

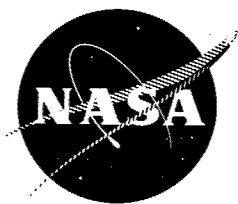
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**SPACE VEHICLE
DESIGN CRITERIA
(CHEMICAL PROPULSION)**

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SOLID PROPELLANT SELECTION AND CHARACTERIZATION



JUNE 1971

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

NASA experience has indicated a need for uniform criteria for the design of space vehicles. Accordingly, criteria are being developed in the following areas of technology:

Environment
Structures
Guidance and Control
Chemical Propulsion

Individual components of this work will be issued as separate monographs as soon as they are completed. This document, part of the series on Chemical Propulsion, is one such monograph. A list of all monographs issued prior to this one can be found on the last page of this document.

These monographs are to be regarded as guides to design and not as NASA requirements, except as may be specified in formal project specifications. It is expected, however, that these documents, revised as experience may indicate to be desirable, eventually will provide uniform design practices for NASA space vehicles.

This monograph, "Solid Propellant Selection and Characterization," was prepared under the direction of Howard W. Douglass, Chief, Design Criteria Office, Lewis Research Center; project management was by John H. Collins, Jr. The monograph was written by Thomas N. Scortia and Howard G. Cutforth, United Technology Center Div., United Aircraft Corporation, and was edited by Russell B. Keller, Jr. of Lewis. To assure technical accuracy of this document, scientists and engineers throughout the technical community participated in interviews, consultations, and critical review of the text. In particular, Dr. John C. Allabashi of Hercules, Inc., William H. Miller of Rocketdyne Solid Rocket Div., North American Rockwell Corporation, and Dr. Harold A. Marsh of the Jet Propulsion Laboratory, California Institute of Technology, reviewed the monograph in detail.

Comments concerning the technical content of this monograph will be welcomed by the National Aeronautics and Space Administration, Lewis Research Center (Design Criteria Office), Cleveland, Ohio 44135.

June 1971

GUIDE TO THE USE OF THIS MONOGRAPH

The purpose of this monograph is to organize and present, for effective use in design, the significant experience and knowledge accumulated in development and operational programs to date. It reviews and assesses current design practices, and from them establishes firm guidance for achieving greater consistency in design, increased reliability in the end product, and greater efficiency in the design effort. The monograph is organized into two major sections that are preceded by a brief introduction and complemented by a set of references.

The *State of the Art*, section 2, reviews and discusses the total design problem, and identifies which design elements are involved in successful design. It describes succinctly the current technology pertaining to these elements. When detailed information is required, the best available references are cited. This section serves as a survey of the subject that provides background material and prepares a proper technological base for the *Design Criteria* and Recommended Practices.

The *Design Criteria*, shown in italic in section 3, state clearly and briefly what rule, guide, limitation, or standard must be imposed on each essential design element to assure successful design. The *Design Criteria* can serve effectively as a checklist of rules for the project manager to use in guiding a design or in assessing its adequacy.

The Recommended Practices, also in section 3, state how to satisfy each of the criteria. Whenever possible, the best procedure is described; when this cannot be done concisely, appropriate references are provided. The Recommended Practices, in conjunction with the *Design Criteria*, provide positive guidance to the practicing designer on how to achieve successful design.

Both sections have been organized into decimally numbered subsections so that the subjects within similarly numbered subsections correspond from section to section. The format for the Contents displays this continuity of subject in such a way that a particular aspect of design can be followed through both sections as a discrete subject.

The design criteria monograph is not intended to be a design handbook, a set of specifications, or a design manual. It is a summary and a systematic ordering of the large and loosely organized body of existing successful design techniques and practices. Its value and its merit should be judged on how effectively it makes that material available to and useful to the designer.

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SOLID PROPELLANT SELECTION AND CHARACTERIZATION

1. INTRODUCTION

The designer of a solid propellant rocket motor must first select a propellant type from the large variety of operational propellants. Those presently available offer a wide range of specific impulses, densities, burning rates, mechanical and hazard properties, and environmental capabilities; further, these basic properties can be adjusted or tailored in a variety of ways. The use of tailoring techniques, however, often forces compromises. Having selected a propellant, the designer then must characterize it completely. The numerous characterization techniques in use complicate this problem. If the designer fails to establish initial propellant parameter envelopes that are broad enough for his needs, or if he fails to appreciate the compromises forced on him by the propellant parameters, he may be faced with a costly redesign or an equally costly selection of new propellant late in the design program.

The purpose of this monograph is to review and evaluate the commonly used techniques of propellant selection and characterization and to emphasize the compromises that may be forced on the designer by the change of a propellant parameter. Even though the designer himself may not be intimately concerned with the propellant characterization, most of the basic techniques are reviewed herein so that he may intelligently assess the work being carried out by propellant specialists.

Rules for the selection of a general propellant type are presented first. The characterization of various propellant properties is then approached parameter by parameter. Tailoring pitfalls and compromises are identified whenever possible, and appropriate cross references are used. The monograph is not intended as a text on solid propellant technology; it presumes a basic knowledge of the technology and access to basic unclassified and classified source material. Related design criteria monographs frequently are cited for a more detailed treatment of the topic under discussion. A list of source references is provided for those seeking more detailed treatment of a particular subject. These references, coupled with established texts in the field, should give the depth of knowledge necessary to the designer to aid in the selection of the most nearly optimum propellant for the design application.

2. STATE OF THE ART

The system analyst, faced with the problem of imparting a given terminal velocity to a payload, determines the total delivered impulse required of the motor, the desired shape of the thrust-time profile, and the volumetric constraints on the motor. The motor length may not be severely constrained initially, but the maximum motor diameter usually is fixed early in the design effort. Within the dimensional constraints, the internal ballisticians work with a range of available propellant density-impulses and burning rates to design an internal geometry that will give the required volumetric loading. He calculates a web dimension such that the propellant will deliver the desired thrust-time profile at a specific burning rate. The stress analyst, using assumed values of mechanical properties for the propellant, makes numerical calculations of the viscoelastic stress concentrations in the grain geometry under all anticipated motor loadings and environments. From these analyses, he defines an envelope of acceptable propellant mechanical properties. The anticipated storage and handling conditions determine the hazard, thermal stability, and storage stability requirements for the propellant. Once the motor design team has established all of these propellant requirements, the list of candidate formulations is reduced to those that require a minimum of ballistic and mechanical property tailoring.

There is a constant interplay of design and propellant tailoring efforts during the motor design program. Compromises of the original propellant requirements and of the original internal geometry may be required. The typical design and development effort shown schematically in figure 1 illustrates this complex interplay. Because of the time lag in hardware procurement, the motor case design usually is completed early in the program and rarely is modified significantly by the propellant tailoring/design interplay. Nevertheless, the hardware design is strongly influenced in the early design effort by the propellant parameter envelopes as shown in figure 2. For this reason, the propellant type is selected as early as possible, and the envelopes for density-impulse, internal ballistics, flame temperature, and mechanical properties are defined. If these envelopes are not realistic, and a propellant parameter outside the early design envelope must later be accepted, costly hardware modifications may become necessary.

2.1 Selection of Propellant Type

Initially, the designer selects a propellant type that is likely to give the required performance, internal ballistics, flame temperature, and mechanical properties as well as the necessary storage stability, the best hazard properties, and any specialized property (e.g., smokelessness). A broad range of properties is available within each general propellant type, but some basic generalizations guide this selection.

The composite propellant contains a crystalline oxidizer to provide oxygen for combustion and often contains a metal to increase the heat of combustion. These materials are slurried in a liquid polymer or polymer-plasticizer, cast, and cured chemically or

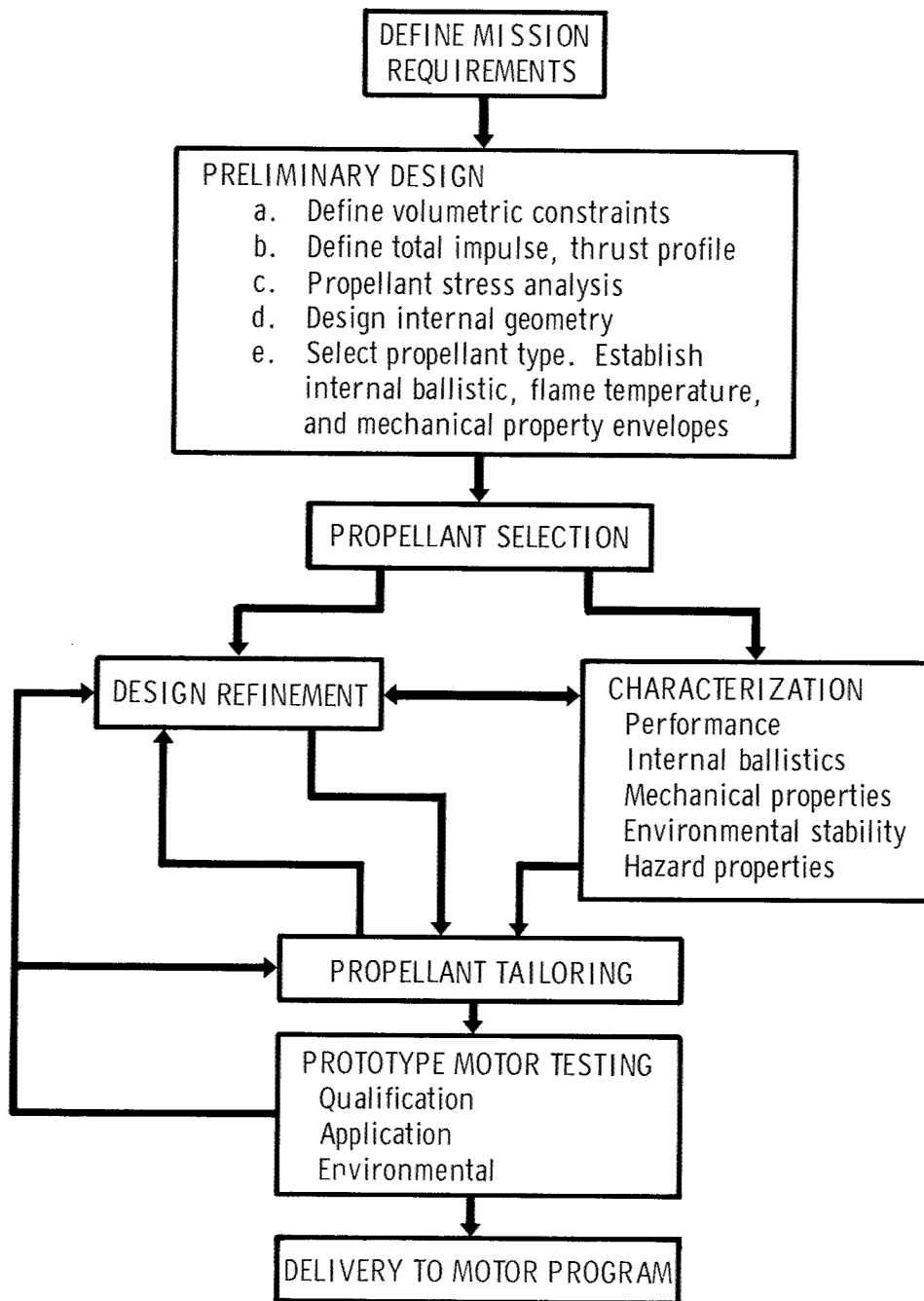


Figure 1.—Propellant selection and tailoring in the design program.

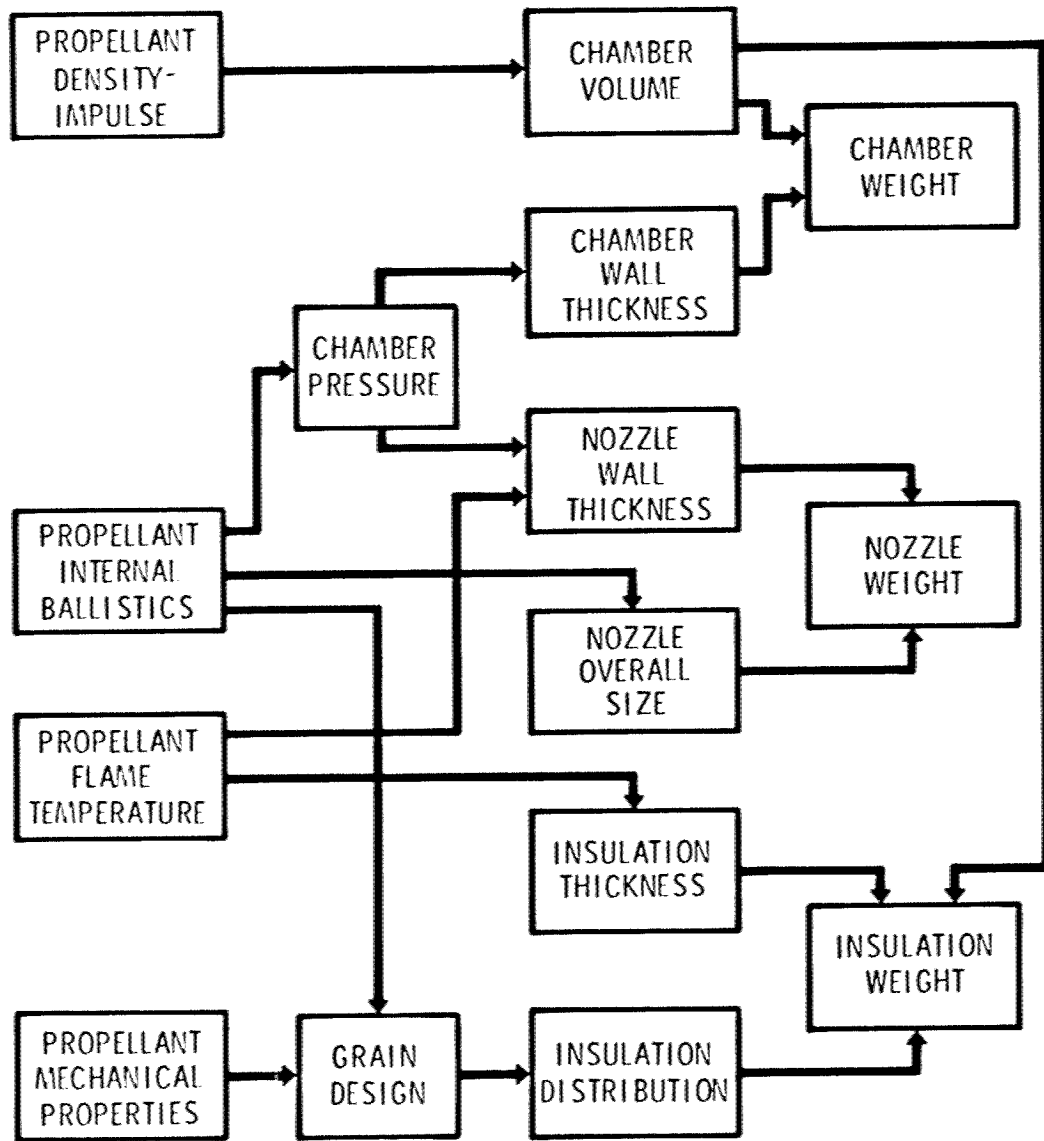


Figure 2.—Influence of propellant properties on weight of motor components.

by physical fusion to an elastomeric propellant. Classical double-base propellants contain no crystalline oxidizer or metal; they are composed of nitrocellulose gelled by a nitrate ester such as nitroglycerin and depend upon the nitro chemical groups in the nitrocellulose and nitrate ester for oxygen. The composite double-base propellants are based on the classical double-base binder but contain a crystalline oxidizer and usually a metal.

Metals are used in high-energy propellants to increase the total heat release during combustion and to increase density. Many propellants contain only nominal amounts of metal to suppress unstable combustion, while propellants for smokeless applications rigidly exclude metals. The most commonly used metal is aluminum (Al), because of its high heat of combustion, its cheapness and ready commercial availability, and its relatively high combustion efficiency. Beryllium (Be) is used in propellants because of its high heat of combustion and its low-molecular-weight combustion products. However, most Be combustion products appear to be toxic, and Be combustion efficiency is less than that of Al except in formulations with flame temperatures above 3600° K (ref. 1). Zirconium (Zr) is used because of its high density (6.49 gm/cc), but its formulations have significantly lower energy than those of Al or Be. Combustion efficiency of Zr is poorer than that of Al except in very high flame temperature, double-base formulations (ref. 2).

The most commonly used crystalline oxidizer is ammonium perchlorate (AP), although lithium perchlorate (LiP) and potassium perchlorate (KP) are used for special applications.¹ Advanced double-base formulations often use HMX or RDX in conjunction with AP as do some of the nitroplasticized polyester polyurethane formulations. Ammonium nitrate (AN), nitroguanidine, and guanidine nitrate (GN) are used in lower energy propellants such as those for gas generators.

Propellants customarily are classified by their binder type. The generic name of the polymer structural backbone most commonly is used, but for proper identification the cure system should be specified as well. The selection of the cure system depends on the chemically active groups on the polymer molecule. Common chemically active groups are the carboxyl group (-COOH), hydroxyl group (-OH), and mercaptyl group (-SH).

A cure reaction must promote extensive crosslinking in the final binder to avoid high-temperature flow and to give adequate mechanical properties. (A crosslink site is a trifunctional branch point in the final binder structure.) For this reason, polymers with only two reactive groups per molecule must be cured with either a trifunctional curative or an auxiliary molecule that is trifunctional. Some binder systems consist of particles of polymeric material slurried in a plasticizer. These systems do not require a curative but cure by swelling in the plasticizer under heat to fuse into an elastomeric gel.

The propellant types most frequently encountered by the designer are described briefly hereafter. A more complete discussion of the chemistry of these binders may be found in reference 3.

¹The chemical names for materials designated by abbreviations may be found in the Glossary.

Polybutadiene Composite Propellants

Polybutadiene propellants are based on binders whose backbones are polymerized butadiene or butadiene copolymerized with other materials. CTPB (carboxy-terminated polybutadiene), PBAA (polybutadiene-acrylic acid copolymer) and PBAN (polybutadiene-acrylic acid-acrylonitrile terpolymer) are the three common polybutadienes with carboxyl cure sites. These polymers can be cured with aziridines such as MAPO, TBM, or BITA. Such cures may revert on aging with a loss of mechanical properties; for this reason, an epoxide often is used to stabilize the cure. These polymers also may be cured with epoxides such as those based on bisphenol A. Such all-epoxy cures do not revert.

Polyurethane Composite Propellants

Classical polyurethane (PU) propellants use binders based on a polyester or polyether backbone with hydroxyl groups as the cure sites. However, polyesters are degraded by moisture, and most PU propellants now use polyethers. A recent PU propellant is based on HTPB (hydroxy-terminated polybutadiene). This polymer is similar to CTPB but with hydroxyl groups instead of carboxyl groups as cure sites. The hydroxy-polyethers and HTPB are cured by di- or triisocyanates, using a cure catalyst such as FeAA. If a diisocyanate is used, a triol such as hexanetriol generally is used to provide necessary branching of the final binder structure. Polyurethanes frequently are plasticized, and a significant group of high-energy polyurethanes use nitroplasticizers (containing the nitro- group: $-NO_2$). These propellants frequently are cured with a nitroisocyanate.

Double-Base Propellants

Double-base (DB) propellants contain nitrocellulose (NC) gelled with a nitrate ester such as nitroglycerin (NG), TEGDN, or TMETN. Inert plasticizers such as triacetin or dibutyl phthalate may be added to the nitrate ester to reduce the handling hazard or to reduce the oxygen content of the final propellant. Nonmetallized DB propellants do not usually contain inorganic oxidizers and frequently are extruded rather than cast. Solvent-cast DB propellants are made by forcing a nitrate ester up through a bed of NC casting powder, after which the mass is gelled by heat. Solvent-cast DB propellants that are metallized and contain AP (often supplemented with HMX or RDX) are referred to as CMDB (composite metallized double-base) propellants. Plastisol double-base (PNC-DB) propellants are made by slurring a fine plastisol-grade NC in the nitrate ester. The slurry, containing metal and oxidizer particles, is cast and heated. Under heat, the plastisol particles swell and fuse to an elastomeric mass. CMDB and PNC-DB propellants frequently are crosslinked to improve the mechanical properties. The unnitrated hydroxyl groups in the NC are crosslinked by isocyanates in the same cure reaction used in a conventional polyurethane propellant. Both CMDB and PNC-DB propellants are referred to as composite-modified double-base propellants.

Polysulfide Composite Propellants

Polysulfide (PS) propellants use a binder whose backbone is a polymerized butyl formal, butyl ether, or ethyl formal. The binder polymer contains mercaptyl groups (-SH) that are oxidized during cure to form -S-S- bridges between molecules. The polymer containing metal and oxidizer is cast and cured to an elastomeric rubber with an oxidizing agent such as paraquinone dioxime, lead dioxide, or a nitro compound. Water is generated during the oxidation of the -SH cure sites.

Polyvinyl Chloride Composite Propellants

Polyvinyl chloride (PVC) propellants (ref. 4) are cast as slurries of fine plastisol polyvinyl-chloride particles with oxidizer and often metal in an inert plasticizer such as dibutyl phthalate or dioctyl adipate. When the temperature is raised to 325°-350° F for about 1 hour, the mixture gels into an elastomeric mass. PVC propellants also may be extruded; the frictional heat of extrusion results in the propellant cure. Casting generally is slower than with other composite propellants because of the high viscosity of PVC propellant mixes.

Saturated Hydrocarbon Binder Composite Propellants

Recently a number of fully saturated difunctional hydrocarbon binders with either carboxy- or hydroxy-termination has been used in composite propellants (ref. 5). These polymers are cured with materials appropriate to their reactive end groups. Trifunctional materials must be used with these polymers to provide branch points for crosslinking.

Fluorocarbon Composite Propellants

Fluorocarbon (FC) propellants (ref. 6) may be made by first coating metal and oxidizer with a fluorocarbon elastomer (e.g., Viton A) deposited from solution. The coated powder then is extruded as a billet. The billet is machined to the desired geometry and potted or cartridge-loaded in the motor.

2.1.1 Performance Properties

The performance capability of a propellant usually is expressed as a theoretical specific impulse I_{sp}^o associated with a density ρ . The value for delivered specific impulse I_{spd} necessary for the mission is specified. The specific impulse efficiency I_{spd}/I_{sp}^o likely to be achieved in a given design can be estimated by various techniques (ref. 7). Thus, the I_{sp}^o necessary to produce the desired I_{spd} is easily derived. On this basis, a propellant type suitable for the intended use may be identified. The theoretical performances of some typical operational propellants are listed in table I (ref. 8).

Table I.—Characteristics of Some Operational Propellants (ref. 8)

| Propellant type | $I_{sp}^{(1)}$ Range, sec | Approximate flame temperature, °F | Approximate density, lb/in. ³ | Metal content, wt-% | Ingredients cost, cents/lb | Processing method |
|-----------------|------------------------------|--|--|---------------------------|----------------------------------|-----------------------|
| DB | 220–230 | 4100 | 0.058 | 0 | 250 | Extruded |
| DB/AP/Al | 260–265 | 6500 | 0.065 | 20–21 | 120 | Solvent cast |
| DB/AP-HMX/Al | 265–270 | 6700 | 0.065 | 20 | 140 | Solvent cast |
| PVC/AP | 230–240 | 4600 | 0.061 | 0 | 30 | Cast or extruded |
| PVC/AP/Al | 260–265 | 5600 | 0.064 | 21 | 30 | Cast or extruded |
| PS/AP | 230–240 | 4700 | 0.062 | 0 | 75 | Cast |
| PS/AP/Al | 240–250 | 5000 | 0.062 | 3 | 75 | Cast |
| PU/AP/Al | 260–265 | 5400–6000 | 0.064 | 16–20 | 40 | Cast |
| PBAN/AP/Al | 260–263 | 5800 | 0.064 | 16 | 35 | Cast |
| CTPB/AP/Al | 260–265 | 5600–5800 | 0.064 | 15–17 | 55 | Cast |
| HTPB/AP/Al | 260–265 | 5600–5800 | 0.064 | 4–17 | 30–100 | Cast |
| FC/AP/Al | 240–245 | 6200 | 0.074 | 19.5 | 180 | Extruded and machined |
| DB/AP/Be | 275–280 | 6500 | 0.064 | 12 | 800 | Solvent cast |
| CTPB/AP/Be | 275–280 | 5800 | 0.060 | 12 | 770 | Cast |
| PU/AP/Be | 275–280 | 5800 | 0.060 | 12 | 770 | Cast |

(1) $I_{sp}^{(1)}$ is the theoretical specific impulse at 1000 psia exhausting to 14.7 psia through a 0° half-angle nozzle.

Nonmetallized propellants generally offer I_{sp}^o in the 220 to 240 sec range, but their efficiencies are higher than those of the metallized propellants. Efficiencies approaching 98 percent may be expected in large motors (ref. 7).

Most of the aluminized propellants will deliver up to 96 percent efficiency in very large motors. The addition of 15 to 20 percent Al to a nonmetallized propellant system results in as much as an 11 percent improvement in delivered specific impulse. Aluminized double-base propellants generally are superior to aluminized composites in both theoretical and delivered specific impulse. The CMDB propellants with HMX yield the highest delivered specific impulses of all of the aluminized propellants. Aluminized nitroplasticized polyurethanes with HMX offer specific impulses nearly as high as the CMDB-HMX propellants.

CMDB-HMX propellants generally give the best combination of density and specific impulse. However, composite propellants with 90 percent solids loading, containing 17 to 18 percent Al, are competitive with the CMDB-HMX propellants in this respect.

The Be propellants listed will deliver efficiencies as much as 4 percent lower than those of similar Al propellants. Beryllium efficiencies in CMDB propellants, however, are comparable to those for Al (ref. 1). Beryllium double-base-HMX formulations usually have very high I_{sp}^o and good efficiencies. Even with lower specific impulse efficiencies, Be composite propellants still deliver over 6 sec more than the analogous aluminum systems. Beryllium propellants frequently have higher flame temperatures than Al propellants. This may lead to greater need for insulation and to greater nozzle erosion in motors operating at chamber pressures above 500 psi. Under these conditions, the erosion rate of high-density graphite, for instance, is as much as 2.5 times that encountered with an Al propellant (ref. 9).

The FC propellants offer high density (0.074 lb/in.³) but yield the lowest specific impulse of the metallized propellants, even with a significantly higher flame temperature (6200° F). Some propellants formulated with Zr (not shown in table I) have even greater densities but have low specific impulse efficiencies. The hotter CMDB-HMX propellants with Zr have efficiencies comparable to aluminized propellants (ref. 2).

2.1.2 Internal Ballistic Properties

Internal ballistics is concerned with those parameters that govern the burning rate and mass discharge rate of the motor. The internal ballistic properties of some typical operational propellants are shown in table II (ref. 8).

The great majority of composite propellants contain AP with a metal fuel. There are wide variations in internal ballistics, but most such propellants have burning-rate exponents less than 0.6. Very low burning-rate exponents often are encountered in narrow pressure ranges in underoxidized, nonmetallized composite propellants.

Table II.—Typical Internal Ballistic Properties of Some Operational Propellants (ref. 8)

| Type | Metal, % | $r^{1000(1)}$ | n , 800-1000 psi range ⁽²⁾ |
|-----------------------|----------|---------------|---|
| AP/FC/Al | 19.5 | 0.30 | 0.54 |
| AP/NC-NG/Al | 20.9 | 0.78 | 0.40 |
| AP/NC-TEGDN/Al | 18.0 | 0.825 | 0.50 |
| | 20.0 | 0.70 | 0.36 |
| AP/PBAA/Al | 14.0 | 0.32 | 0.349 |
| | 16.0 | 0.28 | 0.200 |
| | 5.0 | 0.47 | 0.362 |
| AP/PBAN/Al | 15.0 | 0.55 | 0.33 |
| AP/CTPB/Al | 17.0 | 0.445 | 0.40 |
| | 16.0 | 0.34 | 0.30 |
| | 10.0 | 0.30 | 0.26 |
| AP/CTPB/Be | 11.0 | 0.38 | 0.33 |
| AP/PS | 0.0 | 0.35 | 0.434 |
| AP/PS/Al | 2.0 | 0.31 | 0.333 |
| AP/PU/Al | 15.0 | 0.275 | 0.15 |
| | 7.75 | 0.315 | 0.214 |
| | 20.0 | 0.31 | 0.32 |
| | 2.0 | 0.29 | 0.387 |
| AP/PU/Be | 14.0 | 0.285 | 0.43 |
| AP/PVC | 0.0 | 0.44 | 0.38 |
| AP-HMX/NC-TMETN-TEGDN | 17.0 | 0.47 | 0.64 |
| AP-HMX/NC-NG/Al | 19.8 | 0.55 | 0.49 |
| NC/NG | 0.0 | 0.45 | 0.0 |

(1) r^{1000} = linear burning rate at 1000 psia, in./sec.

(2) n = pressure exponent in burning-rate equation, $r = aP_c^n$ (sec. 2.3.1.1.1).

Propellants based on AN or GN oxidizer have burning rates on the order of 0.06 in./sec.² Without burning-rate catalysts such as ammonium dichromate, these propellants have even lower burning rates; but their combustion frequently is unreliable. Burning-rate exponents on the order of 0.4 to 0.6 are common in GN-AP propellants. Temperature exponents of burning rate in such propellants also are very low.

²All burning rates quoted hereafter will be at 1000 psia and 70° F unless otherwise indicated.

Propellants using KP as an oxidizer frequently have high burning rates in the 0.7 to 0.8 in./sec region with burning-rate exponents of 0.6 to 0.7. Propellants using a mixture of AP and KP will have somewhat lower burning-rate and pressure exponents.

2.1.3 Mechanical Properties

A stress analysis of the preliminary grain design at the anticipated storage and operational temperatures defines the early mechanical property requirements. The stresses on the grain under the design operating pressure must also be considered in this analysis. The mechanical property requirements usually are defined at this time in terms of the lowest acceptable uniaxial stress and strain values at the temperature extremes the grain will likely experience. The use of complex internal geometries with points of high stress concentration often results in uniaxial strain requirements beyond the capacity of most propellants. As a rule of thumb, most useful operational propellants have tensile strengths at maximum stress σ_m of at least 75 psi and elongations of 25 percent at maximum strain ϵ_m when tested at a crosshead rate of 2 in./min (sec. 2.4.1.1). Uniaxial mechanical properties of some typical operational propellants are shown in table III (ref. 8).

CMDB propellants, PU propellants, and the various polybutadiene propellants have excellent properties at 70° F, and elongations above 25 percent are not uncommon at this temperature. Uncrosslinked plastisol double-base propellants rarely show elongations above 20 percent at 70° F, but the crosslinked formulations have properties comparable to the CMDB propellants. The extruded FC propellants have very low elongations with high tensile strengths. Fluorocarbon propellants have anisotropic properties because of flow orientation during extrusion. As a result, they are weak radially and strong axially.

In many applications, the low-temperature properties are particularly critical. Propellant shrinkage results in large internal stresses that must be relieved to avoid grain cracking. CTPB propellants have particularly good low-temperature properties, with elongations often above 25 percent at -70° F accompanied by tensile strengths in the 500 to 1000 psi region. HTPB propellants have good low-temperature properties down to about -40° F, their elongations decreasing sharply past this point. HTPB propellants with the proper bonding agent have low-temperature properties comparable to the other polybutadiene propellants. Double-base propellants of all types have poorer low-temperature properties than most composites, with elongation usually below 15 percent at -70° F. Polyether-PU propellants show relatively high glass-transition points and have low-temperature properties somewhat inferior to the polybutadiene propellants. Low-temperature properties may be improved by a proper choice of plasticizer or bonding agent. The extruded FC propellants become brittle at low temperatures (ref. 6).

Table III.—Typical Uniaxial Mechanical Properties of Some Operational Propellants (adapted from ref. 8)

| Type | $\sigma_m/\epsilon_m^{(1)}$ at— | | |
|-----------------------|---------------------------------|-----------------|------------------|
| | Low temp. (°F) | Room temp. (°F) | High temp. (°F) |
| AP/FC/Al (extruded) | | 700/8 (77°) | |
| AP/NC-NG/Al | 2750/4.5 (-60°) | 390/48 (77°) | 140/44.9 (120°) |
| AP/NC-TEGDN/Al | 900/6 (-60°) | 98/16 (70°) | 63/18 (160°) |
| | 658/14.4 (-60°) | 67.6/16.6 (77°) | 48.8/17 (160°) |
| AP/PBAA/Al | 500/13 (-50°) | 77/33 (77°) | 41/31 (150°) |
| AP/PBAN/Al | | 98/29 (77°) | |
| AP/CTPB/Al | 324/26 (-50°) | 129/57 (77°) | 94/75 (130°) |
| | 700/43 (-70°) | 170/43 (77°) | 120/41 (170°) |
| AP/CTPB/Be | 700/30 (-70°) | 170/30 (77°) | 125/30 (170°) |
| AP/PS | 580/11 (-50°) | 170/85 (77°) | 120/70 (150°) |
| AP/PS/Al | 300/14 (-50°) | 120/33 (77°) | 99/42 (150°) |
| AP/PU/Al | 1168/5.4 (-60°) | 98/41 (77°) | 70/33 (180°) |
| | 467/30 (-60°) | 95/67 (77°) | 45/31 (180°) |
| AP/PU/Be | | 66/68 (77°) | |
| AP/PVC | | 77/175 (77°) | |
| AP-HMX/NC-TMETN-TEGDN | 910/2 (-60°) | 78/9 (70°) | 36/9 (160°) |
| AP-HMX/NC-NG/Al | 2375/2.7 (-60°) | 170/50 (77°) | 61.6/33.0 (120°) |
| NC/NG | 4600/1.5 (-60°) | 1890/40 (77°) | 475/60 (160°) |

(1) Crosshead rate, 2 in./min.

At higher temperatures (ca. 120° F), many propellants lose tensile strength and may flow or slump. Slump may represent a serious problem if propellant deformation affects the geometry and the internal ballistics of the motor. CTPB and PU propellants have tensile strengths in the 50 to 100 psi region at 120° F. Uncrosslinked PNC-DB propellants have tensile strengths in the 50 psi region at this temperature, and uncross-linked plastisol propellant grains frequently show unacceptable flow and slump.

2.1.4 Thermal and Storage Stability

The sensitivity of a propellant to thermal degradation generally is a reflection of its long-term storage stability since the chemical processes that cause age deterioration are accelerated at higher temperatures. Both NC and nitrate esters decompose rapidly at temperatures above 150° F. At lower temperatures, they tend to degrade over longer periods; their decomposition products catalyze and accelerate this degradation. The process can be minimized with the use of materials such as ethyl centralite or resorcinol that scavenge the decomposition products. Long-term degradation can result in loss of elongation, leading to age cracking. However, some CMDB propellants have been stored successfully for 1 year at 100° F (ref. 2). The thermal stabilities of all composite propellants generally are superior to those of DB propellants. However, composite propellants may show longer ignition delays with aging. High-temperature stability is particularly good in the FC, PVC, and epoxide-cured CTPB propellant systems. The limiting factor in these systems appears to be the stability of the AP oxidizer (refs. 6 and 8). PVC propellants can withstand storage at 300° F for days without serious degradation (refs. 4 and 8).

Early polyurethanes were moisture-sensitive and suffered loss of mechanical properties when exposed to moist air over an extended period. More modern formulations have minimized this loss. The mechanical properties of some polysulfides are degraded by moisture; this problem is aggravated by the fact that water is generated in the cure reaction (ref. 3). Polybutadiene binders show a reversible sensitivity to moisture. At relative humidities above 60 percent, some composites show excessive elongation, blistering, internal gassing, and dewetting of the oxidizer and metal by the binder. Classical double-base propellants are not affected by moisture.

The most troublesome problem in CTPB propellants has been the age-reversal of aziridinyl cures with MAPO. New aziridinyl curatives and mixed aziridinyl-epoxy cures have minimized this problem, and the newer all-epoxy cures have eliminated it completely.

2.1.5 Hazard Properties

The combustion or detonation of propellants may be initiated by impact, friction, or static electrical discharge. In many instances propellants will simply deflagrate, but in other instances they may detonate. Under certain circumstances, if the geometry and mass of the grain are large enough, the deflagration may change to detonation. Theoretically, all propellants may be detonated by an impinging high-velocity detonation wave if the propellant grain is large enough so that the propellant's critical diameter is exceeded. As a general rule, the critical diameters of composite propellants are greater than those of double-base and CMDB propellants.

The basic hazard properties of some typical operational propellants are given in table IV (ref. 8) as a guide to general hazard ranking.

Beryllium propellant exhausts are considered highly toxic, but the degree of toxicity has not been definitely established (refs. 10 and 11).

Table IV.—Typical Selected Hazard Properties of Some Operational Propellants (ref. 8)

| Type | 50% Fire impact, kg-cm ⁽¹⁾ | Card gap, 0% fire or 50% fire ⁽²⁾ | Class, DOT/Mil. |
|-----------------------|---------------------------------------|--|-----------------|
| AP/FC/Al | 70-80 | 0:0 | B/2 |
| AP/NC-NG/Al | .. | 50%:75 | B/2 |
| AP/NC-TEGDN/Al | 20 | 0:66 | B/2 |
| | .. | 50%:63 | .. |
| | 9 | 50%:64 | A/2 |
| AP/PBAA/Al | .. | 0:0 | B/2 |
| | .. | 0:0 | B/2 |
| | .. | 0:0 | A/7 |
| AP/PBAN/Al | 46 | 0:0 | B/2 |
| AP/CTPB/Al | 22 | 0:0 | B/2 |
| | 66 | 0:0 | B/2 |
| | 64 | 0:0 | B/2 |
| AP/CTPB/Be | .. | 0:0 | B/2 |
| AP/PS | .. | 0:0 | B/2 |
| AP/PS/Al | .. | 0:0 | B/2 |
| AP/PU/Al | 46 | 0:0 | B/2 |
| | 50 | 0:0 | B/2 |
| | 40 | 0:0 | B/2 |
| | .. | 0:0 | B/2 |
| AP/PU/Be | 70 | 0:0 | B/2 |
| AP/PVC | 48 | 0:0 | B/2 |
| AP-HMX/NC-TMETN-TEGDN | 24 | ... | B/7 |
| NC/NG | .. | 50%:35 | B/7 |

(1) 50% of samples detonate or deflagrate on impact of 2-kg weight dropped from a height measured in centimeters (sec. 2.6.2).

(2) Number of 0.01-in. cellulose acetate cards attenuating test charge when 0% or 50% of samples detonate (sec. 2.6.6).

Little can be done to improve the hazard properties of the propellant without compromising the energy of the system. Composite propellants with nonenergetic binders generally are class 2 (fire hazard); composites with energetic binders such as the nitroplasticized polyurethanes containing RDX or HMX may be class 7 (detonation hazard). Many DB propellants are class 7. The friction hazard of composites, however, is greater than that of most DB propellants but equivalent to that of the composite DB propellants.

2.1.6 Propellant Costs

Usually, hardware costs and developmental costs for a motor far outweigh the basic propellant cost. However, propellant costs can assume unusual significance if unusual processing techniques, unusual insulation techniques, or particularly complex geometries are required. Large reductions in the cost of ingredients or of the processing techniques can rarely be made. However, relatively modest savings can become quite significant when extended over very large quantities of propellant. The cost of ingredients per pound of propellant for some typical propellants is given in table I.

A survey of propellant prices for the 260-in. booster (ref. 12) developed the ingredient costs shown in table V. The low cost of the butadienes stems from their availability and the size of their production runs. The significantly higher costs of the nitrate plasticizers, TEGDN and TMETN, are explained by their low production levels. The significant variation in the costs of curing agents may influence final propellant costs significantly. The more limited availability of CTPB and HTPB polymers results in the cost of \$2.50 per pound as contrasted with the \$0.68 to \$0.70 per pound cost for the PBAN and PBAA polymers, which are produced in large quantities. The high cost of Be reflects its limited availability.

Most ingredients require relatively little preparation before being introduced into a mix. A portion of the AP usually is ground. Aluminum is received from the supplier in the required particle size. A few of the polymers are dried with molecular sieves or with some similar treatment. Some polymers, during the drying treatment, may present a hazard because of their tendency to autopolymerize with the release of heat. TEGDN is shipped undiluted, but other nitrate esters, particularly NG, frequently are diluted in a solvent to reduce their sensitivity. Dilution with a solvent requires an extra step in handling the nitrate ester after it reaches its destination; the nitrate must be displaced by a solvent that is miscible with the shipping solvent but not with the nitrate. For instance, nitroglycerin may be displaced from an acetone solution with water. More commonly, the nitroglycerin is produced near the propellant processing site and may be diluted with an inert plasticizer that becomes a part of the propellant formulation. Some curing agents require special handling, especially in those instances where the ingredient is toxic or can homopolymerize spontaneously (MAPO, for instance, homopolymerizes spontaneously on contact with dry AP, releasing sufficient heat for the mixture to detonate or deflagrate). In many plants, TDI is distilled from molecular sieves before use.

Table V.—1967 Ingredient Prices (ref. 12)

| Ingredient | Designation or symbol | Price, dollars/lb |
|--|-----------------------|---------------------|
| Oxidizers and fuels: | | |
| Ammonium perchlorate | AP | \$ 0.18 |
| Cyclotetramethylene tetranitramine | HMX | 1.25 |
| Cyclotrimethylene trinitramine | RDX | 0.25 |
| Aluminum powder | Al | 0.32 |
| Beryllium powder | Be | 40.00 |
| Polymers: | | |
| Polybutadiene-acrylonitrile-acrylic acid | PBAN | 0.68 |
| Polybutadiene-acrylic acid | PBAA | 0.70 |
| Carboxy-terminated polybutadiene | CTPB | 2.50 |
| Hydroxy-terminated polybutadiene | HTPB | 2.50 ⁽¹⁾ |
| Polysulfide | PS | 2.90 |
| Polypropylene glycol | PPG | 0.17 |
| Polyurethane polyether | PU | 0.35 |
| Nitrocellulose (plastisol grade) | PNC | 4.00 |
| Plasticizers: | | |
| Hydrocarbons | ... | 0.13 |
| Nitroglycerin | NG | 0.30 |
| Triethyleneglycol dinitrate | TEGDN | 1.85 |
| Trimethylolethane trinitrate | TMETN | 3.00 |
| Organic esters | ... | 0.50-0.60 |
| Curing agents: | | |
| Polysulfide curing mixture | ... | 0.25 |
| Epoxide resins | ... | 0.30 |
| Toluene diisocyanate | TDI | 0.32 |
| Hexamethylene diisocyanate | HMDI | 3.00 |
| Aziridines | ... | 25.00 |
| Additives | ... | 2.00 |

(1) Since the survey reported in reference 12, a supplier has offered an HTPB polymer at \$0.55 per pound.

The degree and speed of quality control required represents a source of increased costs. Frequently, propellant ingredients and even propellant mixes must be held for extended periods, pending quality acceptance. If the propellant pot life is short, special provisions for rapid quality control tests must be made or tests must be run on the completed motor with the possibility of costly rejection.

A hygroscopic oxidizer such as AN presents the need to ensure a reproducible water content; an oxidizer from a batch showing iron oxide or other heavy metal contamination necessitates rigid burning-rate controls on the finished propellant. Both kinds of special requirements increase material cost.

The type of processing markedly influences the final cost of the propellant. For large motors with a limited production run, the common technique of mixing in high-shear mixers and casting directly into the motor case to form a cured case-bonded grain is probably the most inexpensive approach. If the grain is sufficiently small that extrusion may be used and the production run is large enough to justify the cost of extrusion dies, this technique is cheaper than casting. Extrusion can be semiautomated, while casting requires a number of specialized personnel in complete attendance on each motor. Because of the hazard in mixing and casting CMDDB propellants, they are processed remotely with consequent saving in labor through semiautomation. Pressing and molding are nearly competitive with extrusion in cost, but few pressing facilities exist in the U.S. except for those in companies specializing in gas generators.

Propellants that exhibit a wide range of energetic, internal ballistic, or mechanical property variations in production often are relatively costly because of the number of rejected mixes and the number of motors failing to meet specifications. Even in those instances where the propellant batch can be modified to meet specifications, the holding time and the second mixing period prove costly.

Processing of composite propellants is relatively uncomplicated. However, the separate ingredients are sometimes hazardous and may require special handling or storage. TDI and MAPO are toxic materials. MAPO reacts explosively with dry AP, which is considered to be a class 7 material when particle size is below 10μ .

Many propellants require special equipment for handling and storage, while others require special environmental controls. Composite and composite DB propellants are not stored at relative humidities over 40 percent without environmental controls or an environmental closure on the motor. If the environmental closure is removed periodically for inspection, the motor is purged with dry nitrogen or air to avoid condensation in the motor on resealing.

Motors that contain a propellant with a relatively long shelf life offer a very significant cost saving. A propellant with a shelf life of 10 years in the anticipated environment will have 20 percent less replacement cost than a propellant with a shelf life of 8 years.

2.2 Performance Characterization

The best possible estimates of theoretical delivered specific impulse I_{spd}^o and density ρ are needed early in the design effort. Not only do such estimates influence the grain design itself, but I_{spd}^o and ρ properties also influence hardware weight and thus the mass ratio of the motor, as shown in figure 2. When reliable performance estimates are available, useful algebraic and graphic tradeoffs between I_{spd}^o and predicted motor mass ratio can be developed.

The estimate of delivered specific impulse is based on a theoretical impulse reduced by efficiency and heat losses. The theoretical specific impulse I_{sp}^o is defined in terms

of the fundamental physical properties of the expanding gases as

$$I_{sp} = \frac{1}{g} \left\{ \frac{2R\gamma}{\gamma - 1} \frac{T_c}{M} \left[1 - \left(\frac{P_e}{P_c} \right)^{\frac{\gamma-1}{\gamma}} \right] \right\}^{1/2} \quad (1)$$

where

- g = acceleration due to gravity, 32.2 ft/sec²
- R = universal gas constant, 1545 ft-lb/mole · °R
- γ = specific heat ratio, C_p/C_v
- T_c = adiabatic equilibrium flame temperature, °R
- \bar{M} = average molecular weight of combustion gases, lb/mole
- P_c = combustion pressure, lb/in.²
- P_e = exit pressure, lb/in.²

If the chamber and exit pressures are specified, I_{sp} may be calculated by determining chamber temperature, average molecular weight of the gas, and the specific heat ratio.

References 13 and 14 give a comprehensive review of industry computer programs for the calculation of I_{sp} . These programs are based on one of two methods of deriving chamber composition: the thermodynamic equilibrium constant approach, and the minimization of Gibbs free-energy approach (ref. 15). Figure 3 illustrates the iterative approach used in both these methods. The validity of the calculation depends primarily on the degree to which the equilibrium chamber and exhaust composition can be defined. Usually, this definition is based on the tables of thermochemical data on combustion products presented in reference 16 (these tables are revised as more precise data become available).

The prediction of a delivered specific impulse in a particular motor configuration is more difficult and less reliable than calculation of I_{sp} . Two methods for predicting delivered specific impulse are described in references 17 and 18. Reference 7 presents a thorough and detailed discussion of the techniques involved in predicting solid rocket motor performance.

2.2.1 Delivered Specific Impulse

Of the factors reducing motor performance below the calculated theoretical value, only kinetic losses and two-phase flow losses can be modified by changes in the propellant formulation, once the burning rate has been fixed. Design-dependent losses are discussed in reference 7. The propellant-dependent losses can be divided into (1) chamber losses from combustion inefficiencies and from failure to reach chemical equilibrium, and (2) nozzle losses from two-phase flow losses. While heat loss to the hardware is dependent on burning time and thus on burning rate, the mission thrust-time profile fixes burning time early in the design effort.

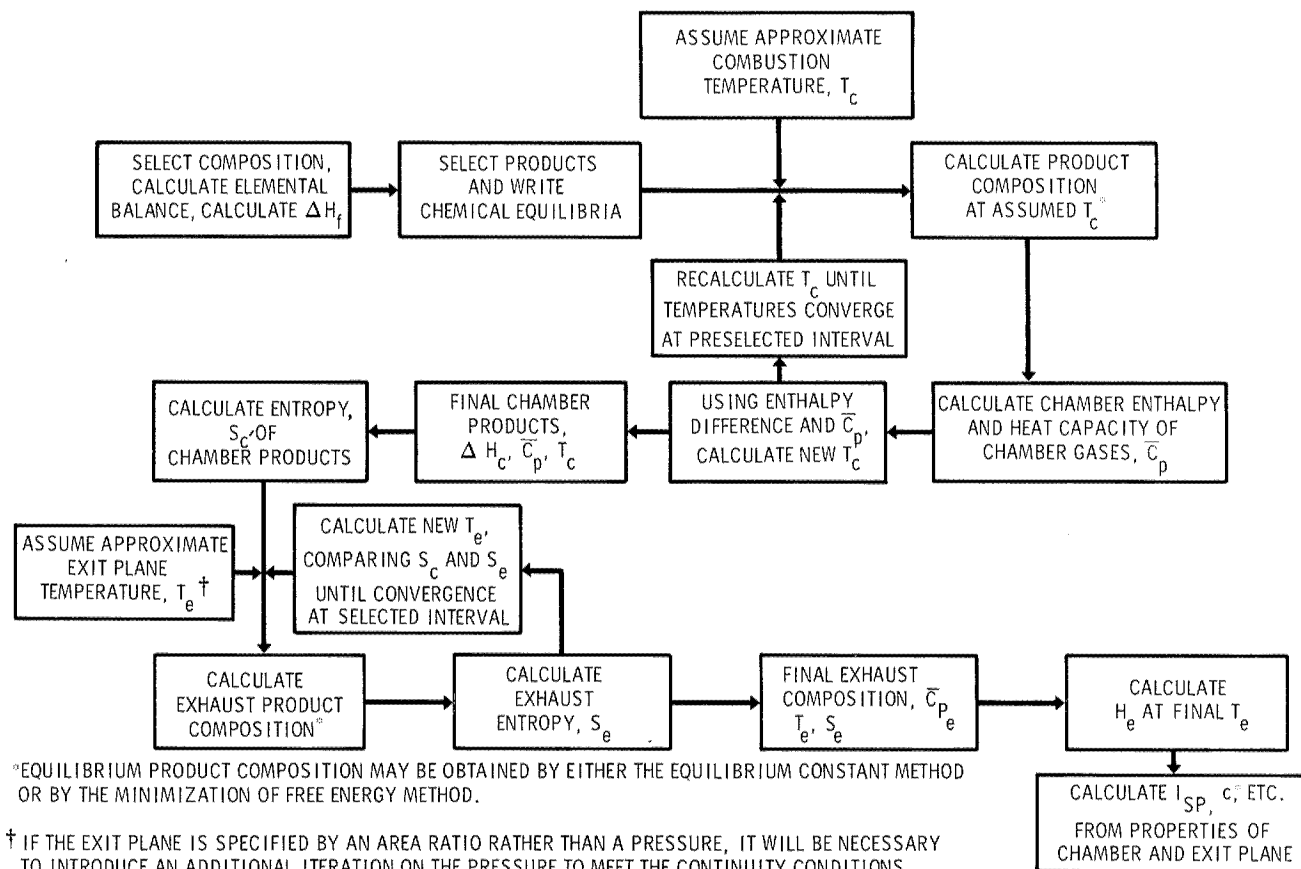


Figure 3.—Flow diagram for calculation of propellant theoretical performance.

2.2.1.1 Combustion Efficiency

Combustion efficiency is determined by the completeness of metal combustion within the motor and by the degree to which combustion products reach chemical equilibrium among themselves. It is dependent on (1) residence time of the metal and gases within the combustion chamber, (2) the combustion chamber pressure, (3) the equilibrium flame temperature of the chamber products, (4) the oxidizing balance of the propellant, and (5) the size of the burning metal droplets.

2.2.1.1.1 Residence Time

Average residence time may be defined from the gas laws by

$$t_r = \left(\frac{V_c}{W} \right) \left(\frac{P_c \bar{M}}{12RT_c} \right) \quad (2)$$

where

t_r = average residence time, msec

V_c = instantaneous volume of combustion chamber, in.³

W = mass discharge rate, lb/sec

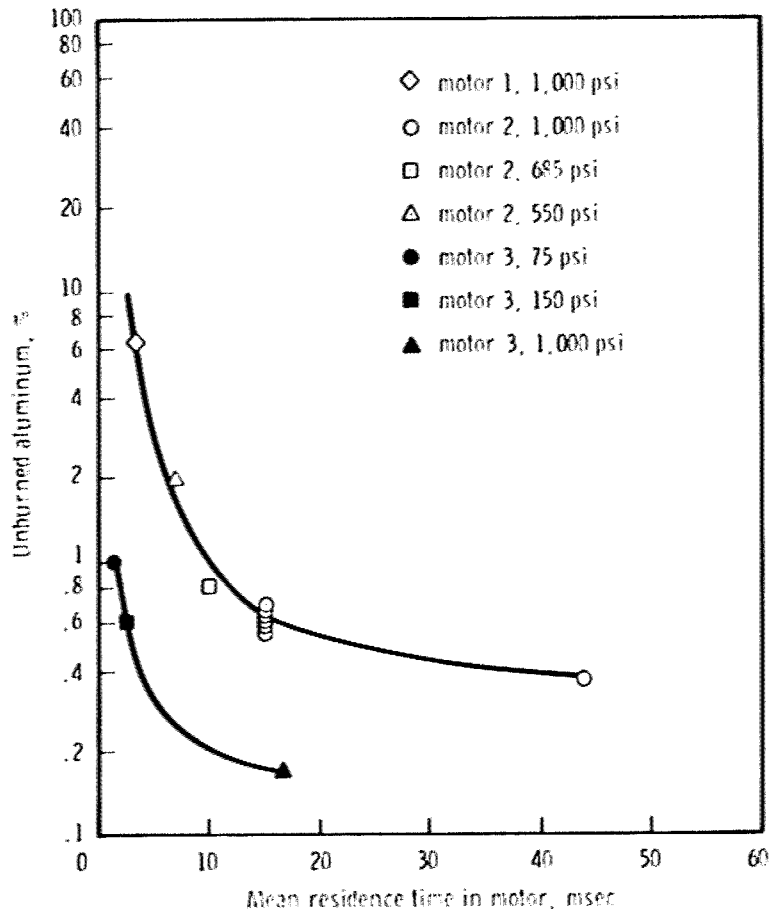


Figure 4.—Effect of residence time on completeness of metal combustion (ref. 19).

From the effect of throat area A_t on W , it may be seen also that t_r varies as L^* , characteristic length; i.e.,

$$t_r \propto L^* = V_c/A_t \quad (3)$$

Metal-particle ignition, combustion, and equilibration of combustion products must occur within the motor residence time to avoid chemical kinetic losses. When motor residence time is too short for adequate combustion, both kinetic lag and the failure of metals to burn completely may produce an equilibrium condition significantly different from the calculated one. The dependence of metal combustion on residence time is illustrated for one propellant in figure 4 (ref. 19), in which percent unburned metal is plotted against residence time. Mean residence times under 10 msec appear insufficient for complete combustion of the aluminum. In figure 5 (ref. 20), specific impulse efficiency is plotted against mean residence for a number of motors of different size. Note the sharp decline in efficiency below a mean residence time of 10 msec (the point of sharp decline is probably closer to 15 msec, since these data have not been corrected for motor heat loss, which, on a relative basis, increases as motor size decreases). The inflection point in such a curve will vary with the propellant. Similar curves for beryllium propellants show an inflection point in the 15 msec region (ref. 21).

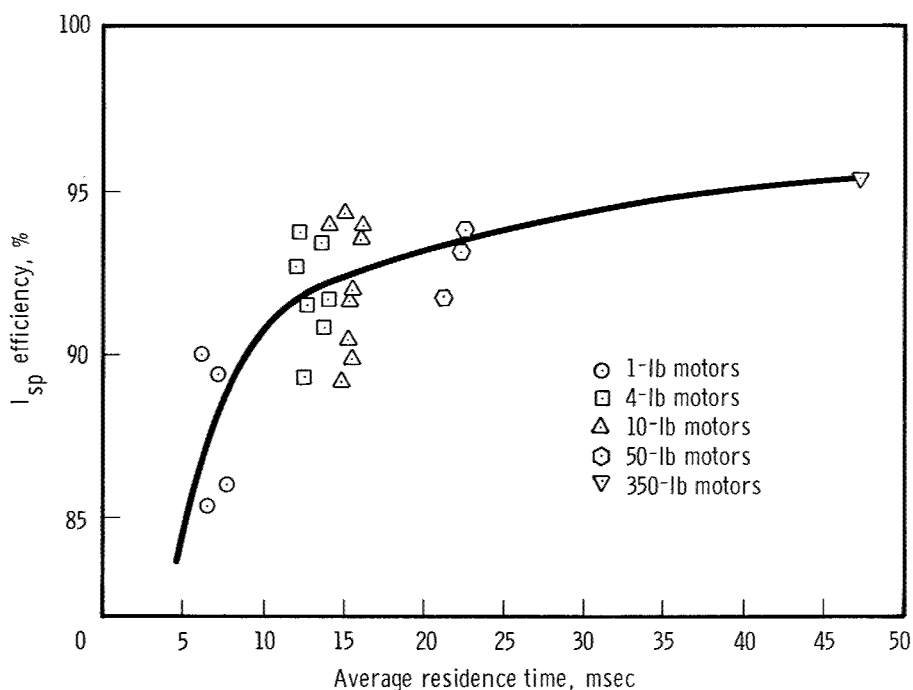


Figure 5.—Effect of residence time on I_{sp} efficiency in an Al-PBAN propellant (ref. 20).

2.2.1.1.2 Chamber Pressure

Window bomb studies have shown that metal combustion rate is a function of chamber pressure for a given equilibrium composition (ref. 22). The effect of pressure on metal combustion efficiency is complicated by the increase in chamber temperature associated with increased pressure and by the tendency of burning metals to form smaller agglomerates at higher pressures. Typical of the many observations of the latter effect are those shown in figure 6 (ref. 23). In one example shown, the average agglomerate

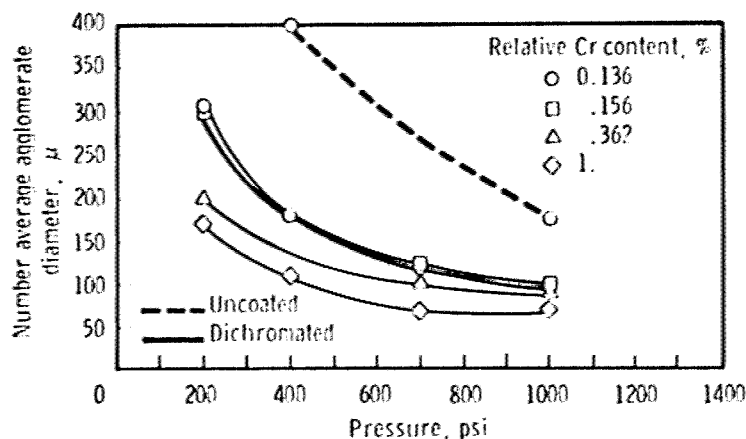


Figure 6.—Variation of aluminum agglomerate size with pressure (ref. 23).

size 400μ at 400 psi was reduced to 180μ at 1000 psi. This dimensional change reduces burning time by two-thirds. Combustion efficiency is improved in all motors by an increase in combustion pressure. However, overall performance efficiency may decline because of increased weight of hardware required to hold the increase in chamber pressure.

2.2.1.1.3 Flame Temperature

Combustion efficiency declines rapidly below a certain critical equilibrium flame temperature. Experimentally, it has been shown that I_p efficiency in highly aluminized propellants declines rapidly below a calculated flame temperature of 3200°K (ref. 20). The data in figure 7 (ref. 20) are not corrected for motor heat loss. Moreover, there is no sound way to correct for combustion inefficiencies at lower calculated temperatures so that the true flame temperature may be derived. However, figure 7 illustrates the dependence of metal combustion efficiency on flame temperature in aluminized propellants. Experiments with beryllium-DB propellants have shown that a minimum calculated flame temperature of 4200°K appears necessary to good combustion efficiency (ref. 24).

Low levels of aluminum (3-4 percent) burn efficiently in propellants having calculated

flame temperatures on the order of 2600° K. For this reason, a sounder approach to defining a minimum temperature for good metal combustion efficiency is the use of the parameter T^* , the equilibrium flame temperature assuming no metal combustion (ref. 25).

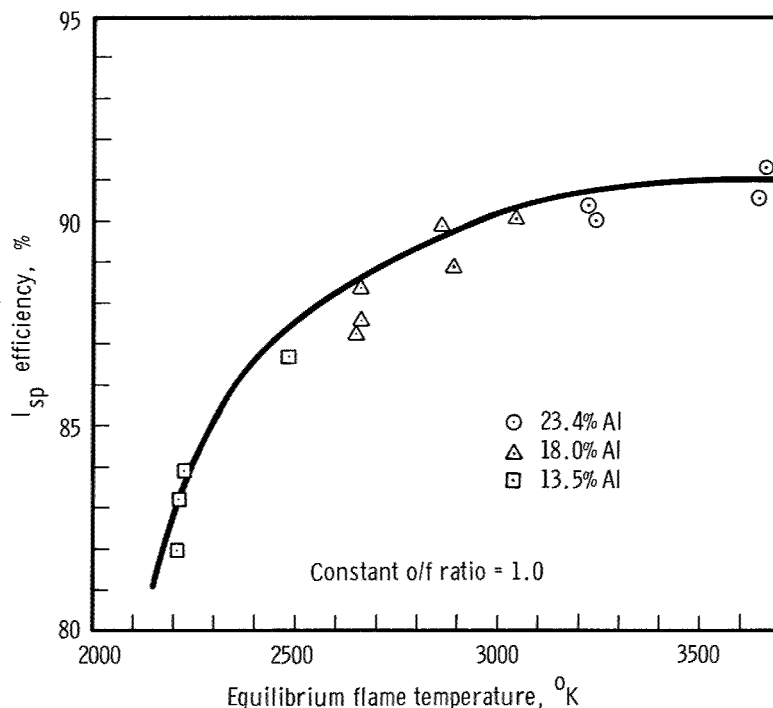


Figure 7.—Effect of equilibrium flame temperature on specific efficiency in highly aluminized propellants (ref. 20).

Metal ignition is slow at flame temperatures too low for rapid heat transfer to the metal particle. Both beryllium and aluminum particles are protected from oxidation by an oxide coating. The melting point of beryllium oxide is 2820° K, and the melting point of aluminum oxide is 2318° K. The metal particle surface must reach the melting temperature before ignition can occur. The following expression (adapted from ref. 26) describes the ignition delay time t_i :

$$t_i = \left(\frac{\rho d^2}{12k} \right) C_p \ln \left[\frac{(T_a - T_o)}{(T_a - T_i)} \right] + \frac{L}{T_a - T_F} \quad (4)$$

where

- k = metal thermal conductivity, cal/cm-sec-°C
- ρ = metal density, gm/cc
- d = metal particle diameter, cm
- C_p = metal heat capacity, cal/gm/°K
- T_a = temperature of hot gases, °K
- L = metal latent heat of fusion, cal/gm
- T_o = initial particle temperature, °K
- T_i = ignition temperature, °K
- T_F = melting temperature of metal, °K

2.2.1.1.4 Oxidizing Balance

A strong correlation exists between combustion efficiency and the oxidizing level of a propellant. The O/F ratio is arbitrarily defined as the ratio of oxidizer chemical equivalent weights to fuel chemical equivalent weights (including metal) for a combustion reaction that results in the products CO, H₂, and the appropriate metal oxide in the highest valence state for the metal. The higher the O/F ratio, the higher the combustion efficiency, approaching a limit characteristic of the motor. A correlation of combustion efficiency and O/F ratio is shown in figure 8 (ref. 20), in which I_{sp} efficiency is plotted against O/F ratio. The residence times in the 4-pound motors

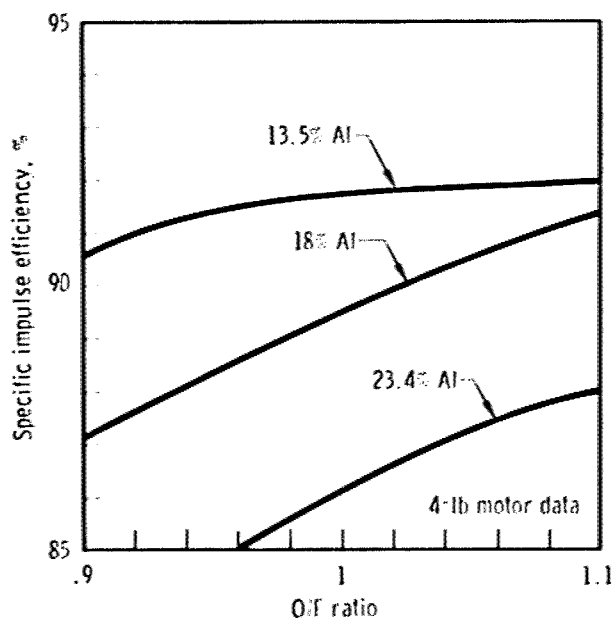


Figure 8.—Effect of O/F ratio on performance efficiency (ref. 20).

used in this experiment were on the order of 10 to 15 msec. O/F ratios of 1.1 and greater were necessary for efficient combustion. A similar principle has been established for beryllium propellants (ref. 27). Very high levels of aluminum, often greater than 20 percent, can be burned in CMDB propellants where high O/F ratios can be achieved (ref. 2).

2.2.1.1.5 Metal Droplet Size

2.2.1.1.5.1 Agglomeration

The burning time of metal droplets in the combustion chamber is a direct function of the droplet diameter, modified by the phenomenon of shattering. There is a tendency for droplet agglomeration in the gas stream after ejection.

Any technique, such as coating the aluminum with aluminum phosphate or with metallic chromium, that will reduce agglomeration in the chamber will promote the rate and efficiency of metal combustion. A significant reduction has been observed in number-average agglomerate diameter by the use of dichromated aluminum (aluminum coated with chromium by chemical deposition from a dichromate solution) (ref. 23); see figure 6.

2.2.1.1.5.2 Oxidizer Particle Size

The droplet size of aluminum may be reduced by reducing the size of the ammonium perchlorate oxidizer in the propellant. High-speed motion pictures of the burning surface of a pressurized composite propellant have shown that aluminum melts on the surface of a burning propellant and accumulates in the interstices between oxidizer particles (ref. 28). The size of the globule ejected from the surface is a function of the size of the pockets between oxidizer particles: smaller pockets give smaller globules leaving the surface, and the rate of combustion is increased. The general effect of oxidizer particle size on combustion efficiency has been observed with all fuels that melt on the surface of the propellant. The effect of oxidizer particle size on beryllium combustion rate is relatively small, since beryllium does not melt on the propellant surface. The effect of pressure on agglomerate size is discussed in section 2.2.1.1.2.

2.2.1.2 Nozzle Efficiency

Nozzle losses are composed of heat losses, inefficient-expansion losses, chemical and physical kinetic-lag losses, boundary-layer frictional losses, and two-phase flow losses. While all of these depend to some extent on the characteristics of the propellant, two-phase flow losses may vary widely with the composition of the propellant. These losses stem from the failure of the condensed oxide droplets to accelerate to the velocity of the gas stream and from the failure of the droplets to reach thermal equilibrium with the gas stream. A measurable, and at times significant, percentage of propellant potential energy is lost in this latter effect, since the oxide droplets fail to solidify and give up their latent heat of fusion to the gas. Ninety-five percent of all two-phase flow losses are estimated to occur in the nozzle throat as a result of the maximum velocity gradient at that location (ref. 29).

Formulation variables may modify two-phase flow losses. Propellant flame temperature to some extent influences the degree of solidification of metal oxides in the exhaust, but recovery of the heat of fusion of the oxide is largely a function of nozzle residence time.

2.2.1.2.1 Condensable Particle Concentration

Two-phase flow losses in metallized propellants are discussed in reference 30, both from a gas dynamic and an aerodynamic standpoint. Velocity-lag losses are a linear

function of the condensable concentration at the throat; this concentration is dependent on the metal content of the propellant (ref. 29).

Nozzle losses increase rapidly with the percent condensed species in the propellant exhaust (refs. 20 and 30). These losses are more than balanced by the increased energy from metal combustion, but eventually nozzle losses outpace the energetic gain. High-performance composite propellants typically contain aluminum loading in the 16 to 18 percent range, and double-base propellants with aluminum loading in the 18 to 20 percent range are common. At higher aluminum loadings, nozzle losses usually outweigh specific impulse gains.

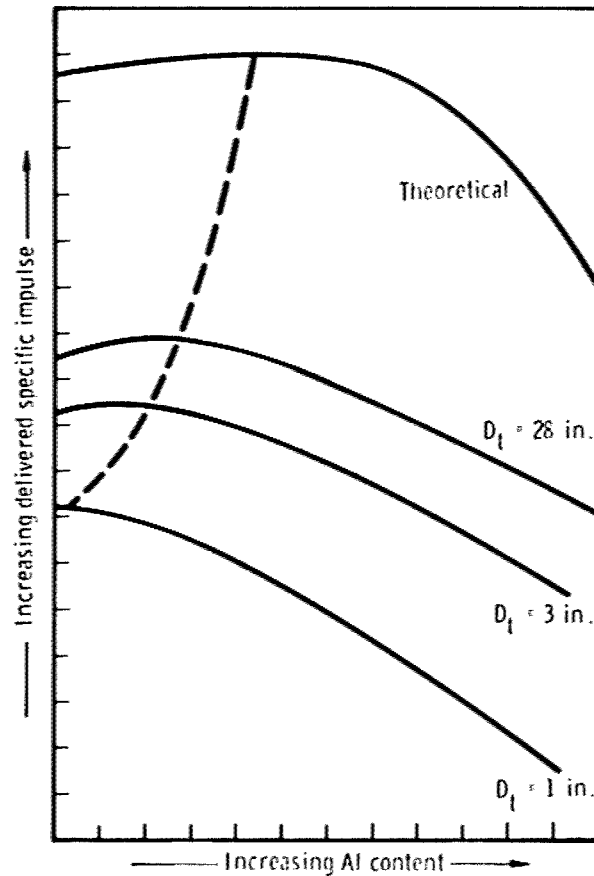


Figure 9.—Al content tailored to nozzle size for peak delivered specific impulse.

Two-phase flow losses are inversely proportional to throat size (ref. 29). Large concentrations of condensables may be tolerated in large throats without efficiency loss. Generally, peak delivered performance occurs with increasing metal content as the nozzle throat size increases, as shown in figure 9. In optimizing propellant performance, the propellant metal content should be related to the final motor size. This principle with experimental verification is discussed in reference 31.

2.2.1.2.2. Condensable Particle Size

Two-phase flow losses decrease as oxide particle size decreases because there is less velocity lag and more rapid thermal equilibrium with smaller particles. Figure 10 (ref. 32) shows the correlation between observed oxide particle size and performance loss in the Air Force BATES motor series. A reduction of particle diameter by 1μ results in a gain in delivered I_{sp} of 2 sec in the motors.

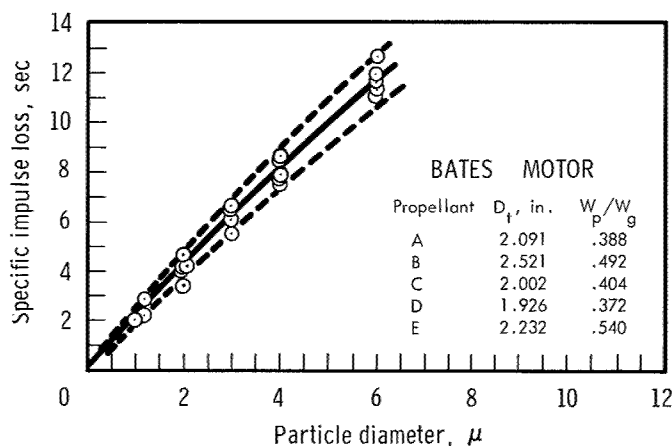


Figure 10.— I_{sp} loss vs. particle diameter for BATES motors (ref. 32).

The type of liner influences particle size (ref. 29). Carbon and other materials from the pyrolysis of the liner are thought to act as nucleating agents for aluminum oxide. Cheung and Cohen (ref. 21) have shown that an increase in the level of aluminum produces a small but definite increase in oxide particle size. An increase in chamber pressure results in increased particle diameter (refs. 33 through 35).

2.2.2 Delivered Density-Impulse

The significance of propellant density cannot be divorced from the specific application. The velocity change Δv_j given to a payload or stage may be calculated from the following (ref. 36):

$$\Delta v_j = g I_{sp} d_j \ln \left(\frac{W_{pj} + W_{wj} + W_{uj}}{W_{wj} + W_{uj}} \right) \quad (5)$$

where

- Δv_j = velocity increment added by stages, ft/sec
- W_{wj} = stage weight at burnout, lb
- W_{uj} = payload weight, lb
- W_{pj} = propellant weight in stage, lb

In a design where the volume is fixed, Δv_j may be improved by increasing $W_{p,j}$, which may be done by increasing the density of the propellant. The influence of propellant density on velocity increment may be approximated by fixing $W_{v,j}$:

$$\Delta v_j \propto I_{sp,j}^n \rho^n \quad (6)$$

Fixing W fixes the propellant volume; the density and $I_{sp,j}$ remain the only variables.

While the relation in equation (6) is a highly restricted approximation, it frequently is used in industry to compare I_{sp} -density tradeoffs in a particular application. The significance of density is such that a density change of 0.10 gm/cc (0.0036 lb/in.³) will balance a change in I_{sp} in the following manner, depending on "n" (ref. 36):

| n | $\Delta I_{sp,j}$, sec |
|------|-------------------------|
| 0.05 | 0.8 |
| 0.10 | 1.6 |
| 0.25 | 4.0 |
| 0.50 | 8.0 |
| 0.75 | 12.0 |
| 1.00 | 16.0 |

In a volume-limited stage,

$$n = \left(\frac{\beta}{\beta + 1} \right) \left(\frac{R - 1}{\ln R} \right) \quad (7)$$

where

$$\beta = \frac{\text{weight of case, lb}}{\text{weight of propellant, lb}}$$

$$R = \text{mass ratio} = \frac{W_p + W_{uc} + W_u}{W_{uc} + W_u}$$

In such a situation, as the weight of the case becomes more important, the significance of n increases. The weight of the case is inversely related to the propellant density and directly related to the combustion pressure. Combustion pressure is the most important parameter. Present case technology is such that β may be approximated by

$$\beta \cong 10^{-4} P_c \quad (8)$$

The performance of a propellant in a volume-limited application may more conveniently be evaluated against a reference propellant by the equation (refs. 36 and 37)

$$\Omega = I_{spd_{ref}} (\rho/\rho_{ref})^n \quad (9)$$

where

- Ω = effective I_{spd} , lb-sec/lb
- $I_{spd_{ref}}$ = delivered propellant specific impulse of reference propellant
- ρ = density of propellant, lb/in.³
- ρ_{ref} = density of reference propellant, lb/in.³
- n = fractional exponent calculated from stage design parameters

For a weight-limited application, the sum of the weights of the propellant W_p , the structure W_w , and the payload W_u are held constant; and the velocity increment may be calculated by

$$\Delta v_j = g I_{spd_j} \ln R_j = g I_{spd_j} \ln \left(\frac{W_p + W_w + W_u}{W_w + W_u} \right) \quad (10)$$

If one divides W_w into a weight W_x , which is fixed, and a weight W_p , which varies with propellant density, then

$$W_w = W_p \text{ (depend. on } \rho_p) + W_x \text{ (const.)} \quad (11)$$

Equation (10) becomes

$$\Delta v_j = g I_{spd_j} \ln \left[\frac{W}{W_p + (W_x + W_u)} \right] \quad (12)$$

where W and $(W_x + W_u)$ are constants, and the mass ratio R now has the form

$$R = \frac{W}{W_p + (W_x + W_u)} \quad (13)$$

One may define a parameter N that is directly proportional to the density of the case material, inversely proportional to the material strength, and has a safety factor and a geometry factor such that the case weight W_p is defined as

$$W_p = NP_c V_p \quad (14)$$

This defines the weight of the case in terms of the volume of propellant, combustion pressure, and the material parameter N . The ratio of case weight to propellant weight β may then be shown to be

$$\beta = \frac{W_p}{W_p} = \frac{NP_c V_p}{V_p \rho_p} = \frac{NP_c}{\rho_p} \quad (15)$$

Assuming a constant chamber pressure,

$$\frac{\beta_{\text{sub}}}{\beta_{\text{ref}}} = \frac{p_{\text{ref}}}{p_{\text{sub}}} \quad (16)$$

Given values for ρ and R for a reference propellant, these quantities may be calculated for the substitute propellant from equation (16). From equation (10), Δv , may be calculated, knowing R . The specific impulse tradeoff between a reference propellant and a substitute propellant may be assessed in a weight-limited system by

$$\frac{\Delta I_{sp_{\text{sub}}}}{I_{sp_{\text{ref}}}} = \frac{\ln R_{\text{ref}} - \ln R_{\text{sub}}}{\ln R_{\text{sub}}} \quad (17)$$

where R is the mass ratio as defined in equation (10).

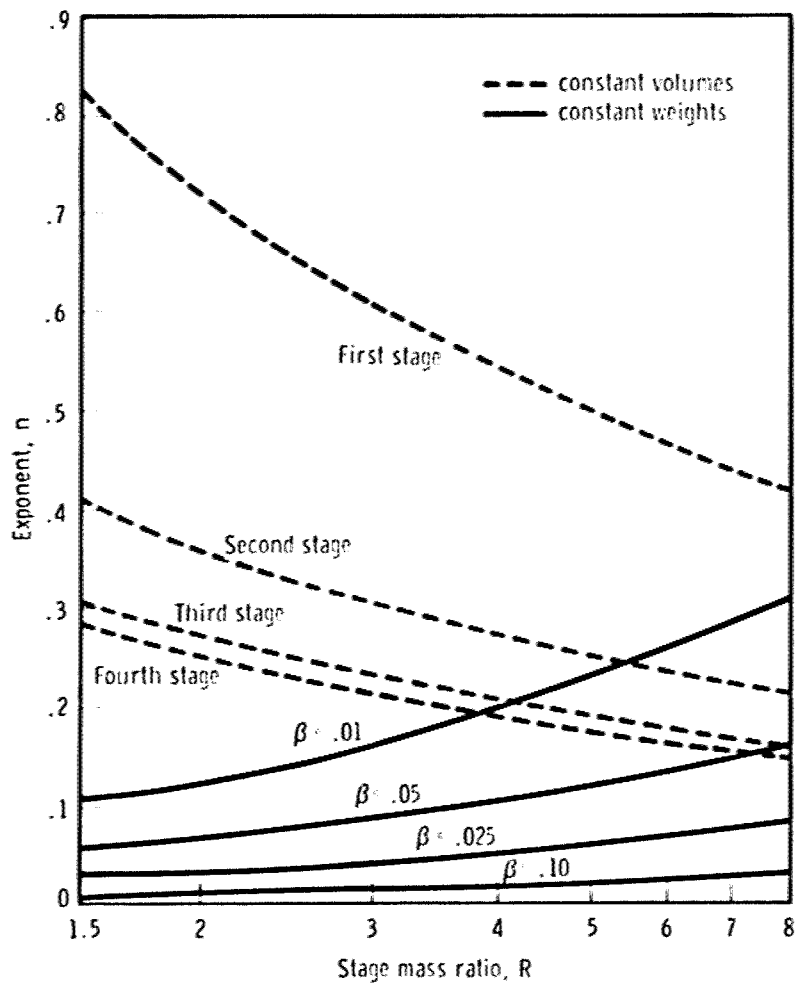


Figure 11.—Variation of density exponent with mass ratio in volume-limited and weight-limited stages.

A density exponent n may be defined as in expression (6) to evaluate the effect of density in a weight-limited system. Figure 11 illustrates the relation of n to mass ratio for various stages in both volume-limited and weight-limited applications.

2.3 Internal Ballistics and Combustion Characterization

After the free volume of the motor has been determined from the internal geometry design and the general propellant type selected, the type and size of the igniter and the placement of the igniter are determined. Subsequently, propellant modifications are made to give the required burning rate and any other needed internal ballistic properties. These modifications may be understood better in terms of recent treatments of propellant combustion. Models of the combustion of double-base propellants are discussed in references 38 through 40. The controversial area of ammonium perchlorate combustion, usually viewed as the rate-determining step in composite propellant combustion, is discussed in references 41 through 43. The many controversial models of composite propellant combustion include those discussed in references 44 through 50. A model of the combustion of aluminum in composite propellants is discussed in reference 51.

2.3.1 Internal Ballistics

2.3.1.1 Burning Rate

2.3.1.1.1 Burning-Rate/Pressure Relation

In both composite and double-base propellants, the primary heat-generating reactions occur among gaseous pyrolysis products and gaseous metals. As a result, the burning rates of solid propellants show a strong pressure dependence that may be described generally by the empirical equation

$$r = aP_c^n \quad (18)$$

where

- r = linear burning rate, in./sec
- a = an empirical constant, characteristic of propellant
- P_c = combustion pressure, lb/in.²
- n = burning-rate exponent

Burning rates usually are plotted as the ordinate against pressure on the abscissa on log-log paper. In the region of 500 to 1500 psi, this usually yields a straight line whose slope is n .

2.3.1.1.2 Burning-Rate Modification

Generally, there are five ways to increase the propellant burning rate:

- (1) Increase the binder heat of explosion.
- (2) Add a burning-rate catalyst.
- (3) Decrease oxidizer particle size.
- (4) Increase oxidizer loading.
- (5) Imbed wires or staples in the propellant.

All the above methods are applicable to CMDB and composite propellants, but only methods (1), (2), and (5) are applicable to classical double-base propellants. Where a method may be applied to increase the burning rate, the reverse of the step generally will reduce the burning rate.

Method (1) is applicable to both classical DB and CMDB propellants in that the heat of explosion is related to the amount of nitroglycerin or other nitrate plasticizer used in the propellant. Figure 12 (ref. 8) illustrates this correlation for a number of operational homogeneous DB propellants. The burning rate of a homogeneous double-base propellant may be reduced by the partial substitution of an inert plasticizer, such as dibutyl phthalate or triacetin, for some of the nitrate ester; the change results in a loss in specific impulse. The burning rate may be increased by increasing the level of nitrate ester plasticizer, the result being an increase in specific impulse. Modifications of the burning rate by the use of inert plasticizer will decrease the overall performance of the system.

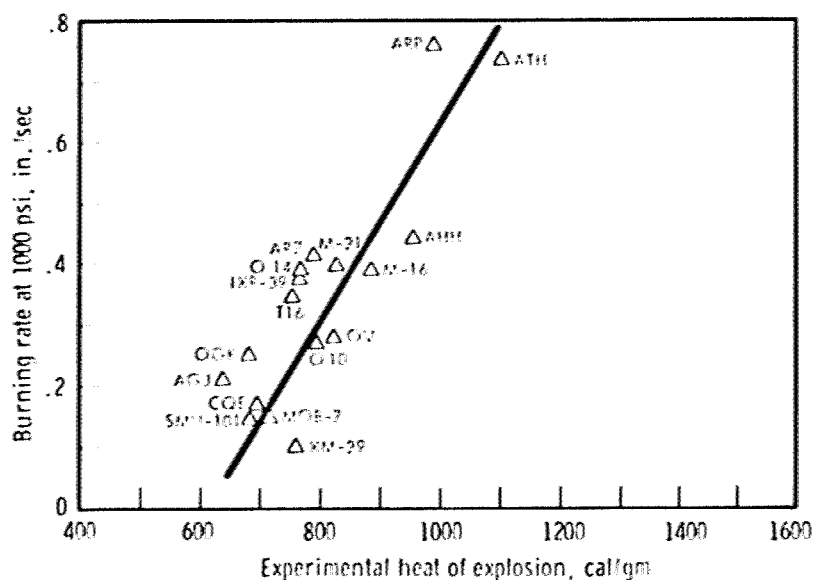


Figure 12.—Influence of heat of explosion on burning rate in nonmetallized double-base propellants (ref. 8).

There is no available technique for significantly decreasing the burning rate of a homogeneous double-base propellant without decreasing its theoretical specific impulse. Carbon black or lamp black may be used for small reductions in rate without measurable loss of specific impulse. In composite propellants, an energetic plasticizer such as a nitrate ester or a nitroplasticizer will increase the binder heat of explosion and result in an increase in burning rate.

Method (2) is applicable to all propellants. The use of combustion catalysts such as ammonium dichromate to increase the burning rate of homogeneous double-base propellants does not usually affect the theoretical specific impulse. Lead and tin organic salts may not be used to introduce plateau and mesa burning (sec. 2.3.1.2.1) in homogeneous double-base propellants. Many of the conventional composite combustion catalysts such as ferric oxide (Fe_2O_3), however, are incompatible with double-base binders.

Ferric oxide is widely used as a burning-rate catalyst in composite propellants. Copper chromite (actually a mixture of cupric oxide and chromic oxide) also is used extensively, although it is incompatible with some polybutadiene binders and with double-base binders. A number of organic iron catalysts have been used in composites. Most notable among these has been ferrocene, an iron organic-coordination compound. The effectiveness of several iron compounds in catalyzing the burning rate of a PBAN propellant is shown in figure 13 (ref. 52). Fe_2O_3 is the least effective of the three with ferric ferrocyanide intermediate and the iron coordination compound, ferrocene, being most effective. Ferrocene is volatile and often is lost during cure or storage, so that exact control of burning rate sometimes becomes difficult. Various less volatile substituted ferrocenes, such as mono-*n*-butyl ferrocene, have been used. Several new nonvolatile polymeric iron catalysts offer reproducible catalyzed burning rates.

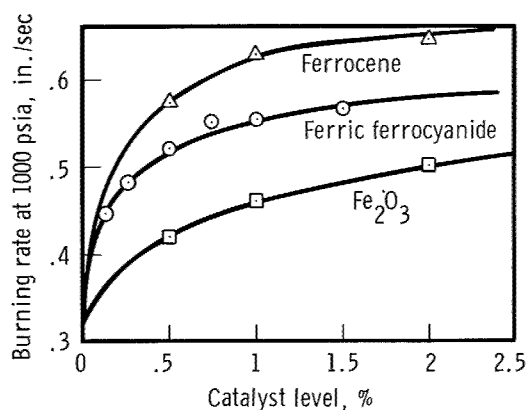


Figure 13.—Effect of several iron catalysts on burning rates of PBAN propellants (ref. 52).

The available catalyst surface area and the degree of catalyst oxidizer contact are important to burning-rate catalysis. Figure 14 (ref. 52) illustrates the changes in the burning rate of a PBAN propellant catalyzed by rhombohedral Fe_2O_3 , spherical Fe_2O_3 , and Fe_3O_4 catalysts. For each catalyst, an increase in the surface area results in significant changes in burning rate at a fixed concentration.

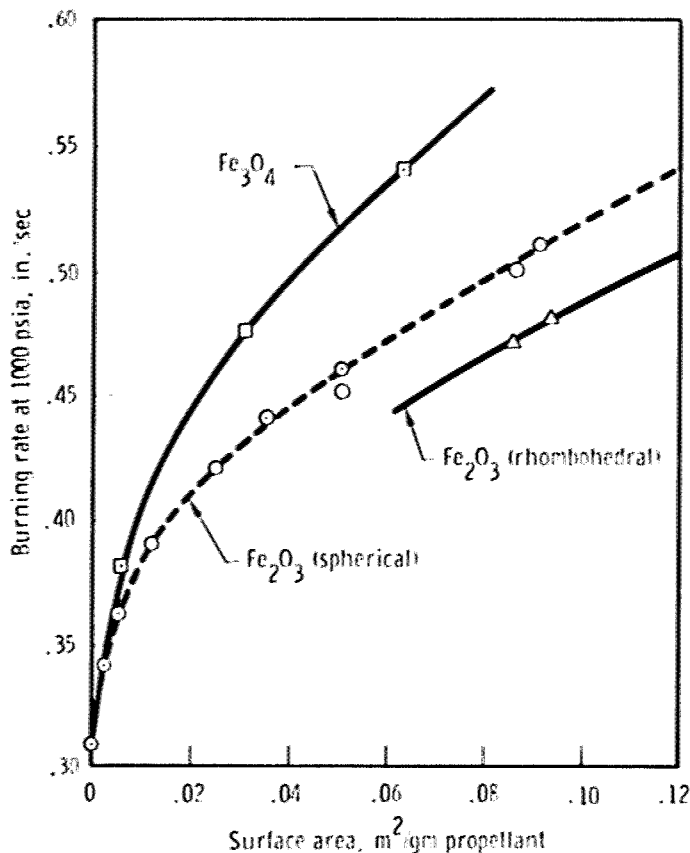


Figure 14.—Effect of iron oxide surface area on burning-rate catalysis in PBAN propellants (ref. 52).

The burning rate of a composite propellant that contains a catalyst may be reduced without loss of performance by reducing the catalyst level. The burning rate also may be reduced by increasing the average size of the oxidizer particles if the residence time remains long enough to avoid combustion inefficiency. Other than these two methods, there is no effective method of decreasing the burning rate of a composite propellant without performance loss.

The burning rate of double-base propellants, CMDDB propellants, and energetic-binder composite propellants may be reduced by lowering the heat of explosion of the binder through the dilution of the oxygenated plasticizer with an inert plasticizer.

Method (3), reducing the size of oxidizer particles, is not applicable to homogeneous DB propellants. The effect of increasing the ratio of fine oxidizer particles to coarse oxidizer particles in a composite propellant or CMDB system is shown in figure 15 (ref. 52). In highly loaded propellant systems, however, the reduction of the oxidizer particle size may result in an increase in propellant viscosity, limiting the final processability of the system. HMX and RDX in CMDB propellants are burning-rate depressants, especially at higher binder-energy levels.

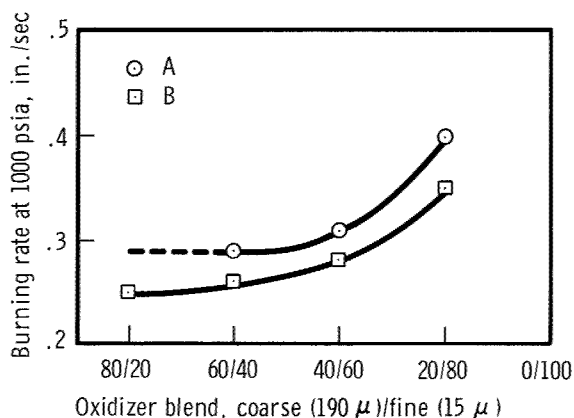


Figure 15.—Effect of oxidizer grind on burning rate in PBAN propellants (ref. 52).

Method (4), changing the oxidizer content, is applicable to all propellants as a method of modifying burning rate. However, a change in oxidizer content often has significant side effects. In particular, decreasing the oxidizer content to reduce burning rate may result in loss of combustion efficiency and loss of specific impulse; increasing the oxidizer loading to increase burning rate may introduce processing problems and possibly reduce reliability.

Significant increases in burning rate can be achieved by method (5). Polyvinylchloride propellants with very high burning rates have been prepared by casting the propellant around a continuous structure of fine silver wires. A recent variation of this technique uses part of the aluminum content in the form of chopped aluminum wires or staples incorporated into the propellant. For ballistically reliable burning rates, the wires must be oriented totally at random or oriented consistently in a known direction. Burning rates in staple-containing composite propellants generally are not reproducible because of staple orientation at the wall and surface that results from wall-flow interaction during casting. No such problem is encountered in CMDB propellants since the staples are incorporated in the casting powder.

In addition to the conventional methods discussed above, there are two other ways in which burning rate may be modified:

- (1) The addition of aluminum to a composite propellant increases the equilibrium flame temperature but often decreases the burning rate of the propellant. This effect is shown in figure 16 (ref. 52). At a constant aluminum content, increasing oxidizer content at the expense of binders increases burning rate. The addition of aluminum or AP usually increases the rate of the double-base propellant. Aluminum has little effect when HMX or RDX are present.
- (2) Burning rate may be reduced somewhat in composite propellants by the use of inert flame-retardant coatings on the oxidizer. Coatings of sodium fluoride, sodium barbiturate, magnesium oxide, and even solvent-deposited fluorocarbons have been used with varying degrees of success. However, all these coatings result in a performance loss.

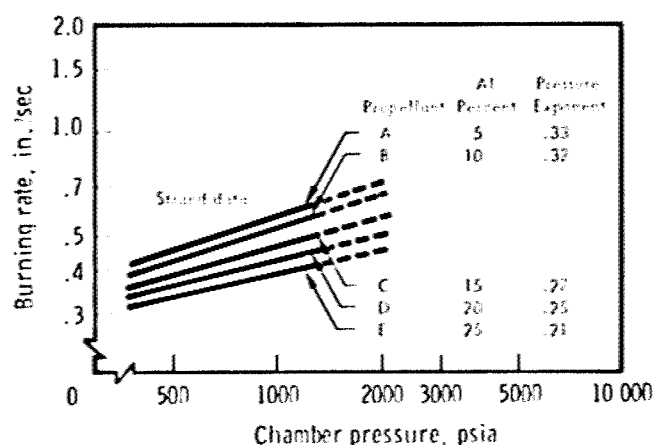


Figure 16.—Effect of aluminum level on burning rate in PBAN propellants (ref. 52).

2.3.1.1.3 Burning-Rate Reproducibility

The reproducibility of the burning rate is critical to good motor design. Careful control of oxidizer size and content as well as catalyst particle size and specific surface is important to this reproducibility. Close control of volatile catalysts such as ferrocene is necessary. Weighing errors in aluminum content are less important to burning-rate reproducibility than weighing errors in oxidizer content, although such errors affect I_p and mechanical properties. The catalyst lot itself often is checked for reactivity in small motors.

2.3.1.2 Pressure Sensitivity of Burning Rate

In most operational propellants, the values for the pressure exponent of burning rate (n) range from a low of 0.2 to a high of 0.8. The effect of n on the combustion pressure of a rocket motor may be inferred from the empirical equation (ref. 53):

$$P_c = b(A_b/A_t)^{\frac{1}{1-n}} \quad (19)$$

where

A_b = burning area, in.²

A_t = area of the throat, in.²

b = a constant, characteristic of the propellant

2.3.1.2.1 Effect of Pressure Exponent

It may be seen from equation (19) that, as n increases, the effect of A_b/A_t on P_c becomes more important. A partial blockage of the throat may result from incompletely burned material or from the deposition of melted aluminum or its oxide. If n is large, a decrease in A_t will result in a correspondingly very large increase in P_c , which may exceed the motor failure limit. Grains with small imperfections or cracks from temperature cycling will show increases in A_b above the design value. If n is large, an increase in A_b will result again in an uncontrolled increase in P_c . Generally, the pressure exponent should be as low as possible so that the motor internal ballistics will not change drastically as a result of such unanticipated changes in burning surface or throat diameter. High-exponent propellants, however, are desirable in controllable motors to facilitate extinguishment.

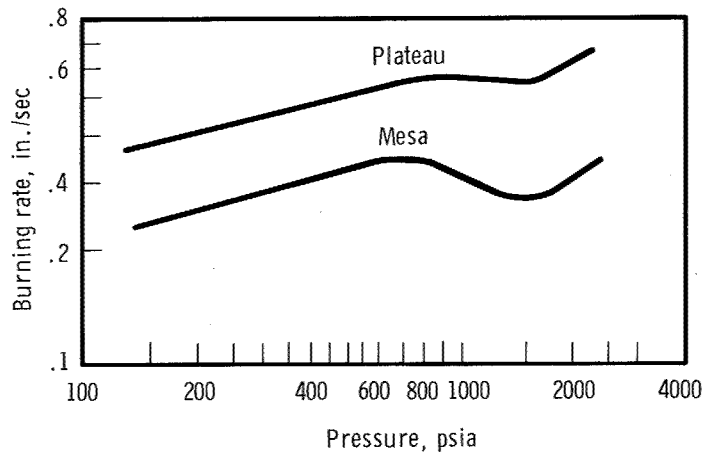


Figure 17.—Mesa and plateau ballistics in double-base propellants.

The most stable ballistic situation is found in the plateau- and mesa-burning double-base propellants (see fig. 17). In these, the pressure exponent may approach zero or may even be negative. If the motor is designed to operate at the pressure at which the characteristic mesa occurs, an increase in burning surface will result in an increase in mass discharge rate and combustion pressure. The increase in combustion pressure will carry the system into the forward slope of the mesa region, the result being a decrease in burning rate. This phenomenon has the effect of damping any

further increases in pressure. However, the values of n on either side of the mesa or plateau generally are very high.

A similar phenomenon occurs in composite propellants with O/F ratios sufficiently low so that free carbon is formed as an equilibrium product.

2.3.1.2.2 Modification of Pressure Exponent

The techniques available for modification of the burning-rate pressure exponent are relatively limited. In homogeneous double-base propellants, lead or tin organic salts introduce a plateau or mesa region, as noted previously. The effect of wires in composite propellants has been discussed in connection with increases in burning rate. The degree of continuity and the type of orientation has an effect on the burning-rate exponent.

As shown in figure 16, increasing the aluminum content of a PBAN propellant decreases the burning-rate exponent. A similar effect is encountered in other composite propellants. A decrease in solids loading results in a decrease in the burning-rate exponent. Some composite propellants with reduced oxidizer content may show a definite plateau in a relatively narrow pressure region.

The burning-rate exponent may be changed by varying the oxidizer grind. The burning-rate exponent increases with increasing average oxidizer particle size or with very fine AP ($<2\mu$). Coating the oxidizer with a flame-retardant material will frequently lower the burning-rate exponent. The magnitude of these effects varies from propellant to propellant and is not predictable without experimental measurements.

The substitution of HMX or RDX for part of the AP in CMDB propellants usually increases the burning-rate exponent. The substitution of potassium perchlorate for part of the ammonium perchlorate in a propellant frequently increases the burning-rate exponent. Such a substitution, however, results in the lowering of the theoretical specific impulse, as the gases resulting from oxidation of the ammonium ion are lost. Moreover, both two-phase flow losses and radar attenuation increase because of condensed potassium chloride in the exhaust.

2.3.1.2.3. Reproducibility of Pressure Exponent

The pressure exponent of burning rate is relatively insensitive to minor errors in formulation and is generally quite reproducible from batch to batch of a propellant. However, large errors in the preparation of oxidizer grind and volatilization of catalyst from ferrocene-catalyzed composite propellants may result in a significant change in n .

2.3.1.3 Temperature Sensitivity of Burning Rate

The burning rate of a propellant is a function of the temperature of the grain. Several models for this temperature/burning-rate relationship are discussed in references 54, 55, and 56.

The temperature sensitivity of burning rate usually is described by the empirical parameters

$$\sigma_P = \left[\frac{\partial \ln r}{\partial T} \right]_P \quad \text{Temperature sensitivity of } r \text{ at a particular value of pressure} \quad (20)$$

$$\sigma_K = \left[\frac{\partial \ln r}{\partial T} \right]_K \quad \text{Temperature sensitivity of } r \text{ at a particular value of } K (= A_b/A_t) \quad (21)$$

However, because of the complex interrelationship of T , P , r , and grain geometry, a complete description of propellant temperature sensitivity requires two additional empirical parameters:

$$\Pi_K = \left[\frac{\partial \ln P}{\sigma T} \right]_K \quad \text{Temperature sensitivity of } P \text{ at a particular value of } K \quad (22)$$

$$\Pi_{P/r} = \left[\frac{\partial \ln P}{\sigma T} \right]_{P/r} \quad \text{Temperature sensitivity of } P \text{ at a particular value of } P/r \quad (23)$$

The Π coefficients are related to the σ coefficients and to n by

$$\Pi_K = \frac{\sigma_K - \sigma_P}{n} \quad (24)$$

$$\Pi_{P/r} = \frac{\sigma_P}{1 - n} \quad (25)$$

Of these coefficients, the most commonly used are σ_P (for strand data) and π_K (for small-motor data). Reference 7 describes how these coefficients are measured and used in characterizing propellant temperature sensitivity.

When the motor may be exposed to a wide range of ambient operating temperatures, the temperature sensitivity of the burning rate is kept as low as possible. The selection of a propellant with a low pressure exponent usually ensures a low temperature sensitivity.

Attempts to modify the temperature sensitivity of burning rate are rare. However, it can be modified by the same techniques used to lower the pressure exponent. The temperature sensitivity generally is lower in propellants with lower burning-rate exponent. For this reason, homogeneous double-base propellants with plateau- or mesa-burning characteristics have very low temperature sensitivities in the plateau and mesa region. In composite and CMDB propellants, those techniques that decrease n (e.g., changes in oxidizer particle size) tend to decrease the temperature sensitivity

of burning rate. Various coatings and additives such as silicone additives have been used to decrease temperature sensitivity, but with some loss in specific impulse.

2.3.1.4 Measurement of Internal Ballistic Properties

Burning-rate measurements frequently are made in the Crawford strand burner. Thin strands of propellant, their outer burning surface suitably inhibited, are burned in a pressure bomb, usually under nitrogen. The linear burning rate is determined by measuring the time interval between the melting of two inserted wires. Strand burning-rate measurements frequently are different from those encountered in actual motors, especially in the 500 psi region; and in some instances the strand-measured pressure exponent of burning rate may be different from that observed in motors. Small ballistic evaluation motors frequently give more meaningful burning-rate measurements (ref. 7).

Although strand-burning measurements frequently are used successfully to define the n of a propellant, the danger in this method is well illustrated in figure 18 (ref. 52). Not only the burning rate but also the pressure exponent of burning rate of a propellant in an internal-burning motor may be greater than or less than that measured in a strand.

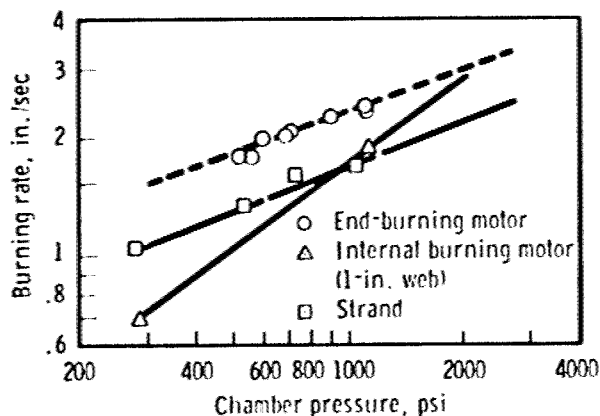


Figure 18.—One example of variations of burning-rate exponent with type of measurement (ref. 52).

Since the pressure exponent is graphically the slope of the line of the plot of the log of the burning rate versus the log of the combustion pressure, its value is sensitive to small errors at the extreme of the experimental combustion pressure range. For this reason, the pressure exponent should be derived from a fairly large number of experimental determinations. While a pressure exponent of reasonable validity may be derived from three burning-rate measurements at three pressures within the range of interest, at least nine measurements covering a range of pressure of at

least 500 psi are desirable. The burning-rate plot is fitted statistically to these data, discarding any widely divergent point. The coefficient of variation (σ/\bar{X}) usually considered acceptable in burning-rate data is 0.020 (refs. 7 and 55).

Frequently, liquid strands (i.e., uncured propellant confined in tubes such as ordinary soda straws) are used for quality control purposes. These liquid strands frequently give good correlation with cured strands. The correlation, however, must be established for each propellant. Liquid-solid strand correlation generally is poor for propellants with burning rates greater than 1.0 in./sec. The use of such strands allows quick determination of burning rates while the propellant is held in the mixer before casting.

2.3.2 Erosive Burning

2.3.2.1 Factors in Erosive Burning

A special instance of burning-rate increase occurs when a rapid flow of gas parallel to the burning surface results in a higher local mass flux (refs. 56 and 57). This effect, erosive burning, stems from increased heat transfer from the flame to the burning surface. Erosive burning becomes particularly troublesome as the J ratio (ratio of the area of the nozzle throat to the cross-sectional area of the grain port) approaches 1.0. Under these conditions, gas velocities at the throat end of the port become very high, and burning rate may be considerably enhanced through increased heat transfer.

Erosive burning is more likely to occur in propellants with flame temperatures below 3000° K. When erosive burning occurs, the selection of a propellant with higher flame temperature frequently will reduce or eliminate the problem. Erosive burning is more pronounced in propellants with lower burning rates. Fluorocarbon composite propellants, however, are particularly sensitive to erosive burning (ref. 58).

2.3.2.2. Characterization of Erosive Burning

There is no completely satisfactory experimental or theoretical treatment of erosive burning. However, the erosive-burning characteristics of a propellant usually are defined in industry empirically by use of the Lenoir-Robillard treatment (ref. 59). Frequently, small motors are fired and their burning interrupted at various times to provide average burning-rate measurements for a particular gas flow regime. In some instances, the grain is instrumented with buried probes that give average burning-rate data for several increments of web. Pressure instrumentation at various stations along the grain also has been used in conjunction with interrupted burning. Lawrence et al. (ref. 60) have developed an effective prediction technique; they use a modified Lenoir-Robillard equation based on turbulent-pipe-flow heat transfer combined with a simple computerized modular treatment to predict pressure, velocity, and mass flow at any point in the port.

2.3.3 Acceleration Effects

When acceleration is applied to a burning motor, either by spin or by a force applied along its axis, any burning surface forming an angle of 60° to 90° with the acceleration vector shows burning-rate enhancement (refs. 61 through 64). This effect is observed in non-aluminized propellants (ref. 65) but is enhanced by metal additives. A cylindrical internal burning grain, rotated about its axis, appears to be the most sensitive to this phenomenon. The effect of axial spin is shown in figure 19 (ref. 20), which presents thrust traces of a motor (16 percent aluminized PBAN propellant) rotated about its axis at various rates.

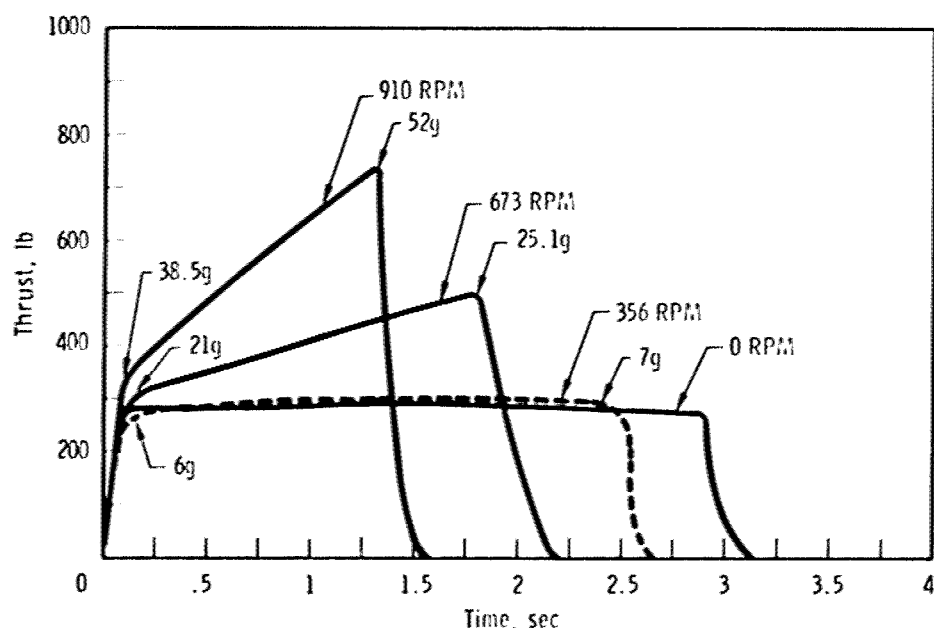


Figure 19.—Effect of axial spin on thrust level of a composite propellant motor (ref. 20).

Above an average particle size of 26μ , the size of the aluminum particle correlates directly with the increase in burning rate (ref. 61). The burning-rate augmentation varies from propellant to propellant but is directly related to the level of aluminum in the propellant. The effect at a particular aluminum level becomes more pronounced at higher acceleration levels (refs. 61 and 64). Slower burning propellants show greater relative augmentation (ref. 65). The phenomenon appears to be transient in nature (ref. 61).

Static spin tests have given misleading results because of the tendency of the aluminum to collect on the burning surface of spinning motors, since it was not accelerated along the axis as would be the case in free flight (refs. 61 and 64). The effect of such augmentation has been met by reduction of aluminum particle size, reduction of burning rate, or reduction of aluminum content.

2.3.4 Oscillatory Combustion

Oscillatory combustion (often referred to as combustion instability) in its extreme form may result in motor failure (ref. 66). The chamber pressure may oscillate at frequencies above 500 cps with amplitudes as high as 50 percent of the design pressure. At other times, the mean chamber pressure may rise more than twice the design pressure for an extended part of the operating cycle. These oscillations may continue during the operation or may damp out and return. Another mode of oscillatory combustion is one in which motors burn in a nonequilibrium manner for a short period and then extinguish, only to reignite after several seconds; this cycle (called "chuffing") may be repeated until all the propellant has been consumed.

Oscillatory combustion appears to stem from a coupling between the transient combustion characteristics of the propellant and the acoustic characteristics of the combustion chamber. Three forms have been identified:

- (1) In pressure-coupled oscillatory combustion, the combustion chamber cavity functions as an acoustic oscillator in establishing acoustic pressure oscillations (refs. 50, 65, and 66).
- (2) Velocity-coupled oscillatory combustion, a special instance of erosive burning, results from the gas oscillating parallel to the burning propellant surface. This oscillation produces changes in the local burning rate by changing heat transfer to the surface. The phenomenon is coupled with the acoustic response of the chamber.
- (3) Bulk-coupled oscillatory combustion in both metallized and nonmetallized propellants results in oscillations at low frequencies (0-500 cps) traceable primarily to the accommodation time lag in the solid propellant when a thermal wave is impressed.

Metal or metallic oxides and other additives generally suppress pressure-coupled oscillations. Aluminum and aluminum oxides appear to suppress high-frequency oscillations by acoustic dampening in the combustion chamber gases (ref. 66). At lower frequencies, this damping mechanism is less efficient than at higher frequencies. Metal addition, however, is not always effective (ref. 67). Motors with high levels of aluminum (16-20%) occasionally have shown instability (ref. 66).

The use of rods and baffles within the combustion chamber is sometimes effective in breaking up the acoustic mode that supports the oscillatory combustion. Grain changes such as the introduction of slots or holes may be used to change the acoustic properties of the combustor by shifting propellant driving surfaces to less responsive regimes (refs. 65 and 66).

2.3.5 Radar Attenuation

The hot exhaust of a high-performance rocket tends to attenuate any RF signal such as a guidance, tracking, or telemetry signal because of ionization in the flame at

high flame temperatures. The principal cause of radar attenuation is the thermal ionization of alkali metals, chiefly sodium and potassium, in nonequilibrium processes during afterburning (refs. 68 through 71). Attenuation is more pronounced at lower altitudes. It increases with higher flame temperatures, smaller nozzle throats, and lower expansion ratios. Aluminum increases radar attenuation by increasing flame temperature and by reducing the propellant O/F ratio so that afterburning is promoted.

The following approaches are taken to reduce attenuation: (1) reducing afterburning by increasing O/F ratio to avoid a higher temperature for ionization (ref. 72), (2) using an electron scavenger additive (refs. 72 and 73), (3) reducing chamber and exit plane temperatures by altering the formulation (ref. 72), and (4) reducing the sodium and potassium content of the propellant and liner (ref. 74).

2.4 Mechanical Properties Characterization

Initially, the designer selects a propellant with mechanical properties that appear to satisfy the requirements of the grain stress analysis. These requirements frequently are more severe for an upper stage motor than for a lower stage application. Subsequent formulation changes during tailoring may affect the mechanical properties of the propellant. For this reason, early mechanical property tests must be made with each formulation tailoring change. Screening tests conducted after each formulation change during any propellant optimization program form the basis for further formulation changes while more elaborate evaluation tests are being run. After the formulation has been fixed and early screening properties appear satisfactory, a more complete mechanical property evaluation generally is made to determine the structural safety properties for the propellant/grain design combination. The degree to which these somewhat costly characterization techniques are used depends on how marginal the design appears. In many instances, simple screening tests are sufficient to establish that a wide failure margin exists and that more elaborate tests are unnecessary.

2.4.1 Screening Tests

Screening tests are conducted with each formulation change and during any mechanical property optimization program. Certain special properties occasionally are determined during the screening period: extreme stability at elevated temperatures, special low-temperature strain requirements, high vibration modulus, etc. However, most mechanical property screening during an optimization program is directed to finding the best set of failure stress-strain limits at three temperatures such as -65° F, 76° F, and 160° F, where -65° F and 160° F are the lower and upper limits of expected temperature exposures.

2.4.1.1 Uniaxial Tensile Properties

Although propellant within the grain is subjected to biaxial and triaxial strain fields, screening programs normally develop uniaxial data with a type A, type B, or type C JANAF uniaxial specimen (ref. 75). Figure 20 shows the standard specimen dimensions. Type A has tabs cemented to the specimen to help maintain a more constant gauge length. Type B is milled from a slab of propellant and has a constant 0.375 by 0.50 in. cross section with a constant gauge length. Type C is a less sophisticated specimen, die cut from slices of propellant that may vary in thickness by 33.3 percent, i.e., from 0.25 to 0.40 in. (ref. 76).

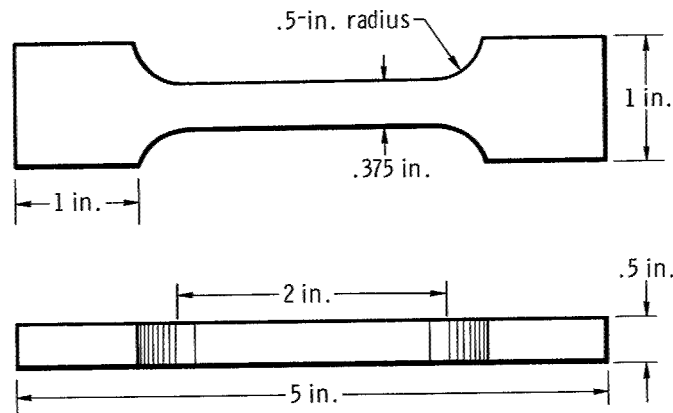


Figure 20.—JANAF tensile specimen.

The fillet regions of the JANAF specimens are placed in the machine holders of a testing device such as an Instron Tester, which pulls the specimen at a constant displacement rate. The force applied to the specimen is measured by a load cell attached to one of the jaws. Because of the viscoelastic response of the propellant, the propellant flows through the holder jaws during testing, leading to a changing gauge length and a variable strain rate. Direct strain-measuring devices such as plastic extensometers are attached to the propellant to measure true strain. Stress data are derived from

$$\sigma = \frac{F}{A_0} \quad (26)$$

where

σ = stress, lb/in.²

F = force applied to the specimen, lb

A_0 = original cross-sectional area of the specimen neck, in.²

An area correction allows for "necking-down" of the sample during the test:

$$\sigma = \frac{F(1 + \epsilon)}{A_0} \quad (27)$$

where ϵ = measured strain, in./in.

The usual test crosshead rate is 2 in./min, although 0.2 in./min often is used for slow strain-rate response measurements.

Uniaxial data usually are related to the true stress-strain fields in the propellant by some convenient conversion factor, often determined empirically for each propellant. A typical approach assumes that the following approximations are valid specifically for highly loaded CTPB composite propellants (ref. 55):

$$\begin{aligned} \text{Biaxial stress} &= \text{Uniaxial stress} \times 1.2 \\ \text{Biaxial strain} &= \text{Uniaxial strain} \times 0.6 \\ \text{Biaxial modulus} &= \text{Uniaxial modulus} \times 1.2 \end{aligned}$$

Such factors are determined for a given family of propellants of similar solids loading.

2.4.1.2 Bond Evaluation

Typically, solid propellants are bonded to the case or liner to withstand the thermal, pressure, and acceleration (including vibrational) stresses of motor. Therefore, the bonding characteristics of new propellants are evaluated during screening. Three different tests are commonly conducted to screen or measure this bonding behavior (ref. 75): (1) peel, (2) shear, and (3) bond-in-tension.

The peel test has been used because of its low cost for sample preparation and test, but the test itself is of doubtful value. The shear and bond-in-tension tests gradually are replacing the peel test as a screening tool because the results from these two are more valid for structural analysis requirements. Shear and bond-in-tension samples are prepared with various substrates consisting of propellant/liner/insulation/steel to simulate all the interfaces that occur in an operational motor. Test procedures for each of the bond tests are included in reference 75. Bond tests are conducted over the temperature range considered for the final propellant application. The bond strength requirement is determined by a grain stress analysis as described in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis," (to be published as NASA SP-8073).

2.4.2 Structural Analysis Properties

Once a final formulation is selected, extensive propellant physical properties may be obtained for use in structural analysis of specific grain designs to calculate grain stress-strain conditions for thermal, pressurization, and acceleration loading condi-

tions. Structural safety factors are determined by comparing propellant failure limits with predicted grain stress-strain requirements. Six propellant properties are used in the calculation of grain stress-strain values:

- Relaxation modulus, $E(t)$, lb/in.²
- Time-temperature shift factor, a_T
- Poisson's ratio, ν
- Coefficient of linear thermal expansion, α , in./in.-°F
- Thermal diffusivity, κ , in.²/hr
- Density, ρ , lb/in.³

The major tool used for predicting grain stress-strain values is a series of finite-element elastic-analysis computer codes such as those presented in reference 77. These computer codes give approximate solutions for the stress, strain, and displacement in grain designs when the state of plane stress, plane strain, or axial symmetry can be assumed. Viscoelastic analysis is performed by consideration of a sequence of elastic solutions corresponding to appropriate values of modulus and Poisson's ratio. The correspondence between a viscoelastic solution (in time) and a suitable sequence of elastic solutions is provided by use of the Laplace Transform or by the use of the Convolution Integral applied to the equations of linear viscoelasticity (refs. 78 and 79), as described in the design criteria monograph, "Solid Propellant Grain Structural Integrity Analysis."

2.4.2.1 Viscoelastic and Thermal Properties

Viscoelastic Properties

Two basic material parameters are required to define a material response to an applied load. The material properties normally selected to identify propellant deformation behavior are the viscoelastic modulus and Poisson's ratio. Viscoelastic modulus is measured with constant-strain-stress relaxation or constant-strain-rate tests over a broad temperature range (ref. 75). The modulus behavior is then shifted by using time-temperature shift factors a_T to obtain one composite master modulus curve that includes data from all of the test temperatures. This master modulus curve is fit to a Prony series form that is compatible with the differential equations of linear viscoelasticity:

$$E(t) = \frac{\sigma(t)}{\epsilon(t)} = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \dots + A_n e^{-t/\tau_n} \quad (28)$$

where

- $E(t)$ = time-dependent modulus, lb/in.²
- $\sigma(t)$ = time-dependent stress, lb/in.²
- $\epsilon(t)$ = time-dependent strain, in./in.
- A_n = characteristic stiffness, psi
- τ_n = characteristic time, sec

Shifting of the data for different test temperatures uses the principal of time-temperature equivalence: all relaxation times are affected the same amount by a temperature change. The time-temperature shift factor a_T is refined as

$$a_T = t/t_0 \quad (29)$$

where

t = relaxation time at temperature T , sec

t_0 = relaxation time at a reference temperature T_0 , sec

The complete form of the Prony series tensile modulus is then represented by

$$E(t) = A_0 + A_1 e^{-t/\tau_1 a_T} + A_2 e^{-t/\tau_2 a_T} + \dots + A_n e^{-t/\tau_n a_T} \quad (30)$$

The a_T parameter is identified over the temperature range of interest by empirical shifting of the data. It also is determined from a relation (WLF) derived by Williams, Landel, and Ferry (ref. 80):

$$\log a_T = \frac{-8.86(T - T_{ref})}{101.6 + (T - T_{ref})} \quad (31)$$

where

T = test temperature, °R

T_{ref} = reference temperature approximately 50° above the glass transition temperature T_G , °R

This equation shows that polymeric viscoelastic response is primarily a function of the glass transition temperature.

The empirical and theoretical a_T -vs.-temperature behavior usually agree except for propellants that exhibit nonlinear behavior. Time-temperature shift response is very important because viscoelastic modulus behavior and failure data are adjusted from the laboratory conditions to motor conditions by means of this parameter.

Poisson's ratio ν or some other representation of propellant volumetric response also is required for structural analysis. One method to evaluate propellant volumetric behavior is to perform tensile tests with the propellant in a gas or liquid dilatometer. Volume-change data are converted into Poisson's ratio with the following equation:

$$\nu = \frac{1}{\epsilon} \left(1 - \sqrt{\frac{V/V_0}{1 + \epsilon}} \right) \quad (32)$$

where

V_0 = initial volume, in.³

V = instantaneous volume, in.³

The Poisson's ratio definition is compatible with the numerical analysis procedures used in grain stress analysis and shows that Poisson's ratio decreases with strain even for incompressible materials (ref. 81).

Thermal Properties

Thermal properties of a propellant are inherent to the binder/filler system and not easily changed. The following thermal properties normally are evaluated for solid propellant even though only three are really required for thermal stress analysis of grains:

- Coefficient of linear thermal expansion, α , in./in.-°F
- Glass transition temperature, T_G , °F
- Thermal conductivity, k , Btu/in.-hr.-°F
- Specific heat, C_p , Btu/lb-°F
- Thermal diffusivity, κ , in.²/hr

Grain thermal analysis can be conducted with only α and κ , but the usual method for obtaining κ is to calculate it from k , C_p , and density data for the propellant. T_G is required so that the time-temperature shift curve for a propellant system may be identified. Of all of the thermal properties, the value of α is of most importance in structural analysis. Grain thermal strains are directly proportional to α , so uncertainty in this parameter would affect structural safety factors. The value of α customarily is obtained by using a quartz tube dilatometer that is programmed to cycle between two temperature limits such as -150° F to 150° F at a very slow rate while propellant sample length change is measured with an electrical displacement transducer. Procedures for all of the thermal test methods are presented in reference 75.

2.4.2.2 Failure Properties

Structural safety factors ideally are determined by comparing the maximum calculated grain stress and strain values with the same failure properties measured under the same multiaxial stress loading conditions as those that occur in the grain. The variability expected (in production) of both failure properties and stress-producing properties must be considered. Solid propellant motors are subjected to a wide variety of severe loading conditions that include low-temperature storage, temperature cycling, acceleration, vibration, and pressurization. Each of these conditions impose on the grain stress-strain conditions that should be simulated. Five propellant failure tests are used to approximate the actual grain conditions:

- Biaxial tension endurance
- Triaxial tension
- Pressurized tension
- Cyclic strain
- Analogue motor tests: thermal—steel case
pressurization—fiber glass case

Failure properties are evaluated at the critical temperature and pressure conditions that a motor is expected to withstand. However, extensive multiaxial propellant characterization is expensive and, therefore, sometimes prohibitive. Generally, two of the most critical tests are performed (ref. 75) at the low-temperature extreme: analogue motor (ref. 82), and biaxial endurance.

Extrapolations from these data to the other motor conditions are made by using wide-range multiaxial data for similar propellant binder systems. Therefore, a complete characterization of each major propellant binder system is necessary to identify the general behavior of the system and to predict changes associated with minor formulation changes.

The various test methods used for evaluating propellant multiaxial failure properties and thermal properties are presented in reference 75 and the ICRPG Working Group Bulletins. Details of grain structural analysis techniques are presented in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis."

2.5 Stability Characterization

Propellant stability in a space application usually is not critical unless the motor must be sterilized or must be exposed for extended periods to space. Most of the available operational propellants have an acceptable stability for the usual space applications and may be expected to have good shelf life under the relatively controlled environment in which such motors usually are stored. Most of the tests used to determine the effects of storage depend on evaluating the mechanical integrity of the motor. Ballistic evaluation rarely is used since changes in delivered specific impulse or burning rate usually are not detectable. However, the severe requirements for biological sterilization may affect ballistic properties.

2.5.1 Storage

A storage time of three years frequently is the minimum time required. A specification of five years is not unusual, but even longer storage times are desirable. The storage time is related to the storage temperature, and compromises often must be made.

2.5.1.1 Binder Stability

Extended storage at elevated temperatures (e.g., 140° F) may cause changes in the composite propellant binder. The internal heat-initiated changes may be complicated by oxidative attack on the binder by the oxidizer or by the atmosphere. The propellant cure reaction may continue on storage, increasing the crosslink density and lowering the propellant elongation. Polymer chain scission may occur, and the re-

active free ends of the split chain may form new combinations. Cleavage, postcuring, and radical crosslinking all change the binder gel structure, increasing or decreasing the crosslink density (refs. 83 through 85). Antioxidants in the formulation often reduce oxidative attack and oxidative crosslinking. Only careful experimentation can identify the source of any troublesome propellant degradation.

The organic nitrate oxidizer in double-base propellants decomposes at a relatively low temperature (e.g., 140° F), and prolonged storage above this temperature is not advisable. Oxides of nitrogen are formed during the decomposition and catalyze further decomposition. Agents such as ethyl centralite are included in the formulation to sequester these products.

The crosslink density of the composite propellant binder is determined periodically during a storage program if degradation of the binder is suspected (ref. 86). These data show any change in crosslinking affecting the mechanical properties of the binder structure. The number of moles of effective chains per unit volume (crosslink density) for polymeric materials can be calculated from the theory of rubber-like elasticity in the form

$$\sigma = \nu_e RT (\lambda - \lambda^{-2}) \quad (33)$$

where

- λ = principal extension ratio ($1 + \epsilon$)
- T = absolute temperature, °K
- R = gas constant, 1205 psi · cm³/°K-mole
- ν_e = crosslink density, moles of effective chains/in.³

Because equation (33) applies to material behavior only in the region of time independent response, care must be taken to ensure that experimental data are obtained under equilibrium conditions and in the absence of high-temperature degradation. Swelling the propellant in a nondegrading solvent provides a method for determining equilibrium properties. The effect of the imbibed liquid on equation (33) is accounted for by

$$\sigma = \nu_e RT (v_2)^{1/3} (\lambda - \lambda^{-2}) \quad (34)$$

where v_2 is the volume fraction of the gel in the swollen gumstock. Tensile stress is based on the unstrained unswollen area corrected for sol fraction, and λ is the extension ratio based on the swollen, unstrained gage length. The linear swelling ratio $((v_2)^{1/3})$ is determined by procedures given in references 87 and 88.

2.5.1.2 Shelf Life

The service life or useful shelf life of a propellant can best be determined by an actual storage-surveillance program under the service conditions of temperature and humidity. Since the propellant ingredients rarely degrade sufficiently on storage to

affect the total energy of the propellant, deterioration of the propellant usually cannot be detected by measurement of thrust of a stored motor unless cracks are present or volatile burning-rate catalyst has been lost. The most reliable method of following the stability of a propellant during a storage program is to measure changes in uniaxial properties during storage that often signal the deterioration of the motor. The appearance of gassing voids or cracks can be detected by x-ray during the program. However, x-raying a grain at elevated temperature may result in premature damage (ref. 89).

Existing techniques for predicting the service life of a propellant are not completely satisfactory. Simulation of all storage conditions is difficult since such factors as degree of access to air, surface-volume ratio of the propellant, and plasticizer migration must be considered. Accelerated aging by storing the propellant at elevated temperature frequently may give some degradative chemical reaction that is not important in the deterioration at service temperature while deemphasizing a reaction that is rate determining in limiting the storage life.

Mechanical properties, (i.e., stress, strain, and modulus) of a propellant after extended storage can be predicted by the method of Marti et al. (ref. 90). Values of mechanical properties are determined at a few temperatures over a period of time. The values are plotted against the log of time to produce a curve for each storage temperature. The low temperature is selected as the reference temperature, and the other curves are geometrically shifted in time to produce a single continuous curve that represents values of the property for a very long storage time at the low reference temperature.

2.5.1.3 Stability to Humidity

Water can attack a composite propellant by dissolving the oxidizer, by hydrolyzing the binder, and by causing binder-oxidizer dewetting. Ammonium nitrate begins to dissolve at a relative humidity of about 35 percent, while ammonium perchlorate begins to dissolve or dewet the binder at 65 to 75 percent. Water attacking the oxidizer can be detrimental to ignition. Classical double-base propellants are not affected by humidity.

Binder hydrolysis may be a serious effect, depending on structure, in a composite propellant. In the hydrolysis reaction, ester linkages are converted to acids and alcohols. In the case of MAPO-cured binders, P-N bonds are broken by water. Early polyurethane binders often were susceptible to hydrolysis, but recently developed polyurethane binders are quite water resistant. Binders based on carboxylated polybutadiene cured by MAPO and similar materials are much more susceptible to hydrolysis than binders of carboxylated polybutadiene and epoxide curatives.

Ammonium perchlorate composite propellant usually can withstand a 1- or 2-week exposure to relative humidities of 50 to 60 percent. Short exposures of a motor to

high relative humidities is not harmful if the wet air is purged with dry air and the motor resealed. However, if most composite propellants are exposed to relative humidities of 50 to 60 percent for more than 6 months, some degradation of the binder will occur. Another problem that may arise on storage is moisture migrating from the liner into the propellant.

The most common method of evaluating stability of the propellant and all critical bonds to humidity is to expose the propellant and propellant bond samples to controlled humidity and then test JANAF specimens prepared periodically from bulk samples.

2.5.1.4 Ingredient Volatility

Operational composite and double-base propellants have very low vapor pressures. Storage of solid propellants in vacuums of about 10^{-6} mm Hg for 6 to 10 months resulted in weight losses of less than 0.5 percent (refs. 91 and 92). These weight losses were caused by water in the case of a polyurethane propellant and by water, antioxidant, and low-molecular-weight molecules in the case of polybutadiene propellant. Volatile ingredients such as tolylene diisocyanate and MAPO are used in propellants, but these compounds become part of the crosslink structure during cure and are not volatile after cure. Nitroglycerin and other nitrate esters used in double-base propellants are relatively volatile at 150° F.

Ingredient volatility generally is evaluated by testing bulk samples stored at a controlled temperature. Strands and JANAF specimens are prepared periodically to determine burning-rate or mechanical property changes. In some laboratories, the samples are stored at reduced pressure.

2.5.1.5 Stability of Liner-Propellant Bond

The stability of the liner-propellant bond during storage is important because failure of the bonds will expose additional propellant burning surface. The liner-propellant bond may fail because the original bond strength was marginal, because the propellant strength has degraded, because the liner strength has been degraded by plasticizer migration, or because the nature of the bond has altered.

An adhesive bond usually is sensitive to any change in strength of the substrates. A liner-propellant bond will weaken if either the liner or propellant weakens. The bulk of the propellant may not necessarily reflect the mechanical properties of the propellant near the bond (refs. 93 and 94). The most common method of studying the time-temperature stability of the propellant-liner bond is the testing of samples of the propellant-liner combination. One approach has been to test a discontinuous JANAF tensile specimen, which is milled from a propellant-liner-propellant "sandwich" so that the neck of the specimen contains a section of propellant-liner-propellant.

A liner formulation frequently consists of a propellant binder with additional curative and inert fillers. The additional curative may migrate into the propellant and form a hard layer of propellant with very low elongation. Strains may cause a crack between the hard and normal propellant. If the liner contains excess curative, the liner may postcure during storage and become brittle. A strain crack between the liner and propellant can occur if the liner becomes brittle. The liner formulation generally is modified in such a situation.

2.5.1.6 Plasticizer Migration

The plasticizer is a high-boiling-point liquid that is completely miscible with the prepolymer of the binder system and, in the final cured state, forms a colloidal gel with the large molecules of the cured polymer. While the plasticizer is somewhat immobilized by steric and electrostatic interactions with the binder polymer, it can and does migrate into adjacent materials in which it also is soluble. Plasticizer migration is significantly reduced if the plasticizer is not soluble in the liner or if the plasticizer is of very high molecular weight. The liner itself may contain plasticizers that will migrate into the propellant. In either instance, an equilibrium state finally occurs in which the plasticizer content of liner and propellant becomes constant. Plasticizer migration into the liner may improve the liner-propellant bond strength if the plasticizer is mutually soluble in both (ref. 95).

The problem of plasticizer migration is a complex one, and the effect of such migration varies from propellant to propellant. Gas chromatographic techniques have been used to detect the interchange of plasticizer between adjacent substances (ref. 96). Analysis of propellant and liner sections allows the development of concentration-incline data. Similar data gathered over a period of time give a time-incline profile of the behavior of the plasticizer in a discontinuous system. Temperature is important to such a study since migration proceeds at a greater rate to equilibrium at higher temperature. JANAF specimens may be prepared from propellant-liner-case samples, and the effect of plasticizer migration on the interface strength can be determined.

2.5.2 Sterilization

Prevention of terrestrial microbe contamination of space probes requires complete heat sterilization. The varying process times at 125° C needed for total sterilization of various geometries and sizes are described in reference 97. Sterilization time at 125° C for an 8-foot-radius shell required almost 51 hours.

Requirements for sterilizing propellants may be as much as 300 hours at 275° F (ref. 98). Double-base binders are excluded as sterilizable propellants. Polyurethane composite propellants based on the use of fully saturated hydroxy-terminated poly-

butadiene binders appear to be successful in withstanding this heating. CTPB propellants with epoxy cures have been used successfully when protected by an antioxidant in the formulation. Polyvinyl chloride composite propellants have demonstrated the capability of undergoing sterilization without adverse effects.

The techniques for reducing the microbial contamination of the polyurethane-ammonium perchlorate-aluminum propellant are discussed in reference 99. During the production of the propellant, the mixer and casting system are presterilized with a mixture of ethylene oxide and Freon 12 followed by pure ethylene oxide. Final sterilization of the propellant grain can take place during the cure phase of the propellant manufacture, or thereafter. Generally, propellants that contain volatile burning-rate catalysts or volatile plasticizers undergo changes in internal ballistics or in physical properties such that they cannot survive the sterilization conditions.

Storage temperatures up to 160° F may cause changes in the binder of composite propellant. The very high temperatures of sterilization produce changes in the oxidizers as well. Few operational propellants will survive a sterilization of 300 hours at 275° F or aerodynamic heating at 320°±30° F. Pure AP begins to decompose at about 220° C (ref. 100). Commercial AP decomposes extensively at 140° C. Recrystallization of AP reduces the concentration of chlorate, sodium, and potassium ions and increases the thermal stability. Decomposition of AP produces very reactive, oxidizing species that may attack the binder. Saturated (carboxy-terminated polyisobutylene) and nearly saturated (hydrogenated carboxy-terminated polybutadiene) polymers that are less susceptible to oxidative attack have been used in binders for propellants that will survive storage at high temperatures, e.g., 320°±30° F. The use of stabilized AP also has improved the stability of sterilizable propellants.

2.5.3 Space Environment

Mugler and Bradford (ref. 101) have reported the effects of vacuum on solid propellant rocket fuels. They have measured the outgassing rates for rocket fuels in vacuum, identified the outgassed products, measured the changes in mechanical properties during vacuum storage, and measured the effects of vacuum storage on the ignitibility of the fuel.

Propellants chosen for space environment are all based on prepolymers with high average molecular weight (ref. 102). Prepolymers are stripped by molecular still or by fractional precipitation to remove any lightweight fractions. No plasticizers are used in the binder since even the high-boiling-point plasticizers will develop a fairly high outgassing rate under vacuum. No volatile catalysts are used in any system exposed to a space environment.

The effect of radiation on ammonium perchlorate as well as the effect of radiation on burning rates and tensile strengths of several composite AP propellants is described in reference 102. Polysulfide propellants in this study suffered burning-rate

decreases after radiation while polyacrylonitrile propellants, polyethylacrylate propellants, and polyurethane propellants showed burning-rate increases after radiation.

Gamma radiation levels corresponding to several years in the Van Allen belt did not seriously alter the ballistic or mechanical properties of composite propellants with ammonium perchlorate oxidizers and polyurethane, polybutadiene-acrylic acid, or polybutadiene-acrylic acid-acrylonitrile binders (ref. 103).

2.6 Hazard Characterization

A propellant rarely is rejected simply because of its hazard characteristics. The results of hazard tests determine the degree of care to be exercised during the motor's manufacture, transportation, and storage. Many companies have developed propellant color codings that tell at a glance the propellant's relative sensitivity to initiation by impact, friction, or spark and its relative susceptibility to detonation.

No single area of propellant characterization is more controversial than that of propellant hazard characterization. No single impact or friction tester is universally accepted by the industry, and no clear rules exist for interpreting the data from any of the available apparatus. The interpretation of hazard data is often semi-intuitive.

2.6.1 General Characterization

Procedures for complete hazard characterization of a propellant are described in reference 104. This characterization includes a detonation test with a no. 8 blasting cap, an ignition and unconfined burning test, a thermal stability test at 75° C for 48 hours, an impact sensitivity test on a Bureau of Mines impact apparatus, and a card gap test. In addition to these minimum tests, other tests may be performed (e.g., a 20-foot drop onto a concrete slab). There is no provision within this series of tests for a static discharge or a friction sensitivity test. Such a complete characterization is costly and is justified only if the end use of the motor is such that this information is essential to successful design.

2.6.2 Impact Hazard

Many propellants can be ignited or detonated by impact. For this reason, it is important that the impact hazard of a propellant be characterized.

The impact hazards of propellant ingredients, uncured propellant mixes, and cured propellant mixes have been characterized in the industry by a wide variety of impact devices. The most common principle for such a device involves calibrated weight falling on a sample. No mechanical impact on a propellant is free of two secondary effects: the effect of adiabatic heating of porous propellant, and the effect stemming

from unavoidable frictional heating during impact. Many propellants that are not particularly impact-sensitive are very friction-sensitive and give unusually low impact test values because of the impact heating effect.

Two types of impact devices are most commonly used within the industry. The Olin-Mathieson impact apparatus uses a 2-kg weight; the impact test results generally are reported in kg-cm (ref. 105). The Bureau of Mines test apparatus (the apparatus specified in ref. 104) uses a 1-lb weight; the impact test results generally are reported in inches (ref. 106). Impact data frequently are given on the basis of a 50 percent impact point, the height at which 50 percent of the samples tested deflagrated or detonated. A higher value, the height at which all samples detonated or deflagrated, the 100 percent impact point, also is frequently quoted in industry. There is disagreement on the question of which value is more meaningful.

The impact apparatus are calibrated with a well-known material such as RDX, tetryl, PETN, or TNT. The materials of construction and the degree to which the apparatus is enclosed result in variations from laboratory to laboratory.

The impact test generally is run on propellant ingredients, the uncured propellant mix, and the cured propellant. The values obtained are useful in assessing the degree to which the ingredients, uncured propellant, and cured propellant should be protected from the common mechanical shocks encountered in processing and handling. An impact sensitivity on the order of 5 kg-cm represents an extremely low value in most devices, and such a propellant properly may be judged as hazardous to handle. Many of the common composite propellants such as the aluminized polybutadiene propellants are relatively insensitive. The impact sensitivities of composite double-base propellants, on the other hand, are sufficiently low that greater care must be taken in processing and handling.

2.6.3 Friction Hazard

Many propellants are particularly sensitive to friction. Aluminum- and beryllium-containing composite propellants, oxidized by AP, are more friction-sensitive than classical double-base propellants.

Uncured propellant mixes frequently have friction sensitivities higher than those of cured propellant. High frictional areas may develop within a highly loaded propellant during mixing. Empirical treatments of the mixer friction are used in some companies in an attempt to relate the friction sensitivity of the propellant to the friction encountered in the mixer (ref. 2). Cured propellant often is subjected to friction during normal handling operations such as mold disassembly, mandrel removal, machining and trimming, and motor assembly.

At the present time, there is no widely accepted standard friction test. Two common friction sensitivity tests are the pendulum friction test and the ESSO screw friction

test. The pendulum friction test machines, the most widely used, use the swing of a pendulum to impart energy to a sliding bar that abrades the test specimen. Several variations of this device have been developed (refs. 106 through 108). In the Bureau of Mines device (ref. 106), the pendulum is fitted with shoes of various composition (fiber, steel, etc.) and allowed to swing directly across the propellant sample. Other variations within the industry include spring-loaded devices and other techniques for imparting mechanical energy to an abrading slide.

The ESSO friction tester is judged by some authorities to be capable of fine distinctions in friction testing while others hold that it is inferior to the pendulum devices. Samples are tested by placing them between two platens on the ESSO screw friction test apparatus (ref. 109). The top screw-threaded platen is slowly lowered until the rotating torque applied to the platen exceeds 100 ft/lb. The severity of the test can be modified by adding different grades of diamond or glass grit. Three general categories of friction sensitivity commonly are recognized in the ESSO test: Category I—manual handling permissible, no initiation with or without glass or diamond grit; Category II—remote handling advised, no initiation with grit, initiation with glass or diamond grit; and Category III—high sensitivity to friction, initiation without grit.

2.6.4 Spark Hazard

Under conditions of low humidity, an ungrounded human body can accumulate a static charge of as much as 0.015 joule (ref. 110). Any propellant with a spark sensitivity lower than this value may be initiated by contact with a human operator carrying a static charge.

Propellants are exposed to mechanical devices with moving parts that may develop static charges. All equipment is grounded; human operators wear grounding straps fixed to some part of the body and may wear conductive shoes. Grounding shoes, however, are useless on a nonconducting floor. Various ionizing devices have been used, but these have limited range or present a radiation or high-voltage hazard.

The amount of electrostatic discharge necessary to ignite a propellant usually is determined by discharging a spark from a needlepoint through a propellant sample to a metal sample support. Typical test energies range from 0.001 to 10.0 joules with corresponding voltages from 3,000 to 7,000 volts dc applied to samples 0.025 in. thick with 0.175-in. diameter. Both unconfined samples and samples partially confined in glass are tested to find the minimum static energy for ignition.

2.6.5 Autoignition Hazard

All propellants have a characteristic temperature at which they will ignite instantaneously. At lower temperatures, however, the propellant may autoignite after a

long exposure time. Many cure reactions are exothermic, and propellants under cure may develop internal heat sufficient to reach the autoignition point if the geometry precludes heat dissipation. Exothermic degradation reactions on storage, particularly at elevated temperatures, may cause the propellant to reach its autoignition point.

2.6.5.1 Environmental Heating

In some laboratories, autoignition temperatures are determined by inserting small propellant samples in metal tubes in a Wood's metal bath (ref. 111). The time to ignition after immersion is recorded for several bath temperatures, and the data are graphically extrapolated back to zero time. In other laboratories, 1-in. and 2-in. cubes are held in temperature-regulated ovens to determine the 1-hr and 8-hr autoignition temperatures (ref. 111). Data are extrapolated back to zero time as in the Wood's metal bath test. The cube tests generally are more accurate because of the better equilibration of temperature between cube and oven.

2.6.5.2 Exothermic Reactions

Measurements of internal heat generation often are made in the industry for a particular geometry by the use of thermocouples buried in the propellant mass. The most common laboratory apparatus for evaluating the exothermic reactions within the propellant under a given cure or thermal environment are the differential thermal analysis (DTA) apparatus and the differential scanning calorimeter (DSC). The DTA heats a test propellant sample and a chemically inert reference sample at a given programmed heating rate. The samples are compared through opposed thermocouples. When the propellant sample undergoes an endothermic or exothermic change, the temperature of the propellant sample falls below or rises above that of the reference sample. Both the temperature at which the onset of reaction occurs and the temperature at the peak of the reaction are significant. In a well instrumented differential analysis apparatus, the amount of heat generated or absorbed by the reaction in the propellant sample can be determined. The differential scanning calorimeter is similar in principal to the DTA but is a more sensitive instrument, measuring the actual heat absorbed or generated when a propellant undergoes endotherms or exotherms.

Pakulak (ref. 112) has used a DTA technique with double-base and composite propellants to predict the autoignition point for a particular geometry. The technique is based on the Zinn and Mader (ref. 113) solution of the Frank-Kamenetsky equation. A critical temperature is defined as that at which heat generation within the propellant is balanced by heat loss from the surface. Above this temperature, the propellant will autoignite. The critical temperature T_m is obtained from

$$T_m = \frac{E}{2.303R \log \frac{\rho a^2 Q Z E}{k R T_m^2 \delta}} \quad (35)$$

where

- a = shortest line distance from center of solid grain to periphery, cm
- Q = heat of decomposition, cal/mole
- Z = frequency factor
- E = activation energy, cal/mole
- R = gas constant, 1.98 cal/mole-°K
- T_m = critical temperature, °K
- k = thermal conductivity, cal/cm-sec-°K
- δ = shape factor

Q , Z , and E are derived from DTA measurements. A log-log plot of propellant radius vs. $1/T_m$ predicts cookoff temperatures for any given grain diameter.

The time to ignition t_i for any environmental temperature T is found by the inexact expression

$$t_i = \frac{\rho C_p a^2}{k} f \left(\frac{E}{T_m} - \frac{E}{T} \right) \quad (36)$$

2.6.6 Detonation Hazard

The most common technique for determining propellant susceptibility to detonation is the standard card gap test developed by the Naval Ordnance Laboratory (ref. 114). A pentolite donor charge is placed at one end of a sample of propellant cast in a rolled steel tube. A signature plate of mild steel is placed at the other end. If the pentolite booster detonates the propellant, the signature plate is perforated. A positive test is a clean perforation with a diameter close to that of the propellant charge. After a positive test, the donor charge is separated from the propellant charge by an increasing number of 0.01-in. cellulose acetate cards. The 50-percent-to-detonation point is reported in terms of the number of cards. The greater the number of cards, the more attenuated the explosive wave reaching the propellant charge and the more sensitive the propellant is to detonation. Aluminized composite polybutadiene propellants normally give a no-detonation result at zero cards, while high-energy CMDB propellants may give card gap values of from 75 to 125 cards. It should be noted that the 1.5-in. diameter of the standard propellant charge in this test is below critical diameter of most composite propellants.

In the commonly used detonation test described in reference 104, a no. 8 blasting cap placed next to a propellant sample is fired to determine whether the sample can be cap initiated. This test does not have the refinement of the card gap test.

2.6.7 Toxic Hazard

Standard double-base propellants have exhaust products that are generally considered nontoxic. However, AP propellants produce large quantities of hydrogen chloride gas,

which is toxic and also is irritating to the eyes and lungs. Double-base propellants may produce lead combustion products in relatively low concentration, but these generally do not represent a toxic hazard. All propellants produce carbon monoxide, which is toxic.

Beryllium and its water-soluble salts produce berylliosis, which is considered an allergenic disease; the individual response may vary widely. The soluble salts of beryllium taken into the lungs are most likely to produce berylliosis. The water-soluble salts of beryllium may be carcinogenic (refs. 11 and 115). All beryllium motor testing in the United States has been in desert areas or in closed installations with deluge systems removing the exhaust products from the air. Open-air firings have now ceased in the United States because of the possibility of atmospheric contamination.

The fluorocarbon propellants and the new experimental difluoramino propellants both produce measurable quantities of hydrofluoric acid gas, HF, which is more toxic and irritating than HCl. Personnel masking indicated where large amounts of HF are found.

Many of the individual propellant ingredients are toxic. Skin reactions are produced by most of the isocyanates and by most of the epoxy resins used for curing CTPB propellants. The vapors of TDI are toxic; MAPO and other aziridinyll curatives are toxic, with individual response varying widely. Most of the metal-containing combustion catalysts are toxic to varying degrees. The nitrate esters produce toxic reactions similar to those of ammonia when ingested or inhaled; protective clothing and gas masks often are needed when large quantities of these materials are handled.

3. DESIGN CRITERIA and

Recommended Practices

3.1 Selection of Propellant Type

3.1.1 Performance Properties

The propellant type shall have the required delivered specific impulse under design conditions combined with a density sufficient to meet performance requirements within grain volumetric constraints.

When high specific impulse in a low-toxicity system is required, an aluminized propellant should be used. Aluminized DB propellants with HMX deliver 3 to 6 seconds more than aluminized composite propellants. Double-base propellants, however, have higher flame temperatures than composite propellants and may require extra insulation. Should high-temperature stability requirements, low-temperature physical property requirements, or a need for a class 2 propellant preclude the selection of double-base³ propellants, an aluminized composite propellant should be chosen, the type of composite being dictated by other than energetic requirements (ref. 8).

If there are no restrictions on the use of beryllium and if specific impulse in an upper stage is of primary importance, a Be-DB propellant with HMX should be considered. These propellants deliver up to 15 seconds more than analogous aluminized systems. If thermal or safety requirements prevent the use of a DB binder, a Be composite propellant is recommended. These propellants deliver 3 to 6 seconds more than their aluminized analogs (ref. 8). The Be propellants, however, have highly toxic exhausts. Their flame temperatures are greater than the analogous aluminum propellants, and extra insulation is required. Their exhaust products produce more severe attrition on nozzles, and heavier nozzles, which degrade total design performances, are required.

If density, as well as high performance, is of importance, a CMDB propellant with HMX should be chosen. Such propellants have densities 1.5 to 6 percent greater than composite propellants. A nitroplasticized polyurethane with HMX offers density and specific impulse advantages nearly as great. If a DB or nitroplasticized PU propellant cannot be used, a high-solids-loading, highly aluminized propellant should be considered; the tradeoff between the decrease in delivered performance with increasing aluminum content and higher density should be assessed for the design.

If density is of such importance that specific impulse may be sacrificed, the FC propellants offer the best choice. However, the higher flame temperatures of the FC propellants may introduce weight penalties because of the need for more insulation. Beryllium

³It should be noted that some CMDB propellants are class 2.

propellants are low in density and should not be considered except in upper-stage applications (refs. 1, 8, and 9).

3.1.2 Internal Ballistic Properties

The propellant type shall have the internal ballistic properties necessary to generate a thrust profile within the desired limits under all anticipated firing conditions.

If burning rates⁴ in the 0.2 in./sec region are desired, propellants considered should include the double-base propellants containing both inert plasticizers and nitrate ester and the uncatalyzed, metallized composites. If higher burning rates are desired, a wide range of burning rates is available in all of the nonmetallized and metallized double-base and composite propellants. These burning rates may be adjusted through suitable use of burning-rate catalysts and adjustment of oxidizer particle size distribution. When very low burning rates (<0.2 in./sec) are required, AN, nitroguanidine, and GN-oxidized propellants should be considered; it should be noted that these propellants generally are of low specific impulse.

When very low pressure exponents are required, plateau- and mesa-burning DB propellants should be considered. If the use of a DB system is precluded by other factors, a nonmetallized, under-oxidized composite propellant should be considered. Many of these propellants show low slopes and, on occasion, even plateau-burning characteristics. If high exponents are required, DB or composite propellants with HMX should be considered. Nitroguanidine-DB propellants also show high exponents as do AP-KP composite propellants, but these propellants have lower delivered specific impulses.

When low temperature sensitivity is needed, a low-pressure-exponent propellant should be considered. Plateau- and mesa-burning double-base propellants show unusually low temperature sensitivities.

3.1.3 Mechanical Properties

The propellant type shall have elongation and tensile strength at all temperatures sufficient to relieve the internal stresses of the grain without loss of structural integrity or unacceptable changes in internal ballistics.

The elongation, tensile strength, and modulus necessary in the propellant are defined by a stress analysis of the grain design. Generally, elongation is the parameter of most concern unless the tensile strength is unduly low.

⁴All burning rates are at 1000 psi and 70° F.

If true elongations above 25 percent⁵ in the 70° F region are needed, then CMDB, polyether polyurethane, CTPB, PBAN, or HTPB polyurethane propellants can be selected. Uncrosslinked plastisol double-base composite propellants should not be chosen where elongations above 20 percent are required at 70° F (ref. 8). Crosslinked PNC-DB composites have excellent elongations at 70° F.

If good low-temperature elongations are required, a CTPB, an HTPB, or polyether-polyurethane propellant should be selected. Generally, DB propellants of either type should not be chosen because the elongations of these propellants are usually under 15 percent at 40° F (refs. 3 and 8).

In higher temperature applications demanding good tensile strength with high elongation, a CTPB, an HTPB, or a PU propellant, suitably formulated for such an application, should be chosen. The tensile strength of these propellants is generally 50 to 100 psi in the region of 140° F. The tensile strength of DB propellants at similar temperatures generally is inferior to this (ref. 8).

3.1.4 Thermal and Storage Stability

The propellant type shall have stability sufficient to withstand all anticipated thermal and chemical environments without unacceptable physical or chemical degradation during the required service life.

The stability of the propellant should be characterized under all service conditions. Motors should be sealed in a dry atmosphere if the propellant is moisture-sensitive.

If the propellant must be stored over a wide temperature range that includes extended periods above 140° F, a composite propellant should be considered. Double-base composite propellants generally are less stable at elevated temperatures than composite propellants. If extended thermal stability in the region of 300° F is required, an FC or a PVC propellant should be considered (refs. 4 and 6). Double-base propellants, because of their lower thermal stabilities and lower cookoff temperatures, may not be used in this thermal environment (refs. 3 and 8). Some polybutadiene propellants may be used in such a thermal environment if the exposure is brief (ref. 8).

3.1.5 Hazard Properties

The propellant type shall have a hazard classification consistent with its intended use and shall not release toxic exhaust products into the atmosphere in excess of NHS standards.

When high operating temperatures are expected or when safety requires, a class 2 composite propellant should always be selected. Double-base composite propellants generally are more sensitive to impact and shock-wave initiation than composites, and many of these are class 7 (ref. 8).

⁵Elongations and tensile strengths quoted in this document are those values at maximum stress, derived from Instron test at a crosshead rate of 2 in./min, corrected for jaw slippage.

Beryllium propellants should not be used in motors operating in atmosphere or under such conditions that an explosive failure will vent their toxic combustion products into the atmosphere (ref. 9).

3.1.6 Propellant Costs

The propellant shall contain the least costly, most readily available ingredients and shall not require unusual or costly quality control, processing, or storage techniques.

Unless processing and shelf-life advantages favor one with a higher cost per pound, the propellant should contain ingredients that are readily available in reasonable quantities from commercial sources without undue delay. These ingredients should require a minimum of preparation for use. The propellant should, when possible, contain standard commercial curatives, standard commercial polymers, and ingredients that are available from commercial sources with specifications as broad as possible with adequate reproducibility.

The propellant should employ the least expensive processing technique available, with a liner that may be applied to the combustion case inexpensively. When relatively small motors in large quantities will be produced, extrusion techniques are recommended over casting techniques. Motors greater than 12 inches in diameter generally should be cast. Special propellant techniques such as the use of continuous wires or wire staples should be avoided since this increases the cost of processing.

The propellant selected should require few quality control steps and quality control tests, particularly at that point where the mix is complete and before it is cast. The propellant should be highly reproducible from batch to batch in delivered specific impulse and in internal ballistic properties, particularly in burning rate. Propellants with highly critical catalyst levels or with catalysts whose activities vary from batch to batch should be avoided. Propellants requiring unusual or costly handling and processing equipment or unusual storage conditions should be avoided. To minimize replacement costs, select the propellant with the longest shelf-life available.

3.2 Performance Characterization

3.2.1 Delivered Specific Impulse

The propellant shall have a high specific impulse efficiency.

The principal propellant-coupled losses associated with combustion inefficiency and with two-phase flow losses in the nozzle should be minimized. Heat losses are dependent on the mass discharge rate of the motor, which in turn is dependent on the propellant burning rate. However, the propellant burning rate should not be altered significantly,

once the grain design and motor time-thrust profile have been established. Specific practices for achieving high I_{sp} efficiency are set forth below.

3.2.1.1 Combustion Efficiency

3.2.1.1.1 Residence Time

The propellant shall burn efficiently within the residence time of the motor.

The residence time of the motor should be calculated from equation (2). If the residence time is significantly greater than 15 msec, good combustion efficiency probably will be achieved (refs. 20 and 21). An alternate assessment of combustion efficiency in the design may be made by calculating L^* , the characteristic length, and comparing it against empirical L^* -combustion efficiency relations available for the propellant type (ref. 55). If combustion inefficiency is suspected, the exhaust of the motor should be sampled by use of a cooled probe or similar device and the solids analyzed for unburned aluminum. If greater than 0.5 percent of the aluminum (ref. 19) is found to be unburned, one of the parameters affecting combustion efficiency should be adjusted. Residence time can be increased by (1) an increase in combustion pressure, (2) an increase in chamber volume, or (3) by a reduction in mass discharge rate. Steps (1) and (2) usually will lead to a heavier case weight, while steps (2) and (3) will result in greater heat loss to hardware with attendant reduction in specific impulse efficiency. A change in combustion pressure will also result in a change in mass discharge rate with a fixed grain geometry. Because of these compromises and the complex interplay of pressure and mass discharge rate, attempts to change residence time to overcome combustion inefficiency are not generally recommended.

3.2.1.1.2 Chamber Pressure

The propellant shall demonstrate acceptable combustion efficiency at the design operating pressure.

It is recommended that the burning rate of the propellant be lowered if inefficiencies in metal combustion are expected. Such a choice will allow a higher combustion pressure and longer residence time while meeting the design mass discharge rate requirements. Combustion efficiency of metals generally is improved by higher pressures (ref. 24). However, it should be recognized that a higher combustion pressure requires a heavier motor case. For this reason the designer should weigh the delivered performance advantages to be gained in such a step against the penalties of increased motor weight.

3.2.1.1.3 Flame Temperature

The propellant shall have a sufficiently high flame temperature to promote combustion efficiency.

Efficient nonmetallized propellants should have flame temperatures in the region of 4000° F; highly aluminized propellants with 16 to 20 percent metal should have flame temperatures above 5000° F (refs. 20 and 25). The most useful methods for increasing flame temperature are to increase oxidizer level or to use a more energetic plasticizer; recognize that either action probably will increase the burning rate and may change n . Also, if the propellant exhaust composition is over-oxidized, higher flame temperatures will lead to increased chemical attack on the nozzle. The penalties arising from greater nozzle erosion and increased insulation must be assessed if flame temperature is increased to promote combustion efficiency.

3.2.1.1.4 Oxidizing Balance

The propellant shall have a high oxidizing balance without incurring excess chemical attack on the nozzle.

No highly metallized propellant should be considered unless it has an O/F ratio above 1.0 and preferably above 1.1 (ref. 20). Lowered performance efficiency may be expected in all metallized propellants at O/F ratios below 1.0, whereas higher O/F ratios favor greater combustion efficiency (refs. 2 and 20). The O/F ratio may be increased by increasing the oxidizer content or by reducing metal level. The designer must assess the effect of such changes on the performance of the propellant, since gains in efficiency may be overshadowed by losses in performance.

3.2.1.1.5 Metal Droplet Size

3.2.1.1.5.1 Agglomeration

Agglomerates expelled from the propellant surface during combustion shall be as small as possible.

Metal combustion efficiency may be improved by any step that effectively reduces the size of the metal droplets burning in the combustion chamber (ref. 27). In aluminized propellants with low combustion efficiency, the use of a dichromated aluminum (ref. 26) is recommended to reduce agglomerate size and increase the rate of metal combustion.

3.2.1.1.5.2 Oxidizer Particle Size

The propellant average oxidizer particle size shall be consistent with internal ballistic, solids loading, and mechanical property requirements and with processing capabilities.

The average oxidizer particle size should be reduced as far as practical if a combustion efficiency problem is encountered, but it should be recognized that the use of finer

oxidizer increases mix viscosity and makes processing more difficult. The use of finer oxidizer will reduce the size of aluminum agglomerates leaving the propellant surface (ref. 28) and will increase the overall decomposition rate of the oxidizer. However, smaller oxidizer grinds give higher burning rates that may result in the selection of too low a combustion pressure for efficient combustion. It is recommended that the tradeoffs between these two effects be determined by an experimental study conducted with small motors at a constant residence time; the techniques described in reference 7 should be used. In extremely troublesome combustion problems, motors may be fired into an inert atmosphere and combustion products analyzed for free metal to determine the degree of metal combustion efficiency.

3.2.1.2 Nozzle Efficiency

Metallized propellant two-phase flow losses shall be as low as possible without sacrifice of delivered performance.

To produce in the nozzle throat the lowest concentration of condensed phases, the propellant metal content should be held to the lowest level that will meet the energy and density requirements of the mission. The metal content should be optimized for the particular throat size. This may be done by the determination of scale-nozzle loss relation, using the techniques described in reference 7. When a choice exists between increasing propellant metal content and increasing the level of another component, all other factors being equal, the latter course should be chosen.

In those instances in which nozzle losses are excessive, as in very small throats, it may be advisable to reduce metal content to achieve a higher absolute delivered performance. A similar step may be indicated if excessive motor or nozzle slagging reduces performance.

The gases resulting from propellant combustion should contain the smallest condensable particle possible. It is advisable that the propellant chosen require a liner that contributes a minimum amount of nucleating particles to the exhaust (ref. 29). The liner material should be held to as low a weight as possible and should ablate cleanly rather than char to produce free carbon.

Data on the delivered specific impulse of the general propellant family in motors of different sizes should be analyzed for nozzle losses. The metal content of the propellant may be tailored to the specific motor and nozzle size to ensure the best delivered performance (ref. 31).

3.2.2 Delivered Density-Impulse

The propellant shall have the highest delivered density-impulse consistent with other necessary properties.

Early in the design effort, the motor application should be examined; and a first approximation of n in the expression $I_{sp} \cdot \rho^n$ should be defined to assess the emphasis to be given density in propellant selection (ref. 36). It is recommended that density be given little emphasis in those systems where n is less than 0.5. In those applications where n is as high as 0.8, beryllium propellants should not be considered and selection should concentrate on the more dense aluminized propellants. It should be recognized that dense propellants with high solids loadings may be difficult to process, while dense propellants with high metal loadings may suffer from combustion or two-phase flow inefficiencies.

3.3 Internal Ballistics and Combustion Characterization

3.3.1 Internal Ballistics

3.3.1.1 Burning Rate

3.3.1.1.1 Burning-Rate/Pressure Relation

The propellant shall have a burning rate well characterized over the operating pressure range.

The burning-rate/pressure relation should be determined during preliminary screening. If the relation is linear in the region of interest, equation (18) may be derived. It is recommended that not less than nine measurements at each of three pressures in the region of interest be made and that the maximum acceptable standard deviation of the data be less than 2 percent of the mean, i.e., that the coefficient of variation (σ/\bar{X}) be less than 0.02 (refs. 7 and 55).

3.3.1.1.2 Burning-Rate Modification

The propellant shall have a burning rate that may be adjusted to deliver the desired mass discharge rate without the use of unusual grain designs or high combustion pressures.

A propellant should be selected with a burning rate in the lower end of the design burning rate envelope, since more options are available for raising the burning rate than for lowering it. The propellant burning rate should be modified by the adjustment of oxidizer particle size or by the adjustment of burning-rate catalyst content. The use of complex grain geometries or undesirably high combustion pressures may thus be avoided in achieving the desired mass discharge rate.

The burning rate of a double-base propellant should not be reduced by decreasing the heat of explosion unless the accompanying decline in specific impulse can be tolerated. The use of flame-retardant coatings on the oxidizer is not recommended because of the loss of energy in the system. Generally the only technique for burning-rate reduction useful in all situations is the use of larger oxidizer particle size.

The burning rate of a composite propellant may be increased by the use of fine oxidizer, but this practice may decrease mix processability (ref. 13). A combustion catalyst should be used if changes in oxidizer grind are insufficient or undesirable. The compatibility of the catalyst with the propellant formulation should be determined, and accelerated aging tests should be made. While ferric oxide and copper chromite are standard catalysts in the industry, it is recommended that ferrocene-derived catalysts be considered in composite propellants because they are more effective than others when compared on an equal weight basis.

For composite propellants, *n*-butyl ferrocene is an effective burning-rate modifier with lower volatility than ferrocene. However, because of its tendency to crystallize at lower temperatures, it is recommended that *n*-butyl ferrocene be used in combination with amyl ferrocene or a similar derivative to avoid this effect. Several proprietary polymeric ferrocene derivatives are now available and should be considered. However, ferrocene-derived catalysts lower the thermal stability of AP and thereby can lower the auto-ignition temperature of a propellant.

Changes in solids loading or in aluminum loading affect propellant energetics, and such changes should not be made except when other techniques cannot be employed.

Wire or staples should not be used in the propellant except in those highly specialized instances requiring very high burning rates. In such instances, the orientation of the staples or wires is of great importance. It is recommended that wire-containing casting powder in a CMDB system be used in high-burning-rate systems with relatively small webs (ref. 2).

3.3.1.1.3 Burning-Rate Reproducibility

The propellant shall have a burning rate that is highly reproducible, relatively insensitive to errors in formulation, and not dependent on volatile burning-rate catalysts.

A propellant with an extensive production history should be chosen where possible. Batch-to-batch reproducibility should be well documented. Data showing the effect of minor variations in the composition on the burning rate should be used to determine permissible errors in formulation. Formulation errors should not lead to burning-rate variations greater than ± 2 percent of the specification (refs. 7 and 55).

3.3.1.2 Pressure Sensitivity of Burning Rate

3.3.1.2.1 Effect of Pressure Exponent

The propellant shall have a pressure exponent appropriate to the design.

In general, it is recommended that the propellant have a pressure exponent of burning rate less than 0.6 and preferably less than 0.5 if other internal ballistic requirements can be met. In applications where very low exponents are required, intermediate performance is acceptable, and service temperature is not extreme, a plateau- or mesa-burning double-base propellant should be used to obtain very low exponents.

The above recommendations do not apply to those situations in which very high burning rates or extinguishment is required. High rates can often only be achieved at high combustion pressures in a propellant with a very high pressure exponent. Low-exponent propellants cannot be extinguished easily by any existing technique.

3.3.1.2.2 Modification of Pressure Exponent

The propellant pressure exponent shall be susceptible to modification without significant losses in energy.

In those rare instances where modification of the pressure exponent of burning rate is required, the most useful approach is the modification of the oxidizer particle size. A decrease in the overall particle size of the oxidizer will result in a decrease of the burning-rate exponent (ref. 52). It should be recognized, however, that any changes in burning-rate exponent usually will affect the burning rate in the pressure region of interest as well as the temperature sensitivity of burning rate. In a program in which a modification of the burning-rate exponent is necessary, it is recommended that sufficient experimental data be gathered on the particular propellant to define the magnitude of the burning-rate exponent changes with changes in oxidizer grind.

The pressure exponent of burning rate frequently may be decreased in aluminized composite propellants by increasing the aluminum content as shown in figure 16 (ref. 52). This approach will result in a change in the energy of the propellant as well as an increase in two-phase flow losses. Unless the design requirements are such that a decrease in the energy of the propellant system is acceptable, this approach is not recommended.

3.3.1.2.3 Reproducibility of Pressure Exponent

The propellant pressure exponent shall be highly reproducible and not affected by minor errors in formation.

The effects on the pressure exponent of minor errors in formulation should be studied to define the acceptable variations in composition in the normal production of the

propellant. Particular attention should be paid to production errors in the preparation of the oxidizer grind and the effect of such errors on pressure exponent. The pressure exponent should not vary from batch to batch of propellant such that the combustion pressure or burning-rate measurements in the final design have a standard deviation greater than 2 percent (refs. 7 and 55).

3.3.1.3 Temperature Sensitivity of Burning Rate

The propellant shall have a temperature sensitivity of burning rate consistent with the requirements of the design and the anticipated thermal operating environment.

The propellant selected should have a low temperature sensitivity of burning rate, particularly in those designs where the thrust level must be held within narrow margins over wide ranges of temperature. When low temperature sensitivity is desirable, it is recommended that the propellant selected have as low a pressure exponent as possible since low temperature sensitivity is associated generally with a low exponent. In general, composite propellants have lower exponents than CMDB propellants. When temperature sensitivity is critical and the performance requirements are intermediate, a plateau- or mesa-burning double-base propellant should be considered.

3.3.1.4 Measurement of Internal Ballistic Properties

The internal ballistic properties of the propellant in a motor shall be measured accurately under the anticipated service conditions.

Burning rates should be measured over the pressure and temperature ranges of interest in internal-burning small motors as described in references 7 and 18. Crawford Bomb strand measurements may be used for preliminary screening, but the internal ballistic parameters used should be derived from motor measurements unless experience has shown that strand measurements are satisfactory.

In determining temperature sensitivity of burning rate, care should be taken that there are no temperature gradients in the grain and that the grain does not cool or warm significantly while held on the test stand. Minimum equilibration time in the conditioning oven may be determined by the use of thermocouples placed throughout a test grain. It is preferable that provisions be made for maintaining the test stand at the conditioning temperature. Failing this, the motor should not be exposed to an unconditioned atmosphere longer than necessary. Thermocouples imbedded in a test grain may be used to determine the critical exposure time for different conditioning temperatures.

As a rule of thumb, nine burning-rate measurements at each temperature-pressure

combination are recommended for minimum statistical validity. The standard deviation of burning-rate measurements should not exceed 2 percent (refs. 7 and 55).

It is recommended that liquid strands be used for quality control of internal ballistic properties if a suitable correlation can be developed between such strands and motor data. Burning-rate measurements over the pressure and temperature range of interest should have a standard deviation not exceeding 2 percent (refs. 7 and 55).

3.3.2 Erosive Burning

3.3.2.1 Factors in Erosive Burning

The propellant shall have an acceptable erosive-burning characteristic.

Where the possibility of erosive burning exists, attention should be paid to choosing a propellant with an erosive-burning characteristic as low as possible. As a general rule, the propellants with higher flame temperatures have lower erosive-burning-rate constants (ref. 38). However, the erosive-burning behavior of a candidate propellant should be established as described in section 3.3.2.2.

Because of the possibility of severe erosive burning in designs with J ratios approaching 1.0, such designs should be avoided.

3.3.2.2 Characterization of Erosive Burning

The propellant shall be characterized for erosive burning in the particular motor application.

The treatment of erosive burning (based on the Lenoir-Robillard analysis) developed by Lawrence et al. (ref. 60) generally has been more successful in predicting erosive burning than was the original Lenoir-Robillard equation (ref. 59). This treatment should be used in conjunction with the program developed by these authors for predicting the gas flow parallel to the surface at any point in the motor. Because of the laboriousness of the hand calculation, this prediction technique should be computerized, and the erosive burning along the bore of the design motor should be calculated to determine whether any serious problems exist.

If computer facilities are not available, the empirical approach to the determination of erosive burning is recommended. An empirical erosive-burning constant can be determined in analogue motors designed so that the flow through the port is analogous to that in the larger motor under consideration. Generally a series of analogue motors should be fired and interrupted at various points in their burning history. The consumed web

is then measured. From such measurements, erosive burning data for the particular design are gathered.

Empirical monographs from motor firings are useful in treating the burning of an analogous propellant of similar composition and similar flame temperature.

3.3.3 Acceleration Effects

The propellant for a motor that operates under a high acceleration vector oriented 60° or greater to the burning surface shall have a minimum burning-rate response to acceleration.

If the motor will be subjected to high levels of radial acceleration such as those encountered in a spin-stabilized rocket, the internal ballistics of the motor should be checked for sensitivity to acceleration effects (refs. 61 and 63). The effect of axial acceleration on end-burning grains should be checked (ref. 64). Ground tests of radially accelerated motors should be interpreted with caution (ref. 63).

The first approach to modifying any accelerative augmentation of burning rate in aluminized composite propellant should be the reduction in the size of the aluminum particle (ref. 61). If this step is insufficient, the burning rate of the propellant should be reduced. If the reduction in aluminum particle size does not have the desired effect and the burning-rate modifications described above are not acceptable or do not have the desired effect, the aluminum content should be reduced. It should be recognized that such a reduction in aluminum content will reduce the specific impulse of the propellant.

A complete history of burning-rate augmentation over the entire burning time of the motor should be developed by suitable instrumentation in the grain or by the use of a number of motors that are interrupted at various stages in their burning. It may be possible to identify a period at the beginning of the burning time when the augmentation effects are most severe, and the design may be changed accordingly. Inflight data of the motor should be gathered as soon as possible to check static test stand measurements.

3.3.4 Oscillatory Combustion

The propellant shall not be subject to oscillatory combustion in the design application.

If the propellant selected is a metallized propellant for use in an intermediate size motor, it is unlikely that the motor will show any pressure-coupled or velocity-coupled oscillation (ref. 66). If the propellant contains no metal, either pressure-coupled or velocity-coupled oscillatory combustion is possible. There is no absolute way of predicting either type of oscillatory combustion before it is actually observed in the motor.

It therefore is recommended that all nonmetallized propellants be modified to include 2 to 5 percent aluminum or aluminum oxide. The use of aluminum is preferred over the aluminum oxide because of the slight energetic effect. If oscillatory combustion occurs in an aluminized propellant, redesign the grain or use internal baffles to change the acoustic characteristics of the combustion chamber (ref. 66).

3.3.5 Radar Attenuation

The propellant in an application in which microwave tracking, sensing, or guidance is needed shall have an exhaust composition that results in the minimum radar attenuation.

If the system under design relies on radio frequency signals for guidance, telemetry, or tracking, the RF attenuation in the exhaust should be measured experimentally early in the motor testing program. As a general rule, it may be expected that some attenuation of ultra-high-frequency RF signals will be measured in the usual metallized propellant.

Initially, if radar attenuation is a problem, the O/F ratio of the propellant should be increased so that the fuel content of the exhaust is decreased (ref. 72), thus decreasing afterburning. The O/F ratio also may be increased by reducing the metal content of the propellant, but with a resulting reduction of the specific impulse of the propellant.

If the O/F ratio cannot be increased, it is recommended that 1 to 2 percent of an electron scavenger metal (ref. 73) be incorporated into the propellant formulation. If attenuation measurements in the plume of the motor show undesirable attenuation even with the addition of the scavenger, the level in the propellants should be increased. If this increase has an undesirable effect on the energy of the system, steps should be taken, as a last resort, to reduce the alkali metal content of the ammonium perchlorate and the binder (ref. 74). It should be recognized, however, that low-alkali-metal-content ammonium perchlorate or binder represents an appreciable increase in cost of these ingredients.

3.4 Mechanical Properties Characterization

3.4.1 Screening Tests

3.4.1.1 Uniaxial Tensile Properties

The propellant shall have stress and strain capability adequate to meet grain design requirements over the service temperature range.

It is recommended that the most severe anticipated stress-strain condition in the grain be determined and expressed in terms of uniaxial properties by the use of an appropriate

conversion factor, determined empirically for the propellant of interest. The minimum allowable stress, strain, and modulus should be determined; and the failure limits at all temperatures should be related to the final grain design by the techniques described in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis." Formulation modifications can be guided by plotting the stress, strain, and modulus over the temperature range of interest as a function of the curative or plasticizer concentration. The entire range of available propellant failure behavior is then identified.

3.4.1.2 Bond Evaluation

The propellant-liner and liner-case bond shall be strong enough to withstand all anticipated stresses over the service temperature range.

Bond tests using shear or bond-in-tension test mode should be run to evaluate various liner-propellant combinations. The peel test is not recommended because of ambiguities in its interpretation. Selection of a good liner-propellant combination should be based on data from tests that cover the temperature range of interest and include many liner candidates. Testing is continued until failures occur in the propellant or some stress requirement from grain analysis is exceeded.

3.4.2 Structural Analysis Properties

3.4.2.1 Viscoelastic and Thermal Properties

The propellant shall have a well-characterized coefficient of linear thermal expansion, thermal conductivity, heat capacity, and thermal diffusivity over the service temperature range and shall have a viscoelastic modulus, Poisson's ratio, and time-temperature shift factor a_T , that provide an acceptable margin of safety from failure over the service temperature range.

The thermal and viscoelastic properties required for grain analysis should be determined by test procedures and data reduction methods set forth in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis."

3.4.2.2 Failure Properties

The propellant shall have multiaxial failure properties that exceed by an acceptable safety factor the predicted grain stress-strain values for all critical grain stress sites over all anticipated loading conditions including storage, temperature cycling, vibration, acceleration, and pressurization.

The propellant failure properties should be measured under conditions expected in the operational motor, since failure properties are very sensitive to the manner in which

loadings are distributed along the three spatial axes. The critical stress conditions for many designs result from low-temperature storage, pressurization, and repeated cycling between two temperature extremes. The recommended appropriate tests and methods of data reduction are described in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis."

3.5 Stability Characterization

3.5.1 Storage

3.5.1.1 Binder Stability

The propellant shall be based on a binder that will not degrade during storage to the point of propellant mechanical failure.

The propellant binder should be relatively free of oxidizer-binder interactions and should not show any extensive postcuring. The use of an antioxidant in the formulation is recommended. The binder should not be subject to reversion under any of the anticipated storage conditions. It is recommended that samples of the propellant be stored and the crosslink density be followed periodically (ref. 86). Any undesirable changes in propellant mechanical properties can be correlated with changes in the binder crosslink density. Care must be taken to ensure that any experimental data are obtained under equilibrium conditions and in the absence of high-temperature degradation. Swelling the propellant in a nondegrading solvent is recommended for determining equilibrium properties (refs. 87 and 88).

3.5.1.2 Shelf Life

The propellant shall not be degraded below acceptable levels by required storage time and temperature.

Existing data on type-life programs should be surveyed to determine whether service temperature aging data exist for a propellant similar to the one chosen. Service life data must be developed for the specific propellant in the end item if no type-life data are available. If the end item cannot be used, smaller motors designed to have analogous strain fields in the grain should be stored at the service temperature. Their physical integrity should be examined periodically by x-ray. It is desirable that blocks of propellant be stored in a parallel program and the mechanical properties of JANAF specimens milled from these be determined periodically. Accelerated aging is not generally recommended except as a guide to gross storage properties. The method of Marti et al. (ref. 90) is recommended as a more reliable technique since deviations that are artifacts of higher temperatures can be detected by a change in the slope of the aging curve.

3.5.1.3 Stability to Humidity

The propellant shall not be degraded below acceptable levels by moisture during fabrication and storage.

The propellant should be composed of ingredients that minimize the deleterious effects of water.

Samples of propellant should be stored in an environment with a constant humidity and temperature. Tables of humidity versus concentration of a salt or acid are in the International Critical Tables and most handbooks on chemistry or physics. These may be used for a stagnant system to maintain the desired humidity. The propellant surface should be exposed during the storage. Chemical analysis of the sectioned propellant may be used to determine the effect of the water versus depth. The effect on propellant mechanical properties should be determined with JANAF specimens milled from stored propellant.

3.5.1.4 Ingredient Volatility

The propellant shall not be degraded below acceptable levels by the loss of volatile ingredients.

The propellant suspected of having a volatile ingredient should be tested for weight loss during exposure to vacuum. A series of tests covering the propellant temperature range should be run. The usual industry practice is to hold a propellant sample at 0.3 μ Hg at 25° C for at least 240 hours. In addition to weight-loss measurements, it is recommended that mechanical properties be tested and burning rates be determined.

3.5.1.5 Stability of Liner-Propellant Bond

The liner shall be tailored for the type of propellant, and the liner-propellant bond shall have adequate strength and stability.

A liner-propellant bond should be studied in environments and under the same storage conditions as the propellant. Peel specimens are easy to make and convenient to store, but bond-in-tension specimens are recommended because the resulting values can be compared with values derived from stress analysis.

3.5.1.6 Plasticizer Migration

The propellant plasticizer when equilibrated between propellant and liner shall not adversely affect the propellant-liner bond.

The liner-propellant bond and the insulation-propellant bond should be studied for plasticizer migration. Gas, liquid, or gas-liquid chromatography is recommended as the best technique for detecting very low concentrations of plasticizer in propellant sections analyzed for plasticizer migration. Sections of propellant along the grain radius may be analyzed, and a time-temperature position plot of plasticizer migration may be developed. Stored propellant-liner-substrate samples should be tested after equilibration for bond strength. Both bond-in-tension and conventional milled JANAF specimens with the propellant-liner bond in the test section are recommended to determine whether propellant-liner or liner-substrate interfaces have deteriorated.

3.5.2 Sterilization

The propellant shall not undergo unacceptable physical, internal ballistic, or energetic changes when exposed to sterilization.

The propellant should contain no materials that will volatilize during the course of the sterilization. For this reason, plasticizers should be selected carefully, and volatile burning-rate catalysts should not be used. Because of the high sterilization temperature, double-base propellants cannot be used. It is recommended that polyvinyl chloride, fully saturated hydroxy-terminated polyurethane-polybutadiene, or CTPIB propellants be used in this application. Alternately, epoxy-cured CTPB composites containing an antioxidant may be used. Stabilized AP should be used in all formulations. The burning-rate catalysts for such an application should be either Fe_2O_3 or some similar inorganic burning-rate catalyst. Care should be taken that the autoignition temperature of the propellant is not so low that there is danger of autoignition during sterilization.

Special thermal stability specifications should be developed for ingredients to be used in propellants that will be exposed to very high temperatures. For instance, these special specifications should describe acceptable weight loss at the desired temperature and acceptable differential scanning calorimeter profiles. It is recommended that each lot of specific ingredients be qualified separately for the sterilization temperature.

3.5.3 Space Environment

The propellant selected for extended exposure to a space environment shall not undergo physical, internal ballistic, or energetic changes when exposed to vacuum or space radiation.

Propellants that may be exposed to vacuum should be based on a high-average-molecular-weight prepolymer. Where commercial binders are used, a high-molecular-weight fraction should be derived by molecular distillation or by solvent-nonsolvent precipitation (ref. 98). The propellant composition will present unusual outgassing problems if either a plasticizer or a volatile burning-rate catalyst is used. For this

reason, it is mandatory that very-high-molecular-weight chemicals or monofunctional chemicals that will become part of the gel be used as plasticizers and that no volatile burning-rate catalyst be used.

In spite of these basic precautions, the propellant outgassing may be excessive. Samples of the propellant should be formulated and exposed to 0.1μ Hg vacuum to measure the outgassing. An outgassing vs. time history should be developed, and an assessment should be made of the actual physical damage to the propellant. If outgassing proves destructive, the polymer and all other components should be outgassed before incorporation and the processing should be carried out under high vacuum.

For those propellants that will undergo extensive exposure to high radiation levels, the changes of the binder physical properties should be determined. Expose binder gumstocks and binder/ammonium perchlorate combinations to radiation in the laboratory; then correlate measured damage with intensity and wave length. Any effects on the internal ballistics of the propellant should be determined after the propellant strands are exposed to radiation for varying periods of time.

Propellants should be tested under space storage environments when those propellants are expected to survive space missions. Conditions simulating space environment have not been standardized officially, but consensus has established a few criteria: temperature in the range of 30° F to 110° F, pressure in the range of 10^{-3} to 10^{-6} mm Hg, and radiation of 10^5 ergs/gm would be equivalent to 1-year exposure in the most severe Van Allen region (ref. 102). Propellants under this condition should not show weight loss and changes in crosslink density sufficient to cause bond or propellant failure or unacceptable changes in internal ballistics.

3.6 Hazard Characterization

3.6.1 General Characterization

The propellant shall be characterized for its hazard properties before the motor development program is well advanced.

The candidate propellant should be characterized for its basic hazard properties before final selection. The complete procedure set forth in reference 104 usually is not necessary but may be desirable in spite of the cost. If the propellant motors are to be shipped by interstate carrier, propellant samples should be prepared and shipped to the Bureau of Explosives⁶ for DOT classification as soon as possible. Particular attention should be paid not only to the hazards in handling and firing the motor but to the hazards associated with manufacture, transportation, and storage.

⁶Association of American Railroads, Bureau of Explosives, Raritan Center, Edison, New Jersey 08817.

3.6.2 Impact Hazard

The propellant shall have an acceptable sensitivity to impact.

The impact hazard of the cured propellant should be determined as early as possible in the program. The impact hazard of the individual ingredients of the uncured propellant also should be determined as a guide to the design of processing and handling equipment. To this end, laboratory impact tests of the propellant ingredients should be conducted in a well-standardized impact tester to establish the 50-percent fire level and 100-percent fire level. The impact tester should be standardized against a well-known ingredient.

A propellant that gives a zero fire at the maximum height of a Bureau of Mines impact tester or its equivalent may be considered safe to handle by unprotected personnel. Propellants in the range of 10 kg-cm or below should be treated with caution. Propellants in the 5 kg-cm range on such an apparatus must be viewed as hazardous to process and handle, and it may be desirable to consider a less hazardous propellant. However, if the hazardous propellant cannot be replaced by another, special provisions for processing and handling should be made. The friction sensitivity of the propellant in this region should be examined closely since often the apparent impact sensitivity of the propellant may stem more from friction sensitivity.

3.6.3 Friction Hazard

The uncured propellant shall have a friction sensitivity low enough that shear stresses in the mixer will not ignite the propellant, and the cured propellant shall have a friction sensitivity low enough that normal handling operations are not likely to ignite the propellant.

The friction sensitivity of the propellant in both the uncured and cured state should be well characterized as soon as possible in the program by standard industry techniques. Of the techniques available within the industry, a form of the pendulum-and-slide friction tester is preferred. However, most of the available devices yield data that are not meaningful per se and require some standard of comparison. A wide range of standards in order of decreasing friction sensitivity should be run on these machines to produce a calibration range whereby an outside organization can judge the frictional data.

3.6.4 Spark Hazard

The propellant shall have a spark sensitivity low enough that the discharge of the normal static charge of a human body will not ignite the propellant.

The propellant in both the uncured and cured state should be characterized for spark sensitivity as early in the program as possible by the use of a standardized spark

apparatus. The spark apparatus should be calibrated against materials of known spark sensitivity such as lead azide, lead styphnate, and HMX in order to give a meaningful standard for the experimental data. A sufficiently large number of samples should be run in order to get a statistically significant set of data (ref. 110).

If the propellant has a spark sensitivity less than 0.015 joule, another propellant with a lower sensitivity to static initiation should be considered. If, however, the propellant cannot be abandoned, a series of standard procedures should be developed to guide processing, handling, and storage. These procedures should include provisions for the grounding of personnel, equipment, and containers to prevent any static charge and, if possible, provisions for the handling and storing of propellant in an atmosphere of controlled humidity sufficiently high to prevent the buildup of the static charge on personnel and critical handling equipment.

3.6.5 Autoignition Hazard

3.6.5.1 Environmental Heating

The propellant shall have an autoignition point so high that its probability of autoignition is low under the thermal environment to which it will be exposed.

The propellant autoignition point should be characterized early in the program, preferably by the 1- and 2-in. cube technique. Heat-transfer analysis of the propellant under all storage and service conditions should establish that probable internal temperatures and their duration are below the autoignition point. It should be recognized, however, that at all temperatures some degree of chemical reaction is going on in the propellant grain and, in a grain with sufficiently large web fraction, the temperature is so slowly dissipated that the propellant may reach its autoignition point. For this reason, the autoignition points should be recognized only as guides and should not be construed as offering a hazard limit independent of the geometry of the propellant grain.

3.6.5.2 Exothermic Reactions

The propellant shall not develop so high an internal temperature during cure or from degradation chemical reactions that there is danger of autoignition.

The propellant should be tested on the differential thermal apparatus, and a complete thermogram of the propellant should be developed for a number of samples. These data should be used to develop a critical temperature/half-thickness plot of the type described previously. In this manner, the probable behavior of the propellant in the specific geometry of the design may be predicted under a variety of thermal environments. If, on completion of this analysis, it appears that the critical temperature for

the design geometry is such that it lies close to the upper limit of the propellant's design thermal envelope, one of the following alternatives should be chosen: (1) replace the propellant with a thermally more stable one, (2) alter the half-thickness of this design, or (3) restrict the upper service-temperature limits of the propellant.

3.6.6 Detonation Hazard

The propellant shall have an acceptable susceptibility to detonation.

The propellant's susceptibility to detonation should be determined as early as possible in the program. While the impact tests previously described are a guide to the susceptibility to detonation, a card gap series should be run on the propellant if detonability is a major parameter. It is not recommended that the propellant be completely characterized following the procedures set forth in reference 104, because of the cost. However, such a procedure may be necessary if all aspects of the hazard must be defined. If the propellants will be shipped interstate by common carrier either in bulk or in a completely loaded motor, propellant samples should be shipped to the Bureau of Explosives for a complete DOT classification.

3.6.7 Toxic Hazard

The propellant exhaust products shall not contain toxic compounds in excess of allowable concentrations.

The combustion products of the propellant should be determined by thermochemical calculation at an early stage in the program. If the propellant contains beryllium, the motor should be used only in those applications in which the exhaust products cannot contaminate the atmosphere.

If the propellant develops large quantities of hydrogen fluoride gas in its exhaust, it should not be used in an application in which personnel are likely to be exposed to the concentrated exhaust product. If such an exposure is unavoidable and the propellant cannot be replaced, standard procedures must be developed for protection of personnel in the immediate area of the firing (e.g., the use of gas masks and, in some instances, protective clothing).

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3.3.1.2 Pressure Sensitivity of Burning Rate

3.3.1.2.1 Effect of Pressure Exponent

The propellant shall have a pressure exponent appropriate to the design.

In general, it is recommended that the propellant have a pressure exponent of burning rate less than 0.6 and preferably less than 0.5 if other internal ballistic requirements can be met. In applications where very low exponents are required, intermediate performance is acceptable, and service temperature is not extreme, a plateau- or mesa-burning double-base propellant should be used to obtain very low exponents.

The above recommendations do not apply to those situations in which very high burning rates or extinguishment is required. High rates can often only be achieved at high combustion pressures in a propellant with a very high pressure exponent. Low-exponent propellants cannot be extinguished easily by any existing technique.

3.3.1.2.2 Modification of Pressure Exponent

The propellant pressure exponent shall be susceptible to modification without significant losses in energy.

In those rare instances where modification of the pressure exponent of burning rate is required, the most useful approach is the modification of the oxidizer particle size. A decrease in the overall particle size of the oxidizer will result in a decrease of the burning-rate exponent (ref. 52). It should be recognized, however, that any changes in burning-rate exponent usually will affect the burning rate in the pressure region of interest as well as the temperature sensitivity of burning rate. In a program in which a modification of the burning-rate exponent is necessary, it is recommended that sufficient experimental data be gathered on the particular propellant to define the magnitude of the burning-rate exponent changes with changes in oxidizer grind.

The pressure exponent of burning rate frequently may be decreased in aluminized composite propellants by increasing the aluminum content as shown in figure 16 (ref. 52). This approach will result in a change in the energy of the propellant as well as an increase in two-phase flow losses. Unless the design requirements are such that a decrease in the energy of the propellant system is acceptable, this approach is not recommended.

3.3.1.2.3 Reproducibility of Pressure Exponent

The propellant pressure exponent shall be highly reproducible and not affected by minor errors in formation.

The effects on the pressure exponent of minor errors in formulation should be studied to define the acceptable variations in composition in the normal production of the

propellant. Particular attention should be paid to production errors in the preparation of the oxidizer grind and the effect of such errors on pressure exponent. The pressure exponent should not vary from batch to batch of propellant such that the combustion pressure or burning-rate measurements in the final design have a standard deviation greater than 2 percent (refs. 7 and 55).

3.3.1.3 Temperature Sensitivity of Burning Rate

The propellant shall have a temperature sensitivity of burning rate consistent with the requirements of the design and the anticipated thermal operating environment.

The propellant selected should have a low temperature sensitivity of burning rate, particularly in those designs where the thrust level must be held within narrow margins over wide ranges of temperature. When low temperature sensitivity is desirable, it is recommended that the propellant selected have as low a pressure exponent as possible since low temperature sensitivity is associated generally with a low exponent. In general, composite propellants have lower exponents than CMDB propellants. When temperature sensitivity is critical and the performance requirements are intermediate, a plateau- or mesa-burning double-base propellant should be considered.

3.3.1.4 Measurement of Internal Ballistic Properties

The internal ballistic properties of the propellant in a motor shall be measured accurately under the anticipated service conditions.

Burning rates should be measured over the pressure and temperature ranges of interest in internal-burning small motors as described in references 7 and 18. Crawford Bomb strand measurements may be used for preliminary screening, but the internal ballistic parameters used should be derived from motor measurements unless experience has shown that strand measurements are satisfactory.

In determining temperature sensitivity of burning rate, care should be taken that there are no temperature gradients in the grain and that the grain does not cool or warm significantly while held on the test stand. Minimum equilibration time in the conditioning oven may be determined by the use of thermocouples placed throughout a test grain. It is preferable that provisions be made for maintaining the test stand at the conditioning temperature. Failing this, the motor should not be exposed to an unconditioned atmosphere longer than necessary. Thermocouples imbedded in a test grain may be used to determine the critical exposure time for different conditioning temperatures.

As a rule of thumb, nine burning-rate measurements at each temperature-pressure

combination are recommended for minimum statistical validity. The standard deviation of burning-rate measurements should not exceed 2 percent (refs. 7 and 55).

It is recommended that liquid strands be used for quality control of internal ballistic properties if a suitable correlation can be developed between such strands and motor data. Burning-rate measurements over the pressure and temperature range of interest should have a standard deviation not exceeding 2 percent (refs. 7 and 55).

3.3.2 Erosive Burning

3.3.2.1 Factors in Erosive Burning

The propellant shall have an acceptable erosive-burning characteristic.

Where the possibility of erosive burning exists, attention should be paid to choosing a propellant with an erosive-burning characteristic as low as possible. As a general rule, the propellants with higher flame temperatures have lower erosive-burning-rate constants (ref. 38). However, the erosive-burning behavior of a candidate propellant should be established as described in section 3.3.2.2.

Because of the possibility of severe erosive burning in designs with J ratios approaching 1.0, such designs should be avoided.

3.3.2.2 Characterization of Erosive Burning

The propellant shall be characterized for erosive burning in the particular motor application.

The treatment of erosive burning (based on the Lenoir-Robillard analysis) developed by Lawrence et al. (ref. 60) generally has been more successful in predicting erosive burning than was the original Lenoir-Robillard equation (ref. 59). This treatment should be used in conjunction with the program developed by these authors for predicting the gas flow parallel to the surface at any point in the motor. Because of the laboriousness of the hand calculation, this prediction technique should be computerized, and the erosive burning along the bore of the design motor should be calculated to determine whether any serious problems exist.

If computer facilities are not available, the empirical approach to the determination of erosive burning is recommended. An empirical erosive-burning constant can be determined in analogue motors designed so that the flow through the port is analogous to that in the larger motor under consideration. Generally a series of analogue motors should be fired and interrupted at various points in their burning history. The consumed web

is then measured. From such measurements, erosive burning data for the particular design are gathered.

Empirical monographs from motor firings are useful in treating the burning of an analogous propellant of similar composition and similar flame temperature.

3.3.3 Acceleration Effects

The propellant for a motor that operates under a high acceleration vector oriented 60° or greater to the burning surface shall have a minimum burning-rate response to acceleration.

If the motor will be subjected to high levels of radial acceleration such as those encountered in a spin-stabilized rocket, the internal ballistics of the motor should be checked for sensitivity to acceleration effects (refs. 61 and 63). The effect of axial acceleration on end-burning grains should be checked (ref. 64). Ground tests of radially accelerated motors should be interpreted with caution (ref. 63).

The first approach to modifying any accelerative augmentation of burning rate in aluminized composite propellant should be the reduction in the size of the aluminum particle (ref. 61). If this step is insufficient, the burning rate of the propellant should be reduced. If the reduction in aluminum particle size does not have the desired effect and the burning-rate modifications described above are not acceptable or do not have the desired effect, the aluminum content should be reduced. It should be recognized that such a reduction in aluminum content will reduce the specific impulse of the propellant.

A complete history of burning-rate augmentation over the entire burning time of the motor should be developed by suitable instrumentation in the grain or by the use of a number of motors that are interrupted at various stages in their burning. It may be possible to identify a period at the beginning of the burning time when the augmentation effects are most severe, and the design may be changed accordingly. Inflight data of the motor should be gathered as soon as possible to check static test stand measurements.

3.3.4 Oscillatory Combustion

The propellant shall not be subject to oscillatory combustion in the design application.

If the propellant selected is a metallized propellant for use in an intermediate size motor, it is unlikely that the motor will show any pressure-coupled or velocity-coupled oscillation (ref. 66). If the propellant contains no metal, either pressure-coupled or velocity-coupled oscillatory combustion is possible. There is no absolute way of predicting either type of oscillatory combustion before it is actually observed in the motor.

It therefore is recommended that all nonmetallized propellants be modified to include 2 to 5 percent aluminum or aluminum oxide. The use of aluminum is preferred over the aluminum oxide because of the slight energetic effect. If oscillatory combustion occurs in an aluminized propellant, redesign the grain or use internal baffles to change the acoustic characteristics of the combustion chamber (ref. 66).

3.3.5 Radar Attenuation

The propellant in an application in which microwave tracking, sensing, or guidance is needed shall have an exhaust composition that results in the minimum radar attenuation.

If the system under design relies on radio frequency signals for guidance, telemetry, or tracking, the RF attenuation in the exhaust should be measured experimentally early in the motor testing program. As a general rule, it may be expected that some attenuation of ultra-high-frequency RF signals will be measured in the usual metallized propellant.

Initially, if radar attenuation is a problem, the O/F ratio of the propellant should be increased so that the fuel content of the exhaust is decreased (ref. 72), thus decreasing afterburning. The O/F ratio also may be increased by reducing the metal content of the propellant, but with a resulting reduction of the specific impulse of the propellant.

If the O/F ratio cannot be increased, it is recommended that 1 to 2 percent of an electron scavenger metal (ref. 73) be incorporated into the propellant formulation. If attenuation measurements in the plume of the motor show undesirable attenuation even with the addition of the scavenger, the level in the propellants should be increased. If this increase has an undesirable effect on the energy of the system, steps should be taken, as a last resort, to reduce the alkali metal content of the ammonium perchlorate and the binder (ref. 74). It should be recognized, however, that low-alkali-metal-content ammonium perchlorate or binder represents an appreciable increase in cost of these ingredients.

3.4 Mechanical Properties Characterization

3.4.1 Screening Tests

3.4.1.1 Uniaxial Tensile Properties

The propellant shall have stress and strain capability adequate to meet grain design requirements over the service temperature range.

It is recommended that the most severe anticipated stress-strain condition in the grain be determined and expressed in terms of uniaxial properties by the use of an appropriate

conversion factor, determined empirically for the propellant of interest. The minimum allowable stress, strain, and modulus should be determined; and the failure limits at all temperatures should be related to the final grain design by the techniques described in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis." Formulation modifications can be guided by plotting the stress, strain, and modulus over the temperature range of interest as a function of the curative or plasticizer concentration. The entire range of available propellant failure behavior is then identified.

3.4.1.2 Bond Evaluation

The propellant-liner and liner-case bond shall be strong enough to withstand all anticipated stresses over the service temperature range.

Bond tests using shear or bond-in-tension test mode should be run to evaluate various liner-propellant combinations. The peel test is not recommended because of ambiguities in its interpretation. Selection of a good liner-propellant combination should be based on data from tests that cover the temperature range of interest and include many liner candidates. Testing is continued until failures occur in the propellant or some stress requirement from grain analysis is exceeded.

3.4.2 Structural Analysis Properties

3.4.2.1 Viscoelastic and Thermal Properties

The propellant shall have a well-characterized coefficient of linear thermal expansion, thermal conductivity, heat capacity, and thermal diffusivity over the service temperature range and shall have a viscoelastic modulus, Poisson's ratio, and time-temperature shift factor a_T , that provide an acceptable margin of safety from failure over the service temperature range.

The thermal and viscoelastic properties required for grain analysis should be determined by test procedures and data reduction methods set forth in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis."

3.4.2.2 Failure Properties

The propellant shall have multiaxial failure properties that exceed by an acceptable safety factor the predicted grain stress-strain values for all critical grain stress sites over all anticipated loading conditions including storage, temperature cycling, vibration, acceleration, and pressurization.

The propellant failure properties should be measured under conditions expected in the operational motor, since failure properties are very sensitive to the manner in which

loadings are distributed along the three spatial axes. The critical stress conditions for many designs result from low-temperature storage, pressurization, and repeated cycling between two temperature extremes. The recommended appropriate tests and methods of data reduction are described in the design criteria monograph "Solid Propellant Grain Structural Integrity Analysis."

3.5 Stability Characterization

3.5.1 Storage

3.5.1.1 Binder Stability

The propellant shall be based on a binder that will not degrade during storage to the point of propellant mechanical failure.

The propellant binder should be relatively free of oxidizer-binder interactions and should not show any extensive postcuring. The use of an antioxidant in the formulation is recommended. The binder should not be subject to reversion under any of the anticipated storage conditions. It is recommended that samples of the propellant be stored and the crosslink density be followed periodically (ref. 86). Any undesirable changes in propellant mechanical properties can be correlated with changes in the binder crosslink density. Care must be taken to ensure that any experimental data are obtained under equilibrium conditions and in the absence of high-temperature degradation. Swelling the propellant in a nondegrading solvent is recommended for determining equilibrium properties (refs. 87 and 88).

3.5.1.2 Shelf Life

The propellant shall not be degraded below acceptable levels by required storage time and temperature.

Existing data on type-life programs should be surveyed to determine whether service temperature aging data exist for a propellant similar to the one chosen. Service life data must be developed for the specific propellant in the end item if no type-life data are available. If the end item cannot be used, smaller motors designed to have analogous strain fields in the grain should be stored at the service temperature. Their physical integrity should be examined periodically by x-ray. It is desirable that blocks of propellant be stored in a parallel program and the mechanical properties of JANAF specimens milled from these be determined periodically. Accelerated aging is not generally recommended except as a guide to gross storage properties. The method of Marti et al. (ref. 90) is recommended as a more reliable technique since deviations that are artifacts of higher temperatures can be detected by a change in the slope of the aging curve.

3.5.1.3 Stability to Humidity

The propellant shall not be degraded below acceptable levels by moisture during fabrication and storage.

The propellant should be composed of ingredients that minimize the deleterious effects of water.

Samples of propellant should be stored in an environment with a constant humidity and temperature. Tables of humidity versus concentration of a salt or acid are in the International Critical Tables and most handbooks on chemistry or physics. These may be used for a stagnant system to maintain the desired humidity. The propellant surface should be exposed during the storage. Chemical analysis of the sectioned propellant may be used to determine the effect of the water versus depth. The effect on propellant mechanical properties should be determined with JANAF specimens milled from stored propellant.

3.5.1.4 Ingredient Volatility

The propellant shall not be degraded below acceptable levels by the loss of volatile ingredients.

The propellant suspected of having a volatile ingredient should be tested for weight loss during exposure to vacuum. A series of tests covering the propellant temperature range should be run. The usual industry practice is to hold a propellant sample at 0.3μ Hg at 25° C for at least 240 hours. In addition to weight-loss measurements, it is recommended that mechanical properties be tested and burning rates be determined.

3.5.1.5 Stability of Liner-Propellant Bond

The liner shall be tailored for the type of propellant, and the liner-propellant bond shall have adequate strength and stability.

A liner-propellant bond should be studied in environments and under the same storage conditions as the propellant. Peel specimens are easy to make and convenient to store, but bond-in-tension specimens are recommended because the resulting values can be compared with values derived from stress analysis.

3.5.1.6 Plasticizer Migration

The propellant plasticizer when equilibrated between propellant and liner shall not adversely affect the propellant-liner bond.

The liner-propellant bond and the insulation-propellant bond should be studied for plasticizer migration. Gas, liquid, or gas-liquid chromatography is recommended as the best technique for detecting very low concentrations of plasticizer in propellant sections analyzed for plasticizer migration. Sections of propellant along the grain radius may be analyzed, and a time-temperature position plot of plasticizer migration may be developed. Stored propellant-liner-substrate samples should be tested after equilibration for bond strength. Both bond-in-tension and conventional milled JANAF specimens with the propellant-liner bond in the test section are recommended to determine whether propellant-liner or liner-substrate interfaces have deteriorated.

3.5.2 Sterilization

The propellant shall not undergo unacceptable physical, internal ballistic, or energetic changes when exposed to sterilization.

The propellant should contain no materials that will volatilize during the course of the sterilization. For this reason, plasticizers should be selected carefully, and volatile burning-rate catalysts should not be used. Because of the high sterilization temperature, double-base propellants cannot be used. It is recommended that polyvinyl chloride, fully saturated hydroxy-terminated polyurethane-polybutadiene, or CTPIB propellants be used in this application. Alternately, epoxy-cured CTPB composites containing an antioxidant may be used. Stabilized AP should be used in all formulations. The burning-rate catalysts for such an application should be either Fe_2O_3 or some similar inorganic burning-rate catalyst. Care should be taken that the autoignition temperature of the propellant is not so low that there is danger of autoignition during sterilization.

Special thermal stability specifications should be developed for ingredients to be used in propellants that will be exposed to very high temperatures. For instance, these special specifications should describe acceptable weight loss at the desired temperature and acceptable differential scanning calorimeter profiles. It is recommended that each lot of specific ingredients be qualified separately for the sterilization temperature.

3.5.3 Space Environment

The propellant selected for extended exposure to a space environment shall not undergo physical, internal ballistic, or energetic changes when exposed to vacuum or space radiation.

Propellants that may be exposed to vacuum should be based on a high-average-molecular-weight prepolymer. Where commercial binders are used, a high-molecular-weight fraction should be derived by molecular distillation or by solvent-nonsolvent precipitation (ref. 98). The propellant composition will present unusual outgassing problems if either a plasticizer or a volatile burning-rate catalyst is used. For this

reason, it is mandatory that very-high-molecular-weight chemicals or monofunctional chemicals that will become part of the gel be used as plasticizers and that no volatile burning-rate catalyst be used.

In spite of these basic precautions, the propellant outgassing may be excessive. Samples of the propellant should be formulated and exposed to 0.1μ Hg vacuum to measure the outgassing. An outgassing vs. time history should be developed, and an assessment should be made of the actual physical damage to the propellant. If outgassing proves destructive, the polymer and all other components should be outgassed before incorporation and the processing should be carried out under high vacuum.

For those propellants that will undergo extensive exposure to high radiation levels, the changes of the binder physical properties should be determined. Expose binder gumstocks and binder/ammonium perchlorate combinations to radiation in the laboratory; then correlate measured damage with intensity and wave length. Any effects on the internal ballistics of the propellant should be determined after the propellant strands are exposed to radiation for varying periods of time.

Propellants should be tested under space storage environments when those propellants are expected to survive space missions. Conditions simulating space environment have not been standardized officially, but consensus has established a few criteria: temperature in the range of 30° F to 110° F, pressure in the range of 10^{-3} to 10^{-6} mm Hg, and radiation of 10^5 ergs/gm would be equivalent to 1-year exposure in the most severe Van Allen region (ref. 102). Propellants under this condition should not show weight loss and changes in crosslink density sufficient to cause bond or propellant failure or unacceptable changes in internal ballistics.

3.6 Hazard Characterization

3.6.1 General Characterization

The propellant shall be characterized for its hazard properties before the motor development program is well advanced.

The candidate propellant should be characterized for its basic hazard properties before final selection. The complete procedure set forth in reference 104 usually is not necessary but may be desirable in spite of the cost. If the propellant motors are to be shipped by interstate carrier, propellant samples should be prepared and shipped to the Bureau of Explosives⁶ for DOT classification as soon as possible. Particular attention should be paid not only to the hazards in handling and firing the motor but to the hazards associated with manufacture, transportation, and storage.

⁶Association of American Railroads, Bureau of Explosives, Raritan Center, Edison, New Jersey 08817.

3.6.2 Impact Hazard

The propellant shall have an acceptable sensitivity to impact.

The impact hazard of the cured propellant should be determined as early as possible in the program. The impact hazard of the individual ingredients of the uncured propellant also should be determined as a guide to the design of processing and handling equipment. To this end, laboratory impact tests of the propellant ingredients should be conducted in a well-standardized impact tester to establish the 50-percent fire level and 100-percent fire level. The impact tester should be standardized against a well-known ingredient.

A propellant that gives a zero fire at the maximum height of a Bureau of Mines impact tester or its equivalent may be considered safe to handle by unprotected personnel. Propellants in the range of 10 kg-cm or below should be treated with caution. Propellants in the 5 kg-cm range on such an apparatus must be viewed as hazardous to process and handle, and it may be desirable to consider a less hazardous propellant. However, if the hazardous propellant cannot be replaced by another, special provisions for processing and handling should be made. The friction sensitivity of the propellant in this region should be examined closely since often the apparent impact sensitivity of the propellant may stem more from friction sensitivity.

3.6.3 Friction Hazard

The uncured propellant shall have a friction sensitivity low enough that shear stresses in the mixer will not ignite the propellant, and the cured propellant shall have a friction sensitivity low enough that normal handling operations are not likely to ignite the propellant.

The friction sensitivity of the propellant in both the uncured and cured state should be well characterized as soon as possible in the program by standard industry techniques. Of the techniques available within the industry, a form of the pendulum-and-slide friction tester is preferred. However, most of the available devices yield data that are not meaningful per se and require some standard of comparison. A wide range of standards in order of decreasing friction sensitivity should be run on these machines to produce a calibration range whereby an outside organization can judge the frictional data.

3.6.4 Spark Hazard

The propellant shall have a spark sensitivity low enough that the discharge of the normal static charge of a human body will not ignite the propellant.

The propellant in both the uncured and cured state should be characterized for spark sensitivity as early in the program as possible by the use of a standardized spark

apparatus. The spark apparatus should be calibrated against materials of known spark sensitivity such as lead azide, lead styphnate, and HMX in order to give a meaningful standard for the experimental data. A sufficiently large number of samples should be run in order to get a statistically significant set of data (ref. 110).

If the propellant has a spark sensitivity less than 0.015 joule, another propellant with a lower sensitivity to static initiation should be considered. If, however, the propellant cannot be abandoned, a series of standard procedures should be developed to guide processing, handling, and storage. These procedures should include provisions for the grounding of personnel, equipment, and containers to prevent any static charge and, if possible, provisions for the handling and storing of propellant in an atmosphere of controlled humidity sufficiently high to prevent the buildup of the static charge on personnel and critical handling equipment.

3.6.5 Autoignition Hazard

3.6.5.1 Environmental Heating

The propellant shall have an autoignition point so high that its probability of autoignition is low under the thermal environment to which it will be exposed.

The propellant autoignition point should be characterized early in the program, preferably by the 1- and 2-in. cube technique. Heat-transfer analysis of the propellant under all storage and service conditions should establish that probable internal temperatures and their duration are below the autoignition point. It should be recognized, however, that at all temperatures some degree of chemical reaction is going on in the propellant grain and, in a grain with sufficiently large web fraction, the temperature is so slowly dissipated that the propellant may reach its autoignition point. For this reason, the autoignition points should be recognized only as guides and should not be construed as offering a hazard limit independent of the geometry of the propellant grain.

3.6.5.2 Exothermic Reactions

The propellant shall not develop so high an internal temperature during cure or from degradation chemical reactions that there is danger of autoignition.

The propellant should be tested on the differential thermal apparatus, and a complete thermogram of the propellant should be developed for a number of samples. These data should be used to develop a critical temperature/half-thickness plot of the type described previously. In this manner, the probable behavior of the propellant in the specific geometry of the design may be predicted under a variety of thermal environments. If, on completion of this analysis, it appears that the critical temperature for

the design geometry is such that it lies close to the upper limit of the propellant's design thermal envelope, one of the following alternatives should be chosen: (1) replace the propellant with a thermally more stable one, (2) alter the half-thickness of this design, or (3) restrict the upper service-temperature limits of the propellant.

3.6.6 Detonation Hazard

The propellant shall have an acceptable susceptibility to detonation.

The propellant's susceptibility to detonation should be determined as early as possible in the program. While the impact tests previously described are a guide to the susceptibility to detonation, a card gap series should be run on the propellant if detonability is a major parameter. It is not recommended that the propellant be completely characterized following the procedures set forth in reference 104, because of the cost. However, such a procedure may be necessary if all aspects of the hazard must be defined. If the propellants will be shipped interstate by common carrier either in bulk or in a completely loaded motor, propellant samples should be shipped to the Bureau of Explosives for a complete DOT classification.

3.6.7 Toxic Hazard

The propellant exhaust products shall not contain toxic compounds in excess of allowable concentrations.

The combustion products of the propellant should be determined by thermochemical calculation at an early stage in the program. If the propellant contains beryllium, the motor should be used only in those applications in which the exhaust products cannot contaminate the atmosphere.

If the propellant develops large quantities of hydrogen fluoride gas in its exhaust, it should not be used in an application in which personnel are likely to be exposed to the concentrated exhaust product. If such an exposure is unavoidable and the propellant cannot be replaced, standard procedures must be developed for protection of personnel in the immediate area of the firing (e.g., the use of gas masks and, in some instances, protective clothing).

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GLOSSARY

Mathematical terms and symbols, chemical symbols, material designations, and abbreviations used in the text are grouped in separate sections in the Glossary. Frequently used subscripts are presented for combination with the general mathematical symbols. For example, subscripts e and t combined with the symbol A are to be interpreted as A_e , the area at the nozzle exit plane, and A_t , the area at the nozzle throat. (Complete symbols are presented with subscripts or superscripts when the usage cannot be divorced from the sub- or superscript, e.g., I_{sp}^0 .)

MATHEMATICAL TERMS AND SYMBOLS

| <u>Symbol</u> | <u>Definition</u> | <u>Remarks</u> |
|---------------|--|-----------------------------------|
| A | area, in. ² | |
| A_n | characteristic stiffness, psi | eqs. (28) and (30) |
| a | coefficient of pressure in burning-rate equation | $r = a P_c^n$ |
| a | shortest line from center to periphery of a grain, in. | eq. (35) |
| a_T | time-temperature shift factor | defined in eq. (29) |
| b | dimensionless constant | eq. (19) |
| C | heat capacity, cal/gm/°C | |
| C_p | specific heat | |
| c^* | characteristic velocity, ft/sec | |
| D | diameter, in. | |
| d | diameter, cm | eq. (4) |
| E | activation energy, kcal/mole | eqs. (35) and (36) |
| $E(t)$ | relaxation modulus, psi | |
| F | force, lb | |
| $f()$ | function of () | unspecified mathematical relation |
| g | acceleration of gravity, 32.2 ft/sec ² | |
| H | enthalpy, kcal/100gm | |

| <u>Symbol</u> | <u>Definition</u> | <u>Remarks</u> |
|---------------|---|--|
| H_f | heat of formation from the elements, kcal/mole | |
| I_{sp} | propellant specific impulse, lb _f -sec/lb _m | <p>This symbol is used only in general reference to propellant specific impulse or in reporting nonstandard corrected values of $I_{sp,t}$. All numerical values must be accompanied by specification of the following assumptions:</p> <ul style="list-style-type: none"> (a) chamber pressure, P_c (b) ambient pressure, P_a (c) nozzle area expansion ratio, ϵ, and whether or not this is optimum (d) nozzle divergence half-angle, α. <p>Use the same time interval and propellant mass assumptions as for $I_{sp,t}$; therefore, do not report a numerical value of I_{sp} without also reporting the corresponding value of $I_{sp,t}$.</p> |
| I_{sp}^o | theoretical propellant specific impulse | <p>Calculated from propellant thermodynamic properties. All numerical values must be accompanied by specification of items (a) through (d) as for I_{sp} plus the following:</p> <ul style="list-style-type: none"> (e) assumption of frozen or equilibrium exit composition (f) physical state of exhaust condensables. |

| <u>Symbol</u> | <u>Definition</u> | <u>Remarks</u> |
|---------------|---|--|
| I_{spd} | measured (delivered) propellant specific impulse | <p>Calculated from data from actual motor firing. All numerical values must be accompanied by specification of motor conditions (a) through (d) for I_{sp} plus the following:</p> <p>(e) time interval used for impulse determination</p> <p>(f) propellant mass assumption.</p> |
| I_{spd}^o | theoretical delivered propellant specific impulse | <p>Calculated from propellant thermodynamic properties assuming the same conditions (a) through (d) as for I_{spd} with the added specifications of either frozen or equilibrium exit composition and physical state of exhaust condensables.</p> |
| I_{sp}^o | standard theoretical propellant specific impulse | <p>Calculated from propellant thermodynamic properties. The physical state of exhaust condensables must be specified. The following standard conditions are implied and need not be stated in reporting numerical values:</p> <p>(a) chamber pressure $P_c = 1000$ psia</p> <p>(b) ambient pressure $P_a = 14.7$ psia</p> <p>(c) nozzle area expansion ratio $\epsilon =$ optimum</p> <p>(d) nozzle divergence half-angle $\alpha = 0^\circ$</p> <p>(e) equilibrium exit conditions.</p> |

| <u>Symbol</u> | <u>Definition</u> | <u>Remarks</u> |
|----------------------|---|---------------------------------|
| <i>J</i> ratio | ratio of nozzle throat area to grain port area | A_t/A_g |
| <i>K</i> | ratio of area of burning to nozzle throat area | A_b/A_t |
| <i>k</i> | thermal conductivity, cal-/cm-sec-°C or Btu/in.-hr-°F | |
| <i>L</i> | latent heat of phase change, cal/gm | eq. (4) |
| <i>L*</i> | ratio of chamber free volume to nozzle throat area (also known as characteristic length) | V_c/A_t |
| <i>ln</i> | Napierian (natural) logarithm | |
| <i>log</i> | logarithm to the base 10 | |
| \bar{M} | average molecular weight of gases, lb/mole | |
| <i>N</i> | material parameter, in. ⁻¹ | eq. (13) |
| <i>n</i> | exponent of density | eqs. (6), (7), and (9) |
| <i>n</i> | pressure exponent of burning rate | eqs. (18), (19), (24), and (25) |
| <i>O/F</i> | ratio of equivalent weights of oxidizing molecules to equivalent weight of fuel molecules for the reaction to yield H ₂ + CO + metal oxide | |
| <i>P</i> | pressure, lb/in. ² | |
| <i>Q</i> | heat of decomposition, kcal/mole | |
| <i>R</i> | universal gas constant, 1545 ft-lb/mole-°R, 1.98 cal/mole-°K, or 1205 psi • cm ³ /°K-mole | |
| <i>R</i> | mass ratio | eqs. (7), (10), (13), and (17) |
| <i>r</i> | propellant burning rate, in./sec | |
| <i>S</i> | entropy | |
| <i>T</i> | temperature, deg | |
| <i>T_n</i> | temperature of hot gases, °K | eq. (4) |

| <u>Symbol</u> | <u>Identification</u> | <u>Remarks</u> |
|---------------|---|---------------------|
| T_c | adiabatic equilibrium flame temperature, °R | |
| T_m | critical temperature, °K | |
| t | time, sec | |
| t_i | time to ignition, sec | defined in eq. (36) |
| V | volume, in. ³ | |
| v | velocity, ft/sec | |
| v_2 | volume fraction of gel | eq. (34) |
| W | weight, lb | |
| \dot{W} | mass discharge rate, lb/sec | |
| \bar{X} | arithmetic mean of X samples | |
| Z | frequency factor in Arrhenius rate expansion | eq. (35) |
| α | coefficient of linear thermal expansion, in./in.-°F | |
| β | weight of case/weight of propellant | |
| γ | ratio of specific heats, C_p/C_v | |
| Δ | change or increment | |
| δ | shape factor | eq. (35) |
| ϵ | elongation; i.e., strain, in./in. | |
| ϵ_m | maximum strain or elongation, in./in. | |
| κ | thermal diffusivity, in. ² /hr or cm ² /sec | |
| λ | principal extension ratio ($1 + \epsilon$) | |
| μ | micron, 10 ⁻⁶ meter | |
| ν | Poisson's ratio, transverse strain/longitudinal strain | |

| <u>Symbol</u> | <u>Identification</u> | <u>Remarks</u> |
|-------------------|---|---------------------|
| ν_c | crosslink density | eqs. (33) and (34) |
| Π_K | temperature sensitivity of pressure at a particular value of K | defined in eq. (22) |
| $\Pi_{P/r}$ | temperature sensitivity of pressure at a particular value of P/r | defined in eq. (23) |
| ρ | density, gm/cm ³ or lb/in. ³ | |
| σ | stress, lb/in. ² | |
| σ_K | temperature sensitivity of burning rate at a particular value of K | defined in eq. (21) |
| σ_m | maximum stress, lb/in. ² | |
| σ_p | temperature sensitivity of burning rate at a particular value of pressure | defined in eq. (20) |
| τ | constant, characteristic of a viscoelastic nonlinear material, sec | eqs. (28) and (30) |
| Ω | effective $F_{s,t}$, lb-sec/lb | defined in eq. (9) |
| <u>Subscripts</u> | | |
| a | ambient | |
| b | burning | |
| c | chamber combustion | |
| d | delivered | |
| e | exit; exhaust | |
| F | fusion | |
| f | formation | |

Subscripts

| | |
|----------|------------------------|
| <i>G</i> | glass transition point |
| <i>g</i> | gas |
| <i>i</i> | initial; ignition |
| <i>j</i> | <i>j</i> th item |
| <i>K</i> | area ratio = A_b/A_t |
| <i>m</i> | maximum |
| <i>n</i> | <i>n</i> th item |
| <i>o</i> | original; initial |
| <i>P</i> | pressure |
| <i>p</i> | propellant |
| <i>r</i> | residence |
| ref | reference |
| sub | substitute |
| <i>T</i> | temperature |
| <i>t</i> | throat |
| <i>u</i> | payload |
| <i>w</i> | stage |
| <i>x</i> | fixed |
| <i>y</i> | port |
| ρ | density-associated |

MATERIAL DESIGNATIONS, CHEMICAL SYMBOLS, AND ABBREVIATIONS

| <u>Designation or Symbol</u> | <u>Identification</u> | <u>Remarks</u> |
|----------------------------------|---------------------------------------|--|
| Al | aluminum | metal |
| AN | ammonium nitrate | |
| AP | ammonium perchlorate | |
| Be | beryllium | metal |
| BITA | butyleneimine adduct of trimeric acid | aziridinyl curing agent for -COOH groups |
| CMDB | composite metallized double base | |
| CO | carbon monoxide | |
| -COOH | carboxylic acid group | active group in carboxy- terminated prepolymers |
| Cr | chromium | metal |
| CTPB | carboxy-terminated polybutadiene | |
| CTPIB | carboxy-terminated polyisobutylene | |
| DB | double base | |
| FC | fluorocarbon | |
| FeAA | ferric acetylacetonate | polyurethane curing cat- alyst |
| GN | guanidine nitrate | oxidizer |
| H ₂ | hydrogen | gas |
| HCl | hydrogen chloride | gas |
| HF | hydrogen fluoride | gas |
| HMDI | hexamethylene diisocyanate | polyurethane crosslinker |

| <u>Designation or Symbol</u> | <u>Identification</u> | <u>Remarks</u> |
|----------------------------------|---|--|
| HMX | cyclotetramethylene tetranitramine | |
| HTPB | hydroxy-terminated polybutadiene | |
| KP | potassium perchlorate | |
| LiP | lithium perchlorate | oxidizer |
| MAPO | tris-[1-(2-methyl)aziridinyl] phosphine oxide | aziridinyl curing agent for -COOH groups |
| NC | nitrocellulose | |
| NG | nitroglycerin | |
| NO ₂ | nitro-group | |
| -OH | hydroxyl group | active group in hydroxy-terminated prepolymers |
| PB | polybutadiene | |
| PBAA | polybutadiene-acrylic acid polymer | |
| PBAN | polybutadiene-acrylic acid-acrylonitrile terpolymer | |
| PETN | pentaerythritol tetranitrate | explosive |
| P-N | phosphorous-nitrogen bond | |
| PNC-DB | plastisol nitrocellulose double base | |
| PPG | polypropylene glycol | |
| PS | polysulfide | |
| PU | polyurethane | |
| PVC | polyvinyl chloride | |

| <u>Designation or Symbol</u> | <u>Identification</u> | <u>Remarks</u> |
|------------------------------|-------------------------------------|--|
| RDX | cyclotrimethylene trinitramine | |
| -SH | mercaptyl groups | active group in poly-sulfide prepolymers |
| TBM | tris-(2-ethylaziridinyl)-S-triazine | aziridinyl curative for -COOH groups |
| TDI | tolylene diisocyanate | polyurethane curative |
| TEGDN | triethylene glycol dinitrate | DB plasticizer |
| TMETN | trimethylol ethane trinitrate | DB plasticizer |
| TNT | trinitrotoluene | explosive |
| Zr | zirconium | metal |

ABBREVIATIONS

| <u>Organization or Term</u> | <u>Identification</u> | <u>Remarks</u> |
|-----------------------------|---|--|
| BATES | Ballistic and Test Evaluation System | series of scaling motors developed at Edwards AFB --Rocket Propulsion Laboratory |
| CPIA | Chemical Propulsion Information Agency | |
| DOT | Department of Transportation | |
| DSC | differential scanning calorimeter | |
| DTA | differential thermal analysis | |
| EAFB-RPL | Edwards Air Force Base --Rocket Propulsion Laboratory | |
| ICRPG | Interagency Chemical Rocket Propulsion Group | |
| JANAF | Joint Army-Navy-Air Force | |
| RF | radio frequency | |

NASA SPACE VEHICLE DESIGN CRITERIA

MONOGRAPHS ISSUED TO DATE

ENVIRONMENT

| | |
|---------|---|
| SP-8005 | Solar Electromagnetic Radiation, June 1965 |
| SP-8010 | Models of Mars Atmosphere (1967), May 1968 |
| SP-8011 | Models of Venus Atmosphere (1968), December 1968 |
| SP-8013 | Meteoroid Environment Model—1969 (Near Earth to Lunar Surface), March 1969 |
| SP-8017 | Magnetic Fields—Earth and Extraterrestrial, March 1969 |
| SP-8020 | Mars Surface Models (1968), May 1969 |
| SP-8021 | Models of Earth's Atmosphere (120 to 1000 km), May 1969 |
| SP-8023 | Lunar Surface Models, May 1969 |
| SP-8037 | Assessment and Control of Spacecraft Magnetic Fields, September 1970 |
| SP-8038 | Meteoroid Environment Model—1970 (Interplanetary and Planetary), October 1970 |
| SP-8049 | The Earth's Ionosphere, March 1971 |

STRUCTURES

| | |
|---------|---|
| SP-8001 | Buffeting During Atmospheric Ascent, revised November 1970 |
| SP-8002 | Flight-Loads Measurements During Launch and Exit, December 1964 |
| SP-8003 | Flutter, Buzz, and Divergence, July 1964 |
| SP-8004 | Panel Flutter, July 1964 |

| | |
|---------|---|
| SP-8006 | Local Steady Aerodynamic Loads During Launch and Exit, May 1965 |
| SP-8007 | Buckling of Thin-Walled Circular Cylinders, revised August 1968 |
| SP-8008 | Prelaunch Ground Wind Loads, November 1965 |
| SP-8009 | Propellant Slosh Loads, August 1968 |
| SP-8012 | Natural Vibration Modal Analysis, September 1968 |
| SP-8014 | Entry Thermal Protection, August 1968 |
| SP-8019 | Buckling of Thin-Walled Truncated Cones, September 1968 |
| SP-8022 | Staging Loads, February 1969 |
| SP-8029 | Aerodynamic and Rocket-Exhaust Heating During Launch and Ascent, May 1969 |
| SP-8031 | Slosh Suppression, May 1969 |
| SP-8032 | Buckling of Thin-Walled Doubly Curved Shells, August 1969 |
| SP-8035 | Wind Loads During Ascent, June 1970 |
| SP-8040 | Fracture Control of Metallic Pressure Vessels, May 1970 |
| SP-8042 | Meteoroid Damage Assessment, May 1970 |
| SP-8043 | Design-Development Testing, May 1970 |
| SP-8044 | Qualification Testing, May 1970 |
| SP-8046 | Landing Impact Attenuation For Non-Surface-Planing Landers, April 1970 |
| SP-8050 | Structural Vibration Prediction, June 1970 |
| SP-8053 | Nuclear and Space Radiation Effects on Materials, June 1970 |
| SP-8054 | Space Radiation Protection, June 1970 |
| SP-8055 | Prevention of Coupled Structure-Propulsion Instability (Pogo), October 1970 |

- SP-8056 Flight Separation Mechanisms, October 1970
- SP-8057 Structural Design Criteria Applicable to a Space Shuttle, January 1971
- SP-8060 Compartment Venting, November 1970
- SP-8061 Interaction With Umbilicals and Launch Stand, August 1970

GUIDANCE AND CONTROL

- SP-8015 Guidance and Navigation for Entry Vehicles, November 1968
- SP-8016 Effects of Structural Flexibility on Spacecraft Control Systems, April 1969
- SP-8018 Spacecraft Magnetic Torques, March 1969
- SP-8024 Spacecraft Gravitational Torques, May 1969
- SP-8026 Spacecraft Star Trackers, July 1970
- SP-8027 Spacecraft Radiation Torques, October 1969
- SP-8028 Entry Vehicle Control, November 1969
- SP-8033 Spacecraft Earth Horizon Sensors, December 1969
- SP-8034 Spacecraft Mass Expulsion Torques, December 1969
- SP-8036 Effects of Structural Flexibility on Launch Vehicle Control Systems, February 1970
- SP-8047 Spacecraft Sun Sensors, June 1970
- SP-8058 Spacecraft Aerodynamic Torques, January 1971
- SP-8059 Spacecraft Attitude Control During Thrusting Maneuvers, February 1971
- SP-8065 Tubular Spacecraft Booms (Extendible, Reel Stored), February 1971
- SP-8070 Spaceborne Digital Computer Systems, March 1971

SP-8071 Passive Gravity-Gradient Libration Dampers, February 1971

CHEMICAL PROPULSION

SP-8052 Liquid Rocket Engine Turbopump Inducers, May 1971

SP-8048 Liquid Rocket Engine Turbopump Bearings, March 1971

SP-8039 Solid Rocket Motor Performance Analysis and Prediction, May

SP-8051 Solid Rocket Motor Igniters, March 1971

SP-8025 Solid Rocket Motor Metal Cases, April 1970

SP-8041 Captive-Fired Testing of Solid Rocket Motors, March 1971