to 980°C) for 12 to 48 hours to diffuse the aluminum. This heat treatment increases the diffusion layer depth to 0.025 to 0.040 in (635 to 1000 μ m) and reduces the average aluminum content to about 25%, thereby improving the ductility and toughness of the coating.

The pack procedure is used for aluminizing light gage work, tubing, structural parts and articles that may be damaged in the rotating retort. The pack technique involves tightly packing the work with powdered-aluminum-mixture materials in a stationary vessel that is then sealed. Heating at 1500 to 1800°F (815 to 980°C) from 6 to 24 hours forms a suitable alloy layer that requires no additional heat treatment.

Aluminizing can also be done on parts coated with a slurry containing the aluminum-powder-mixture ingredients. Steel parts coated with aluminum by hot dipping or flame spraying can be converted to aluminized coatings by heating.

Military Specification MIL-C-81740 covers the production of aluminum and aluminum alloys by metallic compound decomposition.

The aluminized coating is highly resistant to atmospheric corrosion at high temperatures up to 1600°F (870°C). Applications include equipment used for cracking oil, such as tube stills, valves, retorts, etc. Other applications include furnace parts, pyrometric equipment, exhaust pipes for engines, etc. The aluminized steel coating is resistant to sulfurous gases at elevated temperatures. On the other hand, the coating is brittle and will not withstand deformation.

6.1.4 Miscellaneous diffusion processes. Siliconizing produces a surface with good corrosion and wear properties on steel that is heated to 1850°F (1010°) in a retort, using silicon carbide and silicon tetrachloride. Iron-aluminum and nickel-aluminum are proprietary coatings applied to copper, steel, nickel and cobalt alloys to produce surfaces with improved resistance to oxidation at elevated temperatures. Other diffusion coatings with good high temperature properties include chromium-aluminum and chromium-silicon alloys. Specialized silicon-containing coatings have been applied to refractory metals to provide oxidation resistance at elevated temperatures. For example, molybdenum silicide coatings have been applied to molybdenum and its alloys; and tungsten silicide coatings have been applied to tungsten and its alloys. These latter coatings involve sophisticated equipment and are expensive to apply.

AMS Specification 2465 covers disilicide diffusion coating of molybdenum and its alloys by the pack cementation method.

6.2 Hot dipped metallic coatings. Hot dipping is one of the oldest methods of applying metallic coatings and is still in wide use as an inexpensive means of producing protective coatings. Hot dipping consists of dipping or passing a cleaned part through a molten bath of the coating metal, removing excess coating metal and solidifying the covering film of metal. Metals used commercially for hot dipped coatings are generally limited to those of low melting point to avoid thermal changes in substrate metal properties. Zinc, tin, lead,terne plate and aluminum account for most of the hot dipped coatings produced; the basis metal is usually iron or steel. Practically all parts and shapes which can be suitably immersed in the molten bath can be hot dipped. Sheet, strip and wire are usually coated on a continuous basis. The hot dipped coating usually consists of an alloy layer covered with a layer of pure coating metal. The alloy layer is formed by the molten metal diffusing into and combining with the basis metal.

The most widely used commercial coating is zinc and the bulk of zinc coated iron and steel is produced by galvanizing. The zinc coating provides protection to the basis metal against corrosion from exposure to the atmosphere or to the soil. Coating thicknesses generally range from about 0.0015 to 0.0034 in (38 to 86 μ m).

Tin coatings produced by hot dipping resist corrosion, provide a surface that is readily solderable and are especially useful where the metal comes in contact with foods and beverages. Hot dipped coatings are applied mainly to steel, cast iron, copper and copper alloys. The thickness of hot dipped tin coatings generally ranges from 0.0003 to 0.0015 in (7.6 to 38 μ m).

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Lead alloys, which are applied to steel or iron articles by hot dipping, usually contain 2 to 10% tin to assist in bonding. Pure lead coatings exhibit poor adhesion to steel, as the bond is wholly mechanical. The use of lead alloys applied by hot dipping is generally restricted to articles that require the special characteristics of lead, such as good resistance to attack in sulfuric acid. Terne plate is made by immersing steel plate in a molten bath of terne metal, which is a lead alloy containing about 10 to 25% tin. Typical uses of terne plate include roofing, flashing, air cleaners and fuel tanks.

Hot dipped aluminum coating are extensively used to protect iron, steel and alloy steels against outdoor corrosion as well as corrosion and oxidation at temperatures ranging up to 1800°F (982°C). Hot dipping is probably the most economical and most easily controlled method of applying aluminum coatings to steel. Theoretically, the hot dipping process is simple; that is, the article is immersed in a vat of molten metal and when it is removed, a coat of the molten metal alloys to the steel. In actual practice, hot dipping is more complicated. A number of factors must be considered. Proper surface preparation may require not only mechanical or chemical cleaning, but also protection of the surface with an active flux or nonoxidizing atmosphere until immersion in the coating bath. The temperature of the molten bath and rates of immersion and withdrawal must be closely controlled to achieve the desired film thickness and properties. These controls also govern the proportion of the alloyed layer to the purer metallic coating. Fluxes are required for proper surface cleaning and wetting action. Small additions of other metals are often included in the bath to give the coating a desired property, such as ductility. Since the metallic coating is actually alloyed to the basis metal, adhesion is usually good. For comparable thicknesses, particularly of zinc coatings, corrosion resistance is about the same as that of electroplated coatings. However, either thinner or thicker coats can be applied by electroplating. Also, the thickness and uniformity of the coat can be more accurately controlled. If painting is desired, then the problems of paint adhesion are often overcome by the various surface conversion treatments applied to the metal coating.

Applicable specifications for hot dipped metallic coatings are:

Zinc coatings - ASTM A 123, A 153, A 386
QQ-S-775

Tin coatings - MIL-T-10727
QQ-T-425

Terne plate - QQ-T-191

Lead alloy - MIL-L-13762

Aluminum - MIL-S-4174
MIL-A-40147

Military Specification MIL-C-17711 covers the chromate coating of hot dipped galvanized surfaces.

Excellent detailed descriptions of the hot dipping processes for applying zinc, tin, lead alloy and aluminum coatings to steel, iron and other substrates are presented in Volume 2 of the Metals Handbook entitled "Heat Treating, Cleaning, and Finishing", (8th Edition, American Society for Metals, Metal Park, Ohio, 1964).

6.3 Flame sprayed coatings. Sprayed metallic or nonmetallic coatings are produced by heating the coating material to a molten or semimolten condition by passing it through a high temperature heat source and propelling it in a finely divided form at a high velocity at the article to be coated. Upon striking the part, the particles flatten out against the previously prepared surface and interlock and overlap one another to form a tightly bonded coherent coating. Because the molten material is usually accompanied by a blast of air, or some workpiece cooling technique is employed, the workpieces being sprayed are not excessively heated; temperatures usually are below 500°F (260°C).

Some of the principal uses for flame sprayed coatings are to: (1) increase the wear resistance of metallic and nonmetallic surfaces; (2) repair or salvage parts by building up worn or damaged areas; (3) provide corrosion protection; (4) impart or improve heat and oxidation resistance properties; and (5) provide electrically conductive or dielectric surfaces on parts. Flame spraying is employed advantageously on items that are too large or unwieldy to coat by other methods. Flame sprayed metal coatings are generally harder, more porous and less ductile than the corresponding wrought metals. The structure of the coating is nonhomogeneous and coating cohesion is achieved mostly through mechanical bonding. Because of these differences in properties, the sprayed coatings should be considered as distinct metallurgical materials. For bearing applications, the porous nature of the coating is advantageous in that it provides an excellent reservoir for oils and lubricants.

Flame spraying methods are capable of applying a wide range of coating thicknesses. For most applications, the coating thickness generally ranges from 0.005 to 0.060 in. (130 to 1500 μ m). Where close dimensional tolerances are required on parts, heavier coatings are usually applied to permit subsequent machining or grinding down to size. Flame spraying is generally not practical for coating small, intricately shaped objects.

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Sprayed coatings can be applied to practically all metal substrates, as well as many nonmetallic substrates, including ceramics, graphite, wood and some plastics. The most common substrates are ferrous metals. The three principal methods of flame spraying metallic and nonmetallic coatings are (1) oxy-acetylene; (2) detonation; and (3) plasma arc. They differ considerably in the manner in which the heat to melt the coating material is generated and also in the form in which the coating material is fed to the spraying device (which can be wire, powder or rod). Almost any material can be sprayed if it is obtainable in these forms and melts at a temperature within the range of the particular process. Zinc and aluminum are the two most commonly sprayed metals; they are sprayed mostly to provide corrosion protection to steel. Other metals frequently sprayed include steel, nickel, copper, brass, bronze, tin, cadmium, stainless steel, nichrome and molybdenum.

Achievement of a good bond with sprayed coatings requires that the surface to be coated be in a clean and roughened condition. Oil, grease and other contaminants are removed using solvent or alkaline cleaning methods. The surfaces are then roughened to provide the necessary anchorage for the sprayed metal. Surface roughening techniques include threading, grooving, knurling, wire brushing, rotary roughening and abrasive blasting. Abrasive blasting, alone or in conjunction with other roughening operations, is used most often. Molybdenum is sometimes sprayed first to provide a good bonding surface for other sprayed materials.

The oxy-acetylene flame method is the oldest and still probably the most widely used process for spraying metals. In the oxy-acetylene process, metallic and nonmetallic materials in the form of wire, powder or rod are fed into the specially designed chamber of the spray gun where they are melted in the oxy-acetylene flame at a temperature of over 5000°F (2760°C). Different guns are used for the three forms of material. The molten material is then atomized by a blast of compressed air which propels the particles to the surface to be coated, which usually is about 6 to 10 inches from the spray gun nozzle. The most common methods of flame spraying involve the use of the oxy-acetylene gases with metals in the form of wires or rods. Advantageously, a larger variety of metals, alloys and nonmetallic materials can be sprayed by the powder process. The rod technique is often used for flame spraying ceramics. In some instances, hydrogen gas may be used instead of acetylene. The oxy-hydrogen sprayed coatings have a lower oxide content, resulting in a better quality, but more costly, coating than that achieved with the oxy-acetylene method.

Detonation flame spraying (sometimes called flame plating) may be considered as a modification of the oxy-acetylene powder process. In detonation spraying, measured quantities of oxygen and acetylene gases and suspended powder particles of the metallic or nonmetallic coating material are pressure fed into the chamber of the specially designed gun. A timed spark ignites the mixture, setting off a detonation wave which drives the molten coating particles through the gun barrel at speeds of about 2500 ft/sec (762 m/sec) towards the target surface which is about 2 to 4 in (51 to 102 mm) away. The temperature in the detonation gun device is about 6000°F (3315°C), while the work surface temperature is maintained below 300°F (149°C) by use of auxiliary cooling. The controlled detonations occur at a rate of four or more times per second and successive detonations build up the coating to the desired thickness. The detonations produce loud noise; thus, the unit is set up in a special concrete block structure and the coating operation is carried out automatically by remote control.

Plasma spraying is the most recent of the three flame coating methods and greatly extends spraying technology to include coatings of high melting metals, refractory oxides, carbides and nitrides. The thermal plasma, the heat source for the plasma gun, is produced by partially ionizing a gas, such as argon, in an electric arc and passing it through a small orifice to produce a jet of hot gas moving at high velocity. In passing through the arc, the gas is excited to extremely high energy levels, producing temperatures between 10,000 and 30,000°F (5,540 to 16,650°C). Finely powdered metals, cermets, ceramics or other materials are fed through the nozzle into the plasma stream where they are quickly heated to a plastic state and propelled by compressed air at high velocity onto the surface being coated. Other gases used, besides argon, are nitrogen, hydrogen and helium.

In general, plasma sprayed coatings are denser, better bonded, contain less oxide inclusions and have higher tensile strengths than metal and ceramic coatings flame sprayed by the oxy-acetylene or oxy-hydrogen powder methods. With some materials, detonation spraying provides coatings with better bonds and physical properties than plasma spraying. However, in general, plasma spraying is much more versatile and capable of applying more materials than the detonation or other flame spraying processes. The plasma process is generally the most costly of the flame spraying processes. Because of their good wear resistance, high temperature resistance and other properties, aluminum oxide, chromium oxide, zirconium oxide, titanium oxide, tungsten carbide, chromium carbide and titanium are amongst the materials most often plasma sprayed.

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Even though sprayed metal films are usually thicker than those formed by other means, they are generally more porous and this presents problems of corrosion resistance. If the sprayed metal is anodic to the base metal (such as zinc, cadmium and aluminum on steel) the problem is minimized since anodic coatings will protect in the presence of pores in the coating. On the other hand, the porosity of a sprayed coating that is cathodic to the base metal is a source of unfavorable galvanic couples and poor corrosion resistance, unless exceedingly thick coatings are applied. As a result, such parts are usually sealed with wax. Sprayed metal coatings have a matte finish when applied and, if smoothness is desired, they must be either machined, ground or polished. A sprayed metal coating can be treated by surface conversion treatments and painted, if necessary.

For some applications, the metal coatings are fused after spraying. Fusing, which involves heating at elevated temperatures, e.g., 1800 to 2300°F (982 to 1260°C) for nickel-cobalt base materials, increases the density of the coating and also causes the deposited metal to diffuse into the substrate, creating a stronger bond. Fused coatings are generally used to protect the substrate material during service at high temperatures or in abrasive or highly corrosive environments.

Sprayed metal coating is covered by MIL-M-6874.

Materials for flame spraying are covered by:

MIL-W-6712, Wire, Metallizing

MIL-P-83348, Powders, Plasma Spray

Flame spraying metallic parts with aluminum is treated in AMS Specification 2450.

AMS Specifications 2435 and 2436 deal with the flame deposition of tungsten carbide and aluminum oxide, respectively. Plasma spray deposition of coatings is covered by AMS Specification 2437.

6.4 Vacuum coating processes. The three principal processes for depositing thin metallic coatings employing vacuum techniques are (1) vacuum evaporation; (2) cathode sputtering; and (3) ion plating. The first two methods are essentially physical processes whereby the vapors of the coating material produced by thermal or electrical action are condensed on the articles to be coated. With ion plating, the part to be coated is the cathode in a high voltage dc circuit. Vacuum evaporation (sometimes called vacuum metallizing or vacuum deposition) is the most widely used of the three processes. An attractive feature of the vacuum coating processes is their ability to deposit coatings on both metallic and nonmetallic substrates, although nonmetallic materials cannot be coated by ion plating.

In vacuum evaporation, the coating material and the parts to be coated are enclosed in a sealed chamber which is evacuated to a very high vacuum, i.e., about 10^{-4} to 10^{-6} torr. The coating chamber can vary from small glass containers about 1 ft³ (0.028 m³) in volume to large metal vacuum chambers with capacities of several hundred cubic feet. Usually the parts are small and are fixtured, so as to expose the surfaces which are to be coated to the vapor source. In some of the larger chambers, hundreds of parts can be coated at one time. The metal to be evaporated is brought in contact with a resistance heated tungsten or platinum wire, disc or strip filament or is electrically heated in a refractory "boat" or crucible of magnesia, graphite or alumina. For some of the refractory metals, electron-beam heating of the material is employed to generate the vapor. The high vacuum is needed partly to avoid oxidation, partly to reduce the temperature at which the metal evaporates and partly to reduce the frequency of air molecule-vapor molecule collisions which adversely affect coating performance. When the coating metal reaches a high enough temperature, it evaporates. The evaporated atoms and molecules travel in essentially straight lines and condense on all objects in the chamber, coating them with a film of metal. Therefore, it is important that the vapor sources be properly located in the chamber with respect to the work pieces, in order to provide good coating coverage. When the entire surface of the part is to be covered, the part should be rotated to provide direct exposure of all areas to the vapor source. During the process, the temperature in the chamber rarely exceeds 1500°F (660°C), although the metal vapor temperatures may reach 2000°F (1094°C) or higher.

The condition of the surface of the part prior to vacuum deposition determines the character of the metal coating. Parts are sometimes coated with lacquer prior to metallizing, which serves to fill in scratches, imperfections and other low spots and enables the deposition of a high gloss metal finish. Lacquering also serves to seal surfaces, lessening the time required to achieve the desired vacuum in the chamber.

A typical coating cycle consists of the following: (1) cleaned and otherwise suitably prepared work is positioned in the chamber; (2) the metal vapor source is set up; (3) the chamber is closed and evacuated to the desired vacuum; (4) the metal vapor source is heated up and the coating deposited to the desired thickness, usually in seconds or minutes and; (5) the coated work is allowed to cool and the chamber is vented. Some of the newer installations have provisions for continuous coating by feeding work through the chamber. Typical vacuum evaporation coating rates generally range from 0.000005 to 0.00002 in (0.13 to 0.51 μ m) per minute for most materials. The deposition rates for aluminum are higher and generally are about 0.00005 in (1.3 μ m) per minute.

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Practically all metals and many alloys and semiconductors, as well as some nonmetallic materials, can be vacuum coated with varying degrees of difficulty. Aluminum, cadmium, copper, chromium, silver, germanium, selenium, gold, zinc and nickel-chromium base alloys are among the materials which are frequently deposited. They probably account for more than 90% of all vacuum evaporation coatings, with aluminum accounting for the bulk of the coatings. Greater difficulty is experienced with deposition of films of tin, titanium, silicon, palladium, rhodium and magnesium fluoride. The refractory metals such as tungsten, tantalum, columbium and platinum can be deposited using electron beam heating.

For many applications, the vacuum evaporation coatings are usually of the order of 0.000005 in (0.13 μm) in thickness. Vacuum coatings in the range of 0.0001 to 0.005 in (2.5 to 130 μm) are generally classified as thick coatings. The thick coatings are usually functional, whereas the thin coatings may be either functional or decorative. The thick coatings are generally used with no supplemental coating. On the other hand, the thin coatings are almost always coated with a clear lacquer to protect them against marring or abrasion.

Commercial use of vacuum evaporation coatings may be divided into four main categories: decorative, optical, corrosion resistant and electrical-electronic. Aluminum is the most extensively used material for vacuum deposited decorative coatings. Aluminum is used widely for coating molded plastic parts, plastic films and nonmetallic sheet materials. Vacuum deposited optical coatings are useful as mirror or reflective surfaces for applications ranging from automotive rear view mirrors and reflectors for sealed beam headlamps to optical components of scientific instruments, such as microscopes, monochromators and telescopes. Aluminum and cadmium are used in thicknesses of about 0.0003 to 0.001 in (7.6 to 25 μm) to provide corrosion protection to steel and other metals. Relatively heavy cadmium vacuum deposited coatings of 0.0003 to 0.003 in (7.6 to 76 μm) are applied to high strength steel aircraft fasteners, fittings and other parts to provide corrosion resistance without the hydrogen embrittlement attendant to electroplating. In recent years, several steel companies have developed equipment and techniques to vacuum coat aluminum on strip. Vacuum evaporation is also being used considerably to deposit various metals and metal compounds in various thicknesses for use as resistors, conductors, capacitors and other electronic circuit applications. For example, aluminum, bismuth and nickel coatings serve as conductors, while germanium, selenium and silicon coatings are used as semiconductors. Vacuum coatings of aluminum oxide, titanium oxide and tantalum oxide are employed as capacitors.

Vapor coating by cathode sputtering takes place when an electrical discharge is passed between an anode and a cathode of the coating metal within a chamber at low gas pressures (10^{-2} torr), causing the cathode to be slowly disintegrated by bombardment of the ionized gas particles. The cathode, usually in the form of a disc, rod or wire, is vaporized by the positive ion bombardment and some of the vapor diffuses away from the cathode and deposits on the object to be coated. The voltage required varies from 3000 to 5000 volts, depending on the cathode metal. Sputtering of metallic coatings is usually carried out in an argon atmosphere because this gas has the heaviest inert molecule that is readily available for bombarding the cathode.

Cathode sputtering makes the deposition of refractory metals (such as molybdenum, tungsten and tantalum) comparatively easy, relative to vacuum evaporation. Also, alloys can be deposited with little or no fractionation. Furthermore, reactive oxides or nitrides, that might fractionate if direct thermal vaporization was employed, can be deposited by cathode sputtering. More uniform deposits can often be achieved with cathode sputtering because the source can be a plane. On the other hand, the deposition rate with cathode sputtering is very slow. For example, minutes or hours are required to deposit a 0.000004 in (0.1 μ m) thick coating, as compared with only seconds for producing a coating of the same thickness by vacuum evaporation. The high electrical voltage required for cathode sputtering is another disadvantage.

Cathode sputtering is used considerably to produce films of carefully controlled properties in the manufacturing of miniature and microminiature circuits.

Ion plating is the term used to describe a vacuum deposition process, developed by the AEC's Sandia Laboratory, Albuquerque, New Mexico, in which partial ionization of the metal vapor is used to increase the adhesion of the coating to the substrate. In the ion plating process, the part to be coated is the cathode of a high voltage dc circuit in which the evaporation filament is the anode. The coating chamber is first evacuated to almost 10^{-5} torr and is then back filled with argon to give a gas pressure of about 10^{-2} torr. A gas discharge is established by applying 3000 to 5000 volts between the filament and the part. The high energy argon ions bombard the part and clean the substrate by sputtering off the contaminants from the surface. The filament anode is then heated to melt and evaporate the coating material. A portion of the coating atoms are ionized and accelerated to the part. The particles deposited on the substrate have an energy distribution ranging from 0.2 electron volts (typical of evaporative coatings) to 1000 or more electron volts (typical of accelerated ions). The high energy ions are able to penetrate the surface of the coated part to depths of several atomic diameters. As a result, coating adhesion is substantially greater with ion plating than for vacuum evaporation or cathode sputtering. The high energy bombardment and deposition produce good bonds between coating substrate combinations not previously feasible. Because the workpiece is cathodic, coating ions are attracted to it, which enables ion plating to coat some complex shapes not readily coated by vacuum evaporation techniques.

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For ion plating using argon gas, a typical current density with an applied potential of 5000 volts is 3.2 ma/in² (0.5 ma/cm²). Cleaning time is about 30 minutes, with coating times of several minutes. Using regular vacuum deposition equipment, but at slightly higher pressure, ion plating is comparable in speed to conventional electrodeposition and vacuum evaporation coating and faster than sputtering. Although it can vary greatly, a coating rate of 0.0001 in/min (0.0025 mm/min) is considered average.

Ion plating has successfully produced previously difficult to achieve coating-substrate combinations such as Ag-Fe, Cu-Mo, Ag-Ni, Cr-Mo, Au-Al, Zn-Cb, Au-Mo and Al-U. Some examples of metal-to-semiconductor combinations achieved include Ag-Si, Ag-Ge, Cu-Si, Cu-Ge and Al-Si. Ion plating is also used to deposit ceramic coatings on parts.

The advantages of vacuum coating methods are that nonconducting surfaces and intricate shapes can usually be readily coated. On the other hand, the objects to be coated may be limited to small sized ones, easily racked in the chamber. The film is very thin and porous and cannot be used for applications where incidental wear or abrasion is a factor. On a metal article, a coat of the same metal applied by electroplating generally has much superior protective qualities. A metal film applied by vacuum evaporation must often be protected by a coat of lacquer. For some applications, vacuum evaporation may be comparatively costly.

Vacuum deposited cadmium coatings to provide corrosion protection to ferrous parts are covered by MIL-C-8837. Because it avoids hydrogen embrittlement, cadmium deposition by vacuum technology is recommended for use on steels heat treated to or having an ultimate strength of 220,000 psi (1517 MPa) or above (approximately Rockwell C 46) rather than cadmium electroplating, in accordance with QQ-P-416. Vacuum deposited cadmium coatings can be given a chromate treatment to provide increased corrosion protection. Cadmium coatings should not be used on parts which reach a temperature of 450°F (232°C) or higher or come in contact with other parts which reach those temperatures.

Vacuum deposition of cadmium is also covered in AMS Specification 2426.

The use of vacuum deposited aluminum coatings to provide corrosion resistance to ferrous parts is covered by MIL-C-23217. Vacuum deposited aluminum coatings are also used to provide resistance to stress corrosion cracking and pitting corrosion of high strength aluminum alloys. Vacuum deposited aluminum coatings should not be used on steel parts which, in service, reach a temperature higher than 925°F (496°C) or come in direct contact with parts that reach this temperature.

6.5 Electroless nickel and other metal plating. The deposition of nickel by catalytic chemical reduction, generally referred to as electroless nickel plating, is widely used for the production of uniform coatings on surfaces difficult to electroplate, such as deeply recessed areas, the inside of tanks, pipes, etc. The electroless plating methods are also called "chemical" or "autocatalytic" plating processes. Electroless nickel plating was a development of the National Bureau of Standards in the middle-to-late 1940's. The process is employed by both military and industrial establishments to provide hard, wear resistant and corrosion resistant surfaces for operation at temperatures up to 1000°F (538°C), especially on complex shaped objects.

The high nickel, low phosphorus alloy deposited from a phosphate bath is generally equivalent or more corrosion resistant than electroplated nickel or wrought pure nickel. On properly prepared substrates, the deposit is relatively pore free. However, the metal deposited is more brittle than electroplated nickel. Heat treatment can be used to decrease brittleness and increase the hardness. Unlike electroplated nickel, the electroless deposits are distributed more evenly over the surface of complex shapes. Blind holes, threads, small holes, recesses and internal surfaces usually receive the same amount of plating as sharp corners, edges or flat surfaces. Accordingly, the total amount of deposit needed to achieve a minimum thickness at designated areas can be significantly less for electroless than for electrolytic nickel. In addition, close tolerances can be maintained and subsequent machining to size is frequently eliminated with electroless nickel.

Electroless nickel deposits have found wide acceptance on applications involving missiles, rockets, jet engines, oil refineries, chemical plant equipment, tanks for handling nuclear fuels and heat transfer liquids, electronics, automotive hardware, etc. Because of its hardness, wear resistance and uniform deposit thickness, it has also found wide usage in the fields of pumps, compressors, hydraulic pistons and other moving parts.

Most electroless nickel plating is accomplished by exposing the cleaned and conditioned (catalyzed) substrate surface to a solution consisting primarily of a nickel salt (chloride or sulfate), a reducing agent, sodium hypophosphite to provide anions for the chemical reaction and a salt (usually an organic acid), which acts both as a buffer and a mild complexing agent to control the concentration of nickel and prevent deposition of nickel phosphite. Sodium citrate, sodium acetate and hydroxyacetic acid are representative of the organic acid salts or acids, which are being used singly or in combination in bath makeups. The alkaline baths also usually contain ammonium chloride or sodium pyrophosphate. Both acid (pH 4 to 6) and alkaline (pH 7.5 to 10) baths are used in industrial processes. The acid baths are generally easier to maintain and are the more widely used. During operation, the pH of the bath slowly decreases, which requires the frequent addition of small amounts of alkali to keep the pH within the desired range. Dilute solutions of sodium hydroxide are added to the acid baths, while ammonium hydroxide solution additions are made to the alkaline baths.

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Electroless nickel plating is usually carried out by immersing the previously cleaned and conditioned part in the bath for the required time to obtain the thickness of plate desired. Solution temperature is usually maintained at about 190 to 200°F (88 to 93°C). Work agitation or solution circulation is generally desirable for obtaining good plating rates. For coating the inside diameters of long pipes, etc., solution from a reservoir is pumped continuously to and from the part. The container or tank can be glass, an inert plastic or a metal (preferably stainless steel) tank lined with a coating of inert material such as tetrafluorethylene or a phenolic base organic. The rate of deposition generally ranges from about 0.0004 to 0.001 in (10 to 25 μ m per hour). To assure good quality deposits and consistent plating rates, the composition of the plating bath should be kept relatively constant. This requires periodic determinations of pH and nickel and hypophosphite concentrates. Based on these determinations, periodic additions of fresh reagents are made to the bath.

The electroless nickel bath occasionally may suddenly decompose in the presence of fine catalytic nuclei or particles, which may form more or less spontaneously throughout the solution. The tendency for spontaneous bath decomposition is usually greatest with the more rapid plating baths and may be triggered by precipitation of salts (phosphites or hydroxides) or by introduction of particulate matter from the surroundings. Although good periodic batch or continuous filtration of solution helps to minimize this problem, it does not always prevent it. Much of the R&D by proprietary bath formulators on electroless plating has been carried out primarily to increase nickel deposition rates and improve bath stability. For these reasons, the proprietary bath formulations and processes which generally have good stability and high deposition rates are widely used in industry.

In general, the methods employed for cleaning and preparing surfaces for electroless nickel plating are similar to those used for conventional electroplating. A typical cleaning cycle may consist of (1) alkaline cleaning; (2) rinsing; (3) acid dipping; and (4) rinsing. Such a pretreatment would be satisfactory for the "catalytic" metals. Electroless nickel deposition is initiated spontaneously on catalytic metals such as nickel, cobalt, steel, rhodium or palladium, and on some of the more active metals like aluminum or beryllium, probably by first producing a displacement deposit of nickel.

Noncatalytic metals, such as copper, brass and silver, can be made to receive a deposit by touching them with a part that is actively plating in the bath or by momentarily making them cathodic with dc current. Another method is to immerse the part for a short time in a dilute acidic solution of palladium chloride to produce an immersion deposit, which initiates electroless plating. Once a film of electroless nickel has been deposited on a surface, deposition continues because the electroless nickel is also catalytic.

Certain metals such as cadmium, lead, tin and bismuth generally cannot be catalyzed by any of the above techniques. However, they can be made receptive to electroless nickel coatings by first applying a nickel or copper strike plate on them. Although it is possible to plate directly on it, aluminum is usually zincate treated to initiate electroless nickel plating from an acid bath.

Electroless nickel can be deposited on nonconductors such as glass and plastics by first suitably activating or conditioning their surfaces, usually by treating them in a palladium chloride solution. Frequently, only very thin coatings are applied by the electroless method, so that thicker metal deposits can be applied later by the less expensive electroplating method.

Alloys of nickel and phosphorus are obtained with electroless nickel baths when sodium hypophosphite serves as the reducing agent. The phosphorus content can be varied, normally between 2 and 12%, to control strength, ductility, stress, magnetic properties and structure. The alloys are super-saturated, solid solutions of nickel phosphide in nickel. High phosphorus contents, obtained in solutions with a low pH and high ratio of phosphite to nickel ions, favor high strength and low stress.

Nickel phosphide can be precipitated by a postplating heat treatment, which hardens the deposit about twofold. This treatment increases stress toward the tensile direction for deposits on steel and other substrates with low expansion coefficients. The strength and ductility of alloys containing less than 7% phosphorus are increased by heat treatment, but alloys with higher phosphorus-nickel ratios are reduced in strength and ductility. Generally, heat treatment at 750°F (400°C) for one half to 1 hour maximizes hardness. Heat treatment at 1290 to 1470°F (700 to 800°C) is usually employed to avoid or minimize the loss in fatigue strength of high strength steel plated with electroless nickel.

The principal drawbacks to electroless nickel plating are its higher cost and slower rate of deposition when compared with conventional nickel electroplating. For these reasons it is generally employed for those applications where the special features of the process make its use attractive.

When borohydrides or amineboranes are used as the reducing agent for electroless plating of nickel, the deposits contain 1 to 8% boron. The "as plated" electroless nickel-boron deposits containing about 1% boron are harder than electroless nickel-phosphorus alloy. Thus, the Ni-B deposits are useful for providing wear resistance without the heat treatment needed to achieve equivalent hardness with electroless Ni-P deposits. This can be of importance for such substrates as high strength aluminum alloys or plastics, which are affected adversely by heat treatment at 750°F (400°C). The significantly higher costs of borohydride and amineboranes, as opposed to hypophosphite, have limited the commercial use of these reducing agents.

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Electroless nickel deposits, produced by using hydrazine as a reducing agent in an alkaline bath, contains 97 to 99.2% nickel, with oxygen and nitrogen each present in concentrations of tenths of a percent and a number of other trace elements. These deposits were inferior to Ni-P coatings in protecting steel against corrosion.

Electroless nickel coating is covered by MIL-C-26074. Other documents dealing with electroless nickel plating are AMS Specifications 2404 and 2405.

Electroless plating processes for depositing cobalt, copper, gold and palladium are also available. These processes, which are rather limited in industrial usage, are discussed below.

Cobalt, like nickel, is generally electrolessly deposited from hypophosphite baths, but only from alkaline solutions. Cobalt deposition rates are usually lower than those for nickel. Electroless cobalt plating has been used mainly in the production of memory storage devices. The ability of electroless cobalt to be readily deposited on palladium-catalyzed plastic tape, with recording properties superior to conventional iron oxide tapes, accounts for its use in this field and also for its use in producing magnetic coatings on drums, disks and cards.

Most electroless copper baths used commercially contain copper sulfate, sodium potassium tartrate, sodium hydroxide and use formaldehyde as the reducing agent. The greatest volume use of electroless copper is to coat nonconductors with a thin conductive layer upon which further deposition by electrolytic methods could be carried out. Electroless copper is also widely used to produce thin coatings on localized areas of printed circuit board. Here again, the supplemental heavier copper deposits needed on the boards are produced by electroplating.

Electroless palladium deposits are applied primarily to electrical contacts and connectors. Electroless gold deposits find limited use in electronic and integrated circuit applications.

6.6 Porcelain enamels and ceramic coatings. Porcelain or vitreous enamels and ceramic coatings differ from organic coatings (paint) in that they consist essentially of inorganic materials fused in place on the metal base.

Porcelain enamel (PE) can be defined as a substantially glassy, vitreous, inorganic coating bonded to metal surfaces by fusion at a temperature of 800°F (427°C) or above. The PE coatings are applied primarily to products of cast iron, sheet steel and aluminum to improve their appearances and protect against corrosion. Coatings on steel and cast iron are fused at about 1400 to 1600°F (760 to 871°C), whereas coatings on aluminum are fused at 900 to 1000°F (482 to 538°C). Ceramic coatings differ from conventional porcelain enamel coatings in that they usually require higher fusion temperatures, often over 1800°F (982°C). Ceramic coatings are usually formulated to contain mainly crystalline, rather than glassy materials, and to provide greater protection and prolonged stability at elevated temperatures (red heat and above), for example, in connection with the protection of gas turbine, and jet and rocket engine parts.

Porcelain or vitreous enamels usually contain materials known as glass formers--materials such as flint (silica), feldspar and borax--which act as a matrix or carrier for refractory and other materials. To the glass formers are added materials such as soda ash, nitrate of soda, fluorapatite, beryllium oxide, calcium carbonate, etc., which, as fluxing agents, promote chemical durability. Other materials such as cobalt oxide, nickel oxide and manganese oxide are added to promote adherence of the coating to the metal. All these materials are melted together and then quenched slowly in water to yield a shattered glass called frit. The frit acts as the basic vehicle to which other materials such as aluminum oxide, antimony oxide, zirconium oxide, titanium oxide, etc., called mill additions, are added to produce desired properties such as color, opacity, corrosion resistance, hardness, refractoriness, acid resistance, etc. Water is added to the frit and mill additions and the mixture is ground in a ball mill. The result is a fine suspension of the ingredients in water, known as slip. The slip is applied to the metal part, usually by spray or immersion methods, dried and then fired to fuse the material to the surface.

Steel may be prepared for porcelain enameling by chemical or mechanical procedures. A typical cycle for chemical preparation of steel for enameling consists of the following operations: (1) cleaning the fabricated part of oils, drawing compounds and soils; (2) rinsing; (3) pickling the part with acid (usually sulfuric with or without some ferric ion) to remove oxides; (4) rinsing; (5) nickel flashing in a dilute acidified nickel sulfate solution containing approximately 1 oz/gal (7.5 g/L) $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$; (6) rinsing; (7) neutralizing in a very dilute solution containing sodium carbonate and borax; and (8) drying in air at 200 to 250°F (93 to 121°C). Mechanical preparation consists of grit blasting the surfaces. Before grit blasting, oil and drawing compounds are removed by alkaline cleaning or by heating at 800 to 850°F (427 to 454°C) to burn off the organic contaminants.

Dipping and spraying are the two most widely used methods for applying slip to parts. The slip may be applied either as a single cover coat or as a two stage coating, involving first a ground coat and then the cover coat. Both single and two coat enameling methods are widely used in industry; the metals to be coated, the coating material and the particular part application govern the choice of the method. After coating, the parts are dried to remove water before being fired. Drying conditions are carefully controlled to prevent the formation of hard films which can trap moisture and cause tearing of the finished enamel. Parts are usually allowed to enter the dryer at a comparatively low temperature and leave with the air temperature almost 250°F (121°C). Drying cycle times usually range from 2 to 10 minutes.

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Firing of the dried slip coated parts is carried out in box type furnaces or continuous furnaces heated by oil, gas or electricity. A typical firing time period for ground coated and cover coated steel parts in a continuous furnace at 1480 to 1540°F (804 to 838°C) generally ranges from about 3 to 8 minutes, depending on steel thickness. Firing temperatures and times for coated cast-iron parts are generally similar to those for steel parts. Enamels for aluminum are usually fired at about 950 to 1000°F (510 to 538°C) for 5 to 10 minutes, whereas coatings for high temperature alloys may be fired at 1700°F (927°C) or above. With the two coat system, the ground coat is fired prior to the application of the cover coat, which is also fired.

Ceramic coatings may be considered as special porcelains based on silicates and oxides. However, high temperature coatings based on carbides, silicides, nitrides, borides, cermets and some other inorganic materials have also come to be known as ceramic coatings. (The application of these latter materials as coatings by flame and plasma spraying and by cementation techniques are discussed in paragraphs 6.3 and 6.1, respectively.)

Ceramic coatings increase the useful temperature range of metals in three ways: (1) by protecting them from erosion, oxidation and intergranular corrosion; (2) by thermally insulating them, thereby keeping actual metal temperatures appreciably lower than environmental temperature; and (3) by increasing their overall strength and rigidity. Some of the more important applications for ceramic coated metals are furnace components, heat treating equipment, heat exchangers, chemical processing equipment, jet engine parts, rocket motor nozzles and exhaust manifolds.

Coatings prepared from silicate frits, with or without mill added refractories, are the most extensively used of all ceramic coatings. Many of the high temperature service silicate coatings used commercially are proprietary formulations. However, data on some compositions and formulations of coatings made of frits and mill added constituents can be obtained from literature published by the National Bureau of Standards (NBS) and the University of Illinois. For example, the composition (by weight) of NBS silicate coating slip A-417 consists of: 70 parts frit 331, 30 parts chromic oxide, 5 parts enameler's clay and 48 parts water. The raw batch composition for NBS-331 frit used in this NBS coating A-417 is made up of 38 parts quartz, 56.6 parts barium carboante, 5 parts zinc oxide, 7.14 parts whiting, 11.5 parts boric acid and 2.5 parts berylia. Spraying and dipping are the most common ways of applying the silicate slips. The dried NBS A-417 coating is fired for several minutes at 1850°F (1010°C). The coating produced is a smooth, uniform, glass-like, green-colored finish with a controlled thickness, usually ranging from 0.001 to 0.002 in (25 to 50 μ m).

Ceramic coatings based on oxide materials are often used to provide the underlying metal with protection against oxidation at elevated temperatures and provide a high degree of thermal insulation. Alumina (Al_2O_3) and zirconia (ZrO_2) are the oxides most commonly used for this purpose. Alumina coatings are hard and have excellent resistance to abrasion and good resistance to corrosion. Coatings of zirconia are used as a heat barrier because of their low thermal conductivity. The thin oxide coatings are usually applied by flame or plasma spraying methods. Thicker coatings may also be applied by troweling, to provide maximum protection to the underlying metal. A bonding medium (such as sodium silicate, calcium aluminate, or phosphoric acid) is used to prepare a paste like mixture. Frequently, metal mesh or expanded metal is tack welded to the metal substrate to better anchor the trowelled coating. After drying, the coating is cured at temperatures ranging from 450 to 850°F (232 to 454°C).

Another class of ceramic coatings that is widely used is that containing phosphate bonded materials. Such coatings are formed by the chemical reaction of phosphoric acid or fluorophosphoric acid with a metal oxide such as alumina, chromium oxide, hafnium oxide or zirconia. The phosphate bonded coatings are used for the protection of metals against heat. The coatings can be applied by spraying or trowelling techniques and are usually cured over several hours at successively increasing temperatures ranging from about 200 to 800°F (93 to 427°C).

6.7 Mechanical plating. Mechanical plating, which is a relatively new coating process, has some unique characteristics that make it a useful addition to the spectrum of plating and finishing processes. In mechanical plating, coatings of ductile metals can be applied to surfaces of metallic parts by a mechanical means involving a tumbling or vibratory action but no electric current.

The usual sequence of steps in mechanical plating is as follows:

- (1) Degrease in hot alkaline solution.
- (2) Rinse and load in plating barrel.
- (3) Add impact media.
- (4) Clean and descale.
- (5) Rinse.
- (6) Flash-immersion copper coat.
- (7) Mechanically plate.

After the parts are cleaned, promoter chemicals and a small amount of copper powder are added, to deposit a flash coating of copper which enhances adhesion of the main coating. The amounts of fresh powder and chemicals added to a barrel are determined by the surface area of the load. The amount of metal powder added for plating is dependent on both the surface area and the desired coating thickness. Thicker coatings merely require more powder. Thus, thicker coatings can be applied without a proportionate increase in time and costs in contrast with electroplating, where deposition time and chemical consumption are related directly to coating thickness.

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Solid, ceramically coated glass beads, about 0.125 in (0.32 cm) in diameter or smaller, serve as the impact media in a rotating tumbling barrel to smear and cold weld the powder onto the parts being plated. The promoter chemical provides the proper environment and must be included for satisfactory coating. It is a mild pickling agent which must remove the oxide film from the workpiece with little attack on the metal. An inhibitor is used to limit the attack. The promoter can be a carboxylic acid or a complex nitrogenous compound and the inhibitor can be a cellulose derivative or amine. The coating thicknesses produced in 15 to 30 minutes can vary from about 0.0002 to 0.002 in (5 to 50 μ m). The total processing time for the overall cleaning, flashing and plating operation is about 1 hour.

The coating is lamellar in structure and quite uniform in thickness; variations generally fall within $\pm 10\%$, except for sharp edges. Holes, grooves and recesses usually receive adequate deposits but, in contrast to electroplated parts, mechanically plated parts have somewhat thinner deposits on sharp edges and projections. Bending tests through 180 degrees show that coating adhesion is as good as that obtained by electroplating.

Zinc, cadmium and a 50-50% by weight mixture of tin and cadmium are the metals most often mechanically plated. Corrosion resistance imparted by a zinc or cadmium mechanical plate is essentially the same for a given thickness as that applied by other methods. Zinc and cadmium coated parts may be given a chromating treatment, if desired, to provide greater corrosion protection. Other metals that can be plated are lead, copper, brass, indium and silver. Adherent coatings can be deposited on mild steel, alloy steels, type 410 stainless steel and zinc die castings. The type 300 series stainless steels, nickel base alloys and aluminum are among the materials that are unsuitable substrates for mechanical plating at the present time. Currently, part size is limited to about 6 in (15.2 cm) in length and part weight is limited to about 1 lb (454 g).

One important advantage of mechanical plating is that failures arising from hydrogen embrittlement often encountered in electroplated hardened steel parts (high strength steel bolts, springs, lock washers, etc.), can be avoided. Another advantage of mechanical plating is its ability to deposit metal readily in recessed areas. Powder metal parts that have a density ratio greater than 85% percent can be coated without use of wax impregnation. Mechanical plating is being used in many industries including automotive, appliance, outboard motor and electrical fixtures.

Military Specification MIL-C-81562 covers mechanically deposited coatings of cadmium, zinc and tin-cadmium.

Mechanically deposited coatings of cadmium and zinc on ferrous metals are covered by ASTM Standard Specification B 454.

7. HYDROGEN EMBRITTLEMENT RELIEF TREATMENTS

7.1 Hydrogen embrittlement. When atomic hydrogen enters high strength steel (and certain other high strength alloys), it may cause any of several undesirable events to occur. If large quantities of hydrogen are introduced, there may be a general loss in ductility or, if the hydrogen accumulates in certain localized areas, internal bursts or blisters may be produced. Under certain circumstances, hydrogen may react with the alloy to produce catastrophic brittle failures at applied stresses far below the yield strength or the nominal design strength for the alloy. These phenomena are collectively referred to as hydrogen embrittlement. However, only the latter, i.e., the hydrogen induced brittle failure is of primary concern in the plating and coating of high strength steels. Since this phenomenon often happens in materials that exhibit no significant loss in ductility (as measured by a conventional tensile test), it is sometimes referred to as hydrogen induced delayed brittle failure or hydrogen stress cracking. The term "hydrogen embrittlement" as used herein will refer to phenomenon associated with hydrogen induced or hydrogen stress failures.

The exact mechanisms by which hydrogen enters steel and how failures occur are complex and still somewhat conjectural. Studies have shown that the source of the embrittling hydrogen in the metal is not important. The hydrogen can be introduced during fabricating, cleaning, pickling or electroplating processes, or it may be picked up from the service environment as a result of cathodic protection reactions or corrosion reactions. Thus, any process that presents atomic hydrogen to steel, whether by thermally activated dissociation of the hydrogen gas molecules, electrochemical reaction or chemical reaction, is capable of introducing sufficient hydrogen to cause failure. Unless such processes are avoided or the hydrogen introduced is removed from the high strength steels before permanent damage occurs, the potential exists for failure of these materials in service.

The problem of hydrogen embrittlement of high strength steels and alloys is of considerable concern to aerospace, aircraft and other industries, where components fabricated from the high strength materials are electroplated to provide protection against corrosion, increased wear resistance or some other desirable surface quality. The application of the electrodeposited coatings can make the part susceptible to hydrogen embrittlement failure, because hydrogen is often introduced during cleaning, pickling, activating and plating operations.

The susceptibility to hydrogen embrittlement increases with the hardness of the steel. Apparently, the concentration of hydrogen required to cause brittle fracture decreases with increasing ultimate strength of the steel. Certain hardening constituents such as carbon also increase susceptibility. In general, steel parts having a hardness of Rockwell C 40 or higher are subject to hydrogen embrittlement to a degree that warrants relief treatment.

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Results of many comprehensive studies on cleaning and plating operations have shown that most high strength steels were embrittled to various degrees by almost all of the common electroplating processes including chromium, cadmium, zinc, nickel, lead, copper and silver. These studies also show that the amount of hydrogen entering steel specimens during certain electroplating processes may be as great as that introduced during deliberate severe cathodic charging and that more hydrogen is sometimes introduced during pickling or cathodic cleaning than during the actual electroplating operations.

Furthermore, these studies showed that baking treatments to remove hydrogen from plated parts often were not effective in eliminating delayed failures. Also, the sustained load test employing notched specimens was shown to be the most sensitive of the many methods used to evaluate the embrittling tendencies of cleaning, pickling and electroplating procedures.

7.2 Relief from hydrogen embrittlement. Hydrogen embrittlement tends to be dissipated at room temperature. This is generally true for uncoated parts, where the hydrogen embrittlement arose from cleaning and pickling operations. The process is hastened by applying heat. The exact conditions for embrittlement relief depend on the process causing embrittlement and the cross section of the parts. The most common relief treatments are:

- (a) Ordinary aging at room temperature.
- (b) Heat treatment in air, oil or boiling water. In air, parts are usually heated at temperatures of $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) for periods of 3 to 23 hours. The duration of the bake period, together with the maximum time period between plating and start of baking (often within 4 hours), is usually prescribed by the particular specification or standard governing the type of plating and workpiece involved. Some authorities claim that ordinary immersion in boiling water after pickling or plating is the most effective and the most rapid relief treatment. The boiling water treatment can be used on the few hardened parts which would be affected by the 375°F (191°C) temperature of the air heat treatment.

7.3 Precautions in relief treatments. There are several precautionary measures to be taken with hydrogen embrittlement relief treatments. These are:

- (a) The hardness of certain steel parts that have been heat treated below 375°F (191°C) prior to plating may be reduced to less than the required minimum by embrittlement relief treatment above that temperature. In this case, the embrittlement relief temperature is held to approximately 250°F (121°C) but for longer periods, usually five hours or more.

- (b) Some steels lose fatigue strength as a result of chromium plating. When the plated steel is further treated at 400°F (204°C) for hydrogen embrittlement, its fatigue strength is reduced even more. For applications where fatigue strength of a chromium plated part is critical, the embrittlement relief heat treatment should be omitted. Sometimes shot peening before plating helps to minimize fatigue strength loss.
- (c) For a system of plated coatings such as copper-nickel-chromium, the embrittlement relief bake should be given after the final plate has been applied.
- (d) Plated springs and other parts subject to flexure are not to be flexed prior to the embrittlement relief treatment.
- (e) If the plated part is to be given a supplementary surface conversion treatment, such as chromate or phosphate, it should be treated for hydrogen embrittlement after plating but before applying the conversion coating, which would be destroyed by baking. (This applies primarily to zinc and cadmium plates.)

7.4 Prevention of hydrogen embrittlement. Considerable research effort has been expended by the U.S. Government and the electroplating and aerospace industries in developing and evaluating nonembrittling or less embrittling electroplating processes, especially processes for electroplating cadmium. As a result, several cadmium electroplating procedures have been developed which are reported to be nonhydrogen or less hydrogen embrittling. To a lesser degree, research has also been carried out to develop non or less embrittling procedures for cleaning, pickling or activating metals, particularly by the use of inhibited acid pickling baths.

Practical steps to minimize hydrogen embrittlement in parts that would be seriously affected include:

- (1) Avoid or minimize the use of the hydrogen producing treatments in preparing the metal surfaces for plating; this may be accomplished as follows:
 - (a) Avoid cathodic cleaning, pickling or activation treatments when possible by use of alkaline soak cleaning, anodic alkaline cleaning and anodic etching or electropolishing. These latter four operations are essentially nonembrittling.
 - (b) If cathodic or acid pickling treatments must be employed, shorten the treatment time.
 - (c) Use vapor degreasing or solvent cleaning to remove the bulk of grease, oil and other contaminants before cleaning in aqueous solutions.

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- (d) Use mechanical means (such as tumbling, sand or grit blasting, vapor blasting, etc.) for oxide and scale removal, rather than pickling, when possible.
 - (e) Use inhibited acid pickling baths. The inhibitors either cut down on the amount of metal dissolved (and thereby reduce the amount of hydrogen generated) or they can change conditions at the surface so that less of the hydrogen generated enters the metal. In the Battelle's Columbus Laboratories' investigation for NASA on "A Study of Hydrogen Embrittlement of Various Alloys" (cited in the bibliography at the end of section 17), the effectiveness of 25 inhibitors in minimizing the hydrogen absorption by AISI 4130 steel 180,000 psi (1241 MPa) was studied. Of 25 inhibitors studied, eight were effective in minimizing hydrogen absorption in 2N HCl and 2N H₂SO₄ solutions at 140°F (60°C); five were effective only in 2N HCl solution and one was effective only in the 2N H₂SO₄ solution. The eight inhibitors included: 1-Pentyn-3-ol, ethynyl cyclohexanol, hexynol, ethyl octynol and four proprietary inhibitors whose compositions were not known.
- (2) Employ electroplating or coating techniques that avoid or minimize hydrogen embrittlement as follows:
- (a) Use vacuum coating techniques, e.g., substitute vacuum evaporated cadmium coatings for electroplated cadmium.
 - (b) Use organic coatings, rather than electroplated metals.
 - (c) Use low embrittling versions of electroplating processes. For example, the tabulation in paragraph 7.5 lists low embrittling processes for plating nickel, chromium and cadmium, which employ special bath compositions and operating conditions which result in either a lower pickup of hydrogen or in a deposit that allows easier removal of the absorbed hydrogen during the baking treatment. The low embrittling processes generally have higher cathode current efficiencies for metal deposition, which lessens the amount of hydrogen ion reduced at the cathode. Organic brighteners in cadmium cyanide baths should be avoided because they generally intensify embrittlement. Data on bath compositions and operating conditions for the low embrittlement plating processes are given in the documents cited in the tabulation.
- (3) Use appropriate heat treatment to provide hydrogen embrittlement relief.

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7.5 Specification requirements for relief treatments. Hydrogen embrittlement relief treatments are included in the specifications for the particular processes. Data on embrittlement relief treatments for particular electroplating processes are given in the tabulation below:

Specification or Standard Number	Electroplating Process	Hydrogen Embrittlement Relief Treatment at 375 + 25°F (191 + 14°C), minimum hours
QQ-N-290	Nickel	3 or more; 23 (Optional) ^{1/}
MIL-STD-868 ⁻	Low Embrittlement Nickel	23
QQ-C-320	Chromium	3 or more; 23 (Optional) ^{1/}
MIL-STD-1501 ⁻	Low Embrittlement Chromium	23
QQ-P-416	Cadmium	3 or more; 23 (Optional) ^{1/}
MIL-STD-1500	Low Embrittlement Cadmium-Titanium	12 or more
MIL-STD-870	Low Embrittlement Cadmium	23
QQ-Z-325	Zinc	3 or more
MIL-C-14550	Copper	3 or more
MIL-L-13808	Lead	3 or more
QQ-S-365	Silver	3 or more
MIL-R-46085	Rhodium	3 or more
MIL-G-45204	Gold	3 or more

^{1/} For high strength materials (Rockwell C 40 and above) it may be beneficial to extend the baking time to 23 hours.

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Also provided in the specification or standard for the particular electroplating process are the requirements for stress relief of parts prior to cleaning and plating and, also, a description of the tests that are required for determining whether the plated and baked parts are in compliance. The following excerpts of requirements from Federal Specification QQ-C-320B (June 17, 1974) are typical:

High tensile steel parts. Unless otherwise specified, steel parts having an ultimate tensile strength greater than 240,000 psi (1655 MPa) shall not be plated without specific approval of the procuring activity.

Stress relief treatment. All steel parts having an ultimate tensile strength of 150,000 psi (1034 MPa) and above, which are machined, ground, cold formed or cold straightened, shall be baked at a minimum of $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) for three hours or more prior to cleaning and plating for the relief of damaging residual tensile stresses. When peening is required, thermal stress relief shall be performed prior to shot or rotary flap peening.

Embrittlement relief. All coated steel parts having a hardness of Rockwell C 40 and higher shall be baked at a minimum of $375 \pm 25^\circ\text{F}$ ($191 \pm 14^\circ\text{C}$) for three hours or more, within four hours after plating, to provide hydrogen embrittlement relief. The baked parts, when tested in accordance with prescribed procedures, shall not crack or fail by fracture. Plated springs and other parts subject to flexure shall not be flexed prior to hydrogen embrittlement relief treatment.

Baking time. For high strength materials (Rockwell C 40 and above), it may be beneficial to extend the baking time to 23 hours to insure complete hydrogen embrittlement relief.

Embrittlement relief compliance. Compliance with the prescribed embrittlement relief requirement shall be determined with samples of plated parts taken as prescribed in the specification. Parts such as spring pins, lock rings, etc., which are installed in holes or rods, shall be similarly assembled using the applicable parts specifications or drawing tolerances which impose the maximum sustained tensile load on the plated part. The selected samples shall be subjected to a sustained tensile load equal to 115% of the maximum design yield load for which the part was designed. Parts which require special fixtures and/or extreme loads to comply with the above requirements, or where the maximum design yield load is not known, may be represented by separate specimens prepared in accordance with the procedures described in the specification. The notched samples shall be subjected to a sustained tensile load equal to 75% of the ultimate notch tensile strength of the material. The articles, parts or specimens shall be held under load for at least 200 hours and then examined for cracks or fracture.

Although, the stress relief, hydrogen embrittlement relief and test procedures for the several electroplating processes are generally similar, there are some marked differences. Accordingly, it is important that one adhere to the requirements as designated in the latest version of the specification or standard governing the particular electroplating process involved. For example, in the tabulation above, both Federal Specification QQ-C-320 and Military Standard MIL-STD-1501 deal with chromium plating and are in close agreement on most of their requirements. However, MIL-STD-1501 indicates that where there is a conflict with QQ-C-320, MIL-STD-1501 requirements will govern.

ASTM Standard B 242 covers the recommended practice for the preparation of high carbon steel for electroplating. It includes recommendations on cleaning and activating practices to minimize hydrogen embrittlement and also on an embrittlement relief heat treatment.

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8. ORGANIC COATINGS (PAINT, VARNISH, LACQUER, AND RELATED PRODUCTS)

8.1 General comments. The foregoing sections of this handbook describe the cleaning of metals and their protection by inorganic finishes (for example, electroplated finishes, surface treatments, anodic coatings and miscellaneous inorganic finishes). The following sections of the handbook are directed towards organic coatings for the protection of metal and wood surfaces of concern to the Army. Organic coatings for use as house and barn paints and paints for brick, concrete and plaster, are not discussed in this handbook.

Paint offers probably the most versatile type of coating for protecting metals against corrosion and for protecting wood against weathering. A properly applied paint coating can offer much higher corrosion resistance than an inorganic finish, such as a plated coating or a bare surface conversion coating. Therefore, painting is a preferred method for protecting metals. Incidentally, the word "paint" is used broadly in this handbook to indicate all types of protective and decorative organic coatings, applied hot or cold. While it is recognized, in the definitions that follow, that materials such as varnish, lacquer, sealer and certain bituminous coatings, strictly speaking, are not paint, they are, for the present purposes, referred to in a broad sense by the term "paint".

An important consideration is that paint, as purchased, is in liquid form. Unlike a piece of cloth, a piece of paper, a plastic floor or wall tile, a piece of asphalt roofing material or a wood shingle, paint, as purchased, is not a finished product, but has to be applied to the surface and allowed to dry. Thus, the skill and conditions of application of the liquid paint are of importance for the protection of the surface.

Of major importance in painting is the proper preparation of the surface prior to the application of the paint. If the surface is improperly prepared, the best paint may fail to give the desired protection. On the other hand, a paint of only medium quality may give good service, when applied to a properly prepared surface. A clean and dry surface -- one free from grease, dirt, dust, moisture, rust, mill scale and any other foreign matter -- is of prime importance. Methods of cleaning the surface are discussed in an earlier section on cleaning materials and processes. After the surface is thoroughly clean, another step in the preparation of the surface (metal) to receive the paint is the application of a surface treatment. This process is described in an earlier section on chemical treatments and pretreatments and anodic coatings. Proper surface treatments applied to clean steel, zinc, aluminum and magnesium prolong the protective life of the paint coating.

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A further important consideration in painting is the thickness of the dry film. Assume that the correct paint has been selected and that it has been applied in a workmanlike manner to a clean surface. If the coat is too thin, the protection of the painted surface may be inadequate. Up to a practical limit, the thicker the paint coat, the more durable the paint job. Generally, the paint is applied in several coats in order to obtain the proper total film thickness. Military Standard MIL-STD-171 gives the required limits in painting military materiel.

Other important considerations are using the correct type of paint and using paint of good quality. Three paints may be of satisfactory quality, but one may be designed to prime wood, another steel and the third aluminum. The quality of the paint (provided it is tested) is assured by the detail requirements of the many Military and Federal specifications. In general, the title of the specification indicates the intended use of the paint. This information may also be found in the specification under "Scope" and in section 6, "Notes".

After the surface had been properly prepared -- cleaned, given a surface treatment and allowed to dry -- it is ready for the priming paint. Generally, the composition of this paint differs from the top or finish paint. A priming paint for metal, exposed to the weather, contains corrosion inhibitive pigments, such as red lead and/or zinc yellow, in addition to other pigments.

8.2 Definitions of terms. Before considering the various kinds of paints and their properties, a clear idea of the meaning of the more common terms relating to paint, varnish and lacquer may be in order. The definitions marked by an * are, wholly or substantially, those published by the American Society for Testing and Materials (Designation D 16).

Air dry: To dry in an atmosphere of average temperature and relative humidity, say 70 to 90°F (21 to 32°C) and 30 to 80% relative humidity, and form a coating film.

***Baking finish:** A paint or varnish that requires baking at temperatures above 150°F (66°C) for the development of desired properties.

Binder: In a pigmented composition, the nonvolatile vehicle which is the film forming ingredient that binds the pigment particles together.

Catalyst: A compound that accelerates the rate of a chemical reaction and the cure (film formation) of a coating.

***Coating:** A liquid, liquifiable or mastic composition that is converted to a solid protective, decorative or functional adherent film after application as a thin layer.

- *Drier:** A composition that accelerates the drying of oil, paint, printing ink or varnish. Driers are usually metallic compositions and are available in both solid and liquid forms.
- *Drying oil:** An oil that possesses, to a marked degree, the property of readily taking up oxygen from the air and changing to a relatively hard, tough, elastic substance when exposed in a thin film to the air.
- *Enamel:** A paint that is characterized by an ability to form an especially smooth film.
- Hiding power:** The ability of a paint to hide or obscure the surface over which it has been uniformly applied.
- *Lacquer:** A coating composition which is based on synthetic, thermoplastic, film forming material dissolved in an organic solvent and which dries primarily by solvent evaporation. Typical lacquers include those based on nitrocellulose, other cellulose derivatives, vinyl resins, acrylic resins, etc.
- *Nonvolatile vehicle:** The liquid portion of a paint, excepting its volatile thinner and water.
- Paint:** A pigmented liquid composition that converts to an opaque solid film, after application as a thin film.
- *Emulsion paint:** A paint, the vehicle of which is an emulsion of binder in water. The binder may be oil, oleoresinous varnish, resin or other emulsifiable binder.
- *Latex paint:** A paint containing a stable aqueous dispersion of synthetic resin, produced by emulsion polymerization, as the principal constituent of the binder. Modifying resins may also be present.
- *Oil paint:** A paint that contains drying oil or oil varnish as the basic vehicle ingredient.
- *Paste paint:** A paint in which the pigment is sufficiently concentrated to permit a substantial reduction with vehicle before use.
- *Water paint:** A paint, the vehicle of which is a water emulsion, water dispersion or ingredients that react chemically with water.
- Pigment:** A finely divided, insoluble material used in the preparation of paint or printing ink.
- *Plasticizer:** A substance added to paint, varnish or lacquer to impart flexibility.

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Pigment volume concentration: The ratio of the total volume of pigment to the total non-volatile volume (pigment plus non-volatile vehicle) in a paint.

Primer: A specifically formulated base coating used to promote adhesion between the substrate and topcoat and to improve the protective qualities of the coating system.

***Resin, natural:** A solid organic substance, originating in the secretion of some plants or insects, which is thermoplastic, flammable and nonconductive of electricity, breaks with a conchoidal fracture (when hard) and dissolves in certain specific organic solvents (but not in water).

Resin, synthetic: A synthetic substance physically similar to a natural resin.

***Acrylic resin:** A synthetic resin made from derivatives of acrylic acid.

***Alkyd resin:** A synthetic resin made from polyhydric alcohols and polybasic acids; generally modified with resins, fatty oils or fatty acids.

Epoxy resin: A resin containing an epoxy group and generally made by the condensation of phenol, acetone and epichlorohydrin.

***Ester gum:** A resin made from rosin or rosin acids and a polyhydric alcohol, such as glycerine or pentaerythritol.

***Maleic resin:** A resin made from a natural resin and maleic anhydride or maleic acid.

***Melamine resin:** A synthetic resin made from melamine and formaldehyde.

***Penta resin:** Ester gum made from rosin and pentaerythritol.

***Phenolic resin:** A synthetic resin made from phenols and aldehydes.

Polyurethane resins: A class of resins obtained by the reaction of diisocyanates with organic compounds containing two or more active hydrogens.

***Styrene resin:** A synthetic resin made from vinyl benzene.

***Urea resin:** A synthetic resin made from urea and formaldehyde.

***Vinyl resin:** A synthetic resin made from vinyl compounds.

***Sealer:** A liquid composition to prevent excessive absorption of finish coats into porous surfaces; also a composition to prevent bleeding.

*Spreading rate: The area covered by a unit volume of coating material, frequently expressed as square feet per gallon.

*Stain: A penetrating composition that changes the color of a surface, usually transparent and leaving practically no surface film.

*Thinner: The portion of a paint, varnish, lacquer, printing ink or related product that volatilizes during the drying process.

*Varnish: A liquid composition that is converted to a transparent or translucent solid film after application as a thin layer.

*Bituminous varnish: A dark colored varnish containing bituminous ingredients. The varnish may be either of the oil or spirit type.

*Oil varnish: A varnish that contains resin and drying oil as the basic film forming ingredients and is converted to a solid film primarily by oxidation and polymerization.

Spar varnish: A varnish for exterior surfaces. The name originated from its use on spars of ships.

*Spirit varnish: A varnish that is converted to a solid film primarily by solvent evaporation.

Vehicle: The liquid portion of any paint, varnish or enamel.

8.3 Discussion of paint ingredients.

8.3.1 General. The basic ingredient in any paint or coating composition is the film forming material. The film former provides adhesion to the substrate and is the binder for all of the other ingredients that impart to each coating system the properties that make it uniquely suited for its intended use. To achieve good adhesion to metal or wood, the film forming ingredient must be in the liquid phase in some stage of the application procedure. This generally requires dilution of the film former with a solvent or thinner. This vehicle is also the carrier for the other functional ingredients that may be part of the finished coating system such as pigments, driers, catalysts, plasticizers and other additives.

Paints are carefully formulated to meet specific use requirements. For example, a primer or undercoat is generally applied first to the surface to be coated. Its main purpose is to form a satisfactory bond between the substrate and the finish coats. Thus, adhesion is more important than weatherability. The primer may be used to impart some other properties to the coating system. Corrosion inhibitive pigments, such as red lead or zinc yellow, in the primer prevent destructive oxidation of the metal. Sometimes, a surfacer is applied over the primer. This is a heavy filler coat used to provide a smoother surface.

The topcoat is applied over the primer or primer surfacer. Its main purpose is to protect the undercoats from the effect of weather, abrasion, etc., and to give the desired color and appearance to the painted object.

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8.3.2 Pigments. By definition, pigments are the solid particles used in the preparation of paint. They consist of fine powders of various compositions and colors. As there are several hundred individual pigments, a description of each is not feasible in this handbook. They are substantially insoluble in the liquid or vehicle portion. Most of them are opaque in the paint vehicle. The types and amounts of each pigment in a paint affect the properties of the paint. Pigments serve to protect the paint binder from weathering and abrasion; they provide color and help to create hiding power; they assist in providing mechanical strength and imperviousness to liquids and gases; they influence the degree of gloss of the finish. Some of the pigments, grouped according to color, are listed below. Only a few of them are needed to produce the colors of Army paints.

Red

Acridone red
Cadmium red
Lithol red
Nitraniline red
Oxazole red
Para red
Red iron oxide
Thio indigo red
Toluidine red

Yellow

Anthrimide yellow
Bensidine yellow
Cadmium yellow
Chrome yellow
Flavanthrone yellow
Hansa yellow
Indanthrene yellow
Raw sienna
Toluidine yellow
Yellow iron oxide
Yellow ocher
Zinc yellow

Orange

Anthraquinone orange
Cadmium orange
Chrome orange
Molybdate orange
Orange mineral

Green

Chrome green
Chromium oxide green
Dibenzanthrone green
Hydrated chromium oxide
Indanthrene green
Phthalocyanine green

Blue

Blue lead
Iron blue
Indanthrene blue
Phthalocyanine blue
Ultramarine blue

Violet

Benzanthrone violet
Carbazole dioxazine
Iso violanthrone
Thioindigo violet

White

(opaque in oil)

Antimony oxide
Lithopone
Titanium dioxide
White lead
Zinc oxide
Zinc sulfide

White

(Not opaque in oil)

Aluminum silicate
Barium sulfate
Calcium carbonate
Calcium sulfate
Magnesium silicate
Silica

Black

Antimony sulfide
Black iron oxide
Bone black
Carbon black
Graphite
Lampblack

Metallic

Aluminum
Zinc
Bronze
Stainless Steel

8.3.3 Vehicle. To perform its intended function, a protective or decorative coating must form a film when applied. This property is imparted essentially by the liquid portion of the paint — the vehicle. The vehicle includes anything that is in solution or in an emulsion. It may consist of one or more of the following materials: drying oils, driers, thinners, solvents, plasticizers, resins and other materials. An oil vehicle, for example, in linseed oil house paint, is made chiefly of drying oils, thinners and driers. A varnish vehicle (for example, TT-E-489 enamel) is made chiefly of an oil-modified alkyd resin, thinners and driers. A lacquer vehicle consists mainly of resins, solvents and plasticizers. The oils, resins and plasticizers are the binder for the pigment and remain in the dry film. The thinners and solvents are volatile and eventually evaporate completely as the lacquer film dries. Water emulsion and other water-borne coatings, while mentioned in this handbook, are not discussed in detail because few such coatings are covered by specifications of interest to the Military. The thinner in such paints is, of course, water. Such coatings may contain acrylic, alkyd, vinyl or even epoxy type binders.

As stated above, the vehicle comprises a non-volatile and a volatile portion. The former includes drying oils, resins and the like and plasticizers. As a group these are the film formers. They are commonly called binders, because they bind the pigment. The most important oil and resin binders are listed below in alphabetical order.

Drying Oils

Dehydrated castor
Fatty acids
Fish

Linseed
Oiticia
Perilla
Safflower
Soybean
Synthetic
Tall
Tung

Natural Resins

Copals
Congo
Kauri

Manila
Dammars
Batavia
Singapore
East Indies
Batu
Black
Pale
Lac
Rosin

Synthetic Resins

Acrylic
Alkyd
Cellulose ester and
ethers
Chlorinated paraffin
Chlorinated rubber
Coumarone-indene
Epoxy
Maleic
Melamine
Petroleum
Phenolic
Polyamide
Polyethylene
Polyurethane
Rosin esters
Rubber
Silicone
Styrene
Terpene
Urea
Vinyl

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8.3.3.1 Solvents, thinners. At ordinary temperatures, the consistencies of practically all mixtures of oils and pigments and of oils and resins are too high to allow easy spreading over a surface in a film of suitable thickness. Also, most resins are solids to begin with and, with few exceptions, must be dissolved before they can be used. Volatile solvents reduce (thin) consistency to practical levels. According to the circumstances, these liquids are called solvents, reducers, thinners or diluents. The difference is mainly one of degree. For example, mineral spirits is often referred to as a diluent. For all practical purposes the terms solvent, reducer and thinner are used interchangeably and all of them may be regarded as solvents or as diluents under some conditions. Other things being equal, a solvent may be a diluent when used on account of lower cost. A solvent is carefully selected for its rate of evaporation, boiling point, flash point, flammability, solvency, odor, cost, conformance with air pollution regulations and other properties. There are a large number of volatile solvents and thinners. Some types, with examples, are listed below.

Terpenes (for example, turpentine)

Hydrocarbons (for example, mineral spirits, toluene and xylene)

Alcohols [for example, ethyl and butyl alcohols (ethanol, butanol)]

Esters (for example, ethyl acetate and butyl acetate)

Ketones (for example, acetone and methyl ethyl ketone)

Ether-alcohols (for example, cellosolve)

Chlorinated hydrocarbons (for example, methylene chloride)

Nitroparaffins (for example, nitropropane)

Furans (for example, tetrahydrofuran)

8.3.3.2 Driers. By definition, a drier is a composition that accelerates the solidification of compositions based on drying oil, such as paint, printing ink or varnish. The ordinary lacquer dries solely by evaporation and thus does not need any drier. Driers are heavy metal soaps of organic acids, the principal metals being lead, cobalt, manganese, zinc, iron, calcium and zirconium. The early ones were soaps of either linseed fatty acids or rosin acids. These are known as linoleate driers and resinates driers, respectively. Today we also have naphthenate, octoate and tallate driers. The organic acid in the naphthenate is naphthenic acid, in the octoates it is octoic acid and in the tallates it is the acid obtained from tall oil. Driers are used in small amounts and, generally, the combination of two or more metals (for example, lead and cobalt) is preferred over a single metal. A lead drier is usually considered to be a "through" drier, promoting hard drying throughout the thickness of the film. However, lead driers have come into disrepute for paints on any surfaces accessible to children because of the potential danger of lead poisoning. A cobalt drier is a very active drier and thus tends to dry the outer layer of the film. A manganese drier is intermediate in its action. Too much drier may adversely affect the durability of the paint film and, ordinarily, driers should not be added to paints in the field.

8.3.3.3 Catalysts. Until some 25 years ago, paints and the like were classed as oxidizing or nonoxidizing types, those that "dried" as a result of the binder (drying oil, etc.) combining with oxygen from the air and those that "dried" solely as the result of evaporation of thinner. As discussed in the preceding paragraph, "driers" catalyzed or accelerated the drying of the oxidizing type. There now exists a third class of paint that contains ingredients that react with each other in the presence of a suitable catalyst (not the metallic soap type) or heat (or both) to form the film. The catalysts include hydrochloric acid, phosphoric acid, amines and other compounds. An example is phosphoric acid, as used in Primer (Wash), Pretreatment, DoD-P-15328.

8.3.3.4 Plasticizers. Plasticizers are liquid or solid organic compounds that are used in some cellulose and vinyl lacquers (for example in lacquers for automobiles, furniture and fabrics; in rubber resin base coatings; and in related finishes) to impart flexibility and other properties to the film. For example, MIL-L-11195 for hot spray lacquer requires 10 to 15% plasticizers by weight of the nonvolatile vehicle. A large number of plasticizers are available. A few types and one or two examples of each type are listed below.

- (a) Vegetable oils, semi or nondrying (for example, castor oil and its derivative, rapeseed, and cottonseed oils)
- (b) Certain liquid compounds having high boiling points (for example, dibutyl phthalate and tricresyl phosphate)
- (c) Nondrying resinous materials (for example, oil-modified sebacic alkyd)

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8.3.3.5 Other ingredients. Other ingredients, known as chemical specialties, are used in small amounts in paints. Among them are wetting agents, stabilizers, antioxidants and antiskin agents.

8.4 Types of clear (transparent) coatings. There are four kinds of clear coatings in which the Army is interested, viz., varnish, shellac, lacquer and linseed oil.

8.4.1 Varnish. Varnish may be classed as spirit or oleoresinous. A spirit varnish is one whose film is converted from the wet to dry state by simple evaporation of the solvent. Shellac, covered by TT-S-300, is an example of spirit varnish. An oil varnish is a combination of drying oil, resin, thinner and drier. When this varnish is spread in a thin film, the wet film is converted to a dry film by oxidation (chemical reaction). Spar varnish covered by TT-V-121 is an example of oil varnish. Sometimes an oil varnish is designated by its oil length (the number of gallons of oil for each 100 pounds of resin). For example, a 25-gallon varnish is one in which 25 gallons of drying oil are used for each 100 pounds of resin.

8.4.2 Shellac. Actually, this product is a spirit varnish, consisting of shellac resin dissolved in alcohol -- usually about four pounds of the shellac resin dissolved in 1 gallon of alcohol. When shellac varnish is spread in a thin film it dries by simple evaporation of the alcohol, leaving a continuous film of the dry shellac as the coating. The usual shellac varnish is not transparent in the container, being rendered turbid by a small amount of naturally occurring wax, but the dry film is practically so. Refined (dewaxed) shellac varnish is clear in the container. Specification TT-S-300 covers shellac varnish.

8.4.3 Lacquer. A typical clear cellulose lacquer consists of nitrocellulose, a resin such as alkyd, a plasticizer and volatile solvents. Federal Specification TT-L-32 for (clear) cellulose nitrate lacquer covers such a product. A film of this lacquer dries by solvent evaporation. There are several other kinds of lacquer (for example, vinyl lacquer covered by MIL-L-14486) in which the non-volatile vehicle consists of vinyl resin and plasticizer. Also, there are clear lacquers based on acrylic ester resin used alone or in combination with cellulose nitrate, ethyl cellulose and vinyl resins.

8.4.4 Linseed oil. This drying oil is used in a few places by the Army as a clear coating. When linseed oil is spread in a thin film, it absorbs and combines with oxygen from the air and is converted to a dry film of linoxyn. A raw linseed oil is covered by TT-L-215, while boiled linseed oil is covered by TT-L-190.

8.5 Types of pigmented coatings. Pigmented coatings may be typed or classified in several ways, e.g., according to the function the coating is to serve, the appearance of the coating film, the composition of the vehicle or the basis of the mode of application or curing. Classification by composition of vehicle is a very useful method because it provides the experienced user with some indication of the properties to be expected from the coating and its potential uses. Pigmented coatings include oil type paints, varnish enamels, lacquer enamels, sealers, undercoaters, surfacers and some stains. It is beyond the scope of this handbook to describe in detail each type of pigmented coating. However, brief descriptions of varnish enamels, lacquer enamels and some paints and coatings, according to vehicle composition, are given in the paragraphs that follow.

8.5.1 Enamels. Historically, the term "enamel" is an abbreviation of enamel paint; that is, a paint suggestive of a porcelain enamel in hardness, smoothness and gloss. These features are imparted by the use of a varnish vehicle in place of oil.

No hard and fast line separates paint from enamel, but the term has come to have a close connection with composition as well as with properties. For example, flat (nonglossy) finish made with varnish is often called flat enamel, although it is not glossy as were the original enamels. But perhaps this is not unusual; semigloss and flat finish porcelain enamels are also being produced.

Since lacquer is a type of varnish, a pigmented lacquer may properly be called an enamel, i.e., lacquer enamel, if necessary, to avoid ambiguity. However, the indexes of both Federal and Military specifications use the term enamel mainly for those made with oleoresinous varnishes. Lacquer enamels are indexed in several ways, often only indirectly revealing the true nature.

The Army uses gloss, semigloss and flat enamels, represented mainly by TT-E-489, TT-E-529 and TT-E-527, respectively. These may be had as air drying or baking types. They are made with alkyd varnish, 10 to 20% of which is replaced with urea or melamine resin to make the baking type. Among other types of enamels used by the Army are those made with styrenated alkyd varnish (TT-E-516) and phenolic resin varnish (TT-E-522).

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8.5.2 Pigmented lacquers. Pigmented lacquers (lacquer enamels) based on cellulose derivatives [for example, cellulose nitrate (popularly called nitrocellulose)], have been used widely by the military on shells, bombs, grenades, tanks, trucks, ammunition and automotive components and on other surfaces. These lacquer coatings dry chiefly by evaporation of the volatile solvents and diluents, with little or no oxidation or polymerization. The clear (unpigmented) nitrocellulose lacquers have been described in a previous section. The pigmented lacquers have the same composition as the clear lacquers except for the addition of pigment. These lacquers are applied by spraying and the film dries rapidly (within a few minutes). Pigmented lacquers can be formulated to dry with a glossy, semiglossy or lusterless finish. Nitrocellulose lacquers drying with glossy and lusterless finishes are covered by MIL-L-12277 and TT-L-20, respectively. Lacquers have a lower solids content than enamels or oil paints. Thus, more coats of lacquer are needed for the same dry film thickness. However, in modern pigmented nitrocellulose lacquers, this drawback has been relieved to a considerable extent in several ways, viz., by selecting nitrocellulose of the lowest possible viscosity, by using a high ratio of resin to nitrocellulose (for example in MIL-L-11195 lacquer, the ratio of phthalic alkyd type resin to nitrocellulose is two to one by weight), by selecting resins which have the best compatibility and solubility with the nitrocellulose and by hot spray application. The hot spray process reduces the viscosity of the lacquer. Thus less thinner (more solids) are present and fewer coats are needed to obtain the desired film thickness. For hot spraying, lacquer is heated to about 160°F (71°C). Pigmented lacquer covered by MIL-L-11195 is an example of hot spray lacquer. Lacquers dry at room temperature, but in automobile finishing, forced drying for about 1 hour at 150 to 180°F (66 to 82°C) is used to speed production.

8.5.3 Oil-type paints. These paints consist principally of drying oil (usually linseed), thinner and drier as the vehicle, mixed with pigments. The exterior surfaces of wood houses and various steel structures may be coated with this type of paint. The paint can be applied by brushing or spraying, but generally it is applied by brushing. Oil type paint brushes easily, has good wetting properties and dries slowly, usually requiring several days between coats. An example of oil type paint is one covered by TT-P-105.

8.5.4 Alkyd resin enamels. Alkyd resins are the products of condensation polymerization of polycarboxylic acids, polyols and fatty acids or vegetable oils. Probably the most common drying and semidrying alkyds are based on linseed and soya oils, respectively. These alkyds are used in coatings where baking is not possible or desirable. Film formation occurs by evaporation of solvent and oxidation-polymerization through the unsaturated sites in the fatty acid portion of the alkyd resin. Alkyds are characterized by good exterior durability and thus form the top coat in many metal finishing applications. However, they are not recommended for continuous immersion or for use where chemical fumes or splash will prevail. They use mineral spirits and other exempt solvents and can be formulated for application by brush, spray, dip or roller.

For baking finishes, either a semidrying type (such as that obtained from soya oil) or nondrying type (such as that obtained from coconut oil) may be used. Generally, the baking alkyds are produced with lesser amounts of oil than those produced for air drying and contain unreacted hydroxyl groups (from excess polyol). Amino resins (urea or melamine) are frequently added to produce a highly cross-linked molecule when cured by baking. The baked alkyds have better hardness, exterior durability and abrasion resistance than the air dried alkyds, so the baking types find wide usage as factory applied finishes on metal objects. The baking types require stronger solvents than the air drying types and are generally formulated for factory application by spray or dip. Some examples of alkyd resin coatings of interest to the Army follow:

- (a) TT-E-489, Enamel, Alkyd, Gloss (for Exterior and Interior Surfaces) is available in a variety of colors in two classes: class A - Air Drying and class B - Baking -- they are general purpose enamels having excellent exterior durability (color and gloss retention) for use on automotive and construction equipment, drums, slow moving aircraft, etc.
- (b) TT-E-491 (for Air Drying and Baking)
- (c) TT-E-515, Enamel, Alkyd, Lusterless, Quick Drying
- (d) TT-E-527, Enamel, Alkyd, Lusterless (for General Use)

8.5.5 Epoxy resin coatings. The epoxy resins are characterized by the reactive epoxy group (oxirane ring) in the molecule, e.g., the



group. This group and the hydroxyl group in many epoxies serve as a reactive site for cross-linking. Most of the resins used in organic coatings are produced by reacting bisphenol A with epichlorohydrin. The resin is diglycidyl ether of bisphenol A. Other types, such as the epoxy novolacs, find less use in coatings.

The epoxy coatings used by the military are those produced from the diglycidyl ether of bisphenol A. This type of resin is produced in a range of molecular weights and varies from brittle solids to viscous liquids. The resins are used to produce the following types of coatings:

1. Two package, solvent free, viscous liquids (epoxy-polyamide)
2. Two package epoxy solution coatings (amine-cured)
3. Single package, baking type epoxies
4. Single package, baking type, epoxy-phenolics
5. Two package, epoxy coal tars with amine or polyamide resins for curing
6. Epoxy esters (air drying or baking types)

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The epoxies have great versatility and impart chemical resistance, exceptional adhesion and good flexibility to coatings. Epoxy coatings tend to chalk when exposed outdoors. However, this is a surface phenomenon that affects appearance only. Otherwise, the coatings will withstand long outdoor exposure.

Epoxy resins are soluble in oxygenated solvents such as ketones, esters and ether alcohols, as well as mixtures of solvents containing aromatic hydrocarbon and alcohol. The epoxy ester resins are soluble in aromatic solvent (such as xylene) and as oil length increases, can tolerate increasing amounts of aliphatic hydrocarbon. The epoxy type coatings can be formulated for application by brush, spray, roller and even by troweling. Some examples of epoxy type coatings of interest to the military follow:

- (a) MIL-P-23377, Primer Coating, Epoxy-Polyamide, Chemical and Solvent Resistant (epoxy-polyamide type).
- (b) TT-C-535, Coating, Epoxy, Two-Component, for Interior and Exterior Use on Metal, Wood, Concrete, and Masonry (epoxy-polyamide type).
- (c) MIL-C-46079, Coating, Epoxy, Baking Type for Magnesium.

8.5.6 Phenolic resin coatings. Phenolic resins are used as the binder in some baking type coatings and are heat treated or cooked with oils to produce oleoresinous (or varnish type) binders for enamels.

Phenolic resins are produced from phenols by reaction with an aldehyde. The following types of phenolics find major usage in coatings:

- 1. Baking phenolics (alcohol soluble).
- 2. Pure phenolics (oil soluble).
- 3. Modified phenolics (rosin is the usual modifier).

A substantial variety of phenolics is produced with properties related to the type of substitution of the phenol, the ratio of phenol to formaldehyde, the type of modifier, the type of catalyst and the reaction conditions.

The high baked, pure phenolic coatings have exceptional chemical resistance. They find usage as linings for cans and steel containers and in other places where extreme resistance to chemicals is required. The baking type coatings may be modified with other resins such as epoxy and vinyl to improve flexibility. Besides being brittle, the pure phenolic coatings are somewhat darker in color than many of the other coatings. They tend to chalk when exposed outdoors.

For exterior service, the phenolics are modified with drying oils. The varnish type phenolic resins are processed (cooked) with such oils as linseed and tung. The so-called "spar varnishes" fit into this category. These oil modified phenolics, when pigmented, find usage in protection of structural steel, bridgework, tankage and ship superstructures. These vehicles are pigmented with various colors, zinc or aluminum for top coats. For primers, they may be pigmented with red lead, zinc chromate or lead silico chromate. Iron oxide, iron oxide-zinc chromate mixtures and zinc dust are also popular in primers for galvanized steel. Phenolic varnishes are baked for some uses, such as can linings, and for coating shell casings. Some examples of phenolic coatings of interest to the military follow:

- (a) TT-E-522, Enamel, Phenolic, Outside Type I - Lusterless, Type II - Semi-Gloss (Rule 66 Solvents)
- (b) MIL-P-12742, Primer Coating, Phenolic, Water Immersible
- (c) TT-P-38, Paint, Aluminum, Ready Mixed -- contains phenolic varnish vehicle

8.5.7 Polyurethane coatings. The isocyanate group (--N=C=O) is the characteristic group of the polyurethane prepolymer. These prepolymers can be cured by reaction with alcohols, amines, carboxylic acids, water, etc., to form coatings. Several types of urethane coatings are produced:

- 1. Oil modified polyurethanes (one package): uralkyds
- 2. Moisture cured prepolymers (one or two package)
- 3. Catalyzed (two package)
- 4. Polyol cured (two package)
- 5. Blocked (one package)

Like other varnishes and alkyd resins, the oil modified polyurethanes dry by oxidation. Suggested uses are in places where the regular alkyds have been used but where faster drying and improved wear, water and chemical resistance are desired. However, color stability cannot match the alkyds.

The two package urethane coating provides excellent chemical resistance. One component is a polyurethane prepolymer containing an unreacted isocyanate group, while the other is generally a polyester or polyether. When combined, the two components react to form a chemically resistant coating superior to the two package epoxy for some uses, but somewhat more expensive. This type of coating is used for chemical resistant maintenance paints, marine coatings and tank linings.

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Aromatic and aliphatic hydrocarbons are solvents for the uralkyds. The two package coatings require a balanced solvent system comprised of polar solvents, preferably ester types. Special urethane-grade solvents (low water content) are necessary. Some examples of polyurethane coatings of interest to the military follow:

- (a) TT-C-540, Coating, Polyurethane Clear, Linseed-Oil Modified, Air Drying Type (Uralkyd) -- for metal, wood, masonry, etc.
- (b) TT-C-542, Coating, Polyurethane, Oil Free, Moisture Curing -- several colors, offers good abrasion and chemical resistance and washability
- (c) MIL-C-81773, Coating, Polyurethane, Aliphatic, Weather Resistant
- (d) MIL-C-46168, Coating, Aliphatic Polyurethane, Low Reflective, Chemical Agent Resistant

8.5.8 Silicone coatings. Silicone coatings are based on a highly stable, inorganic silicone-oxygen structure coupled with organic radicals. Coatings produced from silicone resins have outstanding high temperature resistance and resistance to UV light exposure. The coatings are difficult to wet, so other materials do not bond well to them. Silicone coatings (baked type) will withstand prolonged exposure to temperatures up to 500°F (260°C) and short exposure to temperatures of 1000°F (538°C). Thus they find use on mufflers, stacks, fantails of jet engines, etc. (often with aluminum pigmentation). The silicone resins are also used to modify alkyds, producing coatings which have exceptional resistance to outdoor exposure. The silicones may be reduced with hydrocarbon solvents and can be formulated for application by spray or brush. Some examples of silicone modified coatings follow:

- (a) TT-E-490, Enamel, Silicone-Alkyd Copolymer, Semigloss -- for exterior and interior use
- (b) TT-E-1593, Enamel, Silicone-Alkyd Copolymer, Gloss -- for exterior and interior use
- (c) TT-P-28, Paint, Aluminum, Heat Resisting -- for temperatures to 1200°F

8.5.9 Vinyl resin coatings. Vinyl resins are produced by polymerization of a variety of monomers containing double bonds between adjacent carbon atoms. In a broad sense, acrylics, polystyrene and styrene-butadiene resins fall into the vinyl class. However, in coatings the term vinyl generally refers to such resins as polyvinyl chloride, vinyl chloride-vinyl acetate copolymers, polyvinylidene chloride and polyvinyl butyral. Because of limited solubility, polyvinyl chloride resin finds limited use in solution type coatings. It does, however, find use in vinyl plastisol and organisol type metal coatings. The vinyl chloride-acetate copolymer is used in both air drying and baking finishes. The air drying types (lacquers) dry by solvent evaporation. They contain modifiers to promote adhesion to metals. Both types also contain stabilizers to impart heat and UV light stability. Excellent maintenance paints (for chemical fume environments) are produced from vinyls. The Navy has developed an excellent vinyl system for marine use: polyvinyl butyral reactive wash primer, vinyl anticorrosive and vinyl top coat. Vinyls require strong solvents such as methyl ethyl ketone but may also contain some hydrocarbons diluent. Application is generally by spray. Some examples of vinyl coatings of interest to the military follow:

- (a) MIL-L-14486, Lacquer, Vinyl Resin, Semigloss -- colors: olive drab and white, uses vinyl chloride-acetate copolymer
- (b) MIL-P-15930, Primer, Vinyl-Zinc Chromate Type

8.6 Non-air polluting coatings.

8.6.1 General. During the latter part of the 1960's, there developed a great concern regarding the release of coating solvents into the atmosphere. Some solvents are particularly undesirable because they produce eye irritants through photosynthesis. The original regulations restricting release of solvents from coatings were adopted by Los Angeles County as Rule 66 in 1966. Similar regulations were subsequently adopted in other areas of the United States. This has led to changing solvents in many coatings formulas and to the search for practical coatings which do not contain organic solvents. Two types of coatings which contain no organic solvents and which offer high potential for use in military applications (powder coatings and electrodeposited coatings) are discussed below.

8.6.2 Powder coatings. Powder coatings, while used in the United States since about the mid 1950's, came into important usage in industrial finishing during the 1970's. Powder coatings are now applied by special electrostatic spray guns in thicknesses comparable to regular solvent systems. Previously, powder coatings were used primarily in specialty applications where 8 to 10 mils of protective film was desired. Such coatings were applied by dipping heated parts into a fluidized bed of powder (dispersed in an air stream).

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In a typical powder finishing process, the part to be coated is carried on a conveyor past one or more spray guns. The spray guns may be either reciprocating or stationary, but reciprocating guns are commonly used to provide a powder spray or cloud over a large work area. Hand held spray guns are also used for touch up work or for applying coatings under limited production conditions.

The powder particles are electrostatically charged by the spray gun and attracted to the ground part (being coated). The electrical attraction of powder to part produces a wrap around effect. Moreover, as the powder coating is laid down it provides insulation over the surface already coated. This directs powder to uncoated areas and also limits the thickness of coating deposited. Thus, electrostatic powder deposition can result in very uniform coating thicknesses.

Even though the charged powder particles are attracted to the ground part, there is still a large amount of overspray. The economics of powder coating generally require collection and recycling of the overspray. The overspray is exhausted from the spray booth into a powder collector, such as a cyclone separator, from which it is returned to the spray guns.

Powder coating is limited to parts that can be heated, because the powder must be melted (fused) to transform the individual particles into a coating film and develop the bond to the metal surface.

Coating powders are made by blending pigments into molten, resinous binder in special melt blending equipment, extruding the melt into a sheet and then breaking and grinding it into a fine powder.

Some advantages of powder coating compared to conventional solvent type industrial finishes follow:

- No solvents present - lowered toxicity, air pollution, fire hazard and odor.
- Good coating uniformity.
- Lower cost potential.

Some disadvantages include:

- Need to heat part to fuse film.
- Difficulty of color change because of the powder recirculation system, which is difficult to clean.

Many of the same generic types of coatings which are applied in solvents can now be applied as powders. The major limitation is the requirement that the coating resin be thermoplastic at the time of application, even though it may subsequently cross-link (thermoset) during the fusion process. Coatings available at the time of this writing include the following:

- Polyolefins
- Cellulosics
- Vinyls
- Acrylics
- Polyesters
- Epoxies
- Nylons

A detailed discussion of powder coating is given in "Fundamentals of Powder Coating", E. P. Miller and D. D. Taft, Society of Manufacturing Engineers, 1974.

8.6.3 Electrodeposited coatings (electropainting). Electropainting with organic coatings is analogous to electroplating with metals. The object to be coated is made an electrode in a tank of water-dispersed coating material. The resinous portion of the paint and the pigments carry a charge and are moved by an applied potential (direct current) to the work.

The resinous portion of the paint can be structured to dissociate into either positive or negative ions in water. The charge on the pigments is obtained by anionic or cationic dispersants on their surfaces. The charges on the resin and pigment must match, so that they move to the same electrode under an applied potential.

Many kinds of metal objects have been electropainted -- from small parts to automobile bodies. Because the coating is an insulator, the coating process is directional and self-limiting. As the coating builds up to a thickness of about 0.75 to 1 mil (19 to 25 μm), the deposition is directed to areas with less coating. Consequently, highly uniform coatings can be obtained over irregular shapes and corners and edges are well protected.

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Acrylic and epoxy coatings have found substantial usage in electropainting, but alkyd and other types of coatings can also be structured for electropainting. The process is highly efficient for primers and single coat finishing. The major advantages of electrocoating are absence of air pollution and fire hazard, coating uniformity on irregular shapes, good coverage of edges, absence of runs and sags, low cost for high volume production and elimination of waste. Disadvantages include difficulty of color change, need for high volume to offset installation costs, bath control and single cost limitations.

A detailed discussion of electropainting is given in Electropainting, R. L. Yeates, Robert Draper Ltd., Teddington, England, 1970.

8.6.4 Water-borne coatings for metals. Water-borne coatings have also been developed for application to metals by methods other than electropainting (spray, dip, etc.). Interest in these water-borne coatings has been considerable because of their ease in meeting air pollution regulations, though it has been common practice to use up to 15 to 20% of solvent in these coatings. The solvent aids in film formulation and better wetting of the metal surfaces, which enhances adhesion of the coating. Baking type water-borne coatings have found the greatest success in metal finishing because the cross-linking of the resin binder improves water resistance of the coating. Examples of water-borne coatings for metal finishing follow:

- (a) MIL-P-28577, Primer, Water Reducible, Corrosion-Resistant, for Metal Surfaces -- primer is air drying type and contains corrosion inhibitive pigments
- (b) MIL-P-28578, Paint, Water Reducible, Semigloss, Exterior and Interior -- an air drying type in a variety of colors

9. PAINT SPECIFICATIONS AND STANDARDS FOR ARMY MATERIEL

9.1 General comments. The Defense Agencies make use of both Federal and Military Specifications for a wide variety of paint, enamel, lacquer and various related materials. The question might be asked, "What is the purpose of paint specifications?" The following comments, quoted from the article "Why Paint Specifications - Their Tests and Controls", C. F. Pickett, ASTM Bulletin 227, January 1958, answers this question. Although this was written more than 20 years ago, the purpose and value of Federal and Military Specifications have not changed.

"The purpose of a specification is to define, particularize and completely state a condition of composition, shape, size, color, procedure, performance or combination of two or more of these, with tolerance limits so that there is a common understanding between the buyer and seller.

"Paint procurement specifications and standards are essential to the Federal government where competitive buying is customary. A paint specification should describe the product so well that a manufacturer knows precisely the quality of the paint required and the buyer, in turn, obtains the desired quality of paint at a reasonable price. Well-prepared specifications permit the buyer to have multiple suppliers of a given quality paint, making possible mixing of products, fewer stripping and finishing rejects, fewer solvents and uniform products from multiple plants. With these, and several other advantages, it is obvious that a specification is a useful tool for a paint buyer. By the same token, it provides fair competition to the seller and an opportunity to exercise ingenuity in formulations and in manufacturing.

"There are many types of specifications describing composition, performance, dimension, procedure or combinations of these elements. Paint specifications frequently fall into the class of composition or performance. It is the opinion of the author that neither one alone is sufficient to completely describe a paint product. Since the very purpose or function of a specification is to describe a product so completely that both buyer and seller know what is wanted, all efforts should be made to do so. It is believed that sufficient parameters of both composition and performance should be included in a specification so that the type, quality and performance are assured."

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New or improved paint products are being developed rapidly by industry. Sometimes the improvement of a particular paint product is the result of experimental work done in a Government laboratory. Later, either a new paint specification is prepared or the older specification is revised to reflect these latest improvements. Thus, it is very important that the Government buyer of paint refers to the latest revision of a particular specification. This can be done by consulting the latest indexes and supplements to Federal and Military Specifications. Some paint specifications cover several classes, types or grades. Hence, it is also very important that the using agency specify the particular type, class and grade wanted. The "Notes" section in Federal and Military Specifications contains valuable information about the intended use of the particular paint, including a description of the types, classes or grades.

9.2 Working list of paint specifications and standards grouped by types. The following pages list, under related categories, available and currently reported Government Specifications for paint and related material (not including new ingredients) in which the Army has an interest. The list is arranged to include (a) the group destination or category; (b) designation of the specifications; and (c) title or name of the specification. The groups or categories are listed in the following order:

Coatings	Roller coat finishes
Coatings, camouflage	Sealers
Coatings, strippable, dipping type	Solar heat reflecting coats
Coatings, strippable, spraying	Stains
Coating compounds in pressurized dispensers	Surfacers
Compounds	Stencil ink and paint
Compounds, cleaning	Test methods & standards
Steam	Treatments & pretreatments
Solvent	for metal
Alkaline	Varnishes
Acid	Wood preservatives
Miscellaneous	Miscellaneous
Corrosion preventatives	
Corrosion removing compounds, rust and	
Enamels	
Lacquers	
Paints	
Paint removers	
Pretreatment (wash) primers	
Primers	

COATINGS

MIL-C-450	Coating Compound, Bituminous, Solvent Type, Black -- for coating interiors of ammunition items before filling
MIL-P-11520	Coating Material, Protective, for Rubber Surfaces
TT-C-520	Coating Compound, Bituminous, Solvent Type, Underbody (for Motor Vehicles) -- protective coating and sound deadener for underbody parts of automotive equipment
TT-C-492	Coating Compound, Paint, Antisweat -- coating for surfaces subject to intermittent condensation
TT-C-499	Coating Compound, Chemical Resistant, Clear -- for maximum protection from concentrated acids
TT-C-530	Coating Compound, Rust Inhibitive, Fish Oil Base -- rust inhibitive primer for use on rusty metal with minimum preparation
TT-C-1883	Coating, Clear, Fire Retardant, Two Component Polyurethane, Thermal Insulating (Intumescent)
MIL-C-21067	Coating Compound, Synthetic Rubber, for Exposed Steel -- coating for protection of exposed steel surfaces
MIL-C-46079	Coating, Epoxy, Baking Type for Magnesium -- for sealing magnesium castings before painting
MIL-C-2750	Coating, Epoxy, Polyamide -- for protection of areas exposed to chemicals and solvents
MIL-C-46168	Coating Aliphatic Polyurethane, Low Reflective, Chemical Agent Resistant
MIL-C-81773	Coating, Polyurethane, Aliphatic, Weather Resistant -- a two component aliphatic polyurethane available in gloss and lusterless types
MIL-C-83286	Coating, Urethane, Aliphatic Isocyanate, for Aerospace Application -- gloss and lusterless oil-free urethane coatings for exterior application on aerospace equipment
TT-C-1060	Coating Compound, Reflective -- used for marking surfaces for safety to insure visibility at night

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CAMOUFLAGE COATINGS

MIL-C-46168 Coating Aliphatic Polyurethane, Chemical Agent Resistant

MIL-E-52798 Enamel, Alkyd, Camouflage

MIL-E-52835 Enamel, Modified Alkyd, Camouflage, Lusterless

MIL-P-52905 Paint Arctic Camouflage, Removable

MIL-L-52909 Lacquer, Acrylic, Camouflage, Lusterless

MIL-L-52926 Lacquer, Camouflage, Lusterless, Hot Spray, Forest Green

MIL-E-52929 Enamel, Alkyd, Camouflage, Flash Dry

COATINGS, STRIPPABLE, DIPPING TYPE

MIL-P-149 Plastic Coating Compound, Strippable (Hot Dipping) -- used for preservation and packaging of small metallic parts

MIL-P-45021 Plastic Coating Compound, Strippable Cold Dipping 120°F (49°C) -- intended for preservation of parts containing heat sensitive material and optical lenses and elements

COATINGS, STRIPPABLE, SPRAYING

TT-C-517 Coating, Strippable, Masking -- for spray booths and glass

MIL-C-3254 Coating System, Bridging, Strippable, Sprayable -- this top coat is an asphalt vehicle which is applied over a vinyl base coat

MIL-C-6799 Coating, Sprayable, Strippable, Protective, Water Emulsion -- can be used over painted surfaces without lifting paint

MIL-C-16555 Coating Compounds, Strippable Sprayable -- this vehicle is usually vinyl

MIL-C-23760 Coating, Sprayable, Strippable, Protective, for Preservation and Packaging of Weapons Systems and Components, Application of -- covers the application of MIL-C-6799 and MIL-C-16555

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COATING COMPOUNDS IN PRESSURIZED DISPENSERS

- TT-L-48 Lacquer, Nitrocellulose and Acrylic, High Solids, Hydrocarbon Propellant (In Pressurized Dispensers) -- quick and convenient method of applying nitrocellulose or acrylic lacquers to small objects or areas
- TT-E-488 Enamel, Primer Coating, and Clear Lacquer (In Pressurized Dispensers) -- primer with maximum corrosion resistance on metals
- TT-P-600 Primer Coating, Zinc Chromate (In Pressurized Dispensers) -- primer with maximum corrosion resistance on metals
- TT-P-605 Primer Coating, All Purpose Gray, Alkyd (In Pressurized Dispensers) -- all-purpose primer for wood, metal and plastics

COMPOUNDS

- MIL-C-3301 Compound, Asphaltic, Hot Melt (Cavity Lining) -- protective lining of metal cases to contain high explosives
- MIL-S-11388 Sealing Material for Metal Container Seams -- for sealing seams of metal containers for packaging dry materials
- MIL-C-13783 Compound, Waterproofing (For Small Arms Ammunition) -- water proofing compound based on high grade asphalts
- MIL-S-3105 Sealing Compound, Inert (For Use in Ammunition) -- nonreactive material for sealing or padding in nose and tail portions of bombs
- MIL-C-46157 Coating Compound, Temporary Protective For Retrograde Materials -- temporary protection of aluminum or painted metal surfaces
- MIL-C-82604 Compound, Asphaltic, High Melting, Hot Melt (Cavity Lining) - for coating inner walls of explosives cases prior to filling
- MIL-C-82633 Compound, Polymeric Elastomer, Thermosetting (For Use As Bomb Tail Pad) -- two part, cured-in-place thermosetting compound for sealing or padding tail portion of bomb cavities
- MIL-S-81733 Sealing and Coating Compound, Corrosion Inhibitive -- room temperature curing synthetic rubber compounds

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STEAM CLEANING COMPOUNDS

P-C-436 Cleaning Compound, Alkali, Boiling Vat (Soak) or Hydrosteam
 P-C-437 Cleaning Compound, High Pressure (Steam) Cleaner
 MIL-C-22542 Cleaning Compound, High Pressure Cleaner, Liquid

SOLVENT CLEANING COMPOUNDS

O-A-51 Acetone, Technical
 O-C-1824 Cleaning Compound, Solvent, Heavy Duty, Liquid
 O-C-1889 Cleaning Compound, Solvent
 O-T-236 Tetrachloroethylene, (Perchloroethylene); Technical Grade
 O-T-634 Trichloroethylene, Technical
 P-C-444 Cleaning Compound, Solvent Soluble, Grease Emulsifying
 P-C-446 Cleaning Compound, Solvent-Detergent (For Cleaning Coils and Filters)
 TT-M-261 Methyl Ethyl Ketone, Technical
 MIL-C-372 Cleaning Compound, Solvent (For Bore of Small Arms and Automatic Aircraft Weapons)
 MIL-C-6864 Cleaning Compound, Solvent, Oil-Cooler
 MIL-C-11090 Cleaning Compound, Degreasing and Depreserving Solvent, Self-Emulsifying
 MIL-C-81302 Cleaning Compound, Solvent, Trichlorotrifluoroethane
 MIL-T-81533 1,1,1 Trichloroethane (Methyl Chloroform) Stabilized

ALKALINE CLEANING COMPOUNDS

P-C-433 Cleaning Compound, Alkali, Pipeline
 P-C-436 Cleaning Compound, Alkali, Boiling Vat (Soak) on Hydrosteam
 MIL-C-25769 Cleaning Compound, Aircraft Surface, Alkaline Waterbase
 MIL-C-43616 Cleaning Compound, Aircraft Surface

ACID CLEANING COMPOUNDS

O-I-501 Inhibitors, Pickling (For Use with Sulfuric Acid)
O-S-809B Sulfuric Acid, Technical
MIL-C-10578 Corrosion Removing and Metal Conditioning Compound (Phosphoric Acid Base)
MIL-C-22183 Metal Cleaner, Scouring Powder, Rust Removing and Surface Brightening

MISCELLANEOUS CLEANING COMPOUNDS

ASTM A-380 Cleaning and Descaling Stainless Steel Parts, Equipment and Systems
A-A-202 Cleaning and Polishing Compound, Hard Surface (Aerosol Spray Buff)
P-C-435 Cleaning Compound, General Purpose (Powdered, Heavy Duty)
P-C-449 Cleaning and Polishing Compound, Floor (Paste Emulsion)
P-C-535 Cleaning Compound, General Purpose (Powdered, Heavy Duty)
P-C-1121 Cleaning and Polishing Compound, Stainless Steel
MIL-C-5410 Cleaning Compound, Aluminum Surface, Non-Flame-Sustaining
MIL-C-7907 Cleaning Compound, Decontaminating (For Soiled and Radio Active Contaminated Surfaces)
MIL-C-22230 Cleaning Compound, Fuel Tank and Bilge
MIL-C-81964 Cleaning Compound, Avionic Components
MIL-C-83360 Cleaning and Lubricating Compound, Electrical Contact

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CORROSION PREVENTATIVES

MIL-C-5545 Compound, Corrosion Preventive, Aircraft Engine, Heavy Oil Type

MIL-C-15074 Compound, Corrosion Preventive, Fingerprint Remover -- temporary preservative for metal items

MIL-C-6529 Corrosion Preventive, Aircraft Engine

MIL-C-8188 Corrosion Preventive Oil, Gas Turbine Engine, Aircraft

MIL-C-11796 Corrosion Preventive, Petrolatum, Hot Application

MIL-C-16173 Corrosion Preventive Compound, Solvent Cutback, Cold Application

MIL-C-62218 Corrosion Preventive Compound, Cold Application (For Fielded Motor Vehicles) -- uses similar to MIL-C-83933, but for use on vehicles in the field

MIL-K-81576 Kit- Touch Up, For Corrosion Control of Weapons Systems -- kit for treating small areas of corrosion on weapons systems

MIL-C-82594 Corrosion Preventive Compound and Surface Sealer For Nonferrous Metals -- solvent dispersed compound which penetrates metal pores

MIL-C-83933 Corrosion Preventive Compounds, Cold Application (For Motor Vehicles) -- cold application to enclosed and concealed areas of automotive equipment

MIL-C-81309 Corrosion Preventive Compound, Water Displacing, Ultrathin Film -- for protection during shipment and storage and for in-service treatment

RUST AND CORROSION REMOVING COMPOUNDS

MIL-C-10578 Corrosion Removing and Metal Conditioning Compound (Phosphoric Acid Base)

MIL-C-14460 Corrosion Removing Compound, Sodium Hydroxide Base -- for electrolytic or immersion application

MIL-H-13528 Hydrochloric Acid, Inhibited, Rust Removing

MIL-C-19647 Corrosion Removing Compound, Paste (Phosphoric Acid Base)

MIL-C-38334 Corrosion Removing Compound, Prepaint. -- for aircraft aluminum surfaces

MIL-C-46156 Corrosion Removing Compound, Sodium Hydroxide Base For Immersion Application

ENAMELS

MIL-E-480 Enamel, Baking, Phenol or Urea-Formaldehyde -- baking enamel for protecting steel and zinc-coated steel

TT-E-489 Enamel, Alkyd Gloss (For Exterior and Interior Surfaces) -- for use in finishing and refinishing automobiles and construction equipment

TT-E-491 Enamel, Gloss, Synthetic (For Wood and Metal Hospital Furniture) -- provides a finish coat of maximum washability and durability

TT-E-515 Enamel, Alkyd Lusterless, Quick-Drying -- quick drying finish coat for military equipment

TT-E-516 Enamel, Lusterless, Quick-Drying Styrenated Alkyd Type -- quick-drying durable enamel for finishing ammunition items

TT-E-522 Enamel, Phenolic Outside -- for use in high humidity or for partial immersion in fresh or salt water

TT-E-485 Enamel, Semigloss, Rust-Inhibiting -- contains rust-inhibiting pigments, can be used as primer or top coat

TT-E-527 Enamel, Alkyd, Lusterless -- camouflage finish for exterior of military equipment

TT-E-529 Enamel, Alkyd Semigloss -- air drying or baking enamels

TT-E-490 Enamel, Silicone Alkyd Copolymer, Semigloss, Exterior -- semigloss on primed metal surfaces, especially smooth exterior metal

TT-E-1593 Enamel, Silicone Alkyd Copolymer, Gloss For Exterior and Interior Use -- for primed metal surfaces, particularly smooth exterior metal

TT-E-1793 Enamel, Semigloss, For Wood and Metal Furniture -- air dry or bake enamel with good washability and durability

MIL-E-16663 Enamel, Semigloss, For Metal Surfaces of Ammunition and Ammunition Containers -- for identification by color

MIL-E-46145 Enamel, Fungus Resistant, Lusterless, Quick Drying, Styrenated Alkyd Type -- for ammunition and other metal surfaces, not gasoline resistant

MIL-E-52227 Enamel, Semigloss, Quick Drying -- for interior and exterior metal surfaces

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LACQUERS

MIL-L-13629 Lacquer, Air-Drying, For Crimped Parts -- covers lacquers for brass, steel and aluminum

MIL-L-12277 Lacquer, Automotive, Hot Spray -- for high gloss, quick-dry, durable finish

MIL-L-10287 Lacquer, Cellulose Nitrate -- for identification of small arms ammunition

TT-L-32 Lacquer, Cellulose Nitrate, Gloss -- for aircraft use

TT-L-20 Lacquer, Camouflage -- available in either lusterless or semigloss lacquer

MIL-L-1195 Lacquer, Lusterless, Hot Spray

MIL-L-46171 Lacquer, Lusterless, Hot Spray for Tip Identification of Ammunition -- can be reduced and sprayed at room temperature

TT-L-40 Lacquer, Lusterless Obliterating -- for obliterating old markings and mismarkings and as an undercoating for marking shipping containers

MIL-L-296 Lacquer, Purple -- for sealing flash holes and water proofing artillery ammunition primers

MIL-L-46075 Lacquer, Red, For Ammunition Primers -- for applications over foil and anvil of ammunition primer after anvil sealing

MIL-52043 Lacquer, Semigloss, Cellulose Nitrate -- can be applied at elevated or room temperature

TT-L-54 Lacquer, Spraying, Acid-Resistant -- for aluminum surface around storage batteries

TT-L-58 Lacquer, Spraying, Clear and Pigmented (General Interior Use) -- for general interior use as finish coat over primed metal or sealed wood

MIL-L-14486 Lacquer, Vinyl Resin, Semigloss -- for use where severe abrasion conditions or exposure to fresh or salt water is expected

PAINTS

TT-P-28 Paints, Aluminum, Heat Resisting -- [1200°F (650°C)] aluminum paint that will withstand heat, solvent and normal weather exposure

TT-P-38 Paint, Aluminum, Ready-Mixed -- for use on exterior surfaces exposed to salt atmosphere and brine

MIL-P-16406 Paint, Black, High Gloss Quick-Drying -- provides an insulating protective coating for electrical equipment

MIL-P-52024 Paint, Fire Retardant, Olive Drab (For Wooden Crates) -- for use on packing crates, not on building or structures

MIL-P-14105 Paint, Heat Resisting (For Steel Surfaces) -- for steel surfaces exposed to high temperature [1400°F (769°C)] and exterior weathering, such as mufflers, manifolds and stacks

MIL-P-14458 Paint, Rubber, Red Fuming Nitric Acid Resistant

MIL-P-13983 Paint, Temporary, Lusterless, Gasoline Removable -- for temporary camouflage and blackout purposes

TT-P-1561 Paint, Zinc-Aluminum, Rust-Inhibitive -- for rusty galvanized and other metal surfaces; for use over rusted galvanized or metallic structural surfaces, especially rust chain-link fence

PAINT REMOVERS

TT-R-230 Remover, Paint (Alkali-Type for Hot Application) -- granular free-flowing product for use in boiling water

TT-R-243 Remover, Paint (Alkali-Organic-Solvent Type) -- for removing multiple coats of paint from motor vehicles

TT-R-248 Remover, Paint and Lacquer, Solvent Type -- water rinsable organic solvent remover for stripping lacquer and enamel from aircraft metal surfaces

MIL-R-25143 Remover, Paint and Lacquer, Solvent Type -- for use on aircraft and other metal surfaces

MIL-S-6892 Stripper, Cleaner and Paint, For Ferrous Surfaces

MIL-R-7751 Remover, Paint and Varnish (Silicate Type) -- granular powder for stripping oil or cellulose-base coating as hot aqueous solution

MIL-R-81294 Remover, Paint, Epoxy System -- for stripping epoxy systems from metal surfaces or aircraft

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- MIL-R-18553 Remover, Paint, Nonflammable Water Rinsable -- usable in contact with synthetic rubber; remover has no deleterious effect on aromatic fuel resistant synthetic rubber parts
- MIL-R-25134 Remover, Paint and Lacquer, Solvent Type
- TT-R-251 Remover, Paint (Organic Solvent Type) -- several types of removers for scrape-off operations
- TT-R-46073 Remover, Paint, Organic Solvent Type, Nonflammable -- water rinsable paint remover requires no neutralization
- MIL-R-46116 Remover, Paint, Solvent Type, For Multiple Coat and Resistant Systems (Including Epoxies) -- for removing paint from mild steel and aluminum by immersion; not for use with magnesium or magnesium alloys
- MIL-R-81835 Remover, Organic Coating, Hot Tank Type
- MIL-R-81903 Remover, Acid Activated, For Amine-Cured Epoxy Coating Systems
- MIL-R-83936 Remover, Paint, Tank Type -- for aircraft wheels, landing gear components and other aircraft and age components

PRETREATMENT (WASH) PRIMER

- MIL-C-8514 Coating Compound, Metal Pretreatment Resin Acid -- this coating is finely ground and recommended for aircraft surfaces where a smooth surface is desired
- MIL-C-8507 Coating, Wash Primer -- pretreatment for metals, application of (for aeronautical use); covers application of MIL-C-8514
- DoD-P-15328 Primer (Wash) Pretreatment, (Formula 117B For Metals) -- for use on clean metal surfaces of all types

PRIMERS

MIL-P-14553 Primer, Coating, Dipping, Automotive -- baking primers for dip application on automotive components, not for use under acrylic top coats

TT-P-664 Primer, Coating, Synthetic, Rust-Inhibiting, Lacquer Resisting -- durable quick drying alkyd primer for metal

TT-P-636 Primer, Coating Alkyd, Wood and Ferrous Metal -- alkyd primer for ferrous metal and wood surfaces

MIL-11414 Primer Coating, Lacquer, Rust-Inhibiting -- quick drying cellulose nitrate primer for ferrous metal and clean aluminum

MIL-P-12742 Primer Coating, Phenolic, Water Immersable -- phenolic primer for use on metal or wood surfaces exposed to partial or total immersion in water

TT-P-662 Primer Coating, Lacquer, Rust-Inhibiting -- quick drying cellulose nitrate primer for ferrous metal and clean aluminum

TT-P-659 Primer Coating and Surfacer, Synthetic, Tints and White (For Metal and Wood Surfaces) -- alkyd primer-surfacer for use on metal or wood

MIL-P-46105 Primer Coating, Weld Through, Zinc-Rich -- for use on ferrous metal surfaces prior to spot welding

TT-P-1757 Primer Coating, Zinc Chromate, Low-Moisture-Sensitivity -- for spray application over pretreated surfaces

MIL-22636 Primer Coating, for Red Fuming Nitric Acid Resistant Paint

MIL-P-15930 Primer, Vinyl-Zinc Chromate Type (Formula 120 For Hot Spray)

MIL-P-23377 Primer Coating, Epoxy-Polyamide, Chemical and Solvent Resistant

TT-P-57 Paint, Zinc Yellow-Iron Oxide-Base, Ready Mixed -- for air dry or bake; good durability to atmospheric exposure

TT-P-86 Paint, Red Lead Base, Ready Mixed -- for iron and steel in bridges and other structures, not dwellings

TT-P-615 Primer Coating, Basic Lead Silico Chromate, Ready Mixed -- linseed oil vehicle; for use on bridges, etc.

TT-P-618 Primer Coating, Styrene/Butadiene-Zinc Chromate -- fast drying exterior primer

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TT-P-641 Primer Coating, Zinc Dust-Zinc Oxide Primer (For Galvanized Surfaces) -- for galvanized metal surfaces; not for use on inside or drinking water tanks

TT-P-645 Primer, Paint, Zinc Chromate, Alkyd Type -- corrosion inhibiting primer for marine service

TT-P-1046 Primer Coating, Zinc Dust, Chlorinated Rubber (For Steel and Galvanized Surfaces) -- primer for steel and galvanized surfaces and for repair of galvanized surfaces

MIL-P-17545 Primer Coating, Alkyd-Red Lead Type, Formula 116 and Formula 116D -- for marine steel surfaces as undercoat for alkyd enamels

MIL-P-22332 Paint, Priming, Exterior and Interior (For Ammunition) -- quick drying, rust inhibiting primer for exterior and interior surfaces of ammunition and rockets

MIL-P-23281 Primer, Vinyl-Red Lead (For Brush or Spray) -- for use over MIL-P-15328 and under vinyl-alkyd or vinyl antifouling paint

MIL-P-28577 Primer, Water Reducible, Corrosion Resistant, for Metal Surfaces

MIL-P-38336 Primer Coating, Inorganic, Zinc Dust Pigmented, Self-Curing for Steel Surfaces -- for use on steel surfaces for severe exposure to adverse weather, condensing moisture, corrosive atmospheres and marine environment

MIL-P-52192 Primer Coating, Epoxy -- air drying or baking, chemical resistant epoxy primer

MIL-P-7962 Primer Coating, Cellulose-Nitrate Modified Alkyd Type Corrosion Inhibiting, Fast Drying -- for spray application over pretreatment coating

DoD-P-15328 Primer (Wash, Pretreatment) -- formula 117-B for metals

ROLLER COAT FINSHES

MIL-P-19602 Primer, Size Coating, Baking for Roller Coat Application

MIL-E-19603 Enamel, Baking, for Roller Coat Application

MIL-V-21064 Varnish, Finishing, Baking, for Roller Coat Application

SEALERS (PAINT TYPE)

TT-S-171 Sealer, Floor, Lacquer Type

MIL-S-1123 Sealer, Sanding, Lacquer Type (For Wood Furniture)

TT-S-190 Sealer, Sanding Lacquer Type (For Wood Furniture)

MIL-S-12935 Sealer, Surface, For Knots

MIL-W-13518 Wood Preservative, Tetrachlorophenol and Pentachlorophenol Surface Sealing Compounds

TT-S-223 Sealer, Floor, Water Emulsion Type

SOLAR HEAT REFLECTING COATINGS

MIL-E-46096 Enamel, Lusterless, Quick Drying, Styrenated Alkyd Type, Solar Heat Reflecting

MIL-E-46117 Enamel, Alkyd, Lusterless, Solar Heat Reflecting

MIL-C-46127 Coating, Gray, Undercoat (Solar Heat Reflecting)

MIL-E-46136 Enamel, Semigloss, Alkyd, Solar Heat Reflecting, Olive Drab

MIL-L-46138 Lacquer, Lusterless, Acrylic, Nitrocellulose, Solar Heat Reflecting, Olive Drab

MIL-E-46139 Enamel, Semigloss, Rust Inhibiting, Solar Heat Reflecting, Olive Drab

MIL-L-46142 Lacquer, Lusterless, Solar Heat Reflecting

STAINS

TT-S-711 Stain, Oiltype, Wood, Interior

SURFACERS

TT-P-659 Primer Coating and Surfacer, Synthetic, Tints and White (For Metal and Wood Surfaces)

TT-P-662 Primer Surfacer, Sanding Lacquer and Enamel Type

STENCIL INK AND PAINT

TT-I-1795 Ink, Marking, Stencil, Opaque (Porous and Nonporous Surfaces)

TT-P-98 Paint, Stencil, Flat

MIL-P-47119 Paint, for Silk Screening

MIL-P-52108 Paint, Water Emulsion Type (For Stenciling and Obliterating)

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**TEST METHODS AND STANDARDS, PAINT
APPLICATION AND RELATED SUBJECTS**

a. Federal

Fed. Std.	1 - Standard for Laboratory Atmospheric Conditions for Testing
Fed. Std.	123 - Marking for Shipment (Civil Agencies)
Fed. Test Method Std.	151 - Metals; Test Methods
Fed. Test Method Std.	595 - Colors (Supersedes TT-C-595 and MIL-STD-795)
Fed. Test Method Std.	791 - Lubricants, Liquid Fuels and Related Products; Methods of Testing
Fed. Test Method Std.	141 - Paint, Varnish, Lacquer and Related Materials; Methods of Inspection, Sampling and Related Items
PPP-P-1892	Paint, Varnish, Lacquer and Related Materials; Packaging, Packing and Marking of

b. Military

MIL-STD-105	Sampling Procedures and Tables for Inspection by Attributes
MIL-STD-129	Marking for Shipment and Storage
MIL-STD-171	Finishing of Metal and Wood Surfaces
MIL-STD-186	Systems for Painting and Finishing Rocket and Guided Missile Material
MIL-STD-193	Systems for Painting and Finishing Tank-Automotive Material
MIL-STD-194	Systems for Painting and Finishing Fire Control Instruments
MIL-P-116	Preservation, Methods of
MIL-T-704	Treatment and Painting of Material
MIL-P-3320	Painting; Freight and Maintenance Cars
MIL-P-3321	Painting; Railway Motive Power and Work Equipment
MIL-P-3846	Painting; Steel-Hull Harbor Craft

MIL-P-6808 Primer Coating, Zinc Chromate, For Aircraft Use, Application of

MIL-F-7179 Finishes and Coatings; General Specifications For Protection of Aircraft and Aircraft Parts

MIL-F-14072 Finishes For Ground Signal Equipment

MIL-F-18264 Finishes, Organic, Aircraft, Application and Control of

TREATMENTS AND PRETREATMENTS FOR METAL
(WITH OR WITHOUT A SUPPLEMENTARY PAINT FINISH)

TT-C-490 Cleaning Methods and Pretreatment of Ferrous Surfaces For Organic Coatings

MIL-F-495 Finish, Chemical, Black, For Copper Alloys

MIL-M-3171 Magnesium Alloy, Processes For Corrosion Protection of

MIL-C--5541 Chemical Films For Aluminum and Aluminum Alloys

MIL-C-8507 Coating, Wash Primer (Pretreatment) For Metals, Application of (for Aeronautical Use)

MIL-C-8514 Coating Compound, Metal Pretreatment, Resin-Acid

MIL-A-8625 Anodic Coatings For Aluminum and Aluminum Alloys

MIL-M-10578 Metal Conditioner and Rust Remover (Phosphoric Acid Base)

MIL-I-13857 Impregnation of Metal Coatings

MIL-T-13867 Treatment, Moisture and Fungus Resistant For Fire Control, Electrical and Electronic Instruments and Equipment

MIL-C-13924 Coating, Oxide, Black, For Ferrous Metals

MIL-C-14460 Corrosion Removing Compound, Sodium Hydroxide Base, For Electrolytic or Immersion Application

DoD-P-15328 Primer (Wash) Pretreatment, (Formula 117-B, For Metals)

MIL-P-16232 Phosphate Coatings, Heavy, Manganese or Zinc Base, For Ferrous Metals

MIL-M-45202 Magnesium Alloys, Anodic Treatment of

MIL-C-46487 Cleaning, Preparation and Organic Coating of Steel Cartridge Cases

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MIL-C-81562 Coating, Cadmium and Zinc, Mechanically Deposited

MIL-C-81706 Chemical Conversion Materials For Coating Aluminum and Aluminum Alloys

MIL-C-81740 Coating, Aluminum and Aluminum Alloys, Metallic Compound Decomposition

MIL-A-81801 Anodic Coatings For Zinc and Zinc Alloys

VARNISH

TT-V-51 Varnish Asphalt (For Indoor Water and Gas Pipes)

MIL-V-13497 Varnish, Impregnating, Electrical-Insulating, (For Fire Control Instruments) -- for impregnating electrical windings of precision rotating mechanisms

MIL-I-24092 Insulating Varnish, Electrical, Impregnating -- for impregnating electrical coils and structures

TT-V-81 Varnish, Mixing, For Aluminum Paint

MIL-V-13750 Varnish, Phenol-Formaldehyde, Clear and Aluminum Pigmented

MIL-V-12276 Varnish, Phenolic, Baking -- for coating cartridge cases and as a lining for ammunitions

TT-V-121 Varnish, Spar, Water Resisting -- for outdoor and indoor use where good durability is a requirement

TT-V-119 Varnish, Spar, Phenolic-Resin -- for marine architectural and structural finishing

MIL-V-13811 Varnish, Waterproofing, Electrical, Ignition

MIL-V-16399 Varnish, Moisture-Proof -- for sealing and moisture proofing surfaces of small explosive devices

MIL-V-83148 Varnish, Electrical Insulating, Moisture, Fingus-, and High-Temperature Resistant

TT-S-300 Shellac, Cut -- for interior use, moisture sensitive

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WOOD PRESERVATIVES

TT-W-570 Wood Preservative; Pentachlorophenol, Solid
 TT-W-571 Wood Preservative; Treating Practices
 TT-W-572 Wood Preservative; Water Repellant
 MIL-W-46101 Wood Preservative; Water Repellant -- for wood to be painted

MISCELLANEOUS

MIL-W-3688 Wax Emulsion (Rust Inhibiting)
 TT-R-771 Rubbing Compound Lacquer
 MIL-E-5558 Enamel; Wrinkle-Finish, For Aircraft Use
 MIL-R-10036 Rust-Arresting Coating -- for treatment of rusted metal
 MIL-W-5044 Walkway Compound, Nonslip and Walkway Matting, Nonslip -- brush-on or matting for aircraft wing walks, with or without grit
 MIL-D-23003 Deck Covering Compound, Nonslip, Lightweight -- one- or two-part compound for application to wood or metal decks

9.3 Comments on individual specifications. - In the same order as the group or category just described in 9.2, the following comments are given on some of the more widely used specifications.

9.3.1 Coatings.

9.3.1.1 MIL-C-450, Coating Compound, Bituminous, Solvent Type, Black. This specification covers acid-proof asphalt coating for cavities of ammunition items such as bombs, shells, rockets and mines. The coating is available in three types:

- Type I - Low solids (spray)
- Type II - Medium solids (spray or brush)
- Type III - Heavy paste

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A composition is also provided for use in areas where air pollution regulations apply. The coating consists of natural or petroleum asphalt dissolved in suitable organic solvents and contains no drying oil, resins or pigments. Suitable asphalt is unharmed by saturated solutions of picric acid and by moderately concentrated solutions of sulfuric, nitric and hydrochloric acid. It also does not react with explosives and protects the explosive from the shell itself.

Federal Specification TT-C-494 covers a similar material for nonammunition uses.

9.3.1.2 TT-C-520, Coating Compound, Bituminous, Solvent Type, Underbody (For Motor Vehicles). This specification covers an asphalt compound for use as a protective coating and sound deadener on the underbody parts of automotive equipment. Two compositions are provided, one of which is suitable for use under air pollution regulations. The compound is a mixture of asphalts, solvents, fillers and additives. While it may be applied with brush on small jobs, the material is visually applied on the field with standard, heavy material spray equipment. It is intended for use in one thick coat on the underside of hoods, fenders, floors, etc., or automobiles, to deaden noise, to act as a seal against fumes and to protect the metal from corrosion.

9.3.1.3 MIL-C-83933, Corrosion Preventive Compounds, Cold Application For Motor Vehicles. This specification covers a solvent dispersed corrosion preventive compound for spray brush or dip application to vehicle underbodies and inclosed or concealed surfaces. Preserved areas that are particularly susceptible to abrasion may require periodic touch up. This material may be used over previously applied underbody coatings if the old coatings are tightly adherent to the substrate. This coating is used chiefly in the "boxed in" areas of automotive equipment, such as inside door panels and window wells.

9.3.1.4 MIL-C-6799, Coatings, Sprayable, Strippable, Protective Water Emulsion. This specification covers water based, sprayable and strippable coating for application over metallic, painted and plastic surfaces. It is available in several types and classes.

Type I - Single coat - Interior or under cover

Class 1 - Transparent

Class 2 - Opaque

Type II - Multicoat system, exterior

Class 1 - Base coat (black)

Class 4 - Contrasting intermediate coat (gray)

Class 5 - Topcoat (white or olive drab)

Type III - Single coat - Exterior (white or olive drab)

Class 1 - Long-term protection

Class 2 - Short-term protection

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These coatings dry to touch within 3 hours (except type II, class 5 - within 2 hours). The coating will withstand sawing, drilling and routing without pulling away from acrylic plastic surfaces. Type I and II materials are intended for use as single or multiple coat strippable protective coatings for acrylic plastic items shipped fully covered and stored under cover. Type III materials are intended for use as exterior single coat strippable protective coatings for application by spraying on plastic, painted and metallic surfaces such as entire aircraft, missiles, rockets and transportation vehicles during outdoor storage and overseas deck load shipment. Class 1 material is intended to provide long-term protection (up to 1 year). Class 2 material is intended to offer shorter term protection (up to 6 months).

9.3.1.5 MIL-C-22750, Coating, Epoxy-Polyamide. This specification covers a two-component epoxy-polyamide finish for spray or brush application. It is available in two classes: class 1 - for use when air pollution regulations do not apply and class 2 - for use where air pollution regulations are in force. Three types of epoxy-polyamide coatings are packaged in one kit: type I, Gloss; type II, Semigloss; and type III, Camouflage. This coating material is formulated for the protection of areas exposed to chemical and solvents and is intended for exterior or interior use on weapons systems and other applications. MIL-C-22751 covers the process for application of this coating.

9.3.1.6 MIL-C-82386, Coating, Urethane, Aliphatic Isocyanate, for Aerospace Applications. This specification covers two component aliphatic isocyanate based oil free urethane coating materials suitable for exterior applications on aerospace equipment. Both type I and type II are suitable for use under local air pollution regulations.

Type I - suitable for application by conventional pressurized air spray techniques.

Type II - suitable for application by unheated, airless spray technique.

The coating is available in a wide range of gloss and camouflage colors. It is intended for use over MIL-P-23377 epoxy-polyamide primer as a general purpose exterior protective coating for metal surfaces.

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9.3.2 Enamels.

9.3.2.1 MIL-E-480, Enamel, Baking, Phenol or Urea-Formaldehyde. This specification covers a semigloss, baking enamel in two types -- type I, phenol formaldehyde resin base and type II, urea formaldehyde resin base. It is available in various colors specified in the contract or order. Type II was designed primarily for use on zinc surfaces. This metal reacts with phenol, enough of which may be present in some type I enamels to adversely affect adhesion. Type I coatings that have been shown to have no effect on adhesion to zinc may also be used over zinc. The enamel is used as a finish for hardware equipment. For fire control applications, MIL-E-480 enamel is used over properly primed metal surfaces that are nonfunctional, but are subject to contact with oil. In general, coatings for both types I and II are very resistant to heat, moisture, many corrosive chemicals, hydrocarbon solvents and oil. Baked at 375°F (182°C) for 45 minutes, both types become hard enough to be handled.

9.3.2.2 TT-E-489, Enamel, Alkyd, Gloss (For Exterior and Interior Surfaces). This specification covers a high gloss, alkyd enamel suitable for use on exterior and interior wood and metal surfaces that have been previously primed. The specification provides for white, black and 50 colors. It can be applied by brushing or spraying. This enamel is highly weather resistant, characterized by good color and gloss retention, good drying, freedom from aftertack and good flexibility. Its main use is for finishing and refinishing automobiles and construction equipment. It is also a suitable finish for machinery, gasoline pumps, trucks and buses, passenger and freight cars, metal drums (exterior), metal signs, metal railings and fences and for marine use (above water). It can be purchased in two classes: class A - Air Drying and class B - Baking. Each class is available in two compositions: composition G - General Use; and composition L - Limited Use (where air pollution regulations apply). Class A enamel may be applied by either brushing or spraying. For spraying, add 1 pint of thinner, TT-T-306, to each gallon of enamel. Class B enamel is intended for spraying only. Reduce class B enamel to spraying consistency by adding 1 pint of xylol, TT-X-916, to each gallon of enamel. Class A enamel will air dry within 8 hours and reach full hardness within 48 hours. Class B enamel will bake hard within 20 minutes at 300°F (149°C) and, within 24 hours after baking, will attain full hardness.

9.3.2.3 TT-E-491, Enamel, Gloss, Synthetic (For Metal and Wood Hospital Furniture). This specification covers a gloss enamel in white, olive drab and tints such as gray, cream and ivory. It is a resin (not rosin) modified alkyd type of enamel. Generally the resin is phenolic. This enamel was designed for wood and metal hospital furniture, where the painted surface has to be scrubbed frequently with cleaning compounds (for example, trisodium phosphate, soap, carbolicizing solutions and alcohol). The enamel comes in two classes: class A - air drying and class B - baking. Class B enamel is intended for factory application of the finish and class A for local application and touch-up.

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9.3.2.4 TT-E-515, Enamel, Lusterless, Quick-Drying. This specification covers one type and grade of quick drying enamel for use as a finishing coat on military equipment. Two compositions are provided: G - for general use and L - for use where air pollution regulations apply. It is a resin (generally phenolic) modified alkyd enamel and can be obtained in white, black and 20 colors. It is usually applied by spraying and dries to a flat finish. It dries faster than TT-E-527 lusterless enamel, becoming hard within 10 minutes. The volatile portion of composition L shall meet the requirements of Rule 66, except that no ketones are allowed. The thinner for use in reducing composition G to spray consistency is one meeting TT-T-306. A quick drying primer to use under this enamel is described in TT-P-664.

9.3.2.5 TT-E-516, Enamel, Lusterless, Quick-Drying. This specification covers one type and one grade of a quick drying, lusterless, durable enamel for use as a finishing coat on shells, bombs, grenades and other ammunition. It can be used for other metal surfaces, but it should be used where gasoline resistance is a prime requisite, as on automotive equipment. The enamel is based on a styrenated alkyl resin and can be obtained in 18 colors. It is applied by spraying or dipping and dries hard within 10 minutes. Thinner for the enamel for spraying or dipping conforms to Specification TT-T-306. Composition L meets Air Pollution Regulations (Rule 66).

9.3.2.6 TT-E-522, Enamel, Phenolic, Outside. This specification covers a lusterless enamel for outside use. The vehicle portion of the enamel is a 25-gallon varnish made with phenolic resin and tung oil. The enamel is available in 13 colors and dries hard in not more than 16 hours. The primer for use with this enamel is phenolic resin primer MIL-P-12742. It is intended for use where high humidity exists as well as where partial to total immersion in fresh or salt water may occur.

9.3.2.7 TT-E-485, Enamel, Semigloss, Rust-Inhibiting. This specification covers one grade semigloss, rust inhibiting enamel for use as a one or two coat priming system. The pigment contains rust inhibiting pigments -- red lead, chrome yellow and zinc oxide. This enamel is intended primarily for priming iron and steel, as a one coat paint for metal ammunition containers, landing mats, pipe line equipment and steel drums (such as gasoline drums). It is also used as a finish coat. There are four types: type I for dip application, type II for brush and spray application, type III for roller coat application and type IV for flash drying. The first three types are straight alkyd resin vehicle and the fourth type has a phenol-modified alkyd resin vehicle. The enamel is furnished in four colors -- olive drab, Marine Corps green, olive green and natural (untinted). It is a combination air drying or baking enamel, i.e., either method of drying may be used. Better properties are usually obtained by baking. Composition L meets Air Pollution Regulations (Rule 66).

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9.3.2.8 TT-E-527, Enamel, Alkyd Lusterless. This specification covers a combination air drying and baking phthalic alkyd resin lusterless enamel for use as a finishing coat on military and other equipment. The enamel is available in 24 colors. It is used as a durable, lusterless camouflage finish for the exterior of military equipment. Ordinarily, surfaces are painted with a semigloss enamel. For war time use, this lusterless finish may be applied directly over the semigloss enamel. As a lusterless finish in black, it is used for the interior metal surfaces of optical instruments (should be baked for this purpose). Composition 1 meets Air Pollution Regulations (Rule 66).

9.3.2.9 TT-E-529, Enamel, Alkyd, Semigloss. This specification covers a semigloss enamel for use on exterior and interior wood and metal surfaces, previously primed. The enamel can be procured in two classes: class A, air drying and class B, baking. The vehicle of both classes is based on drying oil phthalic alkyd resins, but that of class B is modified with 10 to 20% of a urea or melamine formaldehyde resin. The enamel may be applied by brushing or spraying. For brushing, it may be thinned with not over 5 parts by volume of TT-T-306 thinner to 85 parts by volume of enamel. For spraying, up to 15 parts by volume of TT-T-306 thinner may be added to 85 parts by volume of class A enamel or up to 15 parts by volume of TT-X-916 xylol may be added to 85 parts by volume of the class B package enamel. Class A, air drying enamel, dries hard within 8 hours; class B, baking enamel, becomes hard within 30 minutes when baked at 300°F (149°C). The enamel can be obtained in 36 colors. Composition L meets Air Pollution Regulations (Rule 66).

9.3.2.10 MIL-E-52227, Enamel, Semigloss, Quick-Drying. This specification covers one type and grade of quick drying, semigloss enamel for use on interior and exterior surfaces. The vehicle for this enamel is intended for cottonseed oil-phthalic alkyd resin solution. The enamel is intended for use on primed metal surfaces as an exterior finish coat for military and other equipment. It is also used for direct application to bare surfaces, such as metal office furniture and lockers, which have been prepared for painting with type I (zinc phosphate) or type II (iron phosphate) pretreatment in accordance with TT-C-490.

9.3.2.11 TT-E-1593, Enamel, Silicone Alkyd Copolymer, Gloss (For Exterior and Interior Use). This specification covers a copolymerized silicone alkyd enamel for use on primed metal. It may be used in areas with air pollution regulations. This enamel is available in a variety of colors matching Federal Standard 595 color chips. The vehicle is an air drying, silicone modified, long oil alkyd, plus suitable thinner driers and additives. This enamel is highly weather resistant and is characterized by excellent color and gloss retention, good drying, freedom from after tack and good flexibility. The enamel may be applied with brush, roller or spray. Enamels meeting this specification are used as a gloss finish for machinery, trucks and buses (refinishing), passenger and freight cars, metal drums (exterior), metal signs, metal railings and fences, marine use (above water), metal trim, metal siding and metal doors. It is not intended for painting interior plastered walls.

9.3.2.12 TT-E-490, Enamel, Silicone Alkyd Copolymer, Semigloss (For Exterior and Interior Use). This specification covers a copolymerized silicone alkyd enamel for use on primed smooth metal surfaces. The enamel complies with Air Pollution Regulations (Rule 66). This enamel has properties comparable to TT-E-1593 (9.3.2.11), except TT-E-490 is a semigloss enamel.

9.3.2.13 MIL-E-16663, Enamel, Semigloss (For Metal Surfaces of Ammunition and Ammunition Containers). This specification covers an enamel intended for production line application by spraying, dipping, and brushing (meets Rule 66).

Type I - Air drying

Class 1 - Rapid drying

Class 2 - Flash drying

Type II - Baking

The vehicle is a phthalic alkyd resin solution. The enamel is available in white and 13 colors. Type I, class 1 material dries hard in 30 minutes and class 2 dries hard in 20 minutes. Type II material dries hard in 18 minutes at 300°F (149°C). This semigloss enamel has good weather resistance and is intended for use as exterior protective coatings for projectiles, rockets, powder and cartridge tanks and other ammunition, as well as for the identification by color marking of such ammunition.

9.3.3 Lacquers.

9.3.3.1 TT-L-20, Lacquer, Camouflage. This specification covers a lacquer for use on metal surfaces as a camouflage color finish. Thirty colors are available in either lusterless or semigloss lacquers. The vehicle is a nitrocellulose modified phthalic alkyd resin with plasticizers. Best performance will be obtained when the lacquer is applied over metal surfaces properly pretreated and primed with a lacquer resisting primer. It should not be used over bare metal. The specification recommends finishing systems for use prior to the application of the camouflage lacquer to aluminum and steel surfaces.

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9.3.3.2 MIL-L-11195, Lacquer, Lusterless, Hot Spray. This specification covers one type and grade of cellulose nitrate lusterless lacquer enamel which can be applied at an elevated spray gun temperature of $160 \pm 50^\circ\text{F}$ ($70 \pm 30^\circ\text{C}$) or at room temperature. The lacquer is available in two compositions, one of which is suitable for use where air pollution regulations apply. It can be procured in 19 colors. The vehicle is cellulose nitrate modified with phthalic alkyd resin. The lacquer dries through within 10 minutes. The packaged lacquer is suitable for hot spraying. For cold spraying, 2 volumes of the packaged lacquer are thinned with 1 volume of lacquer thinner (TT-T-266). This lacquer is intended for use as a finish coat on phosphated and/or primed shells, bombs, grenades, tanks, trucks and ammunition and automotive equipment. For automotive applications, insufficient preparation of the surface may result in defective adhesion of the lacquer. Surfaces of automotive equipment to be painted should be prepared by use of either a wash primer (DoD-P-15328) or a phosphate metal treatment (TT-C-490, type I) and should then be given a coat of lacquer primer (MIL-P-11414) prior to the application of the finish coat of lacquer.

9.3.3.3 MIL-L-14486, Lacquer, Vinyl Resin, Semigloss. This specification covers one type and one grade of semigloss vinyl lacquer enamel for use as a finish coat on steel prepared with wash primer (DoD-P-15328) and vinyl red lead primer (MIL-P-15029). It does not adhere well to bare metal surfaces of any type. It is particularly useful where severe abrasive conditions or intermittent exposure to fresh or salt water will be encountered, such as on the amphibious equipment. The color of the lacquer is olive, drab or white. The lacquer is applied by spraying and, for this purpose, 5 volumes of the lacquer are thinned with 4 volumes of thinner consisting of equal parts by volume of methyl isobutyl ketone (TT-M-268) and xylene (TT-X-916). This lacquer should be applied to clean steel according to the following system:

0.0002 to 0.0003 in (5.1 to $7.6 \mu\text{m}$) dry film of DoD-P-15328 wash primer

0.0009 to 0.0011 in (22.9 to $27.9 \mu\text{m}$) dry film of MIL-P-15929 vinyl red lead primer

0.0009 to 0.0011 in (22.9 to $27.9 \mu\text{m}$) dry film of vinyl lacquer

9.3.4 Paints.

9.3.4.1 TT-P-28, Paint, Aluminum, Heat Resisting - 1200°F (649°C).

This specification covers one type and grade of aluminum heat resistant paint that will withstand heat, solvents and normal weather exposure. The vehicle is a silicone or modified silicone resin together with the necessary amounts of volatile solvents. The paint is intended for use on superheated steam lines, boiler casings, boiler drums, superheater headers and similar high temperature applications, up to 1200°F (649°C) without failure. It is also intended for painting military equipment such as personnel heaters, rocket launchers and other components, where operating temperatures preclude use of conventional paint. The paint may also be used for application to engrave, stamp or stencil lettering or numerals on metallic gun or weapon components for identification or function purposes, when the components are exposed to temperatures up to 1200°F (649°C). Composition L meets Air Pollution Regulations (Rule 66).

9.3.4.2 MIL-P-13983, Paint, Temporary Lusterless, Gasoline Removable. This specification covers one type and one grade of gasoline removable, lusterless paint for temporary camouflage and blackout purposes. The paint meets Air Pollution Regulations (Rule 66). It can be obtained in 27 colors, including black, white and olive drab. It can be applied by spraying or brushing and dries hard within 8 hours. The paint may be thinned with mineral spirits (TT-T-291) or gasoline (for brushing not to exceed 15% by volume; for spraying not to exceed 30% by volume). The vehicle in the paint is a blend of liquid and resinous chlorinated paraffin (MIL-C-429), with the necessary amounts of volatile solvents. The paint is intended primarily for brush application for temporary blackout and camouflage purposes under the following conditions:

- (a) When the application of a paint is required at subfreezing temperatures.
- (b) When removable camouflage or removable identification markings are required. In this application, the paint should not be used over porous surfaces such as unpainted wood. Where completely removable paint is required, black paint should not be used, because it permanently stains the base coat to which it is applied.

9.3.4.3 MIL-P-14458, Paint, Rubber Red Fuming Nitric Acid Resistant. This specification covers one type and one grade of paint resistant to red fuming nitric acid. It is intended for use as an exterior finish coat on aluminum oxidizer tanks and other aluminum surfaces exposed to possible spraying and splashing of liquid red fuming nitric acid. The aluminum should first be primed with MIL-P-22636. The color of the paint is dark green (34079) or gray (36231).

The vehicle is chlorosulfonated polyethylene (Hypalon) in aromatic solvents. The paint is furnished as a two component material with part A being the curing agent and part B being the elastomer component.

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9.3.4.4 TT-P-98, Paint, Stencil, Flat. This specification covers one type and two classes of opaque, fast drying, flat finish stencil paint as follows:

Class 1 - Paint consistency (brushing consistency)

Class 2 - Semipaste consistency (buttery consistency)

The paint consists of pigment, volatile thinner (conforming to Rule 66) and quick drying varnish. It can be obtained in black, white, yellow, red, orange and blue. Both types are intended for marking or stenciling bales, crates, fiberboard drums and boxes, ammunition, etc., using an ordinary stencil brush. This paint meets Air Pollution Regulations (Rule 66).

9.3.5 Paint Removers.

9.3.5.1 TT-R-230, Remover, Paint (Alkali-Type For Hot Application. This specification covers a granular, free flowing product for use in boiling water solution to strip alkyd resin, modified urea formaldehyde alkyd resin, oleoresinous and nitrocellulose base finishes. The paint remover is available in two classes:

Class 1 - For use with ferrous and magnesium metals (general heavy duty stripper)

Class 2 - For stripping from aluminum and other nonferrous alloys

A wide latitude is allowed for selection of raw materials and processes of manufacture, but the two classes of remover must perform as well as removers made according to formulas given in the specification.

The effectiveness of the class 2 remover in stripping paint from aluminum basis metals can be increased from 50 to 75% by conversion of the aqueous solution of the class 2 compound into a stable, single phase, water-organic solvent solution, which is operated at a boil. The change is accomplished by adding 1 gallon of hexylene glycol (boiling point 192 -200°C, and specific gravity at 20 / 20 C, 0.922-0.925) to 9 gal (34 L) of a 12 oz/gal (90.0 g/L) water solution of the class 2 remover. The hexylene glycol is maintained by periodic test. Rinse parts with hot water after stripping.

9.3.5.2 MIL-R-7751, Remover, Paint and Varnish (Silicate Type). This specification covers a granular powder, silicate type paint and varnish remover intended for use in stripping oil or cellulose base coatings from steel or anodized aluminum surfaces. The formula for the powder is as follows:

Sodium metasilicate, pentahydrate	- 48% by weight
Sodium trisilicate	- 48% by weight
Sodium resinate	- 4% by weight

The powder is dissolved in water in the proportion of a 2% solution by weight. The solution is used boiling hot.

9.3.5.3 TT-R-251, Remover, Paint (Organic Solvent Type). This specification covers liquid paint removers of the organic solvent type, commonly used in scrape-off operations, suitable for use on finished wood and metal surfaces. These removers are generally intended for use indoors, but they may be used out of doors under conditions that warrant their efficient and economical use. The specification covers removers of the following types and classes:

- Type I - Flammable mixture with paintable retardant
- Type II - Flammable mixture nonpaintable retardant
- Type III - Nonflammable mixture with paintable retardant
- Type IV - Nonflammable mixture, water rinsable, with paintable retardant

- Class A - Low viscosity
- Class B - High viscosity

Type I and II removers are flammable and generally are of the benzol-acetone-alcohol type. Type II remover contains paraffin wax to retard evaporation and surfaces on which it has been used cannot be painted successfully unless the wax has been thoroughly washed off with turpentine, mineral spirits, carbon tetrachloride or a similar solvent. On the other hand, types I and III may be used without solvent cleaning prior to refinishing. Type III is nonflammable. It contains chlorinated solvents, particularly methylene chloride. The more viscous removers (class B) are for use on vertical surfaces. The active ingredients of these paint removers are necessarily more toxic and proper ventilation is imperative during their use.

9.3.5.4 TT-R-243, Remover, Paint (Alkali-Organic Solvent Type). This specification covers a homogeneous liquid alkali-organic solvent composition for removing paint, varnish, lacquer, enamel and synthetics. The remover is nonflammable, nonhardening and water rinsable. Its main use is for removing multiple coats of paint from motor vehicles, specifically from the steel parts. It contains a volatile solvent and should be used only with adequate ventilation. The remover should not come in contact with aluminum, aluminum alloys or galvanized surfaces. It will raise the grain on wood surfaces.

9.3.5.5 TT-R-248, Remover, Paint, and Lacquer, Solvent Type. This specification covers a nonflammable, water rinsable liquid paint remover. Its main use is for stripping lacquer and enamel from metal surfaces (aluminum alloy, steel, magnesium alloy) of aircraft. It contains ingredients irritating to the skin and eyes and adequate ventilation should be provided. The composition is not specified in detail, but its paint stripping efficiency must be equal to or better than the control formula given in the specification.

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9.3.5.6 MIL-R-18553, Remover, Paint, Nonflammable, Water Rinsable, Usable in Contact with Synthetic Rubber. This specification covers a nonflammable water rinsable composition for removing paint, varnish, lacquer and enamel from metal surfaces of aircraft. The paint remover has no deleterious effect on aromatic fuel resistant synthetic rubber parts, such as those made from Buna-N synthetic rubber. The remover contains ingredients irritating to the skin and eyes and, where conditions demand paint removal indoors, adequate ventilation should be assured. Composition is not specified in detail, but the remover must strip paint as efficiently as the "control formula" given in the specification.

9.3.5.7 MIL-R-46073, Remover, Paint, Organic Solvent Type. This specification covers a nonflammable, water rinsable, solvent type paint remover suitable for removing dried paint from metallic and nonmetallic surfaces. It will provide a surface ready for recoating without neutralization. The composition is unspecified, providing that it meets the requirements of the specification.

9.3.6 Primers.

9.3.6.1 DoD-P-15328, (Primer Wash), Pretreatment, (Formula 177 for Metals). This specification covers a primer pretreatment coating (Wash Primer) for use on clean metal surfaces of all types as a treatment prior to application of the coating system. The purpose is to increase the adhesion of the coating system. The pretreatment should be coated with the priming paint as soon as practicable (preferably within 24 hours), as it loses its effectiveness after a short exposure to adverse weather conditions. A film of the materials is sufficiently dry for recoating within 15 to 30 minutes after application. It may be applied to damp surfaces (preferably by brushing in this case) but should not be applied to wet surfaces or in rainy weather. The dry film thickness should be about 0.3 - 0.5 mil (8 - 13 μ m). It is supplied in two parts: (1) a 5-gallon (19 L) pail containing 4 gallons (15 L) of the resin component (polyvinyl-butyral resin, zinc chromate, magnesium silicate, lamp black, butyl alcohol and isopropyl alcohol); and (2) a gallon (3.8 L) bottle of the acid component (phosphoric acid, water, and isopropyl alcohol).

The resin component should be well stirred and the acid component added slowly with stirring; the mixture is then ready for use. The pretreatment is most effective when freshly mixed and must be used within 8 hours after the addition of the acid component. The acid component is not a thinner. It is a necessary activator and must be used exactly as directed. The coating is suitable for application by dipping, spraying or brushing. When this pretreatment coating is used on magnesium, the amount of phosphoric acid should be reduced by 50 to 75%.

9.3.6.2 MIL-P-14553, Primer, Coating, Dipping, Automotive. This specification covers two classes of a durable baking primer for dip application on automotive components. They are available for G (general use) and L (limited use) under air pollution control regulations.

- Class 1 - Low bake 30(-3250F (149-1630C)
- Class 2 - High bake 365-3850F (185-1960C)

The color is dark gray or black. The pigment contains black or lampblack, titanium dioxide, zinc chromate (not less than 5%), iron oxide and extenders. The vehicle is pure vegetable oil phthalic alkyd resin. Class 1 cures to full hardness at 300-325°F (149-163°C) within 20 minutes. Class 2 cures to full hardness 365-386°F (185-196°C) within 20 minutes. While primer is not intended for spray application, it can be sprayed for spot priming. Either oleoresinous or lacquer enamels can be used over this primer, but is it not intended for use under acrylic type lacquers and enamels.

9.3.6.3 TT-P-664, Primer Coating, Synthetic, Rust-Inhibiting, Lacquer-Resisting. This specification covers a durable, quick drying, rust inhibiting, lacquer resisting primer for metal. It is suitable for use under either synthetic enamel or lacquer enamel topcoats. The pigment is a mixture of zinc chromate, iron oxide and siliceous extenders. It is primarily a spraying primer, but it may be applied by dipping. Composition L meets Air Pollution Regulations (Rule 66).

9.3.6.4 TT-E-485, Enamel, Semigloss, Rust-Inhibiting. Although designated as an enamel, this specification covers a material that can also function as a primer. It is described under "Enamels" (see 9.3.2.7).

9.3.6.5 TT-P-636, Primer Coating, Alkyd, Wood and Ferrous Metal. This specification covers an oil modified alkyd varnish primer for ferrous metal and wood surfaces. A composition is provided for use in areas where air pollution regulations apply. The pigment is a combination of iron oxide, zinc yellow, zinc oxide and siliceous matter. It is intended for priming clean, rust free, bare or phosphate treated ferrous metal parts of motor vehicles, as well as guns, gun mounts, tanks, metal shipping containers and similar ordnance material. It may also be used as a sealing undercoat on wood parts of motor vehicles. It is primarily intended for air drying, but it may also be baked. In air, it dries through within 18 hours. At 250°F (121°C), it bakes hard enough to handle within 45 minutes. It may be applied by brushing or spraying. For the latter method, 1 pint of mineral spirits (TT-T-291) should be added to each gallon of primer. Where a faster drying and lacquer resistant primer is required, TT-P-664 primer described above (see 9.3.6.3), should be used.

9.3.6.6 MIL-P-11414, Primer, Lacquer, Rust-Inhibiting. This specification covers a quick drying, rust inhibiting, cellulose nitrate primer. It is available in two compositions: G (for general use) and L (limited use, where air pollution regulations apply). It is intended for use on solvent cleaned or phosphated shells, bombs, grenades, tanks, trucks and ammunition and automotive components to be top coated with lacquer. It was developed primarily for application to ferrous metal surfaces, but it has given excellent service over vapor cleaned and/or chemically treated aluminum. The pigment is a blend of zinc yellow, red iron oxide and siliceous extenders. The vehicle is a phthalic alkyd modified cellulose nitrate lacquer. The primer dries through within 6 minutes. It may be applied by dipping or spraying. For spraying, one part by volume of the primer is thinned with one part by volume of lacquer thinner (TT-T-266).

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9.3.6.7 MIL-P-12742, Primer Coating, Phenolic, Water Immersible. This specification covers two types of phenolic primer for use prior to the application of phenolic enamel TT-E-522 (see 9.3.2.6).

Type I - For metal surfaces

Type II - For wood surfaces

In combination with the phenolic enamel, it is used on surfaces exposed to partial or total immersion in fresh or salt water. The pigment is a blend of zinc yellow (type I only), red iron oxide (type II only) and magnesium silicate (types I and II). The vehicle is a 25-gallon tung oil-phenolic resin varnish. It may be applied by brushing, spraying or dipping. Solvents or thinners used must conform with Rule 66.

9.3.6.8 TT-P-662, Primer Surfacer, Sanding, Lacquer and Enamel Type. This specification covers a primer-surfacer for use in both lacquer and enamel finishing systems, primarily for automotive equipment, but it may also be used for similar metal surfaces. It provides for two compositions, one of which is suitable for use under air pollution regulations. The pigment is titanium dioxide and the necessary amount of tinting pigments to produce color 36231 (blue-gray). The vehicle is a phthalic alkyd resin modified cellulose nitrate lacquer. The primer surfacer dries through within 10 minutes. The material is used as a surfacing coat over primed steel (for example, MIL-P-11414, primer) to obliterate slight scratches or dents prior to the application of a gloss enamel (for example, TT-E-489) or gloss lacquer topcoat.

9.3.6.9 TT-P-659, Primer Coating and Surfacer; Synthetic, Tints and White (For Metal and Wood Surfaces). This specification covers a combination air drying and baking oil modified alkyd varnish base primer and sanding surfacer for ferrous metal and wood surfacer. The color is generally white or light gray. The primer-surfacer may be applied by brushing. For spraying and dipping, it is thinned with mineral spirits (TT-T-291). In air it dries through within 18 hours; at 250°F (121°C) it bakes hard enough to be handled within 45 minutes. The primer-surfacer originally was intended for use on metal and wood hospital furniture to be topcoated with TT-E-491 enamel. This material is suitable for use in areas with air pollution regulations.

9.3.6.10 MIL-P-46105, Primer Coating; Weld-Through, Zinc-Rich. This specification covers one type and grade of ready mixed, single package, epoxy based, zinc rich primer for use on ferrous metal surfaces prior to spot welding. The pigment for this primer is primarily metallic zinc and the vehicle is an epoxy resin solution. The purpose of this primer is application to ferrous metal surfaces that are not readily accessible for painting after spot welding, such as interior surfaces on trailer assemblies.

9.3.6.11 TT-P-1757, Primer Coating, Zinc Chromate, Low-Moisture Sensitivity.

This specification covers a low moisture sensitivity, corrosion inhibiting primer, primarily intended for spray application on surfaces treated with pretreatment coatings. The primer may be used with or without top coating. When suitably thinned, the primer may be used for dip or flow coat application. Two compositions are provided: G (general use) and L (limited use under air pollution regulations). The pigment consists of zinc yellow and siliceous extenders. The vehicle is a resin modified drying oil phthalic alkyd resin. Thinner for composition G can be xylene (TT-X-916) or toluene (TT-T-548), or a mixture of both; for composition L the thinner must be nonphotochemically reactive and compatible with the primer. The primer is intended primarily for use on aluminum aircraft or airborne equipment metal and should be applied at a dry film thickness of 0.3 to 0.4 mil (7.6 to 10.2 μ m). For non-aircraft or airborne equipment and on iron or steel surfaces it should be applied at a dry film thickness of 0.6 to 0.8 mil (15 to 20 μ m). The primer is satisfactory for application over a wide range of temperature and humidity conditions.

9.3.6.12 MIL-P-7962, Primer Coating, Cellulose Nitrate Modified Alkyd Type, Corrosion-Inhibiting, Fast Drying (For Spray Application Over Pretreatment Coating).

This specification covers a corrosion inhibiting, fast drying, lacquer type primer for spray application over pretreatment coating conforming to MIL-C-8514. Two compositions are provided, one of which is suitable for use where air pollution regulations are in force. The vehicle for this primer is a cellulose nitrate, modified alkyd resin with zinc yellow pigment and siliceous extender. The primer dries to a hard smooth finish in 6 minutes and acts as a tie-coat between the pretreatment and a top coating of cellulose nitrate or acrylic-cellulose nitrate lacquer.

9.3.6.13 MIL-P-22332, Paint, Priming, Exterior and Interior For Ammunition.

This specification covers a quick drying, rust inhibiting, lacquer resisting primer for coating interior and exterior surfaces of ammunition and rockets. It provides two compositions, one of which is suitable for use under air pollution regulations. The vehicle for the primer is a resin modified, drying oil phthalic alkyd resin. The pigments are zinc chromate, iron oxide and siliceous extenders. This primer may also be used over bare or chemically treated metal surfaces and may be used under synthetic enamel or lacquer topcoats.

9.3.6.14 MIL-P-23377, Primer Coating; Epoxy-Polyamide, Chemical and Solvent Resistant.

This specification covers a two component epoxy polyamide chemical and solvent resistant primer, primarily for spray application. Alternate composition is supplied for use where air pollution regulations are enforced. This material is intended for use with or without a prior coating of MIL-C-8514 wash primer and with top coat of MIL-C-22750 epoxy coating in accordance with MIL-C-22751.

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9.3.6.15 MIL-P-52192, Primer Coating, Epoxy. This specification covers an air drying or baking epoxy resin primer. Two compositions are provided: one for general use and one for use under air pollution regulations. The primer has good exterior durability and is intended for use as a chemical resistant primer coat for material. It may be baked at 300°F (150°C) for 20 minutes or for a longer period of time at a lower temperature.

9.3.7 Roller Coat Finishes.

MIL-P-19602 - Primer, Size Coating, Baking For Roller Coat Application

MIL-E-19603 - Enamel, Baking For Roller Coat Application
Class 1 - Gloss; Class 2 - Semigloss

MIL-V-21064 - Varnish, Finishing, Baking, For Roller Coat Application
Class 1 - Gloss; Class 2 - Semigloss

These three specifications cover a coating system for clean tin-to-terne plate containers. The system is intended for roller coat application at the factory to flat metal sheets prior to fabrication of the containers. Volatile solvent components meet air pollution regulation requirements. Available colors for the enamel are black, olive-drab, blue-gray and medium blue. The vehicle for each of the three coatings is either an epoxy resin solution, a vinyl resin solution or an alkyd resin solution (varnish only). Each coat is applied and then baked for not over 10 minutes at 400°F (205°C).

9.3.8 Sealers (paint type).

9.3.8.1 MIL-W-13518, Wood Preservative: Tetrachlorophenol and Pentachlorophenol, Surface Sealing Compound. This specification covers a ready-for-use sealer for wood and plywood. The sealer is available in two types and two classes:

Type I - Tetrachlorophenol Type
Class 1 - Linseed Oil Vehicle
Class 2 - Alkyd Resin Vehicle

Type II - Pentachlorophenol Type
Class 1 - Linseed Oil Vehicle
Class 2 - Alkyd Resin Vehicle

Each type contains between 5 and 6% by weight of wood preservative. The sealer-preservative provides a moderate degree of resistance to shrinkage, swelling, insects and fungi for wood products that are exposed intermittently to damp conditions. Type I (tetrachlorophenol) is used on surfaces when painting is anticipated. Type II (pentachlorophenol) is for use on rough wooden surfaces that are not to be painted. Class 1 preservatives (linseed oil base) are intended to be used on close grain, dense surfaces and plywood when good penetration is required. Class 2 (alkyd resin base) are for use on open or porous surfaces that permit easy penetration and require some swelling.

9.3.8.2 MIL-S-11388, Sealing Material for Metal Container Seams. This specification covers a material used for sealing seams in the manufacture of hermetically sealed metal containers for packing dry materials. The sealing material consists essentially of a stabilized dispersion of an elastomer and mineral fillers.

9.3.9 Solar heat reflecting and camouflage coatings.

9.3.9.1 Solar heat reflecting coatings. The primary purpose of these coatings referenced in paragraph 9.2 is to minimize heat buildup in the interior of weapon systems components and other equipment and reduce surface temperatures of equipment exposed to solar radiation. MIL-E-46096, MIL-E-46117 and MIL-E-46136 are enamel coatings available in olive drab and characterized by the incorporation of special hiding pigments (such as lead chromate, molybdate orange, titanium dioxide, phthalocyanine blue, carbazole dioxazine violet and quinacridone red) and are further characterized by the exclusion of organic blacks and antimony sulfide.

MIL-L-46138 and MIL-L-46142 are finish coat lacquers used on aircraft to reduce solar heat absorption. MIL-L-46138 is an olive drab color formulated to resist di-ester lubricating oil. MIL-L-46142 is a near black lacquer finish which can be used as a marking coat as well.

MIL-E-46139 is a rust inhibiting olive drab semigloss solar heat reflecting enamel and is intended for use on sheet metal, metal ammunition containers, drums (such as gasoline drums) and vehicular equipment.

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MIL-C-46127 is a gray undercoat for use with heat reflecting finish coats for missiles, vehicles, other weapon systems components and materiel to minimize the effects of solar heating. Comparable specifications are as follows:

<u>Solar Heat Reflecting Coating</u>	<u>Comparable Coating Without a Solar Heat Reflecting Requirement</u>
<u>Undercoat</u>	
MIL-C-46127	
<u>Lusterless Coatings</u>	
MIL-E-46096	TT-E-516
MIL-E-46117	TT-E-527
MIL-L-46138	MIL-L-19538
MIL-L-46142	TT-L-20
<u>Semigloss Coatings</u>	
MIL-E-46136	TT-E-529 MIL-E-52227
MIL-E-46139	TT-E-485

9.3.9.2 Camouflage paint. Camouflage paint is applied to protect equipment from visual observation and photographic or infrared detection. When a paint specification provides a color choice it shall be according to Fed. Std. No. 595. Unless otherwise specified, all new Army materiel and materiel undergoing depot overhaul, except aircraft and other exempted items, shall be painted with a paint system conforming to the Forest Green color. The system used shall be compatible with, and shall provide good adhesion for, subsequent coatings of paint conforming to MIL-E-52798. When Forest Green of the paint system conforming to MIL-C-46168 is used, the top coating with other camouflage colors shall be from MIL-C-46168 only.

For the application of camouflage paint, it is essential that Forest Green paint be applied at a minimum dry film thickness of 1.8 mils to achieve color uniformity and optimum camouflage characteristics. Because of the higher degree transparency of this paint in both the visual and infrared regions of the spectrum, an application of 0.8 - 1.0 mils dry, which is the normal application for an olive drab paint, would allow both the visual and infrared light to partially penetrate the surface and reflect the substrate or base coating. This would cause both nonuniformity in visual color and poor camouflage properties. Due to the extreme flatness of the paint, the color will vary to a degree, depending upon the texture and type of substrate, as well as the orientation of the film and the direction by which the light hits the film. Acceptance of an end item shall not be based specifically on color. It shall be based on whether the paint was approved by the US Army Mobility Equipment Research and Development Command (ATTN: DRDME-VO, Fort Belvoir, VA 22060) and whether application techniques are correct. As specified above, the paint must be applied at least 1.8 mils dry film thickness. A dust coat should be applied first before the two approximate 1 mil dry film thickness coatings are applied. Allow a 15 minute dry time before the second application for solvent flash-off. A single application of 1.8 mils minimum is permissible, provided the paint film is free of imperfections such as runs, sags or orange peel.

9.3.10 Surfacers.

9.3.10.1 TT-P-659, Primer Coating and Surfacers, Synthetic, Tints and White, (For Metal and Wood Surfaces). This specification covers a combination air drying and baking oil modified, varnish base primer surfacer for ferrous metal and wood surfaces. It is described under the category "Primers" (see 9.3.6.9).

9.3.10.2 TT-P-662, Primer Surfacers, Sanding Lacquer and Enamel Type. This specification covers a quick drying primer surfacer for use under lacquer or enamel and is described under the category "Primers" (see 9.3.6.8).

9.3.11 Stencil ink and stencil paint.

9.3.11.1 TT-I-1795, Ink, Marking, Stencil, Opaque (Porous and Nonporous Surfaces). This specification covers three types of light and weather resistant, fast drying, flat finish stencil inks for marking porous and nonporous surfaces.

- Type I - For use on nonporous surfaces (nonpressurized containers)
- Type II - For use on porous surfaces (nonpressurized containers)
- Type III - For use on porous and nonporous surfaces (pressurized containers)

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The inks are mixtures of pigments and a thin, quick drying varnish. Types I and II are available in 12 colors and type III is in black only. Types I and III will not etch, corrode, stain or discolor polished brass. Types I and III are intended for use in marking metals, glass, stone and similar nonporous surfaces. Types II and III are for marking fiberboard cartons, wood crates and boxes, bales, sacks, burlap and similar porous surfaces not having direct contact with food items. Types I and II are intended to be applied with stencil brush, hand lettering brush or roller coater. Type III is applied by spray and stencil board.

9.3.11.2 TT-P-98, Paint, Stencil, Flat. This specification covers a light and weather resistant, opaque, fast drying, flat finish stencil paint in a variety of colors and is described under the category "Paints" (see 9.3.4.4).

9.3.12 Varnishes.

9.3.12.1 TT-V-51, Varnish, Asphalt. This specification covers a black asphalt varnish for exterior and interior surfaces and is particularly suitable for painting indoor water and gas pipes. It dries to a smooth, lustrous, black finish. It is composed of hard native asphalts or asphaltites (Gilsonite, for example) blended with properly treated drying oils, driers and thinners conforming to TT-T-291, type II, or any other solvent complying with Rule 66.

9.3.12.2 MIL-I-24092, Insulating Varnish, Electrical, Impregnating. This specification covers clear heat resistant, insulating, baking varnishes for impregnating electrical coils and structures.

<u>Class</u>	<u>Maximum Operating Temperature, °C</u>	<u>Type</u>
105	105	AN, M
130	130	AN, M
155	155	M
180	180	M
200	200	M
220	220	M

These varnishes are intended for use on armature coils, field coils and other electrical windings for continuous operation at the maximum operating temperature specified. Insulating varnish furnished in type AN, classes 105 or 130 (consisting of only unmodified phenolic resins, drying or semidrying oils, thinners and driers) are intended primarily for application by military personnel. Type M varnishes in classes 155, 180, 200 and 220 are intended for application by both manufacturers of Military equipment and by Military personnel.

9.3.12.3 MIL V-13497, Varnish, Impregnating, Electrical-Insulating (For Fire Control Instruments). This specification covers an electrical insulating varnish for impregnating electrical windings of synchro-servo motors and other low torque precision rotating mechanisms requiring low friction bearings. These units are for use in ordnance fire control instruments. The insulating varnish is furnished in the following type and grade:

- Type M - Material for application by manufacturers of fire control equipment
- Grade CB - Clear impregnating insulating

The varnish must pass the qualification test specified in MIL-T-24092 (see 9.3.12.2) plus a distillation corrosion test. The varnish is intended for use where a distillate from the varnish, or corrosion products that may be produced by the action of distillate on bearings at elevated temperatures, are harmful to the operation of the unit. This varnish should be applied in accordance with type IV treatment of MIL-T-13867.

9.3.12.4 TT-V-81, Varnish; Mixing, For Aluminum Paint. This specification covers varnish suitable for mixing with aluminum powder or paste, on the job, to make aluminum paint. The varnish is not intended to be used as a clear finish.

9.3.12.5 MIL-V-13750, Varnish, Phenol-Formaldehyde, Clear, and Aluminum Pigmented. This specification covers two grades and four types of varnish (clear and aluminized) as follows:

- Grade A - Tung oil para phenyl phenol-formaldehyde resin varnish
- Grade B - Linseed oil para phenyl phenol-formaldehyde resin varnish

Grade A and B varnishes are furnished in four types as follows:

- Type I (clear) - 25% by weight of pure phenolic resin
25% by weight of oil (tung or linseed) as specified
50% by weight of xylene
- Type II (clear) - 50% varnish conforming to type I (above)
50% toluene
- Type III (pigmented) - 84% varnish conforming to type I
16% aluminum powder
- Type IV (pigmented) - 42% varnish conforming to type I
16% aluminum powder
42% toluene

These are high grade products. All types, both clear and aluminized, are used as sealers for detonators. They are air drying products.

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9.3.12.6 MIL-V-12276, Varnish, Phenolic, Baking. This specification covers three types of heat hardening phenolic resin varnish for use as a coating for cartridge cases and as a lining for munitions and other containers. The varnish is furnished in the following types and classes as specified:

Type I - For use on cartridge cases

Class A - For spray applications

Class B - For dip applications

Type II - For use in lining munitions and chemical containers

Type III - For use on cartridge cases under special conditions

Class A - For spray application

Class B - For dip application

Class C - For roller coating application

This is a thermosetting varnish that is converted to an infusible and relatively insoluble condition by heat and does not soften appreciably when reheated. The baked varnish is very resistant to chemicals and solvents.

Type I - varnish is based on a straight thermosetting phenolformaldehyde varnish free from resin or resin derivatives, but may include other materials to improve the leveling, flexibility and adherence of the coating.

Type II - varnish is based on a straight thermosetting phenolformaldehyde varnish free from added plasticizers, rosin or rosin derivatives.

Type III - varnish is based on mixture of bis-phenol epoxide and phenol-formaldehyde resin. It may include other materials to improve the leveling of the coating.

Varnishes I and III are intended for use as the finishes on steel cartridge cases to protect them from atmospheric corrosion. Type I is intended for use where the metal is not deformed or fabricated after coating. Type III is intended for use where the metal is deformed or fabricated after it is coated. Type II varnish covered by this specification is intended for use as a protective finish for lining munitions, chemical and other containers requiring special protection.

9.3.12.7 TT-S-300, Shellac, Cut. This specification covers shellac varnish of the following types, grades and bodies (cut):

Type I - Bleached

Grade A. - Regular

Body 1. - 4 pound cut
Body 2. - 4.5 pound cut
Body 3. - 5 pound cut
Body 4. - 3 pound cut

Grade B. - Refined

Body 1. - 4 pound cut
Body 2. - 4.5 pound cut
Body 3. - 5 pound cut
Body 4. - 3 pound cut

Type II - Orange

Grade A. - Regular

Body 1. - 4 pound cut
Body 2. - 4.5 pound cut
Body 3. - 5 pound cut
Body 4. - 3 pound cut

Grade B. - Refined

Body 1. - 4 pound cut
Body 2. - 4.5 pound cut
Body 3. - 5 pound cut
Body 4. - 3 pound cut

Grade A (regular orange and regular bleached shellac) varnishes will be satisfactory for use as a protective coating for most purposes. When the quality of the work warrants the use of a clear varnish that is practically free from wax and other suspended matter, refined (grade B) varnish should be used. Shellac varnish has the following limitations:

a. As a sealer:

1. Sensitivity to moisture
2. Poor adhesion to succeeding top coats
3. Poor adhesion to hard woods

- b. Bleached shellac varnish may deteriorate if it has been stored for over 6 months. Sticky compounds, which do not dry, are formed. Orange shellac, however, remains stable for somewhat longer periods.

9.3.12.8 TT-V-119, Varnish, Spar, Phenolic Resin. This specification covers one grade of clear, air drying, spar varnish of the drying oil phenolic resin type. The coating air dries hard within 8 hours. The varnish has excellent exterior durability and water resistance and is used as a marine spar varnish as well as for structural and architectural finishing. It also finds use as an aluminum vehicle for certain enamels and primers and as a sealing compound in fabrication and repair of riveted aluminum alloy tanks.

9.3.12.9 TT-V-121, Varnish, Spar, Water-Resisting. This specification covers a clear, air drying spar varnish of the oleoresinous type. It is suitable for both outdoor and indoor exposure where durability is the chief requisite and where high gloss or high hardness of the film is not required. The varnish sets to touch within 2 hours and dries hard within 8 hours. It works. flows and levels well when applied by brushing. It may be applied by spraying.

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The specification is based on physical and performance requirements and composition is not specified in detail. Tung oil and phenolic resins are used widely in this type of spar varnish. For fire control applications, TT-V-121 spar varnish is used in three systems:

- (1) Natural varnish wood; wood sealer plus spar varnish
- (2) Under-surface of wood plotting boards; linseed oil, followed by shellac varnish, followed by spar varnish
- (3) Olive drab finish for wood (tripod legs, etc.); olive drab stain, followed by spar varnish, followed by wax

When new wood is to be finished with spar varnish and exposed to the weather, three coats of spar varnish are desirable.

9.3.12.10 MIL-V-13811, Varnish, Waterproofing, Electrical, Ignition. This specification covers one type and one grade of clear varnish for use primarily on electrical circuits and engine parts of internal combustion corrosion. It is suitable, as received, for brushing or spraying. The varnish dries dust free within 15 minutes and dries through within 1 hour, but may retain some tackiness for as long as 18 hours. The dried coating is clear, smooth and glossy and is resistant to water, heat and gasoline. The nonvolatile vehicle (binder) portion of the varnish is based on a resin formed by the reaction of an acrylic ester, styrene and phthalic alkyd resin.

9.4 Tables of principal organic coatings. Tables II through V summarize the principal organic coatings used in military finishing (painting) applications.

TABLE II. Survey of Principal Primers.

Specification	Vehicle	Intended Use
TT-P-485 Enamel, Semigloss, Rust Inhibiting	Types I, II and III medium length alkyd, type IV phenol modified alkyd	One or two coat primer for steel (bare or phosphated). Used on sheet metal, metal ammunition containers, landing mats, pipeline equipment, drums (gasoline), vehicular equipment, certain types of rail and tactical and combat equipment.
TT-P-636 Primer Coating, Alkyd, Wood and Ferrous Metal	Medium oil phthalic alkyd resin	For clean, rust free bare or phosphate treated ferrous metal parts of motor vehicles, as well as guns, gun mounts, tanks, metal shipping containers and similar ordnance materials.
TT-P-645 Primer, Paint, Zinc Chromate, Alkyd Type	Alkyd resin	Corrosion inhibiting primer on metal surfaces and as an after pickling coating on steel and as a primer for application to steel and aluminum.
TT-P-659 Primer Coating and Surfacers: Synthetic, Tints and White (For Metal and Wood Surfaces)	Oil modified phthalic alkyd resin	Primer and sanding surfacer for ferrous metal and wood surfaces. Not intended for use on metals where rust inhibiting characteristics are required.
TT-P-662 Primer Surfacers, Sanding, Lacquer and Enamel Type	Phthalic alkyd modified cellulose nitrate resin	Primer-surfacer for use in lacquered and enamel finishing systems, primarily for automotive equipment.
TT-P-664 Primer Coating, Synthetic, Rust Inhibiting, Lacquer Resisting	Modified phthalic alkyd resin	Durable, quick drying, rust inhibiting, lacquer resisting primer for metal, suitable for use under either synthetic enamel or lacquer topcoats.
TT-P-1757 Primer Coating, Zinc Chromate, Low Moisture Sensitivity	Phenol modified medium oil phthalic resin	Primer primarily for spray application to surface treated aluminum or aluminum or surfaces treated with pretreatment coatings. Used without top coating in interior areas. Corrosion inhibiting primer on aluminum aircraft or airborne equipment.
TT-P-7962 Primer Coating, Cellulose Nitrate, Modified Alkyd Type, Corrosion Inhibiting, Fast Drying (For Spray Application over Pretreatment Coating)	Cellulose nitrate modified alkyd resin	Corrosion inhibiting, fast drying, lacquer type primer under top coat of cellulose nitrate or alkyd cellulose nitrate lacquer.
MIL-P-11414 Primer Coating, Lacquer, Rust Inhibiting	Cellulose nitrate modified alkyd resin	For shells, bombs, grenades, tanks, trunks, ammunition and automotive parts to be topcoated with lacquer. Developed primarily for ferrous metal surfaces, but has given excellent service on cleaned and treated aluminum.
MIL-P-12742 Primer Coating, Phenolic, Water Immiscible	Tung oil-phenolic resin; Type I for metal and type II for wood	For metal and wood surfaces prior to application of phenolic enamel, where subject to humid atmospheres or partial immersion in fresh or salt water.

TABLE II. Survey of Principal Primers. (CONT'D)

Specification	Vehicle	Intended Use
MIL-P-22332 Primer Coating, Exterior and Interior (For Ammunition)	Modified drying oil phthalic alkyd resin	Quick drying, rust inhibiting, lacquer resisting primer for coating interior and exterior surfaces of ammunition and rockets. Suitable for use over bare or chemically treated surfaces and may be used under lacquer or synthetic enamel topcoats.
MIL-P-23377 Primer Coating, Epoxy-Polyamide, Chemical and Solvent Resistant	Furnished in two components (epoxy resin and polyamide resin): Type I, standard and type II, low infrared reflective (IR)	Two component epoxy-polyamide corrosion inhibiting chemical and solvent resistant primer for spray application.
MIL-P-38336 Primer Coating, Inorganic, Zinc-Dust Pigmented, Self-Curing For Steel Surfaces	Furnished in ready-to-mix, two component material (dry zinc dust and liquid inorganic vehicle)	Inorganic zinc-rich primers for use on steel structures that receive severe exposure to adverse weather, condensing moisture, corrosive atmosphere and marine environment.
MIL-P-46103 Primer Coating: Weld Through Zinc Rich	Epoxy resin modified with phenolic, amine or hydrocarbon resins	Ready-mixed, single package, epoxy based, zinc rich primer for use in ferrous metal surfaces prior to spot welding.
MIL-P-52192 Primer Coating, Epoxy	Epoxy resin with polyamine catalyst	Two component epoxy polyamine, chemical resistant primer for spray application.

TABLE III. Survey of principal lusterless enamels.

Specifications	Vehicle	Intended Use
TT-E-515 Enamel, Alkyd, Lusterless, Quick Drying	Resin modified drying oil phthalic alkyd	Fast drying finish coat for equipment.
TT-E-516 Enamel, Lusterless, Quick Drying, Styrenated Alkyd Type	Styrenated alkyd	Finish coat on phosphated or primed metal surfaces and on ammunition components where gasoline resistance is not required.
TT-E-522 Enamel, Phenolic, Outside	Tung oil phenolic resin: Type I, lusterless and type II, semigloss	For outside use when high humidity conditions exist as well as where partial or total immersion in fresh or salt water may occur.
TT-E-527 Enamel, Alkyd, Lusterless	Drying oil phthalic alkyd resins	A combination air drying and baking enamel for use as a finishing coat on military and other equipment.
MIL-L-11195 Lacquer, Lusterless, Hot Spray	Cellulose nitrate modified phthalic alkyd resin	For use as finish coat on phosphated or primed shells, bombs, grenades, tanks, trucks, ammunition and other automotive components. Although primarily for hot spray, the lacquer may be reduced for spraying at room temperature.
MIL-E-46096 Enamel, Lusterless, Quick Drying, Styrenated, Alkyd Type, Solar Heat Reflecting	Styrenated alkyds	Quick drying enamel used as finishing coat to minimize heat buildup in the interior of Army weapons systems.
MIL-C-22750 Coating, Epoxy Polyamide	Epoxy polyamide	For protection of areas exposed to chemicals and solvents, exterior or interior use on weapons systems.
MIL-C-81286 Coating, Urethane, Aliphatic Isocyanate, For Aerospace Application	Two component aliphatic urethane (polyester-isocyanate)	For exterior application on aerospace equipment.

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TABLE IV. Survey of principal semigloss enamels.

Specification	Vehicle	Intended Use
TT-L-20 Lacquer, Camouflage	Nitrocellulose modified alkyd resin	For use on metal surfaces as camouflage color finish. Best results when applied over proper pretreatment and primer.
TT-L-58 Lacquer, Spraying, Clear and Pigmented (General Interior Use)	Cellulose nitrate	Spraying lacquer for general interior use as a finishing coat over primed metal or sealed wood surfaces.
TT-L-485F Enamel, Semigloss, Rust Inhibiting	Types I, II and III medium length alkyd; Type IV phenol modified alkyd	One coat system over cleared and pretreated metals or two coat system using first coat as a primer. For sheet metal, metal ammunition containers, landing mats, pipeline equipment, drums (gasoline), vehicular equipment and certain types of rail and tactical and combat equipment.
TT-E-522 Enamel, Phenolic, Outside	Tung oil phenolic resin; Type I, lusterless and type II, semigloss.	For outside use where high humidity conditions exist, as well as where partial or total immersion in fresh or salt water may occur.
TT-E-529 Enamel, Alkyd, Semigloss	Drying oil phthalic alkyd resin	For exterior and interior wood and metal surfaces, primarily for military and other special equipment. Also used for direct application to bare metal surfaces such as metal office furniture and lockers which have been properly prepared.
MIL-E-480 Enamel, Baking, Phenolic or Urea-Formaldehyde	Type I, phenol-formaldehyde resin; Type II, urea-formaldehyde resin	Semigloss enamels capable of protecting steel and zinc coated steel. Type I is intended primarily for use over steel and type II over zinc coated steel (personnel hardware such as buckles, hooks, snaps, etc.).
MIL-E-46139 Enamel, Semigloss, Rust Inhibiting, Solar Heat Reflecting, Olive Drab	Drying oil phthalic alkyd resin	One or two coat painting system on metal equipment exposed to sunlight to reduce solar heat absorption.
TT-E-490 Enamel, Silicone, Alkyd, Copolymer, Semigloss (For Exterior and Interior Nonresidential Use)	Silicone-soya alkyd	Highly weather resistant with excellent color and gloss retention for use as a gloss finish for machinery, trucks, metal drums, metal signs, railing fences, etc.
MIL-C-22750 Coating, Epoxy Polyamide	Epoxy polyamide	For protection of areas exposed to chemicals and solvents, exterior or interior use on weapons systems.

TABLE V. Survey of principal gloss enamels.

Specification	Vehicle	Intended Use
TT-E-1593 Enamel, Silicone-Alkyd, Copolymer Gloss (For Exterior and Interior Use)	Silicone-alkyd	For use on primed metal, highly weather resistant and has good gloss and color retention. For a gloss finish on machinery, trucks, buses, metal drums, signs, siding, fences, railings, doors, etc.
TT-L-489 Enamel, Alkyd, Gloss	Class A (air drying) medium oil length phthalic alkyd; Class B (baking) short oil length phthalic alkyd.	For primed exterior and interior wood and smooth metal surfaces. For finishing and refinishing automotive and construction equipment.
TT-E-491 Enamel, Gloss, Synthetic (For Metal and Wood Furniture)	Drying oil phthalic alkyd resin; class A (air drying) and class B (baking)	For use over a primer coat to provide finish of maximum washability and durability for metal and wood hospital furniture and similar uses.
TT-V-51 Varnish, Asphalt	Asphalt or gilsonite with drying oils, driers and thinner	For use around storage batteries, etc., chemical resistant.
TT-L-12 Lacquer, Cellulose, Nitrate Gloss For Aircraft Use	Cellulose nitrate	For use as an exterior protective coating for primed metal surfaces.
MIL-C-22750 Coating, Epoxy, Polyamide	Epoxy polyamide	For protection of areas exposed to chemicals and solvents, exterior or interior use on weapons systems.
MIL-C-83286 Coating, Urethane, Aliphatic Isocyanate, For Aerospace Applications	Two component aliphatic urethane (polyester-isocyanate)	For exterior application on aerospace equipment.

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10. SURFACE PREPARATION AND PAINTING OF FERROUS METAL

10.1 General. Possibly 90 to 95% of the various metals used in ordnance applications and Army equipment is ferrous (iron and steel). Thus the surface preparation and painting of ferrous metal deserves close consideration. Unless protected, surfaces of iron and steel (with the exception of stainless steel) react readily with atmospheric oxygen, particularly in the presence of moisture, to form rust. Rust of any kind must be avoided, as it often continues to form even when the surface is coated with oils or paints. Rust may be considered to be the greatest enemy of ferrous metal. The loss incurred through corrosion of steel runs into the billions of dollars per year in the United States. The most common method of preserving iron and steel and limiting corrosion losses is by means of paint.

10.2 Cleaning. Before any paint is applied to ferrous metal, the surface must be cleaned thoroughly. This is a major consideration and the life of the paint coating depends on how well the surface is cleaned. It is generally agreed that a thoroughly cleaned surface of iron and steel (one completely free from rust, scale grease, wax, dirt, moisture and other foreign matter) offers a satisfactory base upon which to apply a protective paint.

Cleaning is done by means of alkaline and acid treatments, by liquid or vapor organic solvent washes, by mechanical abrasion (as with sand or grit blasting) or by special methods. Various cleaning methods for metal are described in detail in section 2 of this handbook and need not be repeated here. The correct specification to use for cleaning ferrous metal surfaces, prior to the application of organic protective coatings, is TT-C-490. The following methods of cleaning, covered by this specification, prepare the metal surface for painting:

- Method I - Mechanical or abrasive cleaning [sand, shot, grit, glass bead, seed or vapor blasting or tumbling preceded by degreasing, if necessary, to assure a grease-free surface, followed by cleaning to remove dust and metal particles (for ferrous surfaces only)].
- Method II - Solvent (immersion, spray or vapor).
- Method III - Hot alkaline [immersion, spray or electrolytic (for ferrous surfaces only)].
- Method IV - Emulsion (with or without added water, followed by a water rinse).
- Method V - Alkaline derusting (for ferrous surfaces only).
- Method VI - Phosphoric acid (alcoholic, detergent or solvent type with detergent).

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Where practicable, the best mechanical method for removing rust and scale from ferrous surfaces is by blasting with steel grit, steel or chilled iron shot, silica sand or a sharp abrasive such as alundum. Steel grit should not be used on parts containing blind holes or deep interstices, because it is removed from such cavities with great difficulty; silica sand is preferred. After being blasted, the parts should not be handled with bare hands and the phosphate coating (about to be described) should be applied as soon as possible. Abrasive blasting is desirable, when possible, as the last pretreatment step before parts are immersed in the phosphating solution, because it provides the most satisfactory surface to receive the phosphate finish. Dust on abrasive blasted work should be removed by means of compressed air and not by brushing or wiping with a cloth.

Pictorial standards for steel surface preparation of steel in the field have been prepared by the Swedish IVA Corrosion Committee and jointly approved by:

- Steel Structures Painting Council;
- American Society for Testing and Materials;
- Swedish Standards Association; and
- National Association of Corrosion Engineers.

Pictorial surface preparation standards consist of a series of color prints. They represent various conditions of ferrous surfaces prior to painting. The standards show the following initial surface conditions before surface preparation:

- (1) Steel surface covered completely with adherent mill scale, but little or no rust.
- (2) Steel surface which has begun to rust with mill scale beginning to flake.
- (3) Steel surface from which the mill scale has rusted away with pitting visible.
- (4) Steel surface from which the mill scale has rusted away with little or no pitting visible.

The various grade of thoroughness of surface preparation are also represented as follows:

- (5) Manual cleaning, light.
- (6) Manual cleaning, thorough.
- (7) Manual cleaning, very thorough.
- (8) Blast cleaning, light.
- (9) Blast cleaning, thorough.
- (10) Blast cleaning, very thorough.

The actual photographs and details of the applicable definitions appear in the text of the photographic reference standards publications book (SSPC-Vis 1-63T) available from the Steel Structures Painting Council or from the American Society for Testing and Materials (see ASTM D 2200).

Specifications established by the Steel Structures Painting Council are helpful in defining the condition of a blasted steel surface. The following specifications are applicable:

- SSPC-SP5-63, White Metal Blast Cleaning. This describes a surface completely free of rust, mill scale and foreign matter or contaminants. If initially agreed upon, SSPC-Vis 1-63T or other visual references may be used to supplement this specification.
- SSPC-SP 10-63, Near-White Blast Cleaning. Describes a blasted surface which is essentially free of rust and scale, but from which the last traces of shadows, streaks or discoloration have not been removed.
- SSPC-SP 6-63, Commercial Blast Cleaning. Describes a high degree of cleaning expected to give long life with practically any paint system, but where cleaning is not as thorough as described above. This specification permits the optimal use of a visual standard such as SSPC-Vis 1-63T.
- SSPC-SP 7-63, Brush-Off Blast Cleaning. Describes a low cost blast cleaning which only removes loose mill scale, loose rust and loose paint. This method permits the use of SSPC-Vis 1-63T or other visual reference.

10.3 Phosphate surface treatments. After the ferrous metal surface has been thoroughly cleaned, it can be substantially improved for painting by application of a phosphate surface treatment. There are various types of phosphate finishes, some giving a light and some a heavy coating. The one under consideration here as a base for paint is Specification TT-C-490, type I. This is a crystalline zinc phosphate coating. The cleaned ferrous article is exposed to the zinc phosphating solution under controlled conditions. The article or item is then subjected for at least 3 minutes, if the dip coating method is used, or for at least one minute, if the spray method is used. The article is then rinsed thoroughly in clean water, followed by a second rinse in a dilute solution of chromic acid or a combination of dilute chromic and phosphoric acids and then dried. Type II of TT-C-490 covers an iron phosphate coating that was developed primarily for 55-gallon steel drums prior to painting. Type IV of TT-C-490 covers an iron phosphate coating produced in a nonaqueous solution using chlorinated solvents and phosphoric acid.

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Articles processed in types I and II phosphating baths require a clean water rinse in order to remove insoluble salts and unreacted phosphating material. Failure to remove water soluble chemical residues by rinsing in clean water will result in early failure of the paint coating by blistering, flaking and rapid spread of corrosion products when the metal surface is scratched.

Where TT-C-490, type I treatment is not practicable, the cleaned ferrous metal, prior to painting, may be given a pretreatment coating (known as "wash primer") meeting DoD-P-15328 (TT-C-490, type III). This treatment is essentially a combination of phosphate treatment and resin coating in one application and, while listed as a treatment for ferrous metals, is equally applicable as a prepaint treatment for most metals of construction. The wash coat is described in detail in section 9 of this handbook.

Phosphate treatments other than TT-C-490, types I, II or IV and DoD-P-15328 (for example, MIL-P-16232) as well as chromate treatments, are described earlier in section 4.

Paint systems applied directly to cleaned ferrous metals provide a certain measure of protection. However, when the paint systems are applied to surfaces both cleaned and phosphate treated, the measure of protection is increased -- in many case, multiplied.

Thus, the Army almost invariably specifies prepaint treatments. The phosphate pretreatments just described do not, in themselves, provide appreciable protection for the underlying ferrous metal surfaces. They are used solely for one purpose -- that of providing superior paint bases. They increase the adhesion of the paint coating to the metal surface. The phosphate treated surfaces (whether of TT-C-490 or DoD-P-15328) should be coated with the paint primer as soon as practicable (within 24 hours).

Paint systems designed for baking at temperatures up to 300°F (149°C) may be applied over the TT-C-490 preparing treatment but not over the DoD-P-15328 or heavy phosphate treatments. Paint systems designed to be baked at higher temperatures should not be applied over phosphate coatings. Hot spray lacquers may be applied over either type of coating.

10.4 Selection of paint and application. After the ferrous metal surface has been properly prepared (i.e., cleaned, passivated and thoroughly dried) it is ready to receive the priming coat of paint. As is explained in section 8, a priming paint for metal to be exposed to the weather contains corrosion-inhibitive pigments like red lead and zinc yellow in addition to other pigments. A list of primers is given in section 9.

When the priming coat of paint has thoroughly dried, the top coats of paint may be applied. A typical finish for ferrous metal as specified on ordnance drawings consists of:

- (a) A suitable prepaint treatment.
- (b) A specified prime coat of paint.
- (c) When required, an intermediate or surfacer paint coat.
- (d) One or more coats of finish types of paint materials.

A typical semigloss oleoresinous enamel system for ferrous metals consists of:

- (a) Phosphate treat according to type I, Specification TT-C-490.
- (b) Apply priming paint conforming to Specification TT-P-636.
- (c) Apply forest green enamel conforming to Specification TT-E-529.

A typical gloss lacquer enamel system for automotive components consists of:

- (a) Phosphate treat according to type I, Specification TT-C-490.
- (b) Apply lacquer primer, conforming to Specification MIL-P-11414.
- (c) Apply a surfacer coat, conforming to Specification TT-P-662.
- (d) Apply hot lacquer enamel, conforming to Specification MIL-L-12277.

Paint coatings used on Army ordnance equipment are typified by the two types illustrated in the above paint systems. One is enamel made with phthalic alkyd varnish modified with drying oil; the other is lacquer enamel made with cellulose nitrate, alkyd resin and plasticizer.

When properly applied to ferrous metals, specified paint systems may be expected to protect such metals for the life of the component, barring damage or abuse. Premature failures are generally due to improper application of one or more parts of the specified system, not using paint meeting the specification or failure to coat all exposed surfaces of the ferrous metals. Failure to adequately protect ferrous metallic components of military equipment by slighting surface preparation and application of protective paint systems in any phase or manner, for economic or other reasons, constitutes false economy.

The importance of applying paints evenly and uniformly, allowing sufficient time for drying between coats, applying paints under proper conditions of cleanliness, humidity and temperature and obtaining the correct dry film thickness for each coat of paint is stressed in the beginning of this chapter.

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11. SURFACE PREPARATION AND PAINTING OF ZINC AND CADMIUM SURFACES

11.1 Cleaning. Cadmium and zinc surfaces are considered together in this section because their properties are similar. Cadmium and zinc electroplating are described in section 3. Zinc diffusion (Sheradizing) and hot dipped zinc coating are described in section 6. Before painting, cadmium and zinc surfaces must be cleaned and treated. As in the case of ferrous surfaces, cadmium and zinc surfaces are cleaned according to TT-C-490. However, clean zinc surfaces, painted with no prior surface treatment, can give unsatisfactory service because of a reaction between the zinc and the paint vehicle.

11.2 Surface treatments: Successful painting of zinc and cadmium requires the use of special surface treatments. Surface treatments for zinc and cadmium are listed in table VI of MIL-STD-171. When factory parts, comprised of zinc or cadmium (or both) are to be treated for painting, indication is for phosphating according to MIL-T-12879, "Treatments, Chemical Prepaint and Corrosion Inhibitive, for Zinc Surfaces". This process deposits fine crystals of zinc phosphate weighing no less than 150 mg per sq ft. Phosphate coating has a characteristic grayish color, but this is not as important as its uniform texture, nonpowdery nature and good adherence. The specification also describes a chromate treatment. Most of the solutions for this consist of chromic acid, a mineral acid (hydrochloric or sulfuric) or an organic acid (formic). Immersion time ranges from 5 to 30 seconds. The color is characteristic of the particular process, but here again, a uniform color is not as important as a nonpowdery coating. The phosphate treatment is considered superior to the chromate treatment, particularly in respect to adhesion.

For field application or for factory application where parts are too large for treating in dip tanks, treatment with DoD-P-15328, "Primer, Pretreatment", is indicated. Also known as "Wash Primer", this material is described more fully in paragraph 4.7. Its main purpose is to increase adhesion of paint. Its thin consistency allows it to be applied very thin (0.3 to 0.5 mil, dry) and to dry within 15 to 30 minutes, depending on atmospheric conditions. The conventional primer should follow within 24 hours, as the wash primer loses its effectiveness after short exposure to adverse weather. Although it contains water, it should not be applied to wet metal, but may be applied to damp metal with a brush. It is more effective when freshly mixed and must be used within eight hours.

Where zinc and cadmium are present in an assembly comprised mostly of ferrous metal, the pretreatment is that described in paragraph 10.3.

11.3 Selection of paint and its application. After the cadmium or zinc surface has been cleaned, treated and dried, it is ready for painting. Paint systems for treated cadmium and zinc surfaces usually consist of zinc chromate primer, TT-P-1757, followed by the usual oleoresinous enamel or lacquer enamel finish coats.

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For example, the steps in a coating system for a zinc-base alloy surface to be exposed to the weather might read as follows:

- (a) Clean thoroughly by vapor degreasing according to TT-C-490, method II.
- (b) Apply pretreatment coating, DoD-P-15328.
- (c) Apply zinc chromate primer, conforming to TT-P-1757.
- (d) Apply two coats of olive drab enamel, conforming to TT-E-529.

A durable, baked on, oil resistant coating system for zinc coated steel surfaces might read as follows:

- (a) Clean thoroughly by vapor degreasing according to TT-C-490, method II.
- (b) Phosphate treat according to MIL-T-12879, type I, class 1.
- (c) Apply zinc chromate primer, conforming to TT-P-1757.
- (d) Apply enamel, conforming to MIL-E-480, type II; bake at about 375oF (191oC).

12. SURFACE PREPARATION AND PAINTING OF ALUMINUM AND ALUMINUM ALLOYS

12.1 General. One of the outstanding characteristics of aluminum is the excellent protection afforded by the very thin film of aluminum oxide naturally formed on its surface. In dry, rural climates, no further protection is necessary. However, in moist atmospheres, and where the surface may be exposed to chemical fumes or industrial gases, pitting of the metal may occur with the formation of loose corrosion products. To avoid this, the practice of the Military is to clean, treat and paint the metal.

12.2 Cleaning. The aluminum surface may be contaminated with oil, grease and other foreign matter. These contaminants must be meticulously removed prior to surface treating and painting. The usual method of cleaning aluminum is with solvent by immersion, or with spray or vapor. Manual scrubbing or dip washing with mineral spirits may be used. However, it is difficult to remove all the contaminants (particularly oil and grease) on the surface by this method of cleaning. Attacking the soil with spray is a better method. Vapor degreasing in special equipment employing trichloroethylene vapor is still another good method. Solvent cleaning (immersion, spray or vapor) is covered by TT-C-490, method II. Solvent cleaning has the advantage that it does not disturb the natural oxide film on the surface and may prove adequate for many applications. The aluminum surface also may be cleaned by inhibited alkaline cleaners. These do not etch the surface and can be used to remove oil, grease and similar organic soils. Steel wool and uninhibited caustic etching solutions, such as sodium hydroxide, should not be used on aluminum.

12.3 Chemical treatments. An alcoholic phosphoric acid solution may be used both to clean the surface and to provide a slight etching on the metal to improve the adhesion of the paint. The solution may be applied by scrubbing or dipping, is allowed to remain on the surface a few minutes and is then rinsed thoroughly with clean water. This process is covered by TT-C-490, method VI.

Another method is to use a dilute solution of phosphoric acid metal conditioner, as covered by MIL-C-10578.

The additional chemical treatments described in 12.3.1 to 12.3.6 may be applied to the aluminum surface subsequent to removal of all oil, grease and foreign material, preferably by vapor degreasing or inhibited alkaline cleaning.

12.3.1 Sulfuric-chromic-fluoride deoxidizer. This treatment provides a clean and uniform surface without undue roughening and is effective for removing inorganic soils and any film formed during the production of hot dip aluminum. The solution is generally used at a temperature of 70 to 130°F (21 to 54°C) for about 5 minutes and is followed by a water rinse.

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12.3.2 Crystalline phosphate treatment. This treatment consists of applying (by spraying or dipping) a zinc phosphate solution containing oxidizing agents and other salts to the aluminum surface. The immersion time is 30 seconds to 4 minutes and the spraying time is 10 seconds to 2 minutes. The aluminum surface is converted to a crystalline phosphate coating that increases the adherence and durability of the applied paint film.

12.3.3 Amorphous phosphate treatment. This treatment consists of applying (by spraying or dipping) a warm aqueous solution containing phosphoric, chromic and hydrofluoric acids to the clean aluminum surface. Duration of spray application varies from 15 to 45 seconds and that of immersion application, from 30 seconds to 3 minutes.

12.3.4 Carbonate-chromate treatment. This treatment consists of applying a hot dilute solution of sodium carbonate and potassium chromate to the clean aluminum surface for from 2 to 20 minutes, followed by a water rinse. The surface is then given a final treatment in a hot 5% aqueous solution of potassium dichromate followed by a final rinse. This treatment produces a thin, adherent, conversion coating on the surface, increasing the corrosion resistance of the metal and promoting paint adhesion.

12.3.5 Amorphous chromate treatment. This treatment consists of applying an aqueous chromic acid solution, containing suitable accelerating agents such as fluoride materials, to the clean aluminum surface. The aluminum surface is converted to an adherent, amorphous, mixed metallic oxide coating, iridescent golden to light brown in color, that increases the corrosion resistance of the metal and the adherence and durability of an applied paint film. The treating solution may be applied by dipping, spraying or brushing, at room temperature, in 15 seconds to 5 minutes contact time. Usually, this treatment is preceded by the deoxidizer treatment (see 12.3.1). Most of the treatments described in 12.3.3, 12.3.4 and 12.3.5 are covered by MIL-C-5541, "Chemical Conversion Coatings for Aluminum and Aluminum Alloys". They offer a good base for paint, preferably air drying paint systems.

12.3.6 Wash primer treatment. Wash primer treatment, more correctly designated DoD-P-15328, "Pretreatment Primer", covers a pretreatment coating for use on clean metal surfaces of all types (including aluminum) prior to application of the paint coating system. It is described in detail in paragraphs 4.7 and 9.3.6.1.

12.4 Anodic films (electrochemical conversion coatings for aluminum). Under severe exposure, one of the best (if not the best) treatments for cleaning aluminum and aluminum alloys prior to painting is an electrochemical surface treatment known as anodizing. Oxide films produced electrolytically on aluminum surfaces have a resistance to wear far superior to those produced by chemical means. Anodic coatings for aluminum and aluminum alloys are covered by MIL-A-8625 and described in detail in section 5.

12.5 Selection of paint and its application. After the aluminum surface has been cleaned, treated and dried, the priming paint should be applied as soon as possible. A priming paint designed specifically for aluminum (and sometimes used on magnesium) is one meeting TT-P-1757. This specification covers a high quality primer made with alkyd resin and not less than 85% of zinc yellow in the pigment portion. Primers for aluminum and magnesium should contain no red lead, which may pit these metals. Another suitable primer is a lacquer type conforming to MIL-P-11414, which may be used when approved by the procuring activity. Where the aluminum is to be painted in white only, and not exposed to the weather, a suitable primer is one meeting TT-P-659. The usual enamel lacquer finish coats may be applied to the dried priming coat.

Some examples of priming and topcoat paints for aluminum are as follows:

Lusterless Paint Systems

Priming Coats	Top Coats
TT-P-1757 (MIL-P-11414)	TT-E-527 TT-E-515 TT-E-516 MIL-L-11195

Semigloss Paint Systems

Priming Coats	Top Coats
TT-P-1757 (MIL-P-11414)	TT-E-485 TT-E-529 MIL-E-480 MIL-L-52043

Gloss Paint Systems

Priming Coats	Top Coats
TT-P-1757 (MIL-P-11414)	TT-E-489 TT-L-32

Paint systems which give good protection under severe environmental conditions are:

MIL-P-23377: Epoxy primer

MIL-C-83286: Polyurethane topcoat (lusterless or gloss)

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13. SURFACE PREPARATION AND PAINTING OF MAGNESIUM ALLOY SURFACES

13.1 General. When exposed to the atmosphere, magnesium and magnesium alloys corrode readily. The products of corrosion are oxides, hydrated oxides and carbonates of magnesium. These products are easily damaged and give little protection in most outdoor environments, but as long as they are not damaged, they do afford some protection.

Corrosion products of magnesium are alkaline and are destructive to paint oils. Hence, their complete removal is necessary before the metal is painted. Also, because of magnesium's strongly anodic nature, corrosion of the metal left unpainted or exposed by damage to a paint coat is accelerated. Hence, early discovery and repair of such conditions are necessary.

Cleaning methods and treatments to be described in this chapter are the subject matter of MIL-M-3171, "Magnesium Alloy, Process for Pretreatment and Prevention of Corrosion on" and of MIL-M-45202, "Magnesium Alloys, Anodic Treatment of".

13.2 Cleaning. Thorough cleaning is essential to satisfactory chemical treatment and painting of magnesium alloy. The nature of the part, the type of soil and the chemical treatments to follow govern the choice of cleaning method. For details of the methods, see section 2.

Before other cleaning methods are used, gross amounts of grease or oil are removed with organic solvents using vapor degreasing or wiping methods.

Use of sandpaper, wire brush or steel wool is appropriate for removal of corrosion products from wrought articles, sheets and extrusions. Steel wool must not be used on die cast parts, because the acid treatment needed to dissolve small embedded particles of the wool removes too much alloy.

Light blasting with sand, grit or shot may be used to remove corrosion products, discoloration and paint from parts of substantial thickness. Blasting, sandpaper and steel wool leave particles of abrasive on the alloy. To remove the particles, these operations are followed by pickling in solutions of sulfuric or nitric-sulfuric acid. The formulations are as follows:

Solution make-up

(a) Sulfuric acid pickle

	<u>gallon</u>	<u>liter</u>
Sulfuric acid (sp gr 1.84)	4 fl oz	31 mL
Water	to volume	to volume

(b) Nitric-sulfuric pickle

Nitric acid (sp gr 1.42)	10.25 fl oz	80 mL
Sulfuric acid (sp gr 1.84)	2.5 fl oz	20 mL
Water	115 fl oz	900 mL

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Pickling is carried out at room temperature in tanks lined with ceramic, rubber, lead or other suitable material. Depending on temperature, an immersion time of 10 to 15 seconds will remove approximately 0.002 in (51 μ m) of metal in a freshly prepared pickle.

When using flux in the welding operations, the welded sections shall be thoroughly cleaned immediately after the operation to remove all traces of flux. Where possible, hot water and a hard brittle brush shall be used to insure thorough flux removal. Inaccessible welded sections shall be washed with a high velocity stream of water (preferably hot). They shall then be immersed for 1 hour in a 2 to 5% sodium dichromate solution maintained at 180 to 212°F (82-99°C). The parts are then rinsed in cold running water.

Before most chemical treatments are applied, a final cleaning in a hot 190-212°F (88-100°C) alkaline solution is specified.

	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	1.3 oz	10 g
Sodium hydroxide (NaOH)	8 oz	60 g
Soap, or other wetting agent	0.1 oz	0.8 g
Water, to make	1 gal	1 L

In place of the above solution, proprietary alkaline cleaners may be used, but in no case must the pH be lower than 8.

If direct current is available, cathodic cleaning in the above solution may be used. The parts are made cathodic in the bath and a current of 10 to 40 A/ft² (1 to 4 A/dm²) at six volts is applied. Cathodic cleaning requires less time than simple contact cleaning. In either case, the parts must receive a thorough rinse in cold running water.

Graphite lubricant on hot formed magnesium alloy sheet requires a stronger caustic solution for removal. For such parts, a 10 to 20 minute soak in a solution made with 13 ounces of sodium hydroxide per gallon (100 g/L), used hot [190-212°F (88-100°C)], is specified. The pH must be at least 13. After the rinse, the parts are immersed for approximately three minutes in a chromic-nitrate pickling solution.

Chromic-nitrate pickle	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Chromic acid (CrO_3)	24 oz	180 g
Sodium nitrate (NaNO_3)	4 oz	30 g
Water, to make	1 gal	1 L

The use of pickling solutions as a step in cleaning was mentioned in connection with sandblasting and sandpapering. Pickling removes more or less metal and thus frees embedded sand or other matter and allows it to be rinsed off. The usual method is to immerse the parts, but other methods of applying the solution (brushing, spraying, flowing) may be used, provided the other requirements are met.

Three acid pickling solutions (sulfuric acid, nitric-sulfuric acid and chromic acid-nitrate) have been described. Others are:

Chromic acid pickle	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Chromic acid (CrO_3)	24 oz	180 g
Water, to make	1 gal	1 L

The chromic acid pickle is suitable for cleaning parts where dimensional tolerances are small, since it causes no dimensional loss. It removes old chemical finishes and surface oxidation. It is not suitable for parts containing copper inserts. It does not remove contaminants left by sanding with sandpaper or blast.

Chromic-nitric-hydrofluoric pickle	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Chromic acid (CrO_3)	37.5 oz	280 g
Nitric acid (sp gr 1.42)	3.25 fl oz	25 mL
Hydrofluoric acid (60% HF)	1 fl oz	8 mL
Water, to make	1 gal	1 L

The chromic-nitric-hydrofluoric pickle is primarily used for cleaning castings, especially die-castings.

Phosphoric acid pickle	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Phosphoric acid (85% N_3PO_4)	115 fl oz	900 mL
Water, to make	1 gal	1 L

The phosphoric acid pickle may be used for all types of die castings.

Acetic-nitrate pickle	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Glacial acetic acid (CH_3COOH)	25.5 fl oz	200 mL
Sodium nitrate (NaNO_3)	6.7 oz	50 g
Water, to make	1 gal	1 L

The acetic-nitrate pickle is designed to insure maximum protective finishing for magnesium sheet, other wrought forms and on castings heat treated in solutions. It removes from 0.0005 to 0.001 in (13-25 μm) of metal and hence is not suitable for cleaning parts where dimensional tolerances are small.

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13.3 Chemical treatments. About 10 more chemical and anodic treatments take care of most magnesium alloys. Two of these are ceramic-like coatings. The HAF process was developed by Frankford Arsenal and the Dow 17 process was developed by Dow Chemical Company. These ceramic coatings are relatively brittle and suitable for use only on rigid parts (such as castings) and on extrusions and sheets whose dimensions are large enough to make them rigid. Specification MIL-M-45202 covers HAF and Dow 17 anodic processes for magnesium. The Dow 17 coating is not as hard as but smoother than, and somewhat lower in cost than, the HAF coating. These coatings are fully described in section 5. Chemical treatments are the subject matter of Specification MIL-M-3171, Magnesium Alloy, Processes for Pretreatment and Prevention of Corrosion on. They are:

- Type I - Chrome pickle treatment
- Type III - Dichromate treatment
- Type IV - Galvanic anodizing treatment
- Type VI - Chromic acid brush-on treatment
- Type VII - Fluoride anodizing process plus corrosion preventive treatment
- Type VIII - Chromate treatment

These treatments are fully described in section 4, "Chemical Treatments and Pretreatments" and section 5, "Electrochemical Conversion Coatings".

A chemical coating for magnesium (Dow No. 23) was developed by the Dow Metal Products Company and Ordnance Tank-Automotive Command. The Stannate Immersion treatment was developed for use with magnesium parts containing dissimilar metal inserts or fasteners. The coating is produced by the following process:

- a. After (1) alkaline cleaning (section 13.2) and rinsing and (2) hydrofluoric acid pickling (190 mL/L of 60% HF), the material is immersed in the stannate bath consisting of :

	Solution make-up	
	<u>gallon</u>	<u>liter</u>
Potassium stannate ($K_2SnO_3 \cdot 3H_2O$)	6.67 oz	50 g
Tetrasodium pyrophosphate ($Na_4P_2O_7$)	6.67 oz	50 g
Sodium hydroxide (NaOH)	1.34 oz	10 g
Sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$)	1.34 oz	10 g

Time of immersion: 20 minutes, minimum

Temperature of immersion: 170 to 190°F (77 to 88°C)

- b. Rinse in cold water.
- c. If parts are to be painted, dip in a 5% sodium acid fluoride ($NaHF_2$) solution for 30 sec at room temperature.
- d. Rinse thoroughly in cold water.
- e. Hot water rinse as final step will facilitate drying.

This coating can be used where steel is in combination with magnesium (e.g., steel inserts in magnesium castings) and both the steel and magnesium receive a protective coating. Certain aluminum alloys, in conjunction with magnesium, prevent the coating from being formed, but the process works satisfactorily with 5056 and 6061 aluminum alloys in conjunction with magnesium. This coating also gives sacrificial protection to steel, can be easily painted and shows considerable promise in the protection of magnesium.

13.4 Selection of paint and its application. In general the two prepainting treatments are specified for new parts, depending on whether or not the part is rigid. Rigid parts should receive one of the heavy anodic coatings: HAE or Dow No. 17; nonrigid parts, the sealed chromate treatment. In certain cases the light or thin anodic coatings (as specified in MIL-M-45202, type I) can be used on nonrigid parts. When one of the prepainting treatments indicated above is not feasible, wash primer, pretreatment, DOD-P-15328, with 25 to 50% of the required phosphoric acid, may be substituted.

The primer previously specified and used in most instances for magnesium alloy has been Specification TT-P-666, "Primer Coating, Zinc Yellow (Zinc Chromate), for Aluminum Surfaces". The surface of magnesium is ordinarily alkaline with a pH of about 10.5 to 10.8. This alkalinity is partially offset by one of the pretreatments previously discussed but the primer should also be alkaline resistant. Since alkyds are sensitive to alkalis, the TT-P-66 primer is replaced by improved primers for magnesium. Some vehicles which are not alkali sensitive are vinyls and epoxies. Primers specifying these vehicles are: MIL-P-15930, "Primer Coating, Vinyl-Zinc Chromate, (Formula No. 120) for Hot Spray" and MIL-P-23377, "Primer Coating, Epoxy-Polyamide, Chemical, and Solvent Resistant".

Alkyd-zinc chromate primer meeting TT-P-1757, "Primer Coating, Zinc Chromate, Low-Moisture-Sensitivity", may be substituted for MIL-P-15930 or MIL-P-23377, but only when approved by the procuring activity. The use of TT-P-1757 would be dependent upon the top coat that is used.

A pretreatment coating meeting DOD-P-15328 should be specified as a pretreatment prior to application of either TT-P-1757 or MIL-P-15930.

Some examples of painting systems for magnesium are as follows:

	<u>Lusterless</u>	<u>Semigloss</u>	<u>Gloss</u>
Priming	TT-P-1757 MIL-P-15930 MIL-P-23377	TT-P-1757 MIL-P-15930 MIL-P-23377	TT-P-1757 MIL-P-15930 MIL-P-23377
Second or Finish Coat	TT-E-527 TT-E-515	TT-E-485 TT-E-529 MIL-L-52043	TT-E-489

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The steps in a typical finishing system (semigloss) for a magnesium alloy sheet consist of:

- (a) Remove grease or oil using a suitable vapor degreasing solvent according to Specification MIL-M-3171, para. 3.2.1.
- (b) Clean with alkali according to Specification MIL-M-3171, para. 3.2.3.
- (c) Apply sealed chrome-pickle according to Specification MIL-M-3171, para. 3.4.1.
- (d) Apply pretreatment coating conforming to DOD-P-15328, followed by the primer MIL-P-15930, or apply primer conforming to MIL-P-23377.
- (e) Apply finish paint conforming to Specification TT-E-485.

14. SURFACE PREPARATION AND PAINTING OF COPPER, TIN, LEAD, TITANIUM, AND THEIR ALLOYS

14.1 General. Protective paint systems for the nonferrous metals described in this chapter follow the same general pattern as has been described for other metals. The surface is cleaned and receives a prepaint treatment. The primer paint coat is applied, then the intermediate paint coat (if any) and finally, the finish paint coat. To repeat, inadequate or improper cleaning may cause detrimental effects on all succeeding operations. The preparation and painting of each metal will be described briefly.

14.2 Copper and copper alloys. Traditionally, copper has been considered to be a corrosion resistant metal. Protective paint coatings are seldom applied to it or its alloys because of the inherent resistance of the metal. The corrosion of copper and its alloys is affected by the contaminants present and the composition of the alloy. The rate of attack generally is less severe in rural atmospheres and more severe in industrial, tropical and marine atmospheres. On weathering, copper develops a brown or black tarnish that turns to a green patina (mainly basic copper sulfate) over a period of years. This serves to protect the copper from further corrosion. Painting may be necessary to conform to a color scheme, either for camouflage or to indicate function. Prior to painting, any grease or oil on the surface should be removed by solvent cleaning (TT-C-490, method II). Any patina or other corrosion products should be removed by either sandblasting (TT-C-490, method I) or by the use of a phosphoric acid etch (MIL-C-10578, type I). Keep the surface wet with MIL-C-10578 solution for one to three minutes before rinsing. The phosphoric acid treatment should be followed by a thorough rinsing with clean water, using a hose or a sponge and clean water within five minutes after application. Both the sandblasting and the phosphoric acid treatments produce a roughened surface on the metal which improves the adhesion of the paint. On clean copper and copper alloys, a good prepaint treatment is a coat of wash primer (DOD-P-15328). For best results, the wash primer treatment should not be used under baked paint coats, although it may be used under hot spray lacquer. Paint primers covered by TT-P-664, TT-P-1757, MIL-P-11414 and MIL-P-12742 (phenolic primer) are suitable for priming copper and copper alloys. The usual enamels (TT-E-485, TT-E-489, TT-E-527, TT-E-529, TT-E-515, TT-E-516 and TT-E-522, phenolic enamel) and lacquers (TT-L-32, TT-L-58 and MIL-L-11195) may be applied as top coats.

Two suggested paint systems for exterior surfaces of copper, brass or bronze are given below:

I - Enamel

- (a) After cleaning, sand or sandblast thoroughly.
- (b) Apply primer conforming to TT-P-1757, TT-P-636 or TT-P-664; or apply pretreatment coating conforming to DOD-P-15328. Follow with one of the primers listed above.
- (c) Apply one coat of semigloss enamel conforming to TT-E-529.

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11 - Lacquer

- (a) After cleaning, either sandblast or etch with phosphoric acid according to MIL-C-10578.
- (b) Apply one coat of primer conforming to MIL-P-11414 or apply pretreatment coating conforming to DOD-P-15328. Follow with the primer named above.
- (c) Apply one coat of hot spray lacquer conforming to MIL-L-11195.

A clear waterproofing varnish (MIL-V-13811) applied to clean copper electrical assemblies will protect them against moisture and corrosion.

Interior surfaces of optical instruments (copper, brass or bronze) may be given a nonreflecting, black, chemical treatment according to MIL-F-495. When specified, this finish can serve as a base for subsequent coatings (such as lacquer, varnish, oil and wax).

14.3 Tin andterne plate. Tin and terne plate (the latter contains 10 to 25% tin, the remainder being lead) is often painted to protect the surface from wear, abrasion and weathering. Generally, paint coatings adhere well to tin and terne plate, provided that the coating of palm oil acquired in the factory and any other oil or grease is removed with solvent, according to TT-C-490, method II. A good prepaint treatment for clean tin or terne plate is a coat of wash primer (DOD-P-15328). This is followed by a good priming paint (TT-P-1757, for example) and the usual enamels or lacquers.

Specifications MIL-P-19602, MIL-E-19603 and MIL-V-21064 cover a primer size coating (baked on), an enamel (baked on) and a finishing varnish (baked on), respectively, as a coating system for clean tin and terne containers. The system is intended for roller coat factory application to flat stock metal prior to fabrication of the containers.

14.4 Titanium and titanium alloys. Titanium exhibits excellent resistance to corrosion in various types of atmospheres and waters, even after long exposure. The good resistance to corrosion is ascribed to a thin stable film of oxide or absorbed oxygen which readily forms at low temperatures. At high temperatures, titanium becomes embrittled and corrodes. Where painting is necessary, the metal first is freed from oil, grease and foreign matter with solvent (TT-C-490, method II). Then the surface is sandblasted (TT-C-490, method I). When sandblasting is not feasible, the clean surface should receive a pretreatment coating (DoD-P-15328). The usual priming paint (TT-P-1757, for example) is then applied, followed by the customary enamels or lacquers as used by the Military.

14.5 Lead. Lead has good resistance to corrosion in almost all types of atmospheres. It likewise has good resistance to corrosion by a variety of chemicals including chromic, sulfuric, sulfurous and phosphoric acids. On exposure to the atmosphere, a thin film of lead carbonate and lead sulfate (and possibly oxide) form on the surface, which protects the metal from further corrosion. Lead is seldom painted and no serious problem is involved in painting; its paint-holding is good. As a precaution, in case of doubt, wash primer (DOD-P-15328) or proprietary oxalate or chromate treatments might be used. Suitable priming paints for use under enamel top coats are TT-E-485, TT-P-636, TT-P-659, TT-P-664, TT-P-1757 and MIL-P-11414. Suitable primers for lacquer are TT-P-664, TT-P-1757 and MIL-P-11414.

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15. PRESERVATIVE TREATMENTS AND PAINTING OF WOOD

15.1 General. Mold and other organisms that promote decay of wood are everywhere. Under favorable conditions of moisture and temperature, they grow at the expense of wood. However, with the aid of certain treatments, wood may be preserved, usually for the life of the article made of it. Wood treated with suitable preservatives holds paint longer than otherwise.

Penetrating preservatives play a more important role in preventing decay of wood than does paint. They function particularly when the coat of paint has been damaged. However, paint does contribute to the extent that it remains sound and excludes moisture. Paint also provides color for identification and concealment. Many paints reduce fire hazard of wood to some extent by being less combustible than wood and by covering sharp edges and splinters.

Hence, it is good to treat all wood parts that are exposed to the weather. Most of these are also painted.

15.2 Surface preparation. Before a preservative treatment is applied to it, the wood must be suitably prepared. Wood to be painted after treatment must not contain more than 20% of moisture before the treatment. The surface itself must be dry and free from moisture and foreign matter, such as grease and dirt. Where possible, the wood parts shall be cut to final dimensions and holes, mortises, tenons and grooves shall be made before treatment. In the event that any of these operations become necessary after treatment, the newly exposed wood shall be liberally treated with the preservative.

Practically all wood parts used in ordnance materiel must be treated with preservative. Unless mishandled, a treated part is ready for paint. Occasionally deposits from the preservative treatment may be encountered. These must be brushed or wiped off.

15.3 Preservative treatment. MIL-STD-171 provides for three preservative treatments [preferred (finish 25.1), alternate 1 (finish 25.2) and alternate 2 (finish 25.3)] in decreasing order of effectiveness. The differences in these treatments are the manner and duration of contact of wood with preservative. All three require the same preparation of the wood and the same preservative, pentachlorophenol. These are described more fully in table XI (table XVII, MIL-STD-171).

15.4 Selection of paint and application. Paints for wood, including parts exposed out-of-doors, belong to the alkyd enamel type. Conventional house paint does not dry to film hard enough for service conditions, although weatherwise it would endure somewhat longer than the enamel type. Typical systems are shown in table XII.

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Some Typical Paint Systems for Wood.

	<u>Lusterless</u>	<u>Semigloss</u>	<u>Gloss</u>
Primer	TT-P-636	TT-P-636 or TT-E-485	TT-P-636
Second Coat	TT-E-529 semigloss	TT-E-529	TT-E-489
Third Coat	TT-E-527		

In addition to the two and three coat enamel systems, several special finishing systems are provided for parts like plotting boards, instrument cases, etc. These systems use materials such as olive drab stain, linseed oil, shellac varnish, spar varnish and lacquer enamel.

16. MISCELLANEOUS ORGANIC FINISHES

16.1 General. In addition to the paints, varnishes and lacquers discussed in section 8, there are a few miscellaneous finish types to be considered. These include petroleum oils and the like, used as supplementary corrosion preventives on plain or phosphated metal, underbody coatings for motor vehicles, nonskid coatings, strippable coatings and graduation fillers.

16.2 Corrosion preventives. Most of these are straight lubricating oil or waxes or blends. Their function is to exclude moisture and they are used where paint may be inappropriate. For example, Specification DOD-P-16232, "Phosphate Coatings Heavy", provides for supplementary finishes of the corrosion preventive type.

The preventives most frequently used in conjunction with DOD-P-16232 phosphate coatings are:

- (a) MIL-C-16173, grade 3, Corrosion Preventive, Solvent Cutback, Cold Application
- (b) VV-L-800, Lubricating Oil, General Purpose, Preservative (Water Displacing, Low Temperature)
- (c) MIL-L-3150, Lubricating Oil, Preservative, Medium
- (d) MIL-C-16173, grade 1A, Corrosion Preventive, Solvent Cutback, Cold Application

Others are covered by the blanket clause "supplementary treatment, as specified". In addition to the four mentioned above, practically all others are selected from Specification MIL-P-116, "Preservation, Methods of" (see table VI).

16.3 Underbody coating. The underbody of motor vehicles requires special protection from moisture and abrasion. Because the moisture may contain corrosive materials and because abrasion from flying gravel is severe, heavy coats of the coating are needed, ranging from 0.0625 to 0.125 in (1.6 to 3.2 mm) thickness. The coating is a mixture of asphaltic compounds and fibrous asbestos fiber. It is invariably applied by spray. This coating is covered by Specification TT-C-520.

16.4 Nonskid coating. This is a paint used to provide nonskid surfaces on floors and pedals of tanks. It consists of paint to which abrasive particles have been added. This type of coating is covered by Specifications MIL-D-23003 and MIL-W-5044.

16.5 Graduation filler. This product is wiped into etched graduation marks on instruments to make them more legible. It comes in four colors and in paste or crayon form. This material is covered by Specification TT-F-325.

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16.6 Strippable coatings. Strippable coatings are used for temporary coverage of materials for storage or for protection from contamination or damage during fabrication. Specification TT-C-517 covers a strippable masking for spray booths or glass; MIL-C-3254 is a bridging, strippable coating for storage of materials; and MIL-C-6799 covers a water emulsion based strippable protective coating for application over metallic, painted and plastic surfaces.

16.7 Reflective coating. This is a reflective coating compound for marking surfaces for safety to insure their visibility at night. This coating is covered by Specification TT-C-1060.

TABLE VI. Preservatives (MIL-P-116G, table II).

Type	Description (not title)	Specification
P-1	Thin film preservative (hard drying, cold application)	MIL-C-16173, Gr. 1
P-2	Thin film preservative (soft film, cold application)	MIL-C-16173, Gr. 2
P-3	Thin film preservative, water displacing (soft film, cold application)	MIL-C-16173, Gr. 3
P-6	Light preservative (soft film)	MIL-C-11796, Cl. 3
P-7	Medium preservative oil (cold application)	MIL-L-3150
P-9	Very light preservative oil, water displacing (cold application)	VV-L-800
P-10	Engine preservative oil	MIL-L-21260, Type I, Gr. 10, 30 or 50, or Type II, Gr. 10 or 30
P-11	Preservative grease (application as required)	MIL-G-10924
P-14	Corrosion preventive (nontoxic)	MIL-C-10382
P-15	Hydraulic preservative oil	(as specified)
P-17	Instrument bearing preservative oil	MIL-L-6085
P-18	Volatile corrosion inhibitor	MIL-P-3420 MIL-F-22019 MIL-B-22020 MIL-I-22110
P-19	Thin film preservative (transparent, nontacky)	MIL-C-16173, Gr. 4
P-20	Lubricating oil, contact and volatile corrosion inhibitor treated	MIL-L-46002 MIL-I-23310
P-21	Thin film preservative, water displacing (soft film, cold application, low pressure steam removable)	MIL-C-16173, Gr. 5

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17. PAINT SYSTEMS USED BY THE ARMY FOR ORDNANCE AND EQUIPMENT

17.1 General. Section 9 describes in some detail the individual paints used for Military finishes. Tables II, III, IV and V summarize the important characteristics of the paints. This section considers systems of paint — the specific combinations of primer, intermediate and finish coats — for use on various types of material. Tables VII through X, reproduced from MIL-STD-171, Finishing of Metal and Wood Surfaces, show the systems that account for most ordnance painting requirements.

17.2 Paint systems for metals. The following tables, reproduced from MIL-STD-171, give the principal paint systems which can be specified by reference to that document:

Table VII. Lusterless paint systems for metal surfaces.

Table VIII. Semigloss paint systems for metal surfaces.

Table IX. Gloss paint systems for metal surfaces.

Table X. Miscellaneous paint systems for metals.

The primary subdivision in the tables is by gloss. Lusterless systems are identified by the number 20, semigloss by 21 and gloss by 22. Following the decimal that sets off the above designations, the members of each series are designated in numerical order. Gaps in the series are left by systems that have been dropped or have been consolidated with remaining systems.

Some of the systems give equal protection and may be used interchangeably at the discretion of the procuring agency.

The arrangement of paints according to systems allows specific paints to be added or removed as improvements are made in paint technology. Such changes will not affect the designations of the basic systems and can be made by revising a single document, instead of hundreds of thousands of drawings.

17.2.1 Primers. The primers listed in tables VII, VIII, IX and X are primarily for use on steel. These primers in most cases permit the use of iron oxide pigments which are not recommended in primers for aluminum and magnesium. For use on aluminum and magnesium alloys the following primers should be substituted (see MIL-STD-171):

For Aluminum

MIL-P-1757
MIL-P-15930
MIL-P-23377

For Magnesium

DOD-P-15328 plus
MIL-P-15930 or
TT-P-1757
MIL-P-23377

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17.3 Paint systems for wood. The following tables from MIL-STD-171 give the principal paint systems for wood which can be specified by reference to that document:

Table XI. Wood preservative treatments.

Table XII. Paint systems for wood.

The primary subdivision in table XII is by gloss. Lusterless systems are identified by the number 26, semigloss by 27 and gloss by 28.

In several systems, the priming coat is TT-P-636 or TT-E-485, both of which are rust inhibitive primers. This provision allows the same paint to be used on steel and accompanying wood, saving time and material.

MIL-STD-171 also contains a number of miscellaneous systems for wood. These are rather fully described in that document and are not repeated here.

17.4 Paint uses. Table XIII gives a condensed description of paint systems arranged for quick reference by use.

TABLE VII. Lusterless paint finishes for metal surfaces
(MIL-STD-171, Table XIII).

Finish	First Coat	Topcoat(s)	Remarks
20.1	--	TT-E-516 or MIL-E-52891 }	One coat finish for projectiles, grenades, etc.
20.2	--	MIL-L-11195	One coat finish for projectiles, grenades, etc.
20.4	MIL-P-114141/ or TT-P-664	MIL-L-11195	Two coat lacquer finish for auto- motive and general use.
20.5	TT-P-6641/ or MIL-P-11414	MIL-E-52891	Two coat alkyd finish for general use, except poor gasoline resistance.
20.8	TT-P-6361/ or TT-P-664	TT-E-527	Two coat alkyd finish for general use.
20.9	TT-P-6641/	TT-P-515	Quick drying, two coat alkyd finish for general use.
20.10	MIL-P-114141/ or TT-P-664	TT-P-662 plus MIL-L-11195	Three coat lacquer finish for automotive or general use.
20.13	MIL-P-12742	TT-E-522	Two coat phenolic enamel for parts wholly or partly immersed in water.
20.18	MIL-P-12742 (2 coats)	TT-E-522	Three coat phenolic enamel for parts wholly or partly immersed in water; also used on wood.
20.19	TT-P-636 or TT-E-4852/ 3/	MIL-E-52798	General camouflage finish.
20.20	TT-P-664 or TT-E-4853/ 4/	MIL-E-52835	Baking Forest Green
20.21	TT-P-6643/	MIL-L-52909	Acrylic Forest Green.
20.22	TT-P-664 or 3/ MIL-P-11414	MIL-L-52926	Hot spray Forest Green.
20.23	TT-P-6643/	MIL-E-52929	Flash dry enamel Forest Green.
20.24	MIL-P-521925/	MIL-C-46168	Chemical agent resistant camouflage.

1/ When these finishes are specified for aluminum or magnesium, the primers shall be as specified in MIL-STD-171, paragraph 5.3.1 for aluminum and paragraph 5.3.2 for magnesium.

2/ When using TT-E-485, types II or IV can be used.

3/ For aluminum, TT-P-1757 or MIL-P-23377 should be used.

4/ When using TT-E-485, type IV should be used.

5/ For aluminum, MIL-P-23377 should be used.

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TABLE VIII. Semigloss paint finishes for metal surfaces
(MIL-STD-171, Table XIV).

Finish	First Coat	Topcoat(s)	Remarks
21.1	---	TT-E-485	One coat finish for ammunition containers, gasoline drums, etc.
21.3	TT-P-6361/ or TT-P-664	TT-E-529	Two coat alkyd finish for general use.
21.5	TT-E-4851/	TT-E-485	Two coat alkyd finish for general use.
21.7	MIL-P-52192 (bake)	MIL-E-480 (Bake)	Two coat baked finish.
21.9	TT-P-6361/ or TT-P-664	TT-E-529 (2 coats)	Three coat alkyd finish for general use.
21.11	MIL-P-114141/ or TT-P-664	MIL-L-52043	Two coat lacquer finish for automotive materials.
21.12	MIL-P-114141/ or TT-P-664	TT-P-662 plus MIL-L-52043	Three coat lacquer finish for automotive materials.
21.13	MIL-P-114141/ or TT-P-664	MIL-L-52043 (2 coats)	Three coat lacquer finish for automotive materials.
21.19	TT-P-1757	TT-E-485 (2 coats)	Three coat finish for general use.
21.20	MIL-P-14553 (Dip and bake) or TT-P-664 (Spray and bake)	TT-E-485 or TT-E-529 (Baking type)	Two coat baking finish for automotive equipment.
21.21	TT-P-6641/ or MIL-P-11414	MIL-E-52227	Two coat fast drying alkyd finish for general use.

1/ When these finishes are specified for aluminum or magnesium the primers shall be as specified in MIL-STD-171, paragraph 5.3.1 for aluminum and paragraph 5.3.2 for magnesium.

TABLE IX. Full gloss paint finishes for metal surfaces
(MIL-STD-171, Table XV).

Finish	First Coat	Topcoat(s)	Remarks
22.2	TT-P-6361/ or TT-P-664	TT-E-489	Two coat alkyd finish for general use.
22.3	MIL-P-114141/ or TT-P-664	MIL-L-12277 (2 coats)	Multiple coat lacquer finishes, automotive use.
22.4	MIL-P-114141/ or TT-P-664	TT-P-662 plus MIL-L-12277 (2 coats)	Multiple coat lacquer finishes, automotive use.
22.9	MIL-P-14553 (Dip and bake) or TT-P-664 (Spray and bake)	TT-E-489 (Baking type)	Two coat baking finish.
22.10	TT-P-6361/ or TT-P-664	TT-E-1593	Two coat silicone-alkyd finish for general exterior use. Outstanding gloss and color retention.

1/ When these finishes are specified for aluminum or magnesium the primers shall be as specified in MIL-STD-171, paragraph 5.3.1 for aluminum and paragraph 5.3.2 for magnesium.

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TABLE X. Special paint finishes for metals
(MIL-STD-171, Table XVI).

Finish	Description of Coating	Remarks
23.1	TT-E-485 plus MIL-E-5558, type 1	Wrinkle finish.
24.1	MIL-P-46105, 2-3 mil dry film thickness	Weld through primer.
24.2	MIL-C-450	Asphalt coating for painting the interior of ammunition items prior to being filled with explosives. Not suitable as primer coat for painting.
24.3	TT-C-520 (0.0625 in minimum dry film thickness)	Underbody coating for motor vehicles.
24.4	MIL-P-22636 (0.2-0.4-mil dry film thickness) plus MIL-P-14458 (2.5-3.0-mil dry film thickness)	Red fuming nitric acid resistant coating.
24.5	TT-P-28	Heat resistant aluminum finish for temperatures to 1200°F (649°C).
24.6	MIL-P-22332	Primer for painting the interior of ammunition items prior to being filled with explosives. It may also be used to prime exterior surfaces.
24.7	TT-C-494	Acid resistant asphalt paint for general use.
24.8	MIL-C-22750 (1.5 mils min dry film thickness)	Epoxy topcoat resistant to hydraulic fluid spray.
24.9	MIL-P-23377 (2 coats-bake) plus TT-E-529 (2 coats-baking type)	For magnesium or other metals subject to severe exposure.
24.10	TT-V-51 (2 coats)	Two coat acid resistant finish for general use.
24.11	MIL-P-52192	Primer for rocket motor cases. Will withstand vapor degreasing and provide corrosion resistance.
24.12	TT-P-1757 Color Y (2 coats)	For missile use on parts requiring primer only. Apply over pretreatment.

TABLE X. Special paint finishes for metals. (Cont'd)

Finish	Description of Coating	Remarks
24.13	TT-V-119 pigmented with 20 ounces per gallon of TT-P-320, type II class B, 0.5-0.7 mil dry film thickness	Oil resistant aluminum coating for interior of gear cases or housings.
24.14	MIL-C-4556 (2 coat system, 3.0 mil minimum dry film thickness per coat)	Epoxy coating kit for interior of fuel transportation and storage tanks.
24.15	MIL-P-23236 class 3 (3.0-4.0 mil dry film thickness)	Zinc rich primer for steel structures that receive severe exposure to adverse weather, condensing moisture, corrosive atmospheres and marine environments.
24.16	MIL-P-38336 (3.0-4.0 mil dry film thickness)	
24.17	MIL-C-23377, MIL-C-22750	For protection of areas exposed to chemicals and solvents.
24.18	TT-P-664 ² / ₁ , MIL-C-46127 plus MIL-E-46096	Lustreless olive drab solar heat reflecting enamel. Performance equivalent to TT-E-516.
24.19	TT-636 ² / ₁ , MIL-C-46127 ³ / ₁ plus MIL-E-46117	Lusterless olive drab solar heat reflecting enamel. Performance equivalent to TT-E-527.
24.20	TT-P-664 ⁴ / ₁ , MIL-C-46127 ³ / ₁ plus MIL-L-46138	Lusterless olive drab solar heat reflecting lacquer. Performance comparable to MIL-L-19538.
*24.21	MIL-E-46136	Semigloss olive drab solar heat reflecting enamel.
24.21.1	TT-P-636 ² / ₁ , MIL-C-46127 ³ / ₁ plus MIL-E-46136, type I	Performance equivalent to TT-E-529, class A.
24.21.2	TT-P-664 ² / ₁ , MIL-C-46127 ³ / ₁ plus MIL-E-46136, type II	Performance equivalent to MIL-E-52227.
24.21.3	TT-P-664 ² / ₁ , MIL-C-46127 ³ / ₁ plus MIL-E-46136, type III	Performance equivalent to TT-E-529, class B.
*24.22	MIL-E-46139 (2 coats)	Semigloss rust inhibiting olive drab solar heat reflecting enamel for ferrous metal.

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TABLE X. Special paint finishes for metals. (Cont'd)

Finish	Description of Coating	Remarks
24.22.1	MIL-E-46139, type I (2 coats)	Performance equivalent to TT-E-485, type II.
24.22.2	MIL-E-46139, type II (2 coats)	Performance equivalent to TT-E-485, type IV.
24.23	MIL-L-46142	Gray or near black lusterless solar heat reflecting lacquer for marking of finish coat. Performance equivalent to TT-L-20.
24.24	TT-P-1757 ^{4/} , MIL-L-46142	Gray or near black lusterless solar heat reflecting lacquer for finish coat.

* These are general headings and shall not be specified. The specific finish number(s) only shall be specified.

- 1/ MIL-E-5558 coating shall be applied at a wet film thickness of 5 to 8 mils, unless otherwise specified. When this finish is specified for aluminum or magnesium the primers shall be as specified in MIL-STD-171, paragraph 5.3.1 for aluminum and paragraph 5.3.2 for magnesium.
- 2/ When these finishes are specified for aluminum or magnesium the primers shall be as specified in MIL-STD-171, paragraph 5.3.1 for aluminum and paragraph 5.3.2 for magnesium, except that MIL-P-15930 shall not be used.
- 3/ MIL-C-46127 is required when these finishes are specified for ferrous metal. It is not required when used on aluminum or magnesium.
- 4/ When this finish is specified for aluminum or magnesium, MIL-P-7962 primer shall be used.

TABLE XI. Wood preservative treatments
(MIL-STD-171, Table XVII).

Finish	Requirements
25.1	<p><u>Vacuum pressure or vacuum soak treatment.</u> The clean, dry, well seasoned wood, free of outer and inner bark, shall be surfaced to the correct cross-sectional dimension and then treated by vacuum and pressure or vacuum and soak. The treating material shall conform to composition A of TT-W-572. Retention on treatment shall be not less than 3 pounds per cubic foot and not more than 6 pounds per cubic foot for hard woods, or more than 8 pounds per cubic foot for soft woods. If retention is less than 3 pounds per cubic foot on initial test cycle, treatment shall be to refusal, using a soak cycle of not less than 24 hours. A maximum of 14 days after treatment, two representative samples from each charge shall be removed and tested for paintability in accordance with applicable section of TT-W-572. The temperature of the preservative during the treating process is to be at the discretion of the contractor, so long as the requirements of TT-W-571 as to penetration and the above retention requirements are met.</p>
25.2	<p><u>Immersion treatment.</u> Dress the wood part to correct cross-sectional dimensions. Immerse in pentachlorophenol solution, TT-W-572, for not less than 4 hours. Allow the treated wood to air dry or kiln dry before it is painted.</p>
25.3	<p><u>Surface treatment.</u> Dress the wood part to correct cross-sectional dimensions. Apply one liberal coat of pentachlorophenol solution, TT-W-572. When practical, apply the solution by immersion for not less than 3 minutes. Otherwise, brushing or low pressure spraying (no atomization) is acceptable. Allow the treated wood to air dry or kiln dry before it is painted.</p>

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TABLE XII. Paint finishes for wood
(MIL-STD-171, Table XVIII).

Finish	First Coat	Topcoats(s)	Remarks
LUSTERLESS			
26.1	TT-P-636	TT-E-529 plus TT-E-527	Three coat alkyd finish for general use.
26.3	MIL-P-12742 (2 coats)	TT-E-522	Three coat phenolic finish for wood or metal.
SEMIGLOSS			
27.1	TT-P-636	TT-E-529 (2 coats)	Three coat alkyd finish for general use.
27.3	TT-E-485 or TT-P-636	TT-E-485 or TT-E-529	Two coat alkyd finish for general use.
FULL GLOSS			
28.1	TT-P-636 ^{1/}	TT-E-489	Two coat or three coat alkyd finish for general use.
28.2	TT-P-659 ^{1/}	TT-E-489	Two coat or three coat alkyd finish, in white, not for exposure to weather.
28.3	TT-P-336 When needed for filling	TT-V-121 (2 coats)	Spar varnish.
28.5	TT-S-300; specify type and grade	TT-S-300	Shellac varnish.

^{1/} An additional coat of TT-P-636 primer or TT-P-659 primer surfacer shall be applied, if necessary for proper surfacing, prior to applying the indicated topcoat.

TABLE XIII. Condensed description of paint systems.

Use on Metal	Type Binder	Number of Coats	Finish		
			Lusterless	Semigloss	Gloss
General, including automotive, except paint TT-E-516, top coat in system 20.5; not suitable where gasoline may contact it; anticorrosive primers contribute to weather resistance.	Alkyd	2	(20.5, 20.8, 20.9)	21.3, 21.5	22.2
		3		21.9	
	Cellulosic	2	20.4	21.11	--
	Lacquer	3	20.10	(21.12, 21.13)	22.3
		4	--	--	22.4
High humidity, continuous or intermittent immersion.	Phenolic-	2	20.13	--	--
	tung	3	20.18	--	--
White only, including primer, for interiors of automotive tanks.	Alkyd	2	20.8	21.3	22.2
Steel only. Ammunition--shells, grenades, etc.	Styrenated alkyd	1	20.1	--	--
	Lacquer	1	20.2	--	--
Steel only. Ammunition boxes, gasoline drums, pipeline equipment, landing mats, etc.	Alkyd	1	--	21.1	--
Special baked finish--alkyd primer phenolic top coat.	Alkyd-phenolic	2	--	21.7	--
Around storage batteries, where acid resistance required; interiors of high explosive shells, etc.	Asphalt	2	--	--	24.10
	Varnish				
	Cuttack asphalt	1	--	--	24.2
		1	--	--	24.7
Wrinkle: alkyd primer; one coat primer top coat mfr's choice; all systems glossy.	Alkyd	2	23.1		
Weld-through primer; primer only, for places inaccessible after spot welding.	Epoxy	1	--	--	24.1

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TABLE XIII. Condensed description of paint systems. (Cont'd)

Use on Metal	Type Binder	Number of Coats	Finish		
			Lusterless	Semigloss	Gloss
Underbody coating, on wood or metal	Cut-back asphalt	1	24.3	--	--
Use on Wood					
General; exterior, interior	Alkyd	2	--	27.3	--
		3	26.1	27.1	--
White only, including primer, for	Alkyd	2	--	27.3	--
		3	26.1	27.1	--
Natural, +filler, when needed	Oleo-resinous	2	--	--	--
	Shellac	2	--	--	--
High humidity, continuous or intermittent immersion.	Phenolic- tung	3	20.18	--	--

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