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SPACE VEHICLE
DESIGN CRITERIA
(CHEMICAL PROPULSION)

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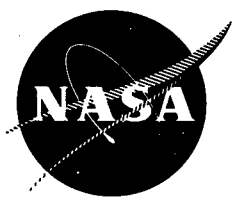
SOLID PROPELLANT PROCESSING FACTORS IN ROCKET MOTOR DESIGN



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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 final pages 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 Processing Factors in Rocket Motor Design," 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 Carlton L. Horine and E. W. Madison of the United Technology Center, a Division of 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, H. Bankaitis of Lewis Research Center, Ernest D. Brown of Thiokol Chemical Corporation, Rudolph A. Peterson of Aerojet Solid Propulsion Company, and O. D. Ratliff of North American Rockwell Corporation collectively and individually 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.

October 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 propellant processing operations and related 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 design problems related to propellant processing 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 PROCESSING FACTORS IN ROCKET MOTOR DESIGN

1. INTRODUCTION

In order to design a solid rocket motor that can be produced effectively and efficiently, the designer must consider the propellant processing problems involved in producing the motor. In general, there are a variety of ways to produce a motor that will satisfy a given set of specifications. Each method affects in different ways the reliability of the finished product and the cost of processing the propellant. Since high reliability usually is a prime design objective, reliability factors are much more important than cost factors.

This monograph describes the ways in which propellant processing is affected by the choices made by the designer, and it sets forth the bases on which tradeoff studies, design proof or scaleup studies, and special design features should be accomplished in order to obtain high product quality and to optimize processing costs whenever these costs are a significant factor in total motor cost. Only those design elements that affect processing are discussed, and only their relation to processing is treated. Other design criteria monographs suitably referenced in this monograph present detailed treatments of the considerations involved in the selection of a propellant and in the design and evaluation of the propellant grain.

For purposes of this monograph, processing is considered to include (1) the operational steps involved with the lining and preparation of the motor case for the grain, (2) the procurement of the propellant raw materials, and (3) propellant mixing, casting or extrusion, curing, machining, and finishing. Specifically excluded are processes involved with the application of motor case insulation and the operational aspects of static firing; these subjects are covered in other NASA design criteria monographs.

The end item performance and operational requirements of a solid propellant motor dictate the particular areas where processing is important to motor performance. For example, severe storage and operational environments require propellants that retain acceptable mechanical properties over a wide range of external conditions. Variations in the propellant formulation or variations in the process of bonding or incorporating the rocket motor grain into the case must be closely controlled to ensure proper performance of the motor. Rocket motors requiring precise output in terms of ballistic performance require precise control of the weighout and incorporation of raw material ingredients as well as control of the many factors that influence

the final burning rate of the propellant. Total impulse is extremely important in many rocket motors, and the specific impulse and the total weight of the propellant in the rocket motor must be controlled closely. These examples illustrate some of the many areas where processing in relation to the system design and performance must be fully understood prior to the establishment of a rocket motor design that will optimize reliability and processing costs.

This monograph is not intended to be a complete discussion on processing, nor is it presented in a format that relates to processing sequences. The information in the monograph is based on industry surveys and literature searches completed in 1967. The material has been arranged in accordance with the usual major steps in the design of a solid rocket motor. These include the selection of a propellant formulation, grain design, liner system selection, and motor case design. Design elements for each of these steps are discussed as they are materially related to propellant processing, and the advantages and disadvantages of the designer's available choices are clearly shown.

2. STATE OF THE ART

A generalized sequence in successful solid rocket motor design may be summarized as follows:

(1) Selection of propellant (covered in detail in reference 1). Propellant ingredients and properties that affect processing are considered thoroughly.
(2) Grain design and evaluation of grain structural integrity (covered in detail in references 2 and 3). Grain design elements that affect processing are examined carefully.
(3) Selection and design of the liner and evaluation of its relation to processing (covered in detail in reference 4).
(4) Design of the motor case (covered in detail in reference 5) and establishment of its relation to propellant processing.

In each of these steps, the factors that influence reliability generally are far more important than those that influence processing cost. In turn, processing costs may be minor compared with other design, development, and manufacturing costs, especially when only a few motors are to be produced. Since generalized, standardized approaches for reliability and cost factors cannot be used for all designs, tradeoff studies are tailored to fit each design and propellant processing program. Process engineers are consulted whenever the available information is not adequate for meaningful studies.

2.1 Propellant Formulations and Properties

2.1.1 Polymeric Ingredients

Polymers constitute the key binding ingredient in solid propellants. Polymer selection in propellant formulations affects reliability, raw material costs, and process conversion costs of the finished rocket motor (refs. 6 through 8).

The polymer structures of concern to the designer are those of the finished propellant binder systems; the structures include those that are formed by polymerization or by other chemical reactions during processing as well as those that do not involve molecular reactions (e.g., plasticization). The molecular structure of the polymers in cured propellant, including the nature of reactive sites or radicals as well as the nature, location, and orientation of branch chains and crosslinking components, varies in complexity. Reliability often is enhanced by limiting the number of ingredients and by selecting relatively simple polymers that can be specified more effectively. There are designs, however, in which increased raw material costs as well as additional complexity can be justified by the gain in reliability produced by improved properties or by tradeoff with cost reductions in other parts of the solid rocket motor system.

Polymers may be divided into four groups according to their impact on propellant processing: (1) plastisol polymers; (2) oxygen-rich binders used in double-base (DB)[1] propellants; (3) prepolymers or monomers used as fuel binders in so-called cast composite propellants; and (4) polymers based on rubber gum stocks.

In plastisol propellants, the first group, all polymerization reactions are completed before propellant processing begins; and the propellants are solidified through solvation of fully polymerized resin particles in the nonvolatile liquid. Polyvinyl chloride (PVC), which consists of a relatively simple polymer suspended in a fluid medium that also serves as the plasticizer, is a typical plastisol propellant (ref. 9). Applications for this type of system are somewhat limited, primarily because of the high cure temperatures. For this reason, PVC seldom is used in case-bonded or thick-web applications.

Nitrocellulose (NC), an example of the second group, is a relatively complex molecule; however, its chemical, mechanical, and ballistic properties can be reproduced accurately. The cost of NC is moderate because its manufacture is based on cotton linters or wood pulp and because it has been manufactured in large quantities for a long time. On the other hand, grain shrinkage during processing causes design and processing problems.

The prepolymer polybutadiene-acrylic acid-acrylonitrile (PBAN) used in composite propellants is an example of the third group (ref. 10). One of the least expensive raw material butadiene polymers used in solid rocket propellant binder systems, PBAN generally is used in applications requiring moderately high elongations (on the order of 30 percent true elongation) and service conditions of 0° to 120° F (256 to 322 K). Other binder components such as crosslinking agents and chemical modifiers commonly are reacted during mixing and curing of this type of propellant. The addition of a crosslinking agent such as an epoxy often is the last step of the mixing process. The PBAN system usually is very reliable, and the processing costs generally are low because of good operational control of schedules and downtime. Prepolymer PBAN plus associated binder ingredients costs about $1.00 to $2.00 a pound ($2.20 to $4.40 a kilogram).

Design performance at temperatures from −65° to +150° F (219 to 339 K) usually requires a prepolymer of carboxy-terminated polybutadiene (CTPB) or a polyurethane. In the CTPB case, the curing agent usually is an imine such as tris [1-(2 methyl)aziridinyl] phosphine oxide, known in the industry as MAPO (ref. 10). However, since the imine curing agent may react chemically with ammonium perchlorate (AP) to liberate heat, precautions are taken to reduce this hazard. Prepolymer CTPB plus associated binder ingredients costs about $2.00 to $4.00 a pound (about $4.40 to $8.80 a kilogram).

[1] See Glossary for material designations, classification of explosive hazards, definitions of terms and symbols, and organization abbreviations.

PBAN and CTPB make up the bulk of binders used in solid composite propellants. Other prepolymers, used in highly specialized applications, are similar in complexity and in impact on process conversion costs. For example, polyurethane, which has been used for several years, is formed in a chemical reaction when a high-molecular-weight glycol, preferably having hydroxyl groups at both ends of the linear chain (alpha-omega termination), is cured with a diisocyanate to form a urethane-linked binder (ref. 10). The chemistry of polyurethane binders has been studied intensively, and polyurethane propellants have been used in a variety of applications. Because the isocyanate curing agent reacts with moisture usually present as an impurity in propellant ingredients, processing of polyurethane propellants requires careful control of ambient relative humidities to avoid additional moisture contamination (ref. 11).

The fourth group of polymers consists of synthetic gum rubbers such as neoprene (GR-M), styrene-butadiene (SBR or GR-S), butyl (GR-1), and butadiene/methyl vinyl pyridine copolymer (Bd/MVP) (ref. 12). These polymers require relatively-heavy-duty equipment for propellant processing (molding and extrusion) in order to incorporate other ingredients in the relatively-high-viscosity rubber gum stocks, and the complexity of the polymer molecule introduces additional cost. The use of this binder system is somewhat limited at present because of difficulties with case bonding and other problems.

2.1.2 Oxidizers

The solid oxidizers currently in common use are limited to those commercially available from the chemical industry. Ammonium nitrate (AN) and ammonium perchlorate (AP), the only ones of significant interest, have the characteristics given in table I.

Table I. — Characteristics of AN and AP

Oxidizer	Available oxygen content, wt-%	Specific gravity	Maximum I_{sp} in optimized formulation, lbf-sec/lbm (N-sec/kg)	Comments
AN	20	1.73	200 (1961)	Hygroscopic nature and phase/volume changes can result in processing problems; used in motors when it is desirable to obtain low burning rate, low flame temperature, and smokeless exhaust.
AP	34	1.95	250 (2452)	Widely used; provides high burning rates, low exhaust signature.

The size of the oxidizer particle has a significant effect on propellant properties, as described in reference 1. In addition, the complexity of the particle-size distribution specified in the propellant formulation can have a significant effect on processing costs. For example, handling and storing several different ranges of oxidizer raw material involve increased costs. Increased costs also result from adjustments of equipment and quality control tests required in the grinding of different sizes of oxidizer for formulations specifying complex particle-size distribution.

Although oxidizers are available in a variety of particle-size distributions, the propellant processors, to reduce costs, purchase AP in two or, at most, three particle-size ranges:

Range I:	400 to 600 μ (μm) diameter
Range II:	50 to 200 μ (μm) diameter
Range III:	5 to 15 μ (μm) diameter

Because material in range III is classed as a high explosive and is subject to restrictive shipping regulations, most propellant processors produce it themselves by grinding range II material.

Propellant formulations may contain any one of the three ranges (a unimodal particle-size distribution), or they may contain various combinations of any two or all three ranges (a multimodal particle-size distribution). The term "modal" refers to the number of peaks (or modes) in a plot of the particle-size distribution. The particle-size distribution for a propellant containing a blend of material from ranges II and III, a typical combination, is shown in figure 1. To maximize the oxidizer content per propellant unit volume, the majority of propellants processed today contain two ranges so chosen that the smaller particles are placed within the voids bounded by the curved surfaces of the larger particles (ref. 13).

Some of the high-solids-loaded formulations of composite fuel-binder propellants use a trimodal AP system. Trimodal systems usually are made up of material from each of the three common ranges described above, although some contain several other distributions of ground material. For example, aluminum powder is usually different in size from the AP and thus adds another size mode. Use of multimodal systems generally improves processability (sec. 2.1.5.1).

A parameter that normally is not specified is the AP shape characteristic, which is highly dependent on the crystallizing and drying processes. Relatively rapid flash drying results in some fracturing of crystals and in a relatively rough overall shape characteristic because of the rapid removal of moisture. The slower rotary drying results in nearly spherical particles with little or no internal cracking. The AP shape characteristic can in turn influence both the propellant processability and the propellant burning rate. Crystal friability is another AP property that is difficult to measure. For this reason, it has not yet been included in raw material specifications. AP friability, however, which can vary significantly from supplier to supplier and sometimes from lot to lot, is important to the user because of the variations in particle sizes caused by attrition when the AP is handled and processed into propellants.

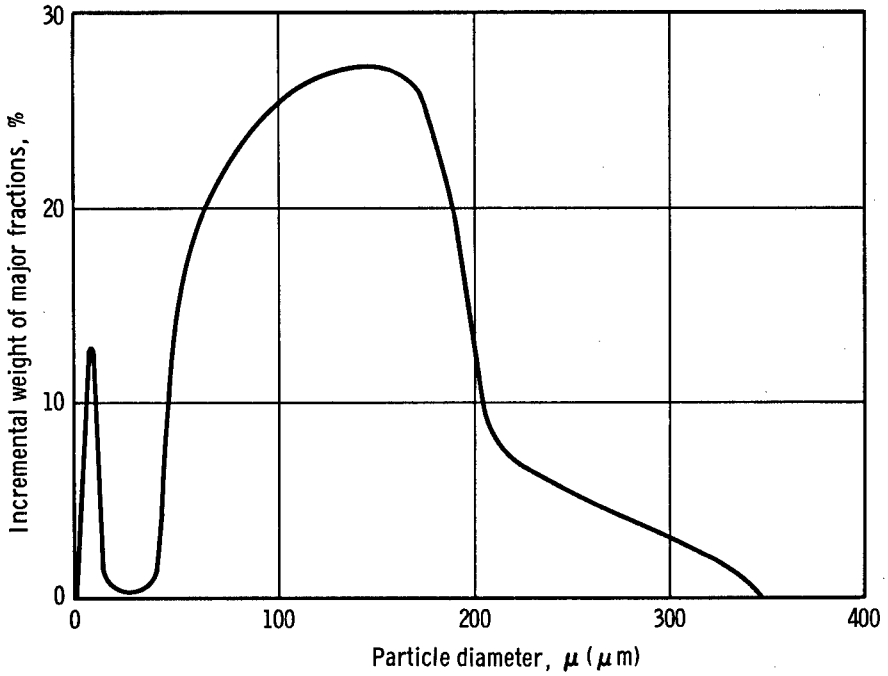

Figure 1. — Typical AP particle-size distribution, bimodal blend of ranges II and III.

Oxidizer specifications, handling, and processing can have significant effects on certain other design factors (e.g., burning rate) as described in the following sections.

2.1.3 Hazards

Processing of solid propellants in special cases involves the hazards of toxic materials but, more generally, the hazards of deflagration and detonation. All solid propellants and many of the ingredients that go into solid propellants are high-energy materials; under certain conditions they can release large quantities of energy in the form of heat or shock waves at very fast rates. It is important to note the distinction between the terms "deflagration" and "detonation" that are used to describe these energy releases. Preventive measures against detonations generally are more costly than those against deflagrations.

Deflagration is the rapid release of large quantities of gas and energy. Although the rate of release may result in an explosion under certain conditions, the reaction front advances

through the solid mass at less than sonic velocity. A typical deflagration is that of the carefully controlled burning that occurs on the surface of solid propellant; it progresses at a predictable rate depending on physical conditions. One of the major factors that determines the safety hazard of a deflagration is the area of solid propellant or other burning solid material, since the rate of gas evolution is directly proportional to the area of surface exposed to burning. Thus, finely divided powder can be much more hazardous than an equal weight in a thick solid propellant grain.

Detonation is an explosion characterized by the propagation of the reaction front within the reacting mediums, such as solid propellant, at supersonic velocity. Whether a given material under given conditions will detonate or deflagrate is a function of probability. A reaction that begins as a deflagration may, under a given set of conditions, become a detonation. In other situations, a high-energy material may detonate when subjected to impact forces or may undergo what has been termed a low-order reaction or a rapid deflagration. Still another possibility is that it will undergo no reaction at all.

Several different systems for classifying the explosive hazards of high-energy material are in use. The Department of Defense, for example, distinguishes two basic classes of explosive hazards: detonation hazards (class 7), and deflagration hazards with very low probability of a detonation (class 2) (ref.14). The appropriate hazard classification for a propellant is established by conducting standardized tests described in reference 14.

Another system of classifying materials for explosive hazard (ref. 15), also using a standard laboratory test to determine the probability of explosion, is used by agencies responsible for regulating the safe transportation of hazardous materials. Class A materials are those likely to detonate during certain types of accidents that can occur during transportation. Class B materials are those with a high-energy deflagration hazard but with little or no probability of detonation under the same circumstances.

Sensitivity to detonation is a function of physical conditions as well as chemical composition. For example, fine AP (sec. 2.1.2) is much more sensitive to shock or friction than coarse AP. Likewise, some propellants are more susceptible to detonation if they contain small air voids and are not in the form of a completely solid grain.

Processing facilities (structures and equipment) are not designed or operated according to uniform standards for safety. Although basic guidelines for the design of facilities and the handling of explosives, including solid propellants and ingredients that go into these propellants, are given in certain handbooks, many of the more important safety considerations are peculiar to a specific processing facility or to specific ingredients and propellant formulation. Handbooks often must be interpreted, supplemented, or modified to provide specific designs, operating procedures, and regulations to cover the hazards for particular materials

and facilities. Handbook discussions of safety generally are divided into considerations of materials and facilities.

As for the safety of materials, laboratory tests are run on every new material and combination of materials developed for solid rocket propellants. These tests establish the sensitivity of these materials to applied inputs of energy and the type and extent of damage that might be expected if they are accidentally deflagrated or detonated. Sensitivities to friction, impact, electric discharge, and heat (cookoff) are discussed in reference 1.

2.1.3.1 Toxicity

Industry practice in general is to avoid highly toxic materials wherever possible because toxic materials pose special storage and handling problems in propellant processing with consequent increases in processing costs. There are, however, several toxic materials whose cost effectiveness cannot be equaled by nontoxic materials. Many solid propellants, therefore, contain at least one toxic material. The epoxide and imine crosslinking agents used with polybutadiene derivative prepolymer system propellants are examples of toxic materials commonly found in composite propellants. PBAN formulations usually contain only one toxic material (the epoxy crosslinking agent, which has dermatological effects). CTPB formulations usually contain two toxic materials: an epoxy, which has dermatological effects, and an imine, which attacks the central nervous system. Problems in processing these materials have been solved by using protective devices and special facilities and by training personnel in proper handling methods.

The increasing use of beryllium in solid propellants poses unusual toxicity problems in both propellant processing and motor firing. In order to reduce the hazards of dust generated during normal processing and the extensive spread of toxic dust in fire or explosion, facilities often are located in isolated areas with favorable wind conditions. Exhaust from static tests is collected in special tanks, and the waste beryllium combustion products are carefully collected. The toxic agents in these propellants are elemental beryllium and beryllium oxide particles approximately 5 to 10μ (μm) in diameter. Normal dust toxicity hazards of elemental beryllium are greatly reduced by handling the beryllium in a beryllium-binder slurry (ref. 16). The toxic-dust hazards to processing personnel have been effectively controlled by facility designs directed toward minimizing personnel exposure.

2.1.3.2 Deflagration and Detonation

The catastrophic effects of accidental deflagration and detonation of ingredients are minimized by design of facilities; for example, water-quench systems (triggered by devices that sense the rate of pressure or temperature rise) are installed at mixing stations, or quantity/

distance factors are considered in locating the various propellant processing stations. Propellant formulations that specify few, if any, sensitive high-energy ingredients usually result in lower processing costs, i.e., lower capital cost for storage and processing facilities and less labor to handle and store raw material ingredients.

From a processing standpoint, composite propellants are among the easiest and safest formulations to produce. DB propellants and some composites that contain high-energy material are more sensitive to handling and to process-induced ignition or detonation and therefore require a more complex processing procedure.

2.1.3.2.1 Ingredient Hazards

Nitroglycerin (NG) is used in DB propellants. It is one of the most hazardous ingredients because of the ease with which it is detonated. Also, being a liquid, it requires special care to avoid leaks or spills. However, NG usually is manufactured in the proximity of the propellant line and is desensitized to a degree by dilution with plasticizers. These precautions plus others established through extensive use of this material over a long period of time have resulted in a very low accident rate.

When the physical state of NC, another ingredient of DB formulations, offers a large specific surface, there are special deflagration hazards, although knowledge gained through the extensive use of NC has kept accidents at a low rate of occurrence. One unsatisfactory feature of NC is its chemical instability during storage unless properly protected by stabilizer ingredients in the propellant mix; fortunately, stabilizers that give NC a shelf life adequate for most applications have been developed.

AP is of particular interest because of its widespread use in solid propellants. Produced by a process involving the reaction of sodium perchlorate with ammonia and hydrochloric acid (ref. 17), AP is a colorless compound that crystallizes from water as an anhydrous salt, forming no hydrates. Its decomposition is discussed in reference 18. When the thermal behavior of AP is studied in a differential scanning calorimeter, a major exotherm (attributed to solid-phase decomposition) is observed at pressures above one atmosphere and temperatures approximating 430°C (703 K). The addition of copper, chromium, or iron salts to AP catalyzes the decomposition, lowering the temperature of the exothermic reaction. This phenomenon is the reason that burning-rate modifiers such as iron oxide and copper chromite are effective.

AP dust decomposes rapidly under excessive friction, impact forces, or pressure. AP is handled in the plant as class 2 material unless it is range III or finer; then it is class 7. The sensitivity and rate of decomposition are increased by contamination with fuel-type materials such as hydrocarbon greases. Processors minimize these contamination hazards by the control of

lubricants and dusts and by the complete enclosure of all processing equipment. The use of sealed bearings is desirable and, where possible, special lubricants that are relatively unreactive with AP are used. Thus, there are significant process costs for special housekeeping and maintenance procedures. Facility designs usually require the separation of personnel from the grinding operations and the control of relative humidity wherever oxdizer is brought in contact with ambient air. However, the classification of AP (other than very fine) does not require significant costs for quantity/distance separation of facilities.

AN also is used as an oxidizer in propellants. This material is produced in very large quantities at low cost for the fertilizer industry. The basic manufacturing processes are well established. AN must be protected against contamination by carbonaceous materials such as lubricating oils because they constitute a deflagration hazard. However, housekeeping and maintenance procedures are not particularly costly.

Aluminum powder must be protected against exposure to moisture during storage and handling; this protection involves process labor and special facilities costs. Aluminum can react with water to form explosive mixtures of hydrogen and air. Dry mixtures of aluminum and iron oxide powders are avoided. The reaction between these two is highly exothermic and can be initiated by friction or by static electric discharge (e.g., by a workman sweeping a contaminated floor).

2.1.3.2.2 Process Combination Hazards

Special hazards associated with individual ingredients have been described above. Because of the chemical reactivity of many propellant ingredients, other hazards may exist in unusual combinations of two or more of these ingredients. Unusual combinations may result either from accidental accumulations (e.g., spills or dust inside the buildings or equipment) or from a particular addition sequence in mixing. These hazards may have a direct impact on processing and a corresponding effect on costs. Some formulations are likely to involve this special hazard more than others, depending on specific ingredients involved and on processing requirements for addition sequences when mixing. Therefore, hazards are evaluated on the basis of knowledge of the chemical reactions that might be involved in processing and by laboratory sensitivity tests on selected combinations of materials. In some cases, processing hazards are reduced by avoiding particular combinations of ingredients or by the order in which ingredients are added. The industry practice is to take full advantage of any combination that reduces processing hazards so that personnel safety is ensured and the high cost of facility replacement is avoided.

CTPB propellants illustrate how processing order greatly reduces processing hazards. MAPO, the imine crosslinking agent in this system, homopolymerizes with the release of heat. Sensitive to heat, MAPO-AP combinations ignite quite readily, a characteristic that was respon-

sible for loss of life and extensive damage to mixing facilities in two disasters in 1965. The hazard is reduced to a tolerable level when the MAPO is added to the fuel and dispersed prior to oxidizer addition.

2.1.3.2.3 Propellant Hazards

As noted, the tendency for mixed solid propellants to deflagrate or detonate has been grouped into two classes of explosive hazard, class 2 and class 7. Finished propellants of class 7 require greater costs for storage facilities and more labor for safe handling than class 2 propellants. Industry practice in reducing the hazards associated with class 7 propellants (usually DB) is to place buildings used to manufacture or store these materials at considerably greater distances from each other than would be the case for class 2 propellants. Extensive use is made of earthen bunkers around the stations.

2.1.4 Burning Rate of Cured Propellant

One of the most important design elements that affects processing is selection of propellant to provide the required burning rate, because very significant changes in burning rate may be caused by relatively small variations in formulation, processing conditions, or chemical or physical properties of the raw materials. In addition, some of the propellant selection and processing factors related to burning rate also affect mechanical properties (sec. 2.1.6).

2.1.4.1 Control and Reproducibility

Burning rate is influenced by the chemical composition and, in some cases, by the physical properties of ingredients. After a propellant system has been selected, small variations in the burning rate are affected by tailoring the propellant composition (usually by adjusting the relative quantities of ingredients) as described in reference 1. Finally, even smaller changes are made at the processing plant after a propellant is in production; these quality control changes are made in order to maintain production within specifications and to compensate for variations from lot to lot. The processing plant utilizes response mechanisms that result in a reliable system for meeting burning-rate specifications and reproducibility. The use of these response mechanisms is complicated by many factors, as described below; in addition, these methods often affect the burning-rate sensitivity to temperature and pressure, and thus produce results that vary if temperature and pressure change.

Varying the ratio of coarse to fine oxidizer particles is one method used for the control of burning rates; varying the oxidizer particle size is another. Oxidizer concentration generally is held constant. The practicality of controlling burning rate with changes in oxidizer particle

size depends on the operating pressure of the motor, on the modality of particle size distribution (sec. 2.1.2), and on the propellant formulation and the physical properties of the oxidizer. Adjustments to burning rates by changing the particle size usually are restricted to small changes so that there are no adverse effects on propellant processability, mechanical properties, or performance.

Small-particle oxidizer (smaller than range II, 50 to 200 μ (μm) diam.) in unimodal distribution may be used in high-burning-rate propellants. In such systems, the burning rate at low pressures increases significantly with a decrease in the particle size (ref. 19). Reference 20 shows the inverse effect of unimodal particle-size diameter on burning rate. Reference 1 points out that in highly loaded propellant systems, however, the reduction of the oxidizer particle size may result in an increase in propellant viscosity because of the concurrent increase in oxidizer specific surface; this viscosity increase limits the final processability of the propellant systems.

Most composite propellants use a multimodal distribution of particle size. This distribution permits the designer to obtain high solids loading without increasing viscosity of the propellant mix to the point where it is impractical to process (secs. 2.1.2. and 2.1.5.3). Formulations with high solids loading often are selected in order to meet high performance (specific impulse) requirements.

At chamber pressures above 500 psia (3.45 MN/m^2), the decomposition of large oxidizer particles dominates the combustion process. Thus when formulations containing AP in a multimodal distribution of ranges II and III particle size are used in motors operating at such pressures, the particle size of the range II AP has the dominant effect on burning rate (ref. 20). This behavior of multimodal systems at chamber pressures above 500 psia (3.45 MN/m^2) also was reported in reference 21; this study (based on constant concentration of total AP) concludes that (1) the particle size of the coarse oxidizer (approximately 100 to 200 μ (μm)) affected burning rate significantly and (2) at the same time, there was no significant effect on burning rate because of variance of fine oxidizer particle size (approximately 20 μ (μm)) when the fine oxidizer was used in a bimodal system with coarse oxidizer.

Processors make quality control adjustments to burning rates by changing the ratio of coarse-to-fine fractions of AP in bimodal systems, as described in reference 22. Typical data usually made available to processors are shown in figure 2, which also shows a typical effect of varying the burning-rate modifier from 0.5 to 0.7 weight-percent. This method of adjusting burning rates by changing the ratio of coarse-to-fine fractions is more effective in propellant systems having either high burning rates (above 0.3 in./sec (7.62 mm/sec)) at a pressure of 1000 psia (6.895 MN/m^2) or AP coarse-to-fine weight ratios that are less than 50/50.

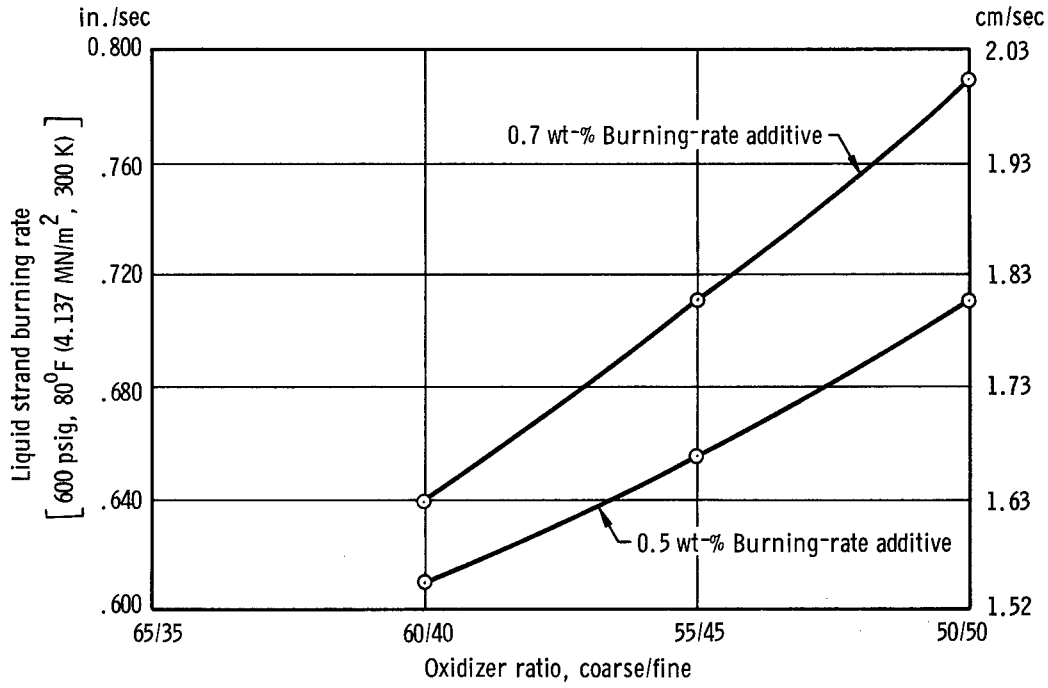

Figure 2. – Typical effect of oxidizer-blend ratio and burning-rate-modifier level on burning rate (ref. 22).

Many solid propellant formulations contain modifying ingredients that, in small amounts, have a large effect on burning rate. In some of these propellant systems, the variation in concentration of the burning-rate modifier has a very marked effect on burning rate, although usually there is an upper limit above which increasing the concentration is not effective. The effectiveness of the modifier often increases markedly at higher levels of fine oxidizer (ref. 19). In others, the quantity of modifiers can be varied over wide limits with only a very small effect on burning rate (ref. 22).

One of the most widely used modifiers in composite propellants is iron oxide; recently, however, there has been a trend favoring the use of compounds other than iron oxides. Quality control charts maintained during production runs of this type propellant record small changes in burning rate that probably are caused by small variations in the properties of some of the ingredients or by changes in process conditions. Once an unfavorable trend has clearly been established, fine adjustments to control burning rate can be made with very little added cost by adjusting iron oxide levels during the mix process. Burning-rate modifiers thus are a good process quality control tool; they are less useful in the tailoring of compositions.

The total weight fraction of oxidizer in a propellant has a significant effect on burning rate, as described in reference 1. But since variation in total oxidizer weight fraction affects specific impulse, this method of modifying burning rate is of limited use in process quality control.

Variations in aluminum weight fraction also can have a significant effect on the burning rate of the specific propellant formulation (refs. 9 and 23). Knowledge of these variations is important in determining the level of control that must be exercised during propellant processing. The manner in which the aluminum is handled, weighed out, and dispensed must be controlled carefully to ensure that consistent concentrations of aluminum are added in a repeatable manner to the propellant batch. During the Titan III-M program, for example, it was found that a 1-percent increase in aluminum fuel increased the uncured propellant burn rate by 3 percent while the same increase resulted in a 6-percent increase in the burn rate of cured propellant when measured in the 15-lb (6.8 kg) test motor (ref. 24). Thus, the response of burning rate to changes in aluminum content is not as significant as with AP. The particle size of aluminum has a significant effect on burning rate, as indicated in figure 3 (ref. 13).

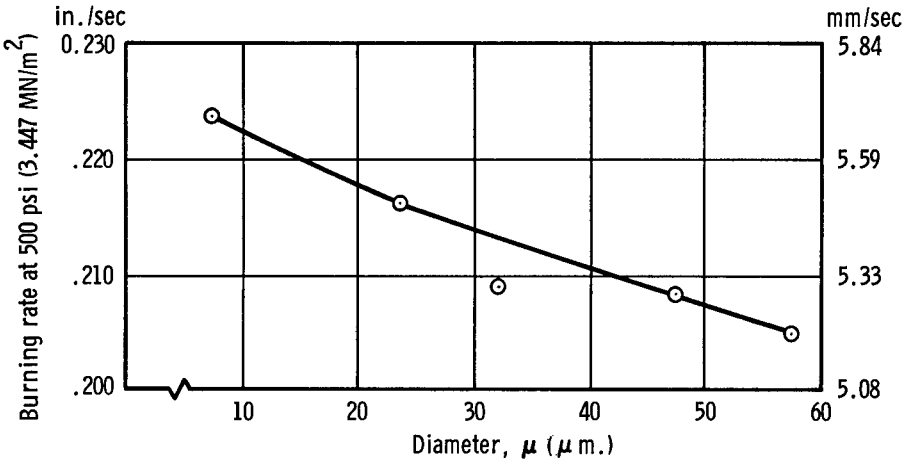

Figure 3. – Typical effect of aluminum particle size on burning rate (ref. 13).

Variations in particle size of aluminum may have significant effects also on combustion efficiency and other propellant properties, as discussed in reference 1. Variation of metal-fuel particle sizes generally is not used for process control, because this method usually is more expensive and less effective than other techniques.

The original DB propellant formulations did not contain any solid oxidizers or metallic fuel ingredients. Many of the formulations developed recently are of the CMDB type that contains relatively small amounts of solid oxidizers such as AP as well as solid metallic fuel. A variation in AP particle size is used to tailor burning rates of CMDB propellants, but this method generally is not used for quality control during processing.

Although many CMDB propellants contain burning-rate modifiers, the rate is not easily adjusted during processing by varying the concentration of the modifiers; other methods of adjusting propellant burning rate are employed. One of these methods is the blending of casting powder sublots (ref. 25), a process in which casting powder lots (1 million pounds (454 x 10^3 kg) is not uncommon) requiring many mixer-loads and many days of operation are combined as homogeneous lots; this operation often is performed in a 5000-lb (2268 kg) tumbling barrel. The practice of blending large lots is the basis of the high level of reproducibility in cast DB propellants. Minor variations in material and processing conditions during the manufacture of casting powder are evened out by this technique, and reproducibility is ensured because the properties of the final cast propellant are determined largely by the properties of the casting powder. In addition, the blending step is used to provide precise adjustments in propellant burning rates based on the measured properties of sublots.

2.1.4.2 Proprietary Ingredients

The variability in mechanical and chemical properties of some propellant ingredients can have a significant effect on burning rate in the finished propellant. Properties vary from supplier to supplier as well as from lot to lot of the same supplier. In some cases, particularly with a newly developed propellant, it is impractical or difficult to establish procurement specifications for these ingredients that will adequately control burning rate. One approach to obtaining uniformity has been to establish proprietary or sole-source procurement for those ingredients that may have a marked effect on burning rate. But, in some cases, even ingredients procured from a single processor will vary.

Although sole-source procurement contributes to the uniformity of propellant ingredients, competitive bids for nonproprietary ingredients have significant effects on minimizing the cost of raw materials. Each manufacturing plant from which bids are accepted must be qualified to produce the ingredient. Process engineers usually set up qualification programs for selected ingredients. Selection of the ingredients and of the suppliers to be qualified is unique for each propellant formulation and is highly dependent on the quality of material to be purchased. Qualification programs involve engineering and testing expenses that must be weighed against forecasted procurement savings and other advantages. Criticality of program schedules, logistics, and other purchasing factors are additional important considerations.

2.1.4.3 Raw Material Characterization

The control of reproducibility of end-item performance is highly dependent on variations in the properties of raw material ingredients used in propellant formulations. Whenever possible, specifications for raw materials are developed in sufficient detail to relate the critical chemical and physical properties to burning rate in the finished propellant. But since it is usually impossible to specify these raw material properties in a manner that will ensure specific

end-item performance, it is customary to establish a baseline by characterizing large lots of raw material used in a newly developed formulation. Raw materials frequently are characterized by processing development motors made from reserved large lots of ingredients and evaluating their performance to establish nominal burning rate. This method generally is used to characterize the solid oxidizer and metal fuel used in composite propellants. For example, reference 26 reports that unknown and apparently undefinable variations in the properties of AP oxidizer resulted in a variation of nearly 3 percent in burning rates of lots supplied by different suppliers, in spite of the fact that these materials were purchased according to identical specifications and had essentially the same particle-size distribution.

The problem is solved in DB propellants by blending very large base lots of casting powder. Because of the chemical purity and liquid nature of casting solvent ingredients such as NG, there is no significant problem with this category of raw materials.

2.1.4.4 Process Contaminants

Burning rate of some propellants can be varied by inadvertent contamination of the raw materials or the propellant during storage, handling, or processing. Precautions therefore are taken to ensure proper shipping containers, storage facilities, and quality control of raw materials to prevent contamination prior to processing. In addition, processing equipment is constructed of materials that will not contribute to contamination; in some cases, special operating precautions are taken during processing.

The burning rate of a composite propellant formulation without modifiers may be modified by iron oxide contamination. Specifications of raw materials therefore must prevent the unintentional incorporation of significant or variable amounts of iron oxide. Some polymers used in these formulations must be stored in stainless steel tanks and the propellants processed in stainless steel equipment to prevent contamination by iron oxide.

2.1.4.5 Scaleup

New propellant formulations usually are developed with laboratory-size equipment, e.g., glass beakers for handling ingredients and either 1-gal or 5-gal (3.8 or 18.9 dm^3) mixers. This size of equipment and the method of handling introduce little, if any, change in particle size. When the new formulations are produced in production quantities, however, the larger size and the different nature of the process equipment usually introduce changes in burning rate. The most common example is the change in burning rate of a composite propellant that results from a change in particle size of the solid oxidizer. This change is a result of production AP being handled in large bins, screw conveyors, or airveyors in which particles often are reduced in size by attrition. AP is subjected to further attrition and deagglomeration in mixing. The de-

gree of size change is a function of equipment designs and procedures for introducing the AP into the mixer, of mixer design, of clearances or agitator design, and of mixing time.

Although important in handling and mixing operations, the scaleup effect usually is not a factor in grinding oxidizer since most laboratory mixes use oxidizer from a full-scale production grinder. However, suitable precautions must be taken to ensure that the ground oxidizer material selected for laboratory mixes has a particle-size distribution that is representative of a full-production run on the grinder.

2.1.4.6 Process Variables

Special studies of process variables usually are conducted on newly developed propellant formulations in order to determine the effect of variations in the proportion of ingredients that occur during normal processing operations. These studies supplement the scaleup studies of the effects of equipment size and of the environmental conditions of production processing and their variations. The ingredient-variation studies are carried out along the lines of a study (ref. 27) that was conducted to determine the necessary process control limits on a relatively simple propellant formulation containing only four materials: PBAA polymer, epoxy, AP, and aluminum. This study showed the effects of ingredient variation on burning rate. Specific formulations, however, may react uniquely to changes in ingredient proportions, and separate studies have been made on most formulations now in use. The results of such investigations are used in the processing plant to meet required in-process control limits and to aid in the preparation of operating procedures that will ensure that the quantities of materials being incorporated into the production mix are within the limits required to yield reproducible burning rates at the desired values.

2.1.5 Rheology of Uncured Propellant

Propellant mixing and casting probably are the most complex and important operations in composite propellant processing. Complete blending and wetout of solid ingredients, as well as dispersion of any agglomerates, are critical for control of ballistic and mechanical properties. A solid propellant mixer must be capable of thoroughly incorporating and blending a mixture of solid/liquid ingredients with weight ratios as high as 90-percent solids and 10-percent liquids and resultant bulk viscosities ranging up to several kilopoise. Mixing normally is the most hazardous operation in propellant processing, because combining fuel and oxidizer by mechanical action involves the hazard of chemical or mechanical ignition of the mass, with resultant fire or explosion.

Background information on mixing and casting is available in the literature. A highly automated batch weighout system for ingredients is described in reference 28. The newest design

vertical batch mixer for composite propellants is described in reference 29, and continuous mixing is described in reference 30. Several different casting techniques are described, including vacuum (ref. 31) (the most common), bayonet (refs. 30 and 32), and bottom casting (ref. 33).

Propellant mixing and casting processes are affected significantly by the rheological properties of the uncured propellant. This is particularly true of composite propellants because of their non-Newtonian nature in the uncured state. An important characteristic of these non-Newtonian propellants is the dependence of viscosity on applied stress as well as on temperature. The rheological properties of the uncured propellant are particularly important when it is necessary to cast successive batches of propellant into the motor case. There are unique mixing and forming processes associated with the manufacture of the casting powder for DB propellants, but these procedures have been essentially standardized to the point that they no longer constitute significant problems in propellant selection. Since DB casting solvents generally are Newtonian in their flow characteristics, the processes of solvent addition are well standardized and involve no special problems of interest to the designer.

Anisotropic mechanical and ballistic properties of solid propellants can result both from the nature of the ingredients and from the flow channels and processes used in casting composite propellants or in extruding solventless DB propellants. In composite propellants, anisotropic properties develop primarily during casting. As the propellant flows into the motor case, there occurs preferential separation of the heterogeneous matrix of the multisized solid particles from the viscous polymeric binder. The final anisotropic properties are brought about by the different shear stress fields imposed on the propellant as it flows in and around the mandrel and the case wall. Some evidence of the mechanical property variations and small burning-rate variations in the propellant used in the 260-SL-1 and 260-SL-2 motors is reported in reference 34.

Processing methods and their effect on the orientation of wires or staples incorporated in composite propellants have a significant effect on burning rates. Details of grain design, casting tooling design, and propellant rheology as well as shape and size of wires or staples can influence orientation, thus producing anisotropic properties in the cured propellant grain.

In most instances there is insufficient information available on the effects of anisotropy on ballistic or mechanical properties. There is no established practice for accounting for anisotropy in motor design.

2.1.5.1 Viscosity

Prior to curing, most propellant formulations consist of a slurry or liquid mix. Formulations with high-viscosity uncured mixes are relatively difficult to process. As the difficulty of pro-

cessing a formulation becomes greater, the frequency of potential grain flaws increases exponentially. Because reliability of the propellant requires that grains be produced without flaws, there must be a smooth flow of propellant into all parts of the motor during casting. The qualitative term used to describe the relative ease with which the formulation can be mixed and cast into a configured motor case is "propellant processability." The best quantitative measurement of processability is found in the rheological values associated with the system. The rheology of a liquid system is the measurement of its deformation and flow properties in terms of shear rate, stress, and time. Viscosity is the principal standard for defining the rheological properties of a system.

The size and geometry of the propellant grain being cast dictate to some extent the importance of the rheological properties of the uncured propellant. For example, the proper performance of smaller grains requires a very low frequency of voids or flow anomalies; therefore, if highly viscous propellant formulations are selected, specialized casting and curing techniques, tooling, and equipment must be developed.

The particle-size distribution and shape of the oxidizer (usually AP) and of the solid fuel (usually aluminum) have a significant effect on the solid packing fraction and on the rheological properties of high-viscosity uncured composite propellants. The packing fraction is the volume fraction of the solids when packed to minimum volume; therefore it is independent of the volume of unpacked solids loading in the propellant. The viscosity of a bimodal system (sec. 2.1.2) decreases very significantly as the bulk density is increased by packing progressively smaller particles into the interstices of the larger particles. In a study of the significance of the shape effect in actual propellant systems (ref. 35), manufacturers' lots of AP with various particle shapes were used in mixes with a bimodal oxidizer distribution, and the rheological properties of the propellant were measured. It was found that the tap density of the unground AP decreased as the number of irregular crystals increased, and that viscosity of the propellant varied inversely with tap density.

Recent work (ref. 13) demonstrates that the packing fraction of a multicomponent mixture can be calculated and then utilized in adjusting the particle-size distributions for packing to a minimum volume. A mathematical modeling technique has been used to develop a computer optimization program (ref. 36). The results indicate that mathematical methods may be used to produce distributions having relatively high packing densities. Reference 37 shows that a solids loading of 90 percent by weight is theoretically attainable with a bimodal nonaluminized perchlorate system.

Vacuum almost always is applied during mixing of composite propellants in order to remove dispersed air and other gases that have become incorporated in the mix. Upon removal of this air by the vacuum, the viscosity of the propellant may change, and the thicker propellant must be handled accordingly.

2.1.5.2 Pot Life

An important characteristic influencing the casting of composite propellants is the length of time that the uncured propellant remains fluid after mixing. As the propellant begins to cure, it approaches a gel stage; the period of time that it takes to reach this stage is known as the "pot life." Formulations with short pot life can result in lower reliability and increased processing costs. Reliability is lowered because of increased probability of flaws due to the high viscosity, as described previously. Costs are increased by the special handling required to expedite quality control, transfer from mixers, and cast into motors. Plastisol binder systems, such as those using PVC, have indefinite pot life, and therefore do not present a problem in this regard.

Pot life often is determined in the laboratory by testing viscosity as a function of time after mixing at the temperatures planned for processing and curing the propellant. The pot life of the propellant is the length of time from completion of mixing to the time these viscosity tests show an essentially "no flow" condition.

2.1.6 Mechanical Properties of Cured Propellant

2.1.6.1 Control and Reproducibility

The molecular structure of the polymer binder used in most solid propellant formulations is the largest factor in determining the mechanical properties of the mixed and cured propellant. The characteristics of the prepolymer, monomer, or polymer as received by the processing plant are major factors in determining the molecular structure of the binder in the finished propellant. The chemical and physical properties of curing agents, plasticizers, and other modifying chemicals also are important.

Adjustment in concentration of the curing agent is the most widely used method for maintaining process quality control and reproducibility of composite propellant mechanical properties. New propellant formulations usually are characterized in relation to the effect of different curative levels on mechanical properties. Elongation at low temperatures, often the limiting characteristic, usually is sensitive to changes in curative level.

Prepolymer characteristics that influence mechanical properties sometimes vary significantly between suppliers and between lots from a single supplier. Examples of the criteria for the selection of a particular prepolymer and subsequent characterization and specification may be found in the composite-propellant tailoring studies for the 260-SL motor (ref. 34). Figure 4 illustrates the effect of the curative ratio on the mechanical properties of a composite propellant made from polymer lots that were secured from two different vendors.

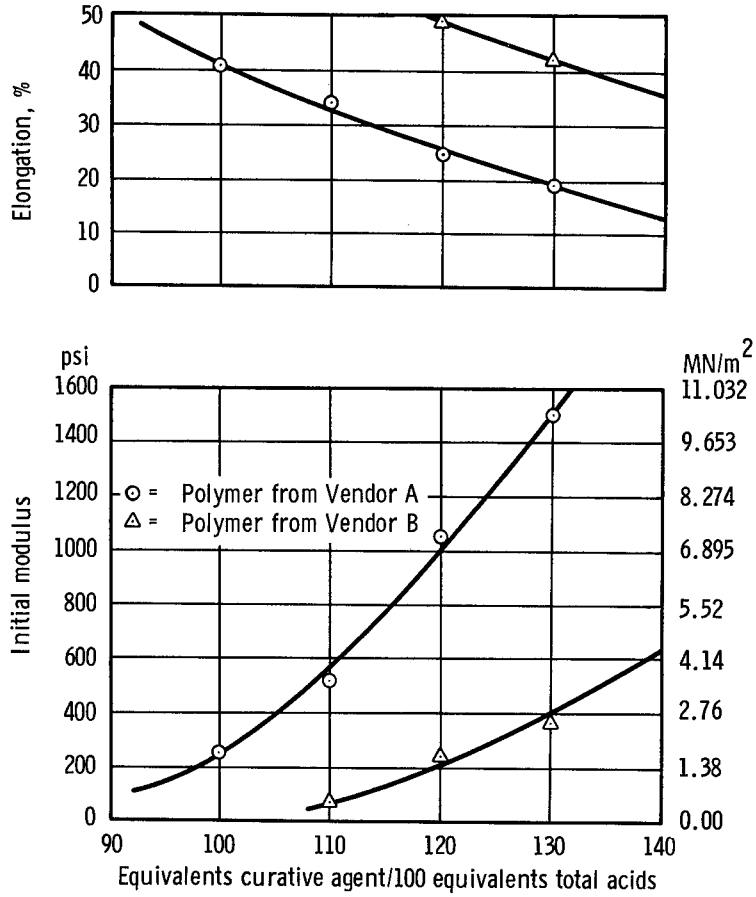

Figure 4. — Typical effect of curative-agent ratio on mechanical properties of composite propellant.

2.1.6.2 Proprietary Raw Materials

The majority of composite propellants use a prepolymer as the basic raw material of the binder. The characteristics of this prepolymer, particularly the molecular structure of the polymer and the number and location of reactive chemical sites or functionality of the prepolymers, have a significant effect on the mechanical properties of the cured propellant. Because of these factors, it is difficult, in the current state of the art, to specify prepolymers completely. Therefore, it is not unusual to specify sole source or proprietary ingredients for binder raw materials, particularly prepolymers for new propellant formulations. For formulations that have been in use for some period of time, it has been possible to develop additional sources of supply by running multisource qualification tests. When there is only a sole source for such materials, costs generally are higher; and even with a sole source there are occasional

changes in raw materials that cause difficulties in maintaining the propellant within required specifications. These changes can be caused by revised methods of manufacture at the prepolymer plant or by unknown causes. Usually they are controlled by careful design of the quality assurance program.

2.1.6.3 Raw Material Characterization

Raw materials for solid propellants usually are characterized to provide a baseline for subsequent control of mechanical properties. This characterization generally is combined with similar studies for burning rate (sec. 2.1.4.3). Most of the effort in characterization for control of mechanical properties is directed toward prepolymers, polymers, and curative agents because these binder ingredients are the raw materials that have the most significant effect on mechanical properties of the cured propellant. Since there are difficult problems in specifying these ingredients, the first production run for a new formulation usually is made from a large blended lot of these binder raw materials. Subsequent purchases of binder ingredients are tested and controlled on the basis of the results of this baseline study and associated subscale propellant batches.

In addition, each new lot of polymer or curative agent is characterized to improve reliability of the process. This procedure identifies small variations in the properties of prepolymers that cannot be controlled by current state-of-the-art specifications. Although the variations are small and sometimes considered nonfunctional by the supplier, they may have major effects on the mechanical properties of the finished propellant. For example, the prepolymer manufacturer has been known to make very minor changes in his methods (e.g., to vary polymerization times and temperatures to increase yields) that did not show up until the subscale lot characterization tests were made by the propellant processor.

2.1.6.4 Process Variables

The process operating conditions and the relative proportion of ingredients can affect the mechanical properties, particularly elongation and tensile strength, of the finished propellant. The amount of binder ingredients and the temperatures and times for casting and curing are the more important process variables for composite propellants. In DB propellants, mechanical properties are not very sensitive to processing conditions but are dependent on the physical properties of the NC casting powder and the ratio of casting powder to casting solvent. When process effects are not well established, the usual practice is to conduct special studies in order to determine the effect of these process variables and different ratios of raw material ingredients on the mechanical properties of the cured propellant. These studies usually are combined with those discussed in section 2.1.4.6. In some cases, byproduct data from these studies give correlations between propellant grain discontinuities and process variables. These

data are used to compensate for lot-to-lot variations and to meet specifications on mechanical properties. Process-variable studies generally include measurements on the effects of mix time, intensity, and vacuum.

The processing of relatively large motors often requires casting many batches over a period of several days, and there are unavoidable interruptions in the casting sequence that can have important effects on the integrity of the mechanical bond between each of the surfaces involved. Studies usually are made to define the process conditions that should be met in order to obtain adequate bonds of propellant to propellant and to other surfaces (ref. 22).

2.1.6.5 Flaws

A major objective of propellant processing is to produce a propellant grain that is free of flaws, i.e., unplanned discontinuities in the grain structure. In general, flaws or voids in the solid propellant degrade ballistic and mechanical properties of cured propellant. The relative size and location of permissible flaws depend on the particular application and propellant formulation. The probability of flaws is a function of the rheological properties of the propellant and of variations in processing. Vacuum and bayonet casting are two of the most common processing techniques used to minimize the formation of voids or flaws.

Special precautions usually are taken to prevent air from being trapped in the cured propellant grain. The production of reliable, reproducible, void-free grains is dependent on the proper removal of air and dissolved gases that can create voids in the propellant grain during either the casting or the curing process. This removal also results in a propellant with maximum density and a reproducible and predictable burning rate. Propellant grain porosity caused by the inclusion of finely dispersed air or gas can result in a propellant with an extremely high burning rate, which can cause catastrophic failure in a rocket motor. Entrapped gas normally is removed by one or more of the following methods: (1) vacuum mixing, (2) intermediate deaeration between mixing and casting, and (3) vacuum casting. In general, good grains can be made without vacuum casting, but vacuum casting the large grains offers an advantage in that it reduces the probability of grains that must be rejected because of air voids.

To provide effective deaeration of extremely viscous propellants, it is necessary to utilize a technique that spreads propellant into a thin sheet for exposure to a vacuum environment. This spreading reduces the mean distance that a gas bubble must travel to break through the propellant surface. Another controlling parameter is the time of exposure to the vacuum. In batch processing, the deaeration process typically consists of pouring the vacuum-mixed propellant into a feeding container connected to an evacuated casting vessel. Propellant flowing into the vessel is passed through narrow slits (in what is commonly called a slitter plate) to produce thin ribbons of propellant or is passed over a conical surface to expose a large surface of the material to a vacuum (ref. 31). Continuous propellant processes use a mechanical

device to expose the mixed propellant to a vacuum environment for deaeration prior to casting (refs. 38 and 39). Some of the more volatile materials contained in the propellant formulation are removed during the degassing or deaeration process; therefore, the control of the vacuum level and duration is often as important as obtaining a very high vacuum in producing a reproducible propellant composition. Viscosity of composite propellant often is sensitive to the level and length of time that vacuum is applied during the mixing and casting processes.

Even the most careful processing, however, is not an absolute guarantee of a void-free grain. To ensure adequate process control, grains are inspected for voids or flaws. Instruments used in nondestructive testing (NDT) for voids include devices with cobalt 60 sources, standard X-ray machines, Van de Graff machines, fluoroscopes, and linear accelerators. In addition, small cartridge-loaded-type grains of uniform cross section are inspected by ultrasonic techniques prior to inhibiting. Bubbles, cracks, and low-density areas are detected if they exceed a certain minimum size. However, the geometry and orientation of a crack or a void may make it difficult to detect with state-of-the-art NDT methods. All exposed propellant surfaces are inspected carefully to determine whether there are any defects observable at these surfaces. Defects that may be minor and insignificant in themselves sometimes can indicate subsurface defects that require more careful investigation. Even separations that are difficult to detect or cracks only a few mils (several dozen micrometers) wide in critical locations may result in catastrophic failure when the motor is fired.

2.1.7 Performance vs. Solids Loading

Achieving high specific impulse by increasing the solids loading of aluminized composite propellants has been an objective of the solid rocket industry for several years. As a result of considerable research in solids-loading technology, 88-percent-solids propellant systems are currently in use. At very high solids loading, oxidizer particle-size distribution must be controlled if maximum fluidity characteristics of a particular fixed formulation are to be maintained. In spite of advances in technology for reduction in viscosities, the designer sometimes is faced with conflicting requirements of high solids loading (for high performance) and processability of the formulation selected. Because of the higher viscosities and increased costs associated with the manufacture of some propellant formulations with high solids loading, there is a continuing problem of trading off ballistic requirements, reliability during processing, and processability.

2.1.8 Effects of Moisture

Many ingredients of solid propellants either are hygroscopic or react with water. The processing facility that handles solid oxidizers usually requires special humidity control to ensure a

free-flowing product and to eliminate any adverse effects on the propellant. When a propellant contains AN, the humidity in the processing area is controlled below 50 grains of moisture per pound (7.14 x 10^{-3} kg of moisture per kilogram) of dry air and the temperature is controlled to approximately 77° F (298 K). In the case of AP, the humidity usually is maintained below 65 grains of moisture per pound (9.28 x 10^{-3} kg of moisture per kilogram) of dry air and the temperature between 85° and 90° F (303 and 306 K). Special shipping containers and desiccants protect these raw materials from moisture during shipping and storage. When such precautions are taken, it is normally unnecessary for AP to be dried at the processing facility; however, AN often is dried in conventional equipment such as tray, rotary, or vacuum dryers at temperatures between 170° and 225° F (350 and 381 K) (ref. 12). If moisture is not controlled, the crystals cake when the oxidizer is temporarily at rest because the moisture migrates to the crystal surface and coalesces the particles. This caking results in serious handling problems.

In addition to the effects on oxidizer described above, deleterious effects result from the exposure of certain binders to excessive moisture. The control of moisture is particularly critical with polyurethane and, to a lesser extent, with CTPB propellants. The environment for these materials must be closely controlled during all phases of processing, including the receiving of raw materials, weighout, premixing, and propellant mixing; this control generally is achieved by providing a controlled atmosphere of either dehumidified air or dry nitrogen gas. In addition, the finished cured grain of CTPB type propellant must be protected from exposure to excessive humidity.

2.1.9 Exhaust-Plume Radar Attenuation

The requirement for low radar attenuation by the propulsion unit exhaust plume sometimes imposes certain restrictions on propellant processing. Currently, there are three techniques for reducing exhaust plume attenuation: (1) reduction of metal fuel content, (2) reduction of alkali metal content in AP oxidizer, and (3) the use of a scavenging agent to neutralize the effect of electrons from the alkali metal ions. These techniques often increase processing costs if performance (specific impulse) is maintained.

2.2 Grain Design

Grain design is discussed in detail in reference 2. The initial steps in grain design (e.g., calculation of volumetric loading) have no direct effect on propellant processing. The grain design considerations having a major impact on processing reliability and costs are (1) the selection of the grain configuration and its detailed geometric design, (2) maintenance of grain structural integrity, and (3) the redesign and tailoring and detailed analysis involved in obtaining the specified performance, specifically thrust control and transient performance.

2.2.1 Geometry

2.2.1.1 Perforation Design

Although grain design is concerned with the total configuration of the propellant, the geometry of the grain perforation is particularly important to processing because of its impact on process tooling. Tooling mandrels for either a propellant casting or for an extrusion-type process have very nearly the same geometry as the perforation. Tooling designs allow for propellant shrinkage as well as mandrel removal. Many grain designs are based on a uniform circular or rounded star design. However, for some ballistic requirements (e.g., those for a boost-sustain motor), it is necessary occasionally that the perforation not be uniform in cross section throughout the entire length of the grain. The process tooling provides for these changes in perforation. Some designs result in two different sets of perforation tooling. Likewise, some ballistic requirements involve geometrical designs more complex than cylindrical or star shapes..

2.2.1.2 Perforation Taper

The design and fabrication of tooling to produce the perforations for cast solid propellant grains are well established. Slight drafts are used to facilitate the removal of tooling after the propellant is cured. Allowances often are made in the design of tooling for large motors in order to take into account propellant cure and thermal shrinkages. Tooling usually is constructed of aluminum and coated with Teflon or other mold-release materials.

2.2.1.3 Propellant Machining

Some ballistic requirements demand grain designs that are not practical to achieve with relatively simple casting or extrusion tooling. In such designs, it is common to perform machining operations on the solid propellant. For example, transverse slots or conicals frequently are produced by machining operations (ref. 40). In addition, the surface exposed at the end of a cast and cure operation often is machined to either a flat or a special configuration. In the case of large motors, this trimming operation usually can be done by hand because minor surface irregularities are not critical.

The relative difficulty in machining a propellant depends on the physical properties of the formulation, the shape and location of the cavity to be formed, the quantity of material to be removed, and sensitivity of the propellant. Special vacuum collection systems usually are installed to remove the propellant cuttings that introduce a special hazard because of their large specific surface. Other steps taken to reduce hazards of accidental deflagration include selec-

tion of special cutting tools, maintenance of sharp edges, and special precautions to prevent the accidental contact of cutting tools with metal parts of the rocket motor.

2.2.1.4 Casting Openings

The configuration and amount of space allowed between the motor case and the casting tooling can have an important effect on process operations. During casting of composite propellants, a viscous and sometimes non-Newtonian material often must be flowed through intricate channels and then deposited uniformly in oddly shaped cavities, all without introducing or entrapping air or forming flow voids. This is a particularly difficult process when non-Newtonian fluids with high viscosities are involved. The details of the flow channels as dictated by grain geometry are an important factor in successful casting of these materials.

An important step in the processing of DB propellants is the insertion of the solid casting powder into the assembled motor case and casting tooling. This casting powder must be dispersed very uniformly and at a constant high density. Success in this operation is a function of both the relative location of and the clearances between the casting tooling and the motor case (or the case insulation).

2.2.2 Structural Integrity

Interactions between the grain and process conditions may significantly affect the residual stresses in the propellant that result from thermal and polymerization shrinkage. This shrinkage most commonly occurs during the curing operations for composite propellants. The purpose of the cure step is to establish and maintain known and controllable temperature gradients in the propellant grain in order to induce and control the polymerization reaction for the particular propellant binder system. The temperature-time program is designed so that the propellant reaches certain mechanical properties at a known point in time after which the grain is cooled at a controlled rate to ensure an upper limit on thermal strains. These strains must not be so severe as to induce a failure of either the grain or the propellant-liner bond. At the same time, the temperature-time conditions of the cure step potentially have an important impact on processing costs. The temperature factors usually are determined by special studies of new propellant formulations or by applications of existing formulations to new grain designs. In some of the more advanced formulations, special cure cycles have been found advantageous (ref. 41).

Composite propellants generally are cured between 100° and 140° F (311 and 333 K) over a period of a few days. Others are cured at higher temperatures, such as 170° F (350 K); AN/Bd/MVP propellants are cured at 190° F (361 K). During cooling and subsequent thermal contraction, changes in volume usually are minimized by curing the propellant at as

low a temperature as practical. The time and temperature depend on the composition and size of the propellant grain. However, with some propellants the improved mechanical properties that can be obtained through higher cure temperatures might offset the higher residual strains. Generally, for a given set of mechanical properties, the lower the cure temperature, the more reliable the motor.

Pressure curing often is used to overcome the effects of grain shrinkage; pressure is applied to dilate the case during cure, the internal case volume being increased by an amount nearly equal to the expected grain thermal contraction. Pressure curing may introduce problems, including difficulties with tool removal caused by compression of the propellant by the case, which was expanded during cure and cool down. Cooling to low temperatures often is required in order to remove the tools. Significant changes in perforation dimensions that can occur when the tooling is removed are taken into account by the processor during tool design.

Excessive strains may occur when certain combinations of grain designs, propellant formulations, and case designs are processed. The strains can be more severe in designs that involve propellants with high moduli of elasticity, motor cases with markedly different coefficients of thermal expansion, or thick-webbed grains. Excessive strains can be reduced by the use of stress relief boots at the interface between the propellant and the motor case. As requirements for wider temperature extremes have increased, the use of stress relief boots in both the forward and aft ends of some motors has become commonplace.

2.2.3 Principal Motor Thrust Control

2.2.3.1 Specifications

Most motor specifications require a control either on total impulse or on thrust as a function of a time-thrust envelope. Often, the thrust performance is specified on the basis of previously demonstrated variability in the operation of motors of a comparable design. These thrust requirements normally are met by specifying dimensions and geometry of grains, propellant weight, and propellant formulation with rigid tolerances during laboratory tests on propellant samples. In most cases, these parameters (such as specific impulse of the propellant and net grain weight) are interdependent to some degree, and rigid specifications result in problems for the propellant processor. Such specification problems usually are resolved through consultation with process engineers and utilization of process-variables data.

2.2.3.2 Prediction of Thrust

There are many applications in which large numbers of production motors are produced in small batches, not in large lots, usually within certain performance limitations. In addition,

the user generally is provided with a predicted thrust-time curve and other predicted performance data. Whenever prediction of performance is required, it is the practice to collect and analyze a large amount of processing and laboratory ballistic data for each grain and each batch of propellant used in the grain in order to predict the thrust-time curve for each motor before it is fired. When the accuracy required in this prediction exceeds the ability of the processor to analyze such dependent variables as burning rate, propellant composition, and grain dimensions, there usually are high costs for the large number of laboratory and static firing tests as well as for the collection of a large amount of inspection and weight data (ref. 42).

2.2.4 Transient Performance

2.2.4.1 Ignition

The design of process tooling and some operating procedures can have a marked effect on the ballistic characteristics of the grain ignition surface. These characteristics, in turn, can affect the ignition delay or the character of the pressure-time or thrust-time curve during the ignition process. The development of anisotropic ballistic properties constitute one way in which process variations can affect ignition transient performance. One of the most common effects is the production of a fuel-rich layer at the surfaces next to the extrusion die or casting mandrel.

It is common practice to use special mold-release agents on casting tooling. If these materials are not selected with care, residual gums may remain on the grain surface and cause an excessive ignition delay time. Some grain designs require the ignition surfaces to be machined or roughened in order to produce proper ignition characteristics. Because process operators cannot always control this surface characteristic, ignition transient performance may vary. With some grain designs, the rapid buildup of the ignition process is inhibited by inert materials added to the ignition surface. With still other designs, it is necessary to use special melt-out mandrels that may leave residual films on the ignition surface; this residue must be removed by special processing steps. One method is dissolution of the film in mercury, but this process may result in contamination of the surface. A more recent method is removal of this thin layer of contaminated propellant by grit blasting.

2.2.4.2 Tailoff

The thrust-time or pressure-time curve during tailoff can be affected adversely by the processor through a lack of careful attention to tooling design and assembly procedures such as exact centering of mandrels or machining of slots. Designs using inert slivers also require careful design of tooling and precise placement and dimensioning of the slivers in order to control tailoff transients. In some applications, variations in burning rate throughout the motor and the accumulation of grain tolerances plus dimensional variations in the motor case can make it

difficult for the processor to meet the tailoff transient performance requirements. Designers take these considerations into account in establishing the tolerances needed (ref. 42).

2.3 Liner

The effects of the large difference in the elastic modulus between propellant and motor case are an important design consideration. Stresses caused by motor operation, acceleration, spin, thermal environment, and cure shrinkage require adhesive bonding of case, insulation, and propellant into an integral unit whenever a case-bonded grain design is used. The liner between the case and the propellant serves as a structural material to transmit stress to the load-bearing components. This transition material is located between the propellant and insulation or, where there is no insulation, between the propellant and the motor case.

Visual inspection of failed composite propellant/substrate bond specimens frequently shows gross cohesive failure in the propellant. But sometimes neither propellant binder nor binder and oxidizer are visible on a failed substrate surface. Failures of this sort usually are described as "clean peel" or adhesive failure, although adhesive detachment has not been proven. These extremes of failure mode indicate that both adhesive and cohesive phenomena are involved. Therefore, both general adhesion principles and factors affecting the cure and strength of propellants near the bond line are important to the interface properties (ref. 43).

Special process steps usually are taken to prepare the surfaces to which liners are to be applied; for example, the insulation usually is abraded, cleaned, and dried to give a satisfactorily fresh surface to which the liner is applied. Primers occasionally are required to ensure good bonds between propellants and the liner or insulation; such primers are considered part of the liner system.

2.3.1 Formulation

The bond for composite propellants is formed by curing the propellant in contact with partially or fully cured liner, and therefore a complex mechanism of bond formation is involved. During cure, many physical and chemical processes that would be insignificant in ordinary adhesive systems may become important; e.g., loss of a reactive ingredient from the binder through slow migration into the substrate can affect the strength of the propellant at the interface. As a result, liner formulations usually are selected so that curing characteristics are compatible with the basic propellant cure cycle and other conditions to which the motor is exposed during processing.

One of the methods used to achieve the insulation-to-propellant bond in DB propellants is the powder-embedment process illustrated in figure 5 (ref. 44).

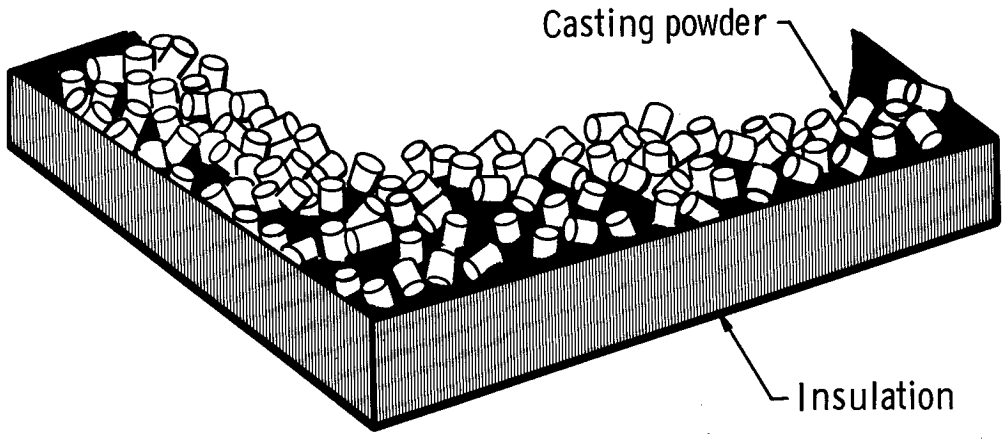

Figure 5. —Typical double-base embedment bonding (ref. 44)

A layer of partly polymerized adhesive such as an epoxy coating of the insulation or interior of the motor case is prepared. Casting powder granules then are carefully injected into this surface so that approximately 50 percent of each granule is embedded in the epoxy adhesive and the other 50 percent is exposed to the action of the casting solvent in the subsequent propellant manufacturing steps. Some of the more important variables that need to be closely controlled in this process to prevent grains from becoming coated on all sides or completely submerged in the adhesive are the viscosity of the embedment adhesive, the flow, and the insertion of the casting powder onto the surface. A recent study (ref. 41) has determined that there is an optimum configuration for the embedment granule and that improved strength of the bond depends on good wetting of the granules and development of a direct propellant-to-insulation chemical bond. In addition, some work has been done on the use of honeycomb structures and improved adhesive coatings. The current practice is to use casting powder shaped as right circular cylinders with the length-to-diameter ratio approximately equal to 1.

2.3.2 Mechanical Properties and Bond Strengths

The propellant-liner interface is one of the most difficult areas of a solid rocket motor to describe quantitatively and to analyze by laboratory techniques. Interface characterization is only partially studied during the development phase of many rocket motor programs. Ref-

erence 45 describes liner testing methods; reference 46 describes the modified double-plate constant-strain tensile test method. In the latter method, a 30° scarf joint is substituted for a joint normal to the direction of tension. One study (ref. 43), using the constant-load test technique on both polyurethane and polybutadiene propellants, showed that failure was always cohesive within the propellant. The site of failure (near the interface) and the mode of failure (cohesive within the propellant) suggest that propellant cohesive strength is the limiting factor in the bond strength of this type of system.

A liner that is satisfactory in laboratory tests and in small motors often is used without further testing. However, what is acceptable under relatively ideal conditions can be subject to deleterious effects of a large number of processing variables and to the detrimental effects of aging, extreme environmental storage conditions, handling, and flight vibration. Special studies sometimes are made to determine the effects of ingredient variations and process variables on the mechanical properties of the bond of liner to propellant and liner to insulation or liner to motor case (ref. 47).

Liner mechanical properties are evaluated with special techniques (ref. 48) that involve the dissection of the motor so that propellant properties in the as-built motor can be determined. Sections of the case, liner, and propellant are cut from the motor at various locations, and normal laboratory tests of the propellant, propellant-liner interface, and liner-case interface are made. These tests provide properties and allowable values for use in the stress analysis. Material properties thus determined disclose incompatibility problems and can show the extent of aging. This section-and-test technique is useful for development work but destroys the motor. For processing of production motors, liner-propellant-case bonds usually are inspected by X-ray, although for large segmented motors often only a simple visual check is made. In addition, quality control of the liner-to-propellant mechanical properties is often maintained by evaluating "peel" test specimens cast at the time the propellant is cast. Liner-to-case or -insulation unbonds have also been detected by ultrasonic techniques.

2.3.3 Rheological Properties

Where required, liners are applied to surfaces in relatively thin and highly uniform layers. Simple techniques for applying a liner to the insulation, including spinning, brushing, and troweling, require no extensive tooling, although skill is required to control both thickness and uniformity. Electrostatic deposition of liners has been used with considerable success and precise control of thickness. With air-operated or airless spray systems, problems may be encountered with air entrapment and environmental moisture control (ref. 46). Most motors are lined by the spraying process.

Measurement of liner thickness is not an exact science. However, thickness can be controlled adequately by application of material on a weight basis and by the use of other process procedure controls.

Most liner formulations are designed to provide good rheological properties of the uncured liner, including proper viscosity, gel characteristics, and pot life (ref. 45). Process reliability is reduced and costs are increased if these properties are not within reasonable limits. Rheological properties are not significant factors in motor designs that use a combination insulation/liner system applied as a solid material to the motor case.

2.3.4 Process Contaminants

Reasonable precautions commonly are taken to maintain cleanliness of all surfaces involved in the liner processing steps, but not to the extent that they involve highly controlled "clean room" environments. Since moisture as well as other contaminants can affect bond strength (refs. 43 and 49), certain liner-propellant systems are processed under humidity-controlled conditions. Most liners are cured at elevated temperature, and this in itself can produce a low-humidity environment. Dust contamination is avoided by the use of inexpensive covers. When special insulation-liner-propellant systems require careful control of common process contaminants, special facilities and procedures are designed to provide protection during handling and storage. Additional precautions generally are taken in preparing the insulation surface before applying the liner; these precautions include grit blasting, cleaning with a solvent wipe to remove dust and insulation particles, and drying to remove residual solvent. Materials and methods used to remove contaminants are described in reference 34.

2.4 Motor Case

Motor case design can affect the cost of casting tooling as well as processing labor costs. In addition, program schedules can be affected by motor case designs that require complex process tooling and long lead times.

2.4.1 Provisions for Tool Removal

Most motor case designs provide an opening, usually through the nozzle flange area, that permits the casting tooling to be removed in one piece and allows flow channels for the proper distribution of propellant or casting powder during the casting operation. However, reference 41 describes tool development for a program that dictated that the mandrels be suitable for producing grain perforations larger than case openings. In other designs, tooling consists of multiple fins mounted inside the motor case with cantilevered support from a central mandrel.

In spherical motor designs, a meltout mandrel often is used. The mandrel is precast from a low-melting-point alloy. The melting point of the alloy must be above the maximum propellant processing temperature (usually cure temperature) and below the temperature at which

the propellant or the other parts of the motor would be affected adversely. As noted previously, the low-melting-point alloys developed for this use often leave a very thin coating of material on the interior perforation of the propellant grain, and special processes then are used to provide adequate ignition surfaces.

2.4.2 Tooling Support

Process operations that tend to distort the motor case must be accounted for in tool design. For example, an unsymmetrical grain or motor design may result in an unsatisfactory degree of out-of-roundness in the motor case unless the castings and curing forces involved are taken into account in the motor case design. In addition the case designer must consider tool support, tool centering or locating, and tool removal after use. Whenever it is not practical to design a motor case that will support tooling, it is necessary to provide for additional process tooling such as rounding rings.

The vacuum-casting system of processing can introduce adverse stresses and strains on the motor case unless a vacuum-casting facility that will contain the entire motor is available.

3. DESIGN CRITERIA and Recommended Practices

3.1 Propellant Formulations and Properties

3.1.1 Polymeric Ingredients

A propellant formulation shall utilize the simplest and cheapest ingredients that will satisfy requirements.

PVC plastisol is an example of a simple, low-cost ingredient as related to processing. However, other design considerations generally limit the PVC binder system to applications in small motors and gas generators.

From the point of view of processing, NC should be considered an acceptable ingredient because it is based on cellulose and has been produced in large quantities for an extended period of time. In most formulations, NC does not undergo any chemical reaction during propellant processing. These qualities make it a reliable and low-cost ingredient. The combination of NC with NG produces ballistic advantages (e.g., specific impulse) that must be justified, however, by tradeoff studies that take into account process quality control limitations and processing costs of DB propellants. Some applications should use crosslinking agents with NC whenever the added processing costs can be justified by improved qualities of the finished propellant. The above applies to the use of NC in conventional DB casting powders; the newer plastisol grade NC has not been produced in large quantities and is expensive.

The group of binders based on high-molecular-weight liquids and partially polymerized materials that have retained functionality for subsequent curing also should be considered. PBAN and CTPB are examples of these somewhat complex prepolymers that should be used whenever the increased raw material, processing, and quality control costs for such things as handling of multiple ingredients can be justified by tradeoff studies against other decreased processing costs. The PBAN system should be selected over the CTPB system whenever possible, because the CTPB raw material costs and processing costs are higher. The increased processing costs result from a difference of sequencing operations and from the mechanics of propellant casting.

Components for improving processability should be added to the formulation when the increased raw material and processing costs can be justified by increased reliability (e.g., as in the addition of cyclic organic acid anhydrides to control crack propagation in PBAN-type

propellants). However, additional ingredients, such as multicomponent crosslinking agents, should be used only when clear advantages can justify increased processing costs or when the improvements obtained are needed to meet design requirements such as operating temperatures or superior mechanical properties.

3.1.2 Oxidizers

The particle-size distribution shall be as simple as possible.

The use of a complex rather than simple distribution is justified only when the performance advantages offset the decreased reliability and increased costs of processing. Cost tradeoffs must take into account the increased costs of purchasing, handling, and storage of more than one unground-oxidizer particle size. There are additional costs to the processor when grind size must be changed to meet the needs of a particle-size distribution of modality greater than two. Of greater importance is the increased risk of inadequate quality control of particle-size distribution when the processor is required to change grind size to meet complex particle-size distributions. A qualified process engineer should be consulted to determine the effect of complex particle-size distribution on the cost and reliability of processing a specific motor design.

3.1.3 Hazards

3.1.3.1 Toxicity

Propellant formulations shall not contain highly toxic materials unless the added costs and hazards are justified.

The selection of formulations that contain toxic ingredients is justified when improved properties offset the disadvantages of increased processing costs and personnel hazards. Because processors must take adequate precautions to minimize hazards of toxic materials in propellant formulations during storage, handling, processing, and testing, tradeoff studies by designers must take the following increased costs into account and weigh them against increased performance as described in reference 1:

Nonrecurring Costs

- Locating facilities in remote areas with favorable wind conditions to minimize the spread of toxic materials in the event of accidental deflagration.
- Equipping facilities with special dust control systems including positive-pressure rooms and systems for safe disposal of toxic combustion products.

- Developing safe methods for storage, handling, and processing toxic materials; thorough training of all personnel involved.

- Supplying workers with protective clothing and, in some cases, auxiliary breathing equipment.

Recurring Costs

- Increased process labor required to ensure adequate housekeeping and personnel cleanliness.

- Equipment and labor for safe handling, transportation, and disposal of toxic wastes and empty containers.

- Equipment and labor for collection of toxic waste products from laboratory and static-firing combustion; includes costs for firing into large evacuated tanks, scrubbing the gases, and disposing of contaminated residues.

3.1.3.2 Deflagration and Detonation

3.1.3.2.1 Ingredient Hazards

Propellant formulations shall not contain materials that are highly sensitive to deflagration or detonation unless the added processing costs and hazards are justified.

Characterization of the hazards associated with a specific propellant formulation is not enough. The hazards associated with each ingredient must be identified (ref. 1), and their effects on processing costs must be assessed. Propellant selection should be based on processing cost considerations developed in tradeoff studies weighing these factors against performance advantages.

Nitrated esters, such as NG and other class 7 materials, are examples of highly sensitive materials requiring added facility and processing costs. NG is very shock sensitive; only small amounts need to be subjected to impact or other initiating forces before a disastrous sequence of reactions is initiated. Facilities require substantial quantity/distance separation and therefore are more costly. In addition, there are certain phases of the processing in which NG may vaporize or diffuse into parts of the manufacturing equipment and thus create additional hazards. These hazards can be reduced by the proper selection of inert plasticizers having the same volatility and diffusion characteristics as NG. These inert plasticizers substantially reduce the sensitivity of NG. Nonrecurring special costs are required for the construction of special facilities for manufacture, storage, and handling of NG. Extra labor costs are required for special housekeeping and care in handling of NG.

3.1.3.2.2 Process Combination Hazards

Laboratory tests shall verify hazards that are likely to arise during processing.

Special processing hazards associated with combinations of two or more propellant ingredients should be evaluated for new ingredients before they are specified in production propellant formulations. Such evaluations should consist of laboratory tests for sensitivity in which weight fractions and physical conditions of ingredients are varied in accordance with recommendations from process engineers. Reference 50 describes these tests for a series of propellants. Test procedures and parameters should be those recommended in reference 1. These tests can reduce processing hazards by identifying a safe order of addition or combination of ingredients. In general, a safe procedure is to add solids to liquids and oxidizers to fuels, but there are exceptions. The safest combinations of the several ingredients should be identified by the laboratory studies.

In some cases, performance requirements cannot be met without formulations that result in this kind of process hazard. The performance advantages of such formulations must, therefore, be traded off against the increased cost of facilities or process labor required to reduce the hazard to a reasonable level.

3.1.3.2.3 Propellant Hazards

The finished propellant shall be class 2 whenever possible and practicable.

Because of the hazards associated with processing, storing, and handling motors containing class 7 propellants, such propellants should be selected only when tradeoff studies show that less sensitive propellants are impractical. The designer should evaluate the increase in processing costs resulting from (1) the increased station-to-station distances required for facilities used to process these formulations, (2) the reduced quantity in process at any one time, and (3) the increased safety precautions required with class 7 formulations. Guidelines to facility layout or to propellant quantities that can be processed in present facilities are available in handbooks and in reference 51. These sources should be supplemented with reliable information on actual accidents.

The basic cost tradeoff is between class 7 and class 2 propellants. The class 2 propellant processing has reduced requirements (as compared with class 7) for quantity/distance separation of buildings and therefore has lower facility costs. One exception is the operation for mixing composite propellants, which usually requires quantity/distance separation for class 7.

3.1.4 Burning Rate of Cured Propellant

3.1.4.1 Control and Reproducibility

Whenever possible, a formulation shall provide a means for control of burning rate during processing.

It is recommended that propellant formulations contain burning-rate modifiers that, when varied in concentration and combined with multimodal oxidizer particle sizes, will provide a practical means of controlling burning rate during processing. In many cases, ballistic requirements cannot be met by available formulations that contain burning-rate modifiers. However, when requirements do allow the selection of formulations with modifier, the propellant processor can achieve higher reliability, better reproducibility of burning rate, and lower processing costs in the finished rocket motors by varying modifier level for fine adjustment of burning rate. Costs are lower because of the lower frequency of reject batches caused by out-of-tolerance burning rate.

All data showing the effect of modifiers on burning-rate of the selected propellant formulation must be available to process engineers, including the data from the process-variables studies (sec. 3.1.4.6), process quality control data from production programs involving similar formulations, and data obtained during development of the formulations. After review of these data, designers should consult with process engineers on process quality control problems before establishing tolerances for the propellant specifications.

When composite formulations with modifiers cannot be used to meet requirements, a propellant in which burning rate can be controlled during processing by some other means (e.g., changes in the particle-size ratio of the oxidizer) should be selected. A propellant of this type will enable the processor to maintain adequate control and to produce a ballistically reliable propellant at optimum cost.

A bimodal oxidizer particle-size distribution should be selected to meet moderate to low burning-rate requirements because it allows for good processability and provides a practical method of burning-rate control during processing. It is further recommended that specifications allow the processor to achieve such controls by changes in the oxidizer coarse-to-fine weight-fraction ratio or in the particle size of the coarse oxidizer.[2] Studies to define the effect of variations in the oxidizer coarse-to-fine ratio should be made prior to production processing. Typical data that should be obtained are shown in figure 2 (ref. 22).

[2]Coarse refers to range I or II (see sec. 2.1.2), averaging over 100 μ (μm) in size. Fine refers to range III, averaging less than 50 μ (μm) and produced by the propellant processor from unground material.

Some propellant formulations such as DB systems contain little, if any, solid oxidizer or burning-rate modifier that can be varied in order to provide a means for adjusting burning rate during processing and compensate for lot-to-lot variations. When this type of formulation must be selected to meet other requirements, the burning rate should be capable of being adjusted by blending sublots of casting powder.

3.1.4.2 Proprietary Ingredients

A formulation shall not depend on sole-source or proprietary ingredients for control of burning rate.

When ballistic requirements cannot be met unless formulations based on proprietary or sole-source ingredients are selected, tradeoffs in reliability, program schedule, and processing production costs should be made in accordance with table II.

Sole-source ingredients that may have a significant effect on burning rate, raw material costs, and processing reliability as described above should be selected by qualified personnel; but specification and qualification of oxidizers for composite propellants should provide for multiple-source supply whenever possible.

3.1.4.3 Raw Material Characterization

Raw material characterization shall provide a baseline for processors to use in meeting design requirements for reproducible and predictable burning rate.

Design proof tests should be conducted with raw material ingredients blended in large lots and subsequently characterized in subscale propellant batches. The baseline thus established will increase the ability of the processor to meet the required burning-rate specifications on the finished propellant, particularly with newly developed propellants. These tests should be repeated for each new lot. In addition, they should be repeated whenever an established propellant has not been produced for an extended period or when a production line is to be started. Data from the tests can be used along with the techniques described in section 3.1.4.1 to compensate for lot-to-lot variations.

3.1.4.4 Process Contaminants

The burning rate shall be insensitive to common types of process contaminants.

The additional costs involved with propellant formulations whose burning rates are changed by common process contaminants should be taken into account in propellant selection. For

Table II. – Comparative Advantages of Multisource and Sole-Source Ingredients

Factors	Advantages of multisource ingredients	Advantages of sole-source or proprietary ingredients
Reliability of newly developed propellants	Qualification tests of several suppliers may reveal that different methods of ingredient manufacture may have significant effects on propellant properties. This knowledge helps prevent surprise changes in propellant properties resulting from process changes by a supplier.	Better control of variations in propellant properties during production processing because of the lower probability of variations between lots of one manufacturer than of variations between lots of different manufacturers.
Program schedule using newly developed propellants	Supply line is more secure after first shipment. Program can shift to alternate suppliers if original source is shut off as a result of strikes, plant damage, or higher priority of other customers.	Production processing can be started immediately without delays for multisource qualification tests. This advantage disappears if the multisource qualification tests are run during propellant development.
Recurring costs	Ingredients purchased on competitive bids will result in minimum raw material costs.	No advantages.
Nonrecurring costs	No advantages. Nonrecurring costs are in the qualification program. Such a program should be designed by qualified personnel using statistically designed experiments and should be tailored to meet the special requirements of each ingredient, propellant, and rocket motor application. However, the qualification program should include both laboratory tests and subscale motor tests as described in reference 1.	No qualification program costs for alternate sources. Cost estimates must be based on net additional costs to qualify a supplier of a particular ingredient.

example, iron oxide is a common process contaminant as well as a good burning-rate modifier; in typical composite propellant formulations without burning-rate modifiers, accidental process contamination with iron oxide may have a deleterious effect on burning-rate control. Water is another common process contaminant that may have a deleterious effect on burning-rate control or on mechanical properties. When formulations that are affected by process contaminants must be used, additional costs that should be taken into account include increased labor costs, higher costs for purified raw material, and costs of special containers; special precautions in shipping and storage also must be observed. Consider also the additional costs in processing equipment as well as in adherence to special operating and handling procedures to prevent contamination of the propellant mix.

3.1.4.5 Scaleup

The value used for burning rate shall take into account the effects of scaleup to production-scale facilities.

Scaleup studies should be performed on each new propellant formulation developed in the laboratory to determine the effects of scaleup equipment and processing environment on burning rate. As indicated previously, variations in oxidizer particle size can have a pronounced effect on burning rates in most composite propellants. The variable attrition of AP or other oxidizer particles should be determined in scaleup studies on burning-rate effects; these studies should include not only the effect of the different size of processing equipment but also the effect of different methods of handling solid oxidizer in production plant as compared with the laboratory. Process engineers should be consulted to determine whether the studies should include scaleup effects on rheological and mechanical properties.

3.1.4.6 Process Variables

Process variables and changes in ingredient proportions shall not affect burning rate adversely.

Design proof tests should be performed with each new propellant formulation to determine the effect of variations in the amount of raw material ingredients on burning rate. Tests should determine the changes in burning rate caused by varying the amount of modifier and the proportion of ground-to-unground solid oxidizer. In CMDB propellants, the tests should demonstrate the effect on the final propellant burning rate of varying the proportions of casting powder sublots having different ballistic properties. The aim of all this information should be to enable the processing plant to maximize reliability of control and reproducibility of burning rate and to minimize costs by avoiding rejection of a propellant that is out of specification for burning rate.

3.1.5 Rheology of Uncured Propellant

3.1.5.1 Viscosity

A composite propellant formulation shall have the lowest viscosity consistent with satisfaction of the requirements for reliability, performance, and cost.

Tradeoff studies should be conducted on the potential decreased reliability and the increased costs of processing associated with the selection of highly viscous formulations. The factors given in table III should be taken into account.

Table III. – Comparative Advantages of High- and Low-Viscosity Formulations

Factors	Advantages of low-viscosity formulations	Advantages of high-viscosity formulations
Reliability	Reduced probability of flaws in the propellant.	None
Recurring costs	Relatively low costs for mixing and casting. No rework costs on cured propellant due to flow voids, etc. Avoids scrap propellant.	None
Specific impulse	None	Generally, high-solids-loaded systems provide higher specific impulse.

Intensive characterization studies (combined with scaleup-effect studies, section 3.1.4.5) should be conducted on the rheological properties of the uncured propellant under various conditions that will simulate the flow patterns of production castings and curing. These studies should consider the effects of shear stress, temperature, and time on the rheological properties of the propellant mix, because these variables may affect the probability of flow voids or anomalies in the grain, at the propellant-to-mandrel interface, and at the propellant-to-liner or -insulation interfaces.

3.1.5.2 Pot Life

The pot life of the formulation shall not affect processing reliability adversely.

The designer should select a formulation with sufficiently long pot life. The pot life required is a function of processing facilities, motor/grain size and configuration, and production rates. It is also a function of propellant mixing and casting temperatures, which are determined in

the optimization studies described in sections 3.1.4.6 and 3.1.6.4. After preliminary designs and data are available on the above factors, an adequate pot life should be determined through consultation with process engineers.

When it is not possible to achieve adequate pot life, a tradeoff study should assess the advantages and disadvantages of the available pot life. A danger of selecting formulations with short pot life is that the processor tends to take additional risks in casting propellant that is near the end of its pot life and has become highly viscous. The net result is a decrease in reliability similar to that associated with high-viscosity uncured propellant. When pot life is short, tradeoff studies should take into account increased labor costs for (1) transfer of propellant, (2) tight scheduling required for coordination of casting and related quality control tests, and (3) more rework of propellant or replacement of rejected grains.

3.1.6 Mechanical Properties of Cured Propellant

3.1.6.1 Control and Reproducibility

A composite formulation shall provide a means for control of mechanical properties during production runs.

Wherever possible, quality control during production runs should be achieved through very simple adjustments in the quantity of the curing agent that is added to the mix. The type and quantity of curing agent should have a negligible effect on other propellant properties. Wherever a single-cure-agent adjustment is not possible, control should be achieved by variations in amounts and blends of several cure agents, such as difunctional and trifunctional imines or epoxides, or by variations in amounts of plasticizers added to the mix.

3.1.6.2 Proprietary Raw Materials

Whenever possible, a formulation shall not depend on sole-source or proprietary ingredients for control of mechanical properties.

When mechanical property requirements cannot be met unless formulations based on proprietary or sole-source ingredients are selected, the tradeoffs in reliability, program schedule, and processing production costs presented in table II should be made.

When the ingredient sources have a significant effect on mechanical properties, raw material costs, and processing reliability as described above, a sole source may be selected by qualified personnel, but specification and qualification of oxidizers for composite propellants should provide for multisource supply whenever possible.

3.1.6.3 Raw Material Characterization

The characterization of raw materials shall provide a baseline for processors to use in meeting design requirements for reproducible and predictable mechanical properties.

Prior to production of a new propellant formulation, raw material ingredients should first be blended (by the vendor or by the propellant processor) into lots for design proof tests that will provide a baseline for later adjustments in mechanical properties of the cured propellant to meet specifications. Process engineers should be consulted for help in establishing lot sizes and kinds of tests. Subsequent procurement of raw material should then be characterized lot by lot through the manufacture of subscale propellant batches and determination of the mechanical properties of the cured propellant. Projection of this subscale data to full-scale processing should be based on scaleup correlations recommended in section 3.1.4.5. For economy, these design proof tests usually can be combined with similar tests conducted for burning-rate adjustments (sec. 3.1.4.3).

3.1.6.4 Process Variables

Process variables and small changes in ingredient proportions shall not affect mechanical properties adversely.

It is recommended that, for all new propellant formulations, the effect of process variables and changes in ingredient proportions on the mechanical properties of the cured propellant be determined by special design proof tests that have been set up in consultation with process engineers. These tests should be concerned primarily with the ingredients of the binder system and with the process variables involved in the mixing, casting, and curing operations. These data are necessary to provide the processor with a quantitative approach to the process control of mechanical properties that is required in the production of a propellant. The tests should be combined with those recommended in section 3.1.4.6 and should be based on experiments statistically designed to determine which variables contribute most to the mechanical properties of the cured propellant (refs. 24, 26, and 27). Figure 6 illustrates the type of data that can be developed to show the effect of process variables on the tensile strength of cured propellant (ref. 52).

These design proof tests should include also a study of the effects on processing conditions that can be achieved by the addition of small quantities of modifying chemicals to the propellant formulation. This is not necessary when such studies have been conducted as part of the propellant development program. For example, a study on a PBAN propellant (ref. 34) showed that the addition of an anhydride could result in a safe delay period of up to 30 days in casting one batch of propellant on top of another batch in large-motor multiple-batch units.

This delay is to be compared with a safe delay period of only 4 days (ref. 19) that can be tolerated with PBAN propellants without an anhydride. Similarly, delays in the casting of CTPB propellant can be extended from 24 to 72 hr if the aged surfaces are treated with a thin film of MAPO (ref. 53).

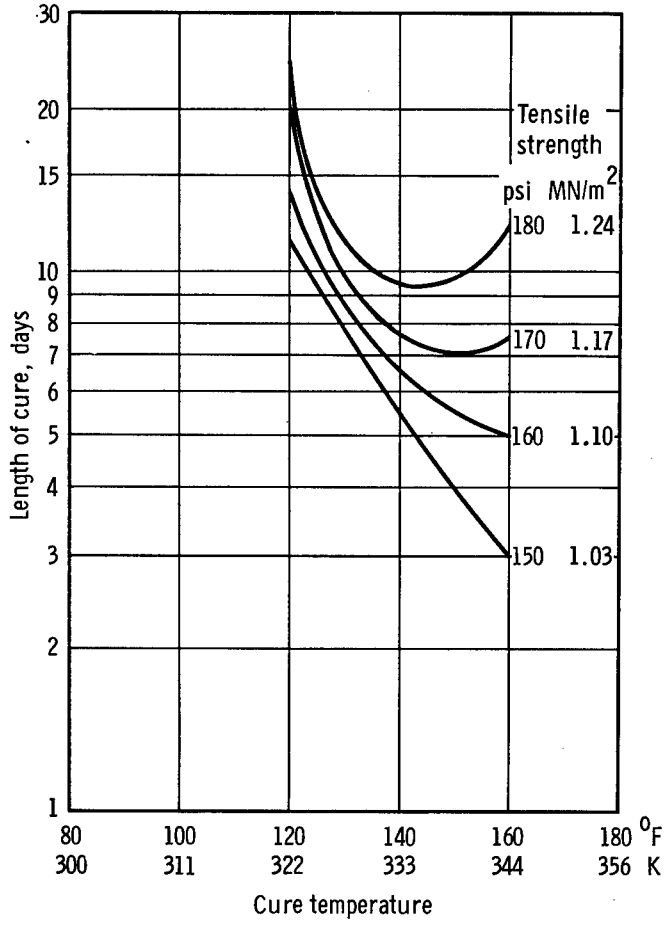

Figure 6. — Typical isotensile lines for PBAN propellant (ref. 52).

3.1.6.5 Flaws

The propellant shall be free of flaws that could degrade mechanical properties and ballistic performance.

Design proof tests for grain flaws or voids should be conducted on new propellant formulations or on the new application of established formulations. In special instances, these tests should

also include the development of NDT methods and equipment to determine the size, shape, and location of voids in the propellant grains. Where practical, such NDT methods should include the use of built-in defects. The effect of grain anomalies or voids on the mechanical properties and ballistic performance of the grain should be considered, and the maximum allowable size and concentration of voids should be established. This is especially important when high density is specified, or the propellant is relatively viscous, or the web thickness relatively small. It is not a significant problem for larger motors with large, thick webs, because small air bubbles in the propellant have a negligible effect on the performance of these large motors.

When requirements cannot be met without a formulation likely to have air voids, tradeoff studies should assess the disadvantages. These disadvantages involve the cost of special equipment to minimize the inclusion of air bubbles during mixing, transfer, and casting operations and the increased labor costs when additional time is required to degas propellant mixes. With existing formulations the likelihood of encountering a problem with air bubbles is shown by the experience in other applications, but with new propellant formulations this information should be developed in the scaleup studies (sec. 3.1.4.5).

Whenever possible, the experience with similar material should be taken as an indicator of the typical quantity and type of defect that can be expected with a propellant of given rheological properties in a given configuration. When additional information is required, design proof tests should cover process variable tests and analyses that provide data on how to control size, frequency, and location of defects. This information is then combined with that described in section 3.1.6.4. Since standardized tests on the effect of flaws are not available, qualified engineers should design each test program for the particular rocket motor involved.

Finally, the design proof tests (special partial-burning tests when practical, and standard static-firing tests) should confirm the permissible level of void defects.

3.1.7 Performance vs. Solids Loading

The solids loading of a composite propellant shall be the lowest that will meet performance requirements.

Composite propellant formulations to meet specific impulse requirements should be selected on the basis of guidelines provided in reference 1. A formulation should contain the lowest possible solids loading in order to obtain good processability. Designers should take into account the lower reliability and higher processing costs generally associated with formulations that provide high specific impulse by the use of high solids loading. The factors given in table IV should be considered.

Table IV. – Comparative Advantages of High and Low Solids Loading

Factors	Advantages of low to moderate solids loading	Advantages of high solids loading
Reliability	Low probability of flow voids and flow line interface anomalies because propellant has low viscosity (sec. 3.1.5.3). Processor is not pushing the upper limits of the processing state of the art.	None
Recurring costs	Relatively low labor costs because of shorter mixing times. Lower rework costs (secs. 3.1.5.3 and 3.1.5.4).	Decrease in total cost of raw materials.

For composite CTPB propellants, the tradeoff analysis should be conducted whenever the total AP and aluminum solids loading exceeds 88 wt-percent. This usually corresponds to a reasonably high delivered specific impulse of 250 sec. In some cases, there are requirements to go higher than 88 wt-percent to increase volume impulse.

For composite PBAN propellants, the tradeoff analysis should be conducted when the total AP and aluminum solids loading exceeds 86 wt-percent.

3.1.8 Effects of Moisture

Whenever possible, the propellant formulation shall not contain hygroscopic or water-reactive ingredients that require special facilities.

When requirements cannot be met without the use of hygroscopic or water-reactive ingredients, tradeoff studies should be made to justify the increased costs for raw materials, more careful storage and handling, and special processing facilities (capital cost) that will prevent the contact of these reactive materials with moisture in the atmosphere or from other sources. It should be noted that these increased costs can vary considerably with different materials. For example, increased costs for handling AP are very small, while those for handling AN are rather substantial.

3.1.9 Exhaust-Plume Radar Attenuation

Designs for low radar attenuation by the exhaust plume shall take into account increased processing costs if special formulations are selected.

Tradeoff studies should be based on the following factors whenever special formulations are selected in order to meet exhaust requirements:

(1) A reduction in aluminum content may require a corresponding increase in AP content to maximize specific impulse. This increase can have a serious effect on the optimized packing arrangement, and it necessitates considerable reformulation work to regain needed processability and mechanical properties.

(2) If special pure AP is selected to eliminate the presence of trace contamination of alkali metals, it will be necessary to implement stringent and costly material control requirements from the procurement of AP through handling, weighing, and grinding in order to eliminate cross-contamination with less pure materials.

(3) If a scavenging material is utilized in the formulation, its deleterious effects on the propellant rheological characteristics, on the cured mechanical properties, and on the ballistic properties can cause processing problems and increased costs.

3.2 Grain Design

3.2.1 Geometry

3.2.1.1 Perforation Design

The geometry of the grain perforation shall be as simple as possible.

Grains should be designed on the basis of guidelines provided in reference 2. Perforations should be uniform in cross section and shaped to minimize process tooling complexity. If requirements dictate a complicated design or one that requires flow of propellant into intricate small spaces, sharp corners, or slots, the designer should take into account decreased reliability during processing and increased process costs. Reliability is decreased by the difficulty of controlling flaws and inspecting surfaces. Tooling costs increase as the geometrical shapes become more complex (right circular cylinders and uniform rounded star perforations are examples of uncomplicated designs). Higher costs are involved if the cross section is not uniform.

Wherever possible, the grain designer should avoid perforations having nonuniform cross sections; e.g., transverse slots. These slots require propellant machining or multipiece tooling (sec. 3.2.1.3). Multipiece tooling is more costly than less complicated tooling, requires more process labor for assembly and disassembly, and presents extra processing hazards because of potential propellant leakage at joints. Grain dimensions should be defined to apply at a specific time (or stage of processing) and temperature after casting.

3.2.1.2 Perforation Taper

The design of a grain perforation for a cast propellant grain shall facilitate mandrel removal.

An axial taper ≥ 0.001 in./in. (≥ 0.001 m/m) length of grain perforation should be provided. Unusual propellant physical properties of the grain and case material or an unusual configuration may require a special taper that should be designed on the basis of experience with similar shapes and propellant formulations. The grain perforation and the tooling mandrels usually are similar in shape and dimension, but design proof tests and measurements of shrinkage and slump should be made. In such a design, processing costs are minimized if the grain perforation design takes into account the taper on the mandrel necessary to assure easy removal after casting and curing.

3.2.1.3 Propellant Machining

A grain design shall not require special machining operations unless designs based on other processing methods cannot be used.

If requirements cannot be met without transverse slots, conicals, or other designs requiring special propellant machining, processing factors that lead to higher costs and lower reliability must be taken into account in tradeoff studies. When grain geometry can be established by the casting or extrusion tooling, the probability of meeting a given grain specification is improved, because this process requires fewer skills and less care to meet a given tolerance in dimensional control. Machining requirements increase processing labor costs and capital investment. Some designs and propellant formulations dictate that propellant machining be conducted remotely to reduce the hazards to operating personnel. Special drill bits, cutters, speed controllers, and propellant chip collection and removal facilities usually are required. In addition, the machining operations introduce a higher probability of rejects caused by the machine operator's errors. Machining is justified only when other design advantages compensate for this decreased reliability and increased cost.

3.2.1.4 Casting Openings

Grain geometry shall provide adequate space for flow of the propellant or casting powder into the motor case.

Design of the grain perforation should take into account the requirements for an adequate flow channel through which the uncured propellant can be cast or, in the case of DB propellants, the casting powder dispersed into the motor case (ref. 34). This requirement is particularly important at the opening through which the material is to be inserted into the assembly, but it is also important in other parts of the grain to reduce the possibilities of voids, low-density areas, or anisotropic properties. In addition, the grain design should permit reasonable configuration for removal of the casting tooling after the propellant is cured. Standardized guidelines are not available, and designs must therefore be reviewed by qualified process engineers for adequacy of casting openings.

In some designs, tradeoff studies can justify the extra cost of meltout mandrels that minimize the problem with the casting opening. This is a tradeoff of increased tooling and propellant finishing costs for increased performance and total impulse.

3.2.2 Structural Integrity

The propellant grain shall tolerate thermal strains imposed during processing and storage.

Design proof tests on new propellant formulations or grain designs should be performed to determine that an optimum balance has been reached between residual thermal strain and process cure temperatures. A process-variable study on casting temperatures should be conducted in conjunction with these design proof tests to provide data for a tradeoff analysis of increased processing costs as a function of the other parameters. These tests should be combined with the process-variable design proof tests on mechanical properties (sec. 3.1.6.4). Certain time and temperature conditions are required during processing to carry out the proper polymerization reactions and to obtain the desired mechanical properties described above. The reaction mechanism can differ markedly at various temperatures and result in significantly different ultimate mechanical properties (ref. 52).

Further problems in processing are the amount of heat generated during various phases of the crosslinking reaction (refs. 54 and 55) and the grain stress induced by the volumetric changes of the propellant matrix caused by polymerization as the system cures. The selection of the curing temperature or programmed time and temperature cycle is very important to the residual thermal stess induced in the solid propellant by the grain cooling from the curing temperature down to ambient temperature or by environmental field conditions that might be as low as −70° F (217 K). Thus, the tradeoff studies must take into account the relative advantages of long-term, low-temperature curing cycles that eliminate much of the thermal stress related to the differences between ambient and curing temperatures. These cures then must be compared with shorter duration, higher temperature cures that have additional induced stresses but also have lower costs for processing facilities and higher production rates. With large motors, the costs saved in faster cures are offset by longer cooldown times (ref. 56). This impact on processing costs related to the factors involved in short pot life of propellant mixes is discussed in section 3.1.5.2.

Designs should provide for relief of excessive strains in the interface areas between motor case and propellant that may result from the propellant formulation or the grain design. The stress concentration usually is greatest at the ends of the grains where propellant interfaces with the motor case; a stress relief boot should be used there whenever stress analysis indicates that the

grain integrity is jeopardized. The drawback to this design is the decreased mass fraction (ratio of propellant weight to total motor weight).

3.2.3 Principal Motor Thrust Control

3.2.3.1 Specifications

Whenever possible, performance specifications for motors produced in large lots shall be based on total impulse.

The use of other parameters should be avoided unless necessary to ensure that the motor will meet requirements for handling and storage life. Minimum processing costs are achieved with total-impulse specifications because of the latitude given to the processor to adjust conditions to meet performance specifications. When total impulse is chosen as the basis of specification control, wide variations should be allowed whenever possible so that processing costs can be reduced.

When other parameters must be controlled to meet requirements or when greater reliability is required, additional processing specifications should be added if the increased costs are justified by the advantages. Increased reliability can be achieved by laboratory specimen tests on ballistic and mechanical properties and by specification of tolerances in propellant chemical composition. In addition, dimensional and geometric tolerances may be set to obtain control on the variation of motor action times. All these procedures tend to increase processing costs because of increased tooling costs (with tighter tooling dimensions), positioning of processing tooling, and dimensional changes resulting from polymerization and thermal shrinkage that might occur in propellant grains.

Further information on specifications for motor performance may be found in reference 42.

3.2.3.2 Prediction of Thrust

Specifications for the prediction of thrust versus time for each motor produced shall take into account practical accuracy in measurement and control of process variables.

The accuracy with which thrust must be predicted should not exceed the accuracy with which the factors that affect burning rate, specific impulse, grain dimensions, and weight can be measured. Factors affecting burning rate and specific impulse are described in reference 42. The designer should establish the accuracy with which these factors can be measured for specific designs through consultation with quality control and process engineers.

3.2.4 Transient Performance

3.2.4.1 Ignition

Design proof tests shall evaluate the effect of special process and tooling variables on the ballistic nature of the ignition surface.

It is recommended that data on the effect of contaminants and process variables on the ignition surface (ref. 57) be obtained. For example, a requirement for a very rapid ignition transient might be met by the roughening of all burning surfaces; or a requirement for a decreased rate of pressurization might be met by the partial inhibiting of some of the burning surfaces. Since the addition of processing steps can add considerably to the overall processing complexity (thus decreasing the system reliability) and to processing costs, the design engineer should consider other methods of meeting these requirements. In addition, the degree of consistency that can be achieved in reproducing the ignition surface should be determined by means of design proof tests. Small changes in the processing conditions or variations in the operator's workmanship can have a marked effect on the ignition performance of each finished motor.

3.2.4.2 Tailoff

Tailoff performance specifications shall take into account commercial tolerances for tooling and motor cases.

Unless the advantages of tighter tolerances can be justified, transient thrust-time or pressure-time performance requirements during tailoff should not be tighter than those that can be met with tooling and motor cases built to commercial tolerances. For tailoff requirements, the important process tool tolerances are those that could result in excessive off-center extrusion dies or warped or off-center casting mandrels. Deficient dies and mandrels produce grains that are not concentric over their entire length; the eccentricity results in an extra quantity of slivers during the tailoff portion of motor performance. Variations in extrusion dies and mandrels can be controlled within limits by exercising stringent quality control on the mandrel itself and on the positioning of the mandrel or the extrusion die. Inert slivers must be oriented precisely to the propellant grain and inhibitor assembly.

Another factor that contributes to the variability of tailoff performance is an out-of-round condition of the motor case. This condition can be controlled in some cases by external-jacketing-type tooling, but precautions must be taken against creep and out-of-roundness after the propellant has been cured.

Tailoff specifications also must take into account variations in burning rates throughout the motor (sec.3.1.4). When the required performance cannot be met by commercially available tolerances, consideration should be given in tradeoff studies to other means for obtaining the tailoff performance required (e.g., the use of thrust termination devices).

3.3 Liner

3.3.1 Formulation

The liner shall be compatible with the propellant cure cycle and process environment.

Liner formulations should be compatible with interface materials and with the temperature conditions to which the motor must be subjected during processing (ref. 45). The effect of variations in process conditions should be determined during the development of a new propellant liner system. For example, the bonding life (the period of time the lined chamber may be stored prior to casting without serious loss of bond strength) must be determined and monitored for any rocket motor program. This useful life period of a liner often is a function of temperature and humidity conditions.

Liner life after the initiation of casting operations on large motors is also an important processing factor. Large monolithic motors require extended casting periods (up to 3 weeks). The liner formulation must have satisfactory properties during the casting period, at casting temperatures (ref. 49) and, in some cases, in vacuum environment.

Additional compatibility factors are covered in references 1 and 4.

3.3.2 Mechanical Properties and Bond Strengths

Design proof tests shall determine the effect of process variables and ingredient proportions on mechanical properties.

No tolerance on mechanical properties of liner should be specified until the effects of process variables have been determined by design proof tests. This requirement is particularly important for each new propellant-liner-insulation combination, but it may be important whenever new insulation materials are involved, because the condition of the bond interface is affected significantly by each item of the combination as well as by processing conditions. Propellant and liner composition factors that influence liner selection include binder type, plasticizer type, catalyst, and filler content (refs. 45 and 46).

In general, a similar binder should be used in both propellant and liner, although this practice alone does not guarantee good bonding. For example, the selection of a plasticizer is highly dependent on its compatibility with both the propellant and the insulation. Since propellant-liner bond strains depend on the condition of the components at the bond interfaces, incomplete cure of the propellant layer next to the liner will cause a severe decrease in bond strength. Improvements in bond strength can be obtained by incorporating a high concentration of cure catalyst in the liner or in primer coatings to improve the cure of both the liner and the propellant at the interface (ref. 46).

The liner development program should provide clear definitions of liner processing techniques and environment. Rigid control of liner application and exposure history should be imposed to protect the bonding interfaces and to ensure bonding system integrity. The most important factors to consider in defining process control for a liner system are type and composition of insulation, conditioning of insulation, application and cure of liner, control of liner thickness, and bonding life (sec. 3.3.1).

When inhibitors are required, they should be incorporated into the design by casting the propellant against a lined surface of the inhibitor to ensure complete surface bonding.

To obtain adequate data from the design proof tests for liner bond strengths, laboratory testing procedures should be used together with other testing devices such as static firing and sampling of fired sections. The two basic test methods recommended are (1) the constant-strain-rate peel and tensile tests (ref. 45), and (2) the constant-load peel and tensile tests. The latter type more closely simulates conditions within the motor where low-level biaxial and triaxial strains prevail for a longer period of time. Because more rapid test results can be obtained, the constant-strain tests often are used as a relative measure of the quality of the bond.

Selection of liner formulation should take into account diffusion of cure inhibitors or plasticizers from substrate to propellant or diffusion of reactive ingredients from propellant mix to substrate, in order to provide adequate initial bond and to prevent deterioration of mechanical properties with time. Specifications for liner thickness must take into account normal process variability (ref. 58).

3.3.3 Rheological Properties

Rheological properties of the uncured liner shall permit relatively thin but highly uniform layers of liner to be applied with commercial process equipment.

Liner formulations should provide good processability of the uncured liner and permit a relatively thin but uniform liner thickness to be applied with a minimum number of coats. Selec-

tion of a liner formulation should take into account process reliability factors as described in reference 34. New formulations should be tested on subscale motors to evaluate processability. An important process variable that must be specified by the design is total liner thickness. Below certain minimum thicknesses, the bond strength decreases rapidly. A minimum total thickness that is consistent with processability (sec. 3.3.2) and bond strength requirements should be specified (ref. 58).

3.3.4 Process Contaminants

The effectiveness of a liner shall not be affected adversely by common process contaminants.

Tradeoff studies should take into account the relative costs involved in protecting liner systems from common process contaminants or in minimizing the effects of such contaminants. Processing costs are increased whenever the selected liner system requires special facilities and procedures to guard against small amounts of surface contamination due to moisture, dust, or condensed volatiles. On the other hand, the reliability of almost all liner systems is improved without appreciable increase in cost when the insulation can be grit blasted, cleaned with a solvent wipe to remove insulation particles, and dried to remove residual solvent. Materials and methods used to remove contaminants are described in reference 34.

If a formulation requires close control of the processing environment (particularly humidity control), the increased processing costs must be taken into account. Process humidity control, for example, is required for liners used with polyurethane and CTPB propellants (ref. 48). In these cases either the propellant surface or the thin, relatively dry liner coat can easily absorb moisture that subsequently may seriously affect the mechanical properties of bond interface regions. Storage, handling, and subsequent processing must provide adequate controls on exposure of the liner surface to excessive moisture.

3.4 Motor Case

3.4.1 Provisions for Tool Removal

Openings in the motor case and in the insulation shall facilitate removal of casting tooling and provide for proper distribution of propellant during casting.

If DB propellant is used, the motor case design should facilitate the placement of the casting powder. Special techniques for producing grain perforations with a major diameter larger than the case opening (e.g., nozzle flange) can increase processing costs.

In certain instances, it is necessary to use a meltout type of mandrel in order to achieve all the design requirements. As noted earlier, this process may contaminate the propellant and thus increase processing costs. The thin layer of contaminated propellant should be removed by grit blasting so that proper ignition surface is obtained.

3.4.2 Tooling Support

The motor case design shall provide a means for accommodating stresses incurred during propellant processing.

Motor case designs should provide a means to distribute and accommodate the loads imposed by process tooling so that no distortion or other adverse effect on the finished motor occurs.

Unsymmetrical case or grain designs should provide a means for adequately locating casting tooling and should take into account the strains imposed on the case by casting and curing the propellant.

A means must be provided for attaching tooling to the case in order to hold down the case when the mandrel is removed.

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GLOSSARY*

Material Designations	Identification
AN	ammonium nitrate, NH_4NO_3, an oxidizer
AP	ammonium perchlorate, NH_4ClO_4, an oxidizer
Bd/MVP	synthetic gum rubber (butadiene/methyl/vinyl pyridine copolymer)
CMDB	composite modified double-base propellant; modification is by addition of oxidizer such as AP and/or fuel such as aluminum powder
CTPB	carboxy-terminated polybutadiene prepolymer
DB	double-base propellant
GR-1	butyl rubber
GR-M	neoprene
GR-S	styrene-butadiene rubber
MAPO	tris [1-(2 methyl)aziridinyl] phosphine oxide
NC	nitrocellulose
NG	nitroglycerin
PBAA	polybutadiene-acrylic acid copolymer
PBAN	polybutadiene-acrylic acid-acrylonitrile terpolymer
PVC	polyvinyl chloride
SBR	styrene-butadiene rubber (also GR-S)

*Divided into four sections: Material Designations, Classes of Explosive Hazards, Terms and Symbols, and Organization Abbreviations.

Classes of Explosive Hazards	Specification
Class A	materials likely to detonate when involved in certain types of transportation accidents. Defined in ref. 15, Part 173.53.
Class B	materials likely to deflagrate when involved in certain types of transportation accidents. Defined in ref. 15, Part 173.88.
Class 2	deflagration hazard, explosives classification per tests described in reference 14.
Class 7	detonation hazard, explosives classification per tests described in reference 14.

Term or Symbol	Definition
ABM	automatic batch mixing
anomaly	irregularity in cured propellant grain (e.g., a void, or a fuel-rich pocket)
casting powder	small (e.g., 0.050-in. (1.27 mm)) grains used in DB and CMDB processes of interstitial casting
characterization	definition of physical or chemical properties of a material in relation to its application or use in a propellant formulation or rocket motor
composite propellant	propellant system comprising a discrete solid phase dispersed in a continuous solid phase
conical	conical slot used to increase burning surface in a cylindrical perforated grain
deflagration	burning process in a solid system comprised of oxidant and fuel in which reaction front advances at less than sonic velocity and gaseous products move away from unreacted material; a deflagration may, but need not, be an explosion
detonation	explosion characterized by propagation of reaction front within reacting medium at supersonic velocity and by motion of reaction products in same direction as reaction front

Term or Symbol	Definition
double-base propellant	propellant with two explosive ingredients such as nitrocellulose and nitroglycerin
end item	the complete space vehicle system or any of its principal subsystems
erosive burning	increase in burning rate that results from high-velocity combustion products moving over the burning surface
explosion	very rapid chemical reaction or change of state involving production of a large volume of gas and resulting in rupture of container (if present) and generation of a shock wave in surrounding medium
filler	discrete material dispersed in substantial quantity in continuous or binder phase of a composite propellant
flaw	unplanned discontinuity in grain structure
friability	tendency of crystalline structure to crumble (i.e., crystal friability of AP)
fuel binder	continuous phase that contributes the principal solid condition to propellant but does not contain any oxidizing element, either in solution or chemically bonded
gel stage	condition reached during curing of a liquid polymer mix when viscosity tests show an essentially "no flow" condition
grain	single piece of solid propellant, regardless of size or shape, used in a rocket motor
I_{sp}	specific impulse
inhibitor	material applied to surface(s) of propellant grains to prevent combustion of the surface
initiation	process of starting combustion, explosion, or detonation of materials by such means as impact, friction, electrostatic discharge, shock, fragment impact, flame, or heat
insulation	material applied to surfaces of the motor case to provide thermal protection

Term or Symbol	Definition
interstitial casting	process that introduces a liquid into a bed of solid granular material (e.g., DB casting powder process)
L/D	length-to-diameter ratio
liner	transition material(s) between propellant and insulation or, when there is no insulation, between propellant and motor case. Function of liner is to provide an adequate adhesive or cohesive bond between propellant and insulation, motor case, or other motor parts. In this monograph, primers used on insulation or liner surfaces are considered part of liner
modality	number of peaks (or modes) in a plot of particle-size distribution
NDT	nondestructive test method, e.g., X-ray
oxidizer	material whose main function is to supply oxygen or oxidizing materials for deflagration of a solid propellant
packing fraction	volume fraction of solids when packed to minimum volume
perforation	central cavity or bore (generally longitudinal) designed in the grain
plastisol	flowable suspension of a polymer in a plasticizer that the polymer may later imbibe to produce gelation
pot life	length of time a temporarily fluid system can be held or worked before setting up to a gel or solid
primer	material applied to surfaces of motor cases, insulation, or liners to enhance bond strengths (see "liner" definition)
processability	measure of relative ease with which a material, propellant, or rocket motor can be produced with state-of-the-art techniques
quality assurance program	planned and systematic pattern of all actions necessary to provide adequate confidence that an end item will perform satisfactorily in actual operation
quality control	management function to control quality of articles to conform to quality standards; includes inspection as well as other controls

Term or Symbol	Definition
quantity/distance	system for specifying safe distances for location of propellant or propellant-ingredients processing or storage buildings
reliability	the probability that a system, subsystem, component, or part will perform its required functions under defined conditions at a designated time and for a specified operating period
sensitivity	measure of relative susceptibility of a material to deflagration or detonation under specified conditions
shelf life	storage time during which an item remains serviceable
slivers	portions of grain remaining at web burnout
tailoff	period of rocket motor thrust decay after the end of effective propellant burning time
tailoring	modification of a basic propellant system by adjustment of properties to meet requirements of a specific rocket motor
tap density	bulk density of solid particles measured after tapping the container several times
transverse slot	slot inside propellant grain, positioned at an angle approximately 90° to axis of rocket motor
void	air bubble in a cured propellant grain
web	thickness of propellant consumed by burning
ρ	density
260-SL	260-in.-diameter, short-length, demonstration motor

Organization Abbreviations	Identification
ACS	American Chemical Society
AIAA	American Institute of Aeronautics and Astronautics

Organization Abbreviations	Identification
AIChE	American Institute of Chemical Engineers
ARS	American Rocket Society
Canadian A.R.D.E.	Canadian Armament Research and Development Establishment
CPIA	Chemical Propulsion Information Agency
ICRPG	Interagency Chemical Rocket Propulsion Group
SAE	Society of Automotive Engineers
SPIA	Solid Propulsion Information Agency
UTC	United Technology Center, division of United Aircraft Corp.

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SP-8005	Solar Electromagnetic Radiation, Revised May 1971
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
SP-8067	Earth Albedo and Emitted Radiation, July 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-8030	Transient Loads From Thrust Excitation, February 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-8045	Acceptance Testing, April 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
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SP-8060	Compartment Venting, November 1970
SP-8061	Interaction With Umbilicals and Launch Stand, August 1970
SP-8062	Entry Gasdynamic Heating, January 1971
SP-8063	Lubrication, Friction, and Wear, June 1971
SP-8066	Deployable Aerodynamic Deceleration Systems, June 1971
SP-8068	Buckling Strength of Structural Plates, June 1971
SP-8072	Acoustic Loads Generated by the Propulsion System, June 1971
SP-8077	Transportation and Handling Loads, September 1971

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
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SP-8071	Passive Gravity-Gradient Libration Dampers, February 1971
SP-8074	Spacecraft Solar Cell Arrays, May 1971
SP-8078	Spaceborne Electronic Imaging Systems, June 1971

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SP-8052	Liquid Rocket Engine Turbopump Inducers, May 1971
SP-8048	Liquid Rocket Engine Turbopump Bearings, March 1971
SP-8064	Solid Propellant Selection and Characterization, June 1971
SP-8039	Solid Rocket Motor Performance Analysis and Prediction, May 1971

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

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