CHAPTER 10

Composite Propellants

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1. Introduction

Composite propellants are made of a polymeric matrix, loaded with a solid powder oxidizer, and possibly a metal powder that plays the role of a secondary fuel component.

In composites the oxidizing and reducing atoms are not in the same molecule, as is the case with double-base propellants, thereby creating a microscopically homogeneous phase, but are rather juxtaposed with a composite structure. A certain number of properties, such as burning rate, rheology, and mechanical behavior, are directly related to this composite character.

The first composite propellants used thermoplastic binders such as asphalt, polyvinyl chloride, and polyisobutylene. Their use required softening or melting obtained through a temperature increase. Around 1950, the first liquid binders allowing crosslinking appeared. Because these binders allowed high ratios of oxidizing and fuel charges, they led to the considerable development of composite propellants in large case-bonded grains (several tens of tons, even several hundreds of tons of propellant) that were impossible to manufacture with other types of propellants.

This development era can be broken down into two major periods:

- From 1950 until 1965, when composite propellants were made with polysulfide binders ("thiokols") and with polyurethane polyethers.
- From 1965 on, new binders emerged, with a functional polybutadiene basis: acrylonitrile-acrylic acid-butadiene, acrylic acid-butadiene copolymers, and homopolymers with functional ends called telechelics. These new polymers led to increasingly better-performing elastomer binders, since they offered higher solids loadings and a wider operating temperature range, especially at low temperatures.

Clearly the significant events in the history of composite propellants are tied to the emergence of high-performance binders and not to new oxidizers.

Indeed, although ammonium perchlorate was not used right away — first potassium perchlorate and ammonium nitrate were used — it rapidly became the oxidizer of choice.

2. Formulation of Composite Propellants

Like all solid propellants, a composite propellant must produce hot gases which create a thrust by expanding in the nozzle, and include an oxidizer-fuel couple with a reaction capable of releasing sufficient energy to ensure the burning of the grain.

Oxidizing and fuel products come in the form of solid powders, which must be incorporated into a binder to give cohesion and homogeneity. This binder must exhibit very specific properties:

- It must be in liquid form during the preliminary phase of the preparation of the intimate mixture of the oxidizer and the fuel charge, although its elements must have sufficiently low volatile characteristics to withstand the high vacuum used during the mixing of the slurry and the casting into a grain.
- It must be chemically compatible with the oxidizer, which means that it will not cause even a slight temperature increase that would result in an exothermal reaction causing an unwanted autoignition of the propellant.
- It must be capable of accepting very high solid loading ratios (up to 80% in volume). The mixing operation must remain feasible, and the resulting slurry must be easily cast into a molding system or into the case of a rocket motor with molding devices with shapes that are often complex and include some fairly narrow sections.
- After the slurry is in the mold, crosslinking must ensure its transformation into a solid through a chemical reaction obeying the following criteria:
  - It must be a polyaddition reaction. Any elimination reaction producing more or less volatile products would result in the creation of cracks or "bubbles" in the crosslinked mass. Additionally, the mixing of the slurry must be done under vacuum to eliminate the gas present in soluble form in the binder. The decrease of the solubility of the gases during the crosslinking would lead to cracks in the propellant during cure.
  - This reaction must have on one hand a sufficiently slow cure kinetic to allow for the casting operations — this useful reaction time of several hours is also known as "pot-life" — and on the other hand must set sufficiently rapidly so as not to require lengthy crosslinking or curing times.

    The curing temperature cannot be too high, so as to prevent severe mechanical loads in case-bonded propellants.

  - It must also be athermic, or not very exothermic, to avoid the release of heat inside the grain, resulting in an increase of temperature inside this material, which is a poor heat conductor. This temperature increase could lead to mechanical loading conditions, possibly leading to cracks and autoignition of the propellant.
- Finally, once it is cured, the binder must lend its mechanical properties to the propellant.

Case-bonded grains are used in most of the composite propellants applications, i.e. the propellant forms one piece with the structure through the use of a bonding material, the liner. During its service life the propellant is subjected to major thermal stresses, resulting in significant strains because the thermal expansion coefficient of composite propellants is approximately ten times greater than that of the metals or composite materials used to make the cases. At firing, the propellant is, in addition, subjected to a range of important stresses and strains due to the deformation of the case under pressure.

The cured propellant must be able to withstand these strains without rupture, requiring it to have elastic type properties, viscoelastic to be more precise. These properties can only be provided to the propellant by the binder, which, taking into account the high proportion of solid loading, must therefore be an excellent elastomer. It is not unusual to require strains of 50% from the propellant, which means that the strains are more than ten times greater for the binder.

In Fig. 1 the tensile strength of a binder is compared to that of a propellant with a solid loading ratio of 88%. This figure demonstrates the effect of the loading ratio on the tensile strength (multiplied by 5) and on the strain at rupture (divided by 8) for a polybutadiene-AP-Al propellant.

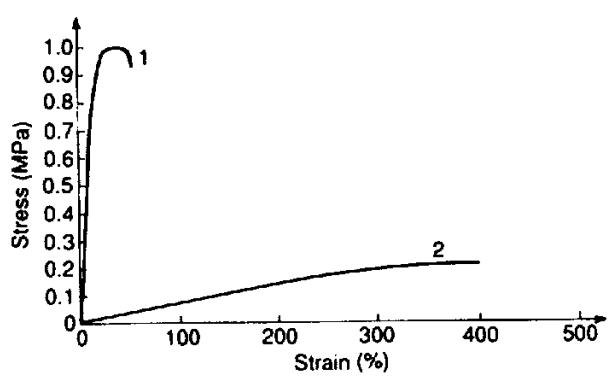


FIG. 10.1. Stress-strain curves.

2.1. THE BINDER

The binder is essentially composed of a liquid prepolymer, with chemical capability to react with a crosslinking system designed to ensure the dimensional stability of the product after the reaction has taken place.

In simplified terms, a prepolymer is a molecule formed by the repetition (several tens of times) of a monomer form (butadiene, polypropylene oxide, etc.), generally ending with reactive functions (telechelic prepolymers).

The crosslinking system may in its most simple state be a polyfunctional molecule (at least trifunctional) with a low molar weight, or a mixture of difunctional molecules, called chain extenders, whose role is to increase the length of the chain of prepolymers and of at-least-trifunctional molecules in order to ensure an average functionality (number of reactive functions, divided by the total number of molecules) greater than 2 for the whole crosslinking system.

After the polyaddition, chemical reaction has occurred between the prepolymer and the crosslinking system and the three-dimensional links are created. If they are in sufficient number — in the areas where it is not glassy — the resulting binder has a vulcanized elastomer type of behavior.

The crosslinked density of a binder, as well as the molecular mass between two links, are the essential characteristics of the network that constitutes the binder. These characteristics determine, in particular, its mechanical properties.

Many attempts have been made to link the mechanical properties (represented by the elasticity modulus) of the crosslinked polymer to the structure of the network defined by the crosslinking density and the molecular mass between two links (from 10,000 to 100,000 in usual composite propellants). They all derive from the statistical theory of rubber elasticity which links strain and stress according to:

where: $\sigma = kT(\alpha - \alpha^{-1})$

σ stress;
k Boltzman constant;
T absolute temperature in K;
α relative deformation of the specimen;
ν number of segments between links
where $\nu = \rho/M_c N$ and $E = \nu kT$
ρ mass per unit volume of the polymer;
N Avogrado number;
M_c molecular mass between two links;
E elastic modulus.

In reality this formula does not apply very well, because the binders of propellants are viscoelastic. It is useful only after long periods of relaxation, when there is equilibrium or quasi-equilibrium.

To be freed from this complication, M_c measurements are done on specimens swollen in a solvent. The Flory-Rehner theory [1] allows us then to determine the mass between links.

Finally, it is necessary to discuss the kinetics of crosslinking in order to describe the formation of the network on which the development of the rheologic characteristics of the slurry will depend.

Theories have been formulated based on the observation of the probability of reaction at the reactive sites [2]. Unfortunately, all of these theories come up against the complexity of the reactional system, whose exact characteristics are difficult to assess, such as: distribution of molecular masses and functionalities of the prepolymer; reactivity of the reaction sites which change during the formation of the network, and in particular, difficulty in measuring the development of reactive functions after the gel point where, through the formation of the first "infinite" molecule, the reacted group becomes partially insoluble. The use of these theories is nevertheless essential in guiding propellant designers.

2.1.1. Prepolymers

Prepolymers are the main element of the binder of composite propellants (70-80%). It is the prepolymer that confers on the binder its essential properties. These can be derived from the nature of the polymeric chain or the properties of the functional ends.

2.1.1.1. Characteristics related to the chain

Several examples are given in Table 1.

(a) ΔH_{f_o} Enthalpy of formation

The higher this quantity is, the more energetic it will help make the propellant (in fact, less negative, because for all usual binders ΔH_{f_o} is negative).

This enthalpy is directly related to the nature of the links between the atoms of the chain, which typically are C, H, O and N.

We will see, later in this chapter, that the binder must consist of light atoms which, through their combustion, will produce gases leading to a high specific impulse.

(b) Oxygen content

It would actually be better to talk about the ratio of the oxidizing valences (O, F, Cl) versus the reducing valences (C, H). In practice, the binders used so far contain, with a few exceptions, only C, H, O and N. Under these

TABLE 1 *Properties of the polymers used in composite propellants*

Polymers	Chain	Density (g/cm³)	ΔH_{f_0} (kcal/kg)	T_g* °C	M_p†	Amount of oxygen mass (%)
Polyisobutylene	$\left(\begin{array}{l}C(CH_3)_2-CH_2\end{array}\right)_n$	0.91	−375	−65	> 100,000 (thermoplastic)	0
Polybutadiene (20% of 1-2)	$(CH_2-CH=CH-CH_2)_n$	0.92	+5	−80	1500/5000	5
Polyether	$\left(\begin{array}{l}CH_2-CH-O\\ \quad\quad\ CH_3\end{array}\right)_n$	1.05	−895	−60 −70	1500/3000	26
Polyester	$\left(O-C-(CH_2)_x-C-O-(CH_2)_y\right)_n$ (O: $=$)	1.19	−1070	−50 −30	1000/2000	35
Polysiloxane	$\left(\begin{array}{l}CH_3\\ -O-Si-\\ CH_3\end{array}\right)_n$	0.87	−1890	−120	30,000	21

* T_g = Glass transition temperature measured by performing a differential enthalpic analysis.
† M_p = Weight average molecular weight.

conditions it seems logical to assume that only the oxygen present in the binder counts as oxidizing valences, and it is customary to consider the mass percentage of the oxygen in the binder. The higher this percentage, the less necessary it is to use high levels of oxidizer to obtain the maximum specific impulse. We must note, however, that the optimum does not correspond to a complete combustion of the reducing valences, as we will see later.

However, the incorporation of high ratios of oxygen in the binder through ether, ester, or carbonate functions is accompanied by a decrease of the enthalpy of formation. This is the reason why there is little interest in these types of binders, except for special applications, such as "cold" propellants or when plasticized by energetic molecules. This is especially true since other parameters intervene adversely: increasing glass transition temperature, and decreasing capability to withstand high solid loading when the amount of oxygen increases.

In practice the polybutadiene chain offers a good energetic compromise in spite of a density somewhat lower that that of oxygenated binders (Fig. 2).

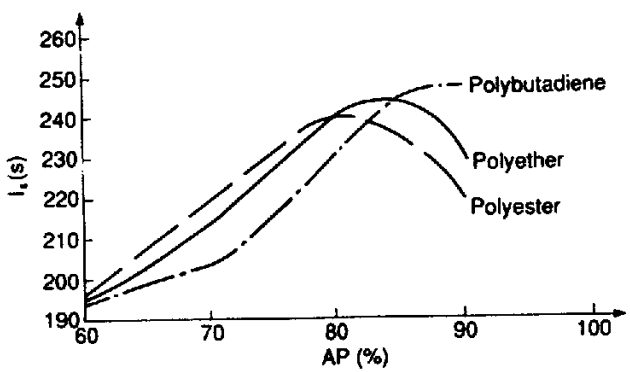


FIG. 10.2. Theoretical specific impulse as a function of AP concentration for three types of prepolymers.

(c) T_g. Glass transition temperature

This transition point of the second order corresponds to an important modification of the mobility of the polymeric chain that occurs when the temperature decreases and goes through a phase called "glass transition", which spreads over approximately 10 degrees Celsius. The physical properties of the polymer are greatly modified. Its elasticity modulus, in particular, increases significantly, and the capability of elongation becomes very small: the polymer has lost the specific qualities for which it was used. Table 1 shows, again, the advantage of using polybutadiene, at least for structures including no more than 20% of vinyl groups.

(d) Average molecular weight

The average molecular weight is tied to the number of monomer units which make up the prepopolymer chain — a few tens of units for the polyethers and polybutadienes — and therefore to the length of the segments of the macromolecular network. Therefore, it plays an important role in:

- The average molecular weight between links in the binder, i.e. its mechanical properties (low masses lead to a highly crosslinked and very rigid network).
- The viscosity of the propellant slurry. The slurry may not exceed a certain viscosity of the order of 15,000 to 20,000 poises if the filling of the molds is to occur under good conditions using classic processes. The viscosity of the prepolymer, which is the main element of the binder, may not exceed certain values. In practice it varies from a few tens of poises to a few hundreds at 25°C.

Beyond that, it is virtually impossible to do the mixing under good conditions without using extremely large quantities of plasticizer, which may lead to undesirable changes in aging properties.

Below several poises the molar mass of the prepolymer is usually too low, and the resulting network will be too rigid.

(e) Polydispersity index, $I = M_p/M_n$

Ratio of the weight average molecular weight versus number average molecular weight, this characterizes the distribution of the molecular weights around the average weight and is, consequently, related to the structure of the network (distribution of the molecular weight between the links). In Fig. 3 the

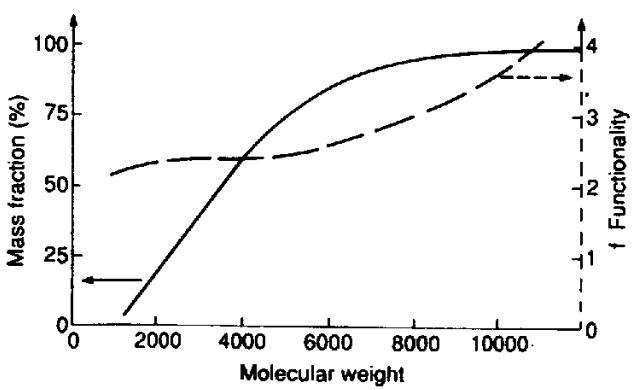


FIG. 10.3. Molecular weight and functionality distribution of an HTPB prepolymer.

distribution curve in weight of a hydroxytelechelic polybutadiene (HTPB) is given as an example.

2.1.1.2. *Characteristics related to the functional ends*

We have already seen that the functionality — the number of reactive functions per molecule — should be at least two to ensure a good formation of the network. This condition has been proven correct for many of the polymers in Table 1.

We must however mention the average functionality of 2.2 to 2.4 for HTPB R45M, which indicates a mixture of molecules with variable functionalities (from 0 to 7). This is related to the synthesis process of this polymer [3], and it has not been an obstacle to its development since 1970.

Ideally, the reactive functions should be located at the end of the chain to take advantage of its entire length and mobility.

In practice, the ends most widely used are the hydroxyl and carboxyl (hydroxy or carboxytelechelic polymers) whose methods of crosslinking are indicated in Table 2.

2.1.2. *The crosslinking agent*

As discussed, the function of the crosslinking agent is to bind the prepolymer molecules and is, when the functionality of the prepolymer is 2, to lead to the crosslinking nodes of the network. Therefore it plays a critical role in the crosslinking kinetic and in the mechanical properties of the propellant.

There are three types of polyaddition reactions used for solid propellants:

- Addition of an alcohol to an isocyanate. Isocyanates $R_1—N=C=O$ react with most of alcohols $R_2—OH$ according to the reaction:

$$R_1—NC=O + R_2—OH \longrightarrow R_1—NH—\underset{\underset{O}{\|}}{C}—O—R_2$$

The link $NH—\underset{\underset{O}{\|}}{C}—O$ is called urethane.

- Addition of an organic acid to an epoxide

$$R_1—\underset{\underset{O}{\|}}{C}—OH + R_2—\underset{\underset{O}{/\backslash}}{C}—CH_2 \rightarrow R_1—\underset{\underset{O}{\|}}{C}—O—CH_2—CHOH—R_2$$

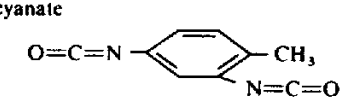
TABLE 2 *Crosslinking systems for prepolymers*

Nature of the ends of prepolymers	Crosslinking system	Functions created
Hydroxyl (polybutadiene, polyester polyoxypropylene)	Triol + diisocyanates Ex: TMP[a] + TDI[b]	Urethane $-O-C(=O)-N(H)-$
Carboxyl (polybutadiene, polyester)	1. Polyepoxide Ex.: Epon 812[c] from Shell	Alcohol ester $-C(=O)-O-CH_2-CH(OH)-$
	2. Polyaziridine Ex.: MAPO[d]	Ester amine $-C(=O)-O-CH_2-CH(NH_2)-$

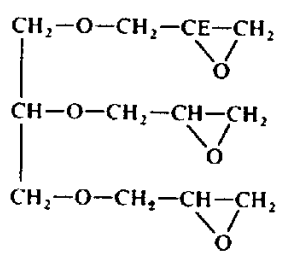
[a] TMP = Trimethylol propane

$$CH_3-CH_2-C(CH_2OH)_2-CH_2OH$$

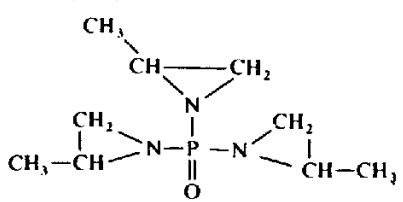
[b] TDI = Toluylene diisocyanate



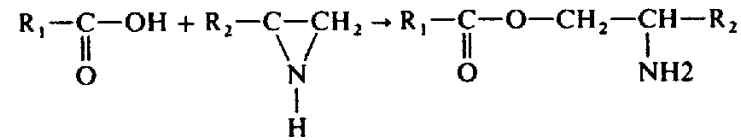
[c] Epon 812 (ideally)



[d] MAPO = Trimethylaziridinyl phosphine oxide



- Addition of an organic acid to an azidirine



(a) Effect on the mechanical properties

Figure 4 gives an example of the important effects of the stoichiometry, and of the percentage of crosslinking agent on the mechanical properties of a polybutadiene-AP-Al propellant. We must note that below a certain level of crosslinking (in this case, 0, 94 for the curing ratio), the propellant is not sufficiently crosslinked. Beyond this limit, maximum strains and stresses increase, which is a very general behavior of these compositions.

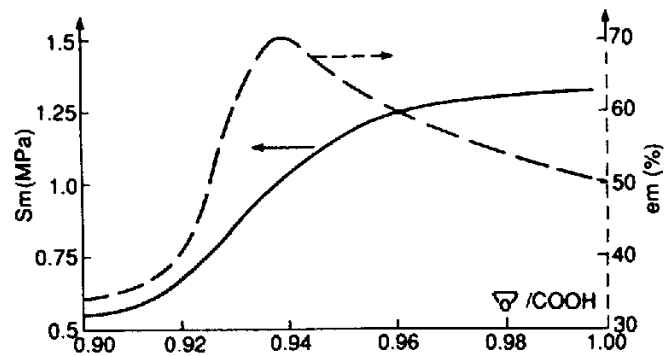


FIG. 10.4. Effect of the cure ratio on the mechanical properties of a CTPB propellant.

(b) Influence on the kinetic of polymerization

The reactivity of the crosslinking functions versus the prepolymer functions must be properly selected. Polyoxypropyleneglycol with secondary hydroxyl functions, for instance, requires an aromatic isocyanate that is fairly reactive (such as TDI), while R45M with primary hydroxyl ends is to be crosslinked with an aliphatic or cycloaliphatic diisocyanate that is less reactive, isophorone diisocyanate (IPDI), for example.

2.1.3. Plasticizer

Plasticizer plays the essential role of complementary element to reduce the viscosity of the slurry, therefore facilitating production, and to affect the mechanical properties by lowering T_g and the modulus of the binder.

Typically, it is an oil that is non-reactive with the polymer, a true diluting agent whose function is to separate the polymer chains, thereby reducing their interaction in the liquid state as well as in the crosslinked state. Table 3 lists the major plasticizers (polyesters for the most part) and Table 4 shows the effect of a plasticizer on T_g. Plasticizers contribute to lowering the mix viscosity and extending the elastic range at low temperatures. However, they have the drawbacks of being able to migrate, particularly at the propellant-liner and/or propellant-inhibitor interfaces, thereby modifying the properties of the propellants in those areas.

TABLE 3 *Major plasticizers for composite propellants*

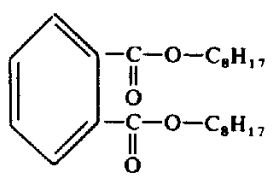
Diisoocytyl azelate	$(CH_2)_7$ with $COO-C_8H_{17}$ and $COO-C_8H_{17}$
Diisoctyl sebacate	$(CH_2)_8$ with $COO-C_8H_{17}$ and $COO-C_8H_{17}$
Isodecyl pelargonate	$CH_3-(CH_2)_7-COO-C_{10}H_{21}$
Polyisobutylene	C_nH_{2n+2}
Dioctyl phthalate	

TABLE 4 *Influence of the percentage of plasticizer on T_g of a polyether + diisooctyl azelate binder*

Plasticizer/polyether (%)	0	10	30	50	70	100
T_g°C	−68	−75	−80	−85	−101	−107

2.1.4. Additives

These are liquid or solid products added at a few percent of the binder. Their function is to modify at will the characteristics of the propellant to improve them, except specific impulse, which they often decrease due to secondary adverse effects. This decrease does not exceed 1-2%.

2.1.4.1. *Burning rate modifiers*

These are used to modify the propellant burning rate — beyond what can be done with variations of the particle size of the solids — and to adjust the exponent "n" of the burning rate-pressure curve in the pressure zone where the propellant grain will be operating.

There are two types of burning rate modifiers: accelerators and moderators.

(a) Burning rate accelerators

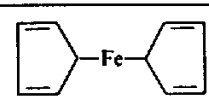
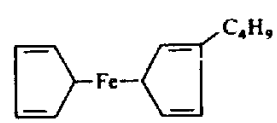
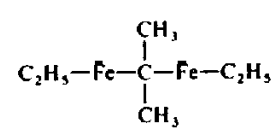
These are products that accelerate the decomposition of the perchlorate, or that lower its decomposition temperature. Virtually all burning rate accelerators are mineral or organic metallic by-products of copper, iron, chromium, or boron.

For many years only solids, iron oxides, and copper chromite were used. Liquid derivatives from iron (ferrocene derivatives) and boron (carboranes) are also used because their incorporation as plasticizers to the binders facilitates the high amounts necessary for high burning rates without lowering the loading ratio of energetic solid charges. The major ferrocene derivatives in use are listed in Table 5.

Unfortunately, because they are not linked with the network, these products, like the plasticizers, have a tendency to migrate at the interfaces. That is why we are now trying to graft the useful functions to the basic polymer chain. Prepolymers resulting from the addition of sililferrocene onto functional polybutadiene vinyl groups are currently being developed [4].

The curves shown in Fig. 5 illustrate the effect of a solid burning rate

TABLE 5 *Major ferrocene derivatives used as burning rate accelerators*

Ferrocene (Fe)	
n-Butylferrocene	
Di *n*-butylferrocene	$C_4H_9-Fe-CH_2-Fe-C_4H_9$
"Catocene"	

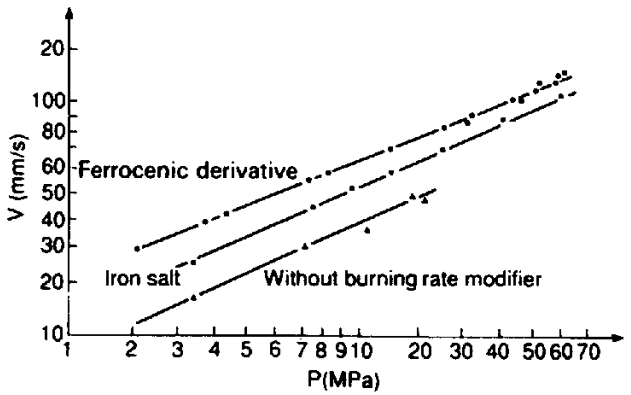


FIG. 10.5. Burning rate vs pressure curves for propellants with burning rate accelerators.

accelerator (copper salt) and a liquid one (ferrocene derivative) on polybutadiene-AP-Al propellants.

The efficiency of burning rate accelerators is highly dependent on the nature of the oxidizer. While there is a large number of burning rate modifiers for ammonium perchlorate and ammonium nitrate propellants, they are rather rare for potassium perchlorate composite propellants, or composite propellants that use organic energetic solids such as HMX or RDX.

(b) Burning rate moderators

There are two types of moderators, based on their mode of intervention.

Additives modifying the kinetic of decomposition of ammonium perchlorate. These generally are alkaline salts, or alkaline-earth solids added in low proportions, not exceeding 1-2% of the propellant.

Like the burning rate accelerators, although to a lesser degree, their efficiency varies as a function of the pressure, and is also associated with a decrease of the pressure exponent. Figure 6 gives an example of the effect of lithium fluoride on an ammonium perchlorate propellant. Although the effect of these additives could be significant (lowering of the burning rate by 50%), very slow burning rates cannot be obtained. Furthermore, they have no effect on aluminized propellants. As a result, "coolants" are preferred.

Coolants, also called "cold oxidizers," are products that also lower the propellant burning temperature, and unfortunately, its specific impulse as well, by:

- a lowering of ΔH_{f_o}, while maintaining a high content of oxygen;
- enriching the combustion gases with nitrogen which, since it takes no part in the combustion, acts as a diluter.

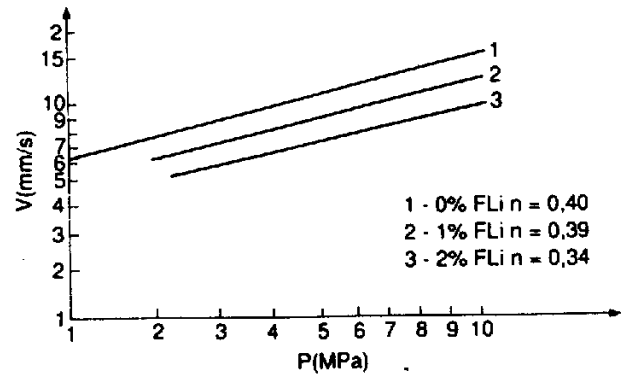


FIG. 10.6. Effect of lithium fluoride on the burning rate of an AP composite propellant.

The more commonly used coolants are:

- oxamide $NH_2—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—NH_2$;
- nitroguanidine $NH_2—\underset{\underset{NH}{\|}}{C}—NHNO_2$;
- ammonium nitrate.

Their main properties are listed in Table 6.

Oxamide has the most severe adverse effect on the specific impulse, but it is also the most efficient of the coolants. In practice, ammonium nitrate is used mainly as the major oxidizer for propellant with very low burning rates (but not very energetic) ranging from 1 to 2 mm/s at 7 MPa.

These products make it possible to reduce by half the burning rate of

TABLE 6 *Some characteristics of the major coolants*

Coolant	O (%)	N (%)	Density (g/cm³)	ΔH_{f_o} (kcal/kg)
Nitroguanidine	30.7	54	1.76	−217
Ammonium nitrate	60	35	1.72	−1090
Oxamide	36	31.8	1.67	−1355

ammonium perchlorate propellants, including those that are aluminized, with a drop in specific impulse up to 10 s.

2.1.4.2. *Surface agents and binder–charge bonding agents*

For many years the only role of these additives, used in low quantities not exceeding 1% of the binder, was to help the manufacturing of the propellant by decreasing the viscosity of the slurry. In this capacity all surface agents that decrease the surface energy of the solid charge, to permit better "wetting" of the surface by the binder, can be used.

However, it was quickly noticed that these agents, as valuable as they may have been in terms of the production, had a detrimental effect on the mechanical properties of the propellant by preventing the adhesion of the binder to the solids, thereby decreasing its tensile strength. Consequently, products called bonding agents have been developed, which through a judicious adaptation of their molecules, of the formulation of the binder, and of the mixing process of the ingredients play a double role, serving as wetting agent for the solids and increasing the cohesion between the binder and the solids [5].

A good bonding agent must satisfy the following criteria:

- Be efficient at very low levels (less than 1%).
- Be capable of bonding itself on a solid (generally the oxidizer, because it is the most important ingredient in terms of quantity). As a result, a bonding agent is specific to the type of solid.
- Be capable of incorporating itself with the binder through a chemical reaction which must be compatible with the crosslinking system.
- Reinforce the mechanical properties of the binder in the vicinity of the solids where the highest mechanical stresses appear in the area close to the surface of the charges [6].

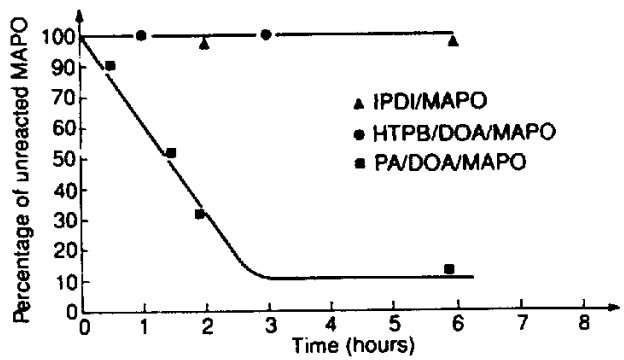
Triethanolamine is a good example of a bonding agent for ammonium perchlorate in polyurethane-type binders through:

- Reaction on the surface of the perchlorate by displacing the ammonia and forming triethanolamine perchlorate.
- Integration in the binder through the highly reactive primary alcohols.
- Trifunctionality of the molecule, ensuring a good crosslinking density in the area close to the ammonium perchlorate particles.

Because of the release of ammonia with amine-type bonding agents, polyaziridine-type additives are often preferred. Several of these additives are listed in Table 7. A good example of this family of additives is MAPO, which polymerizes on contact with ammonium perchlorate by opening aziridine rings. This layer becomes reactive to isocyanates, as illustrated in Fig. 7.

TABLE 7 *Binder-solid bonding agents: imine or aziridine type*

MAPO	Tri (2-methyl-1-aziridinyl) phosphine oxide
HX 752	Bis-isophtaloyl-1-methyl-2-aziridine
MT4	Product resulting from the reaction of 2 MAPO moles: 0.7 adipic acid moles and 0.3 tartric acid moles
Methyl BAPO	Methylamino-bis (2-methyl-1-aziridinyl)-phosphine-oxide



HTPB Hydroxylterminated polybutadiene
DOA Dioctyladipate
IPDI Isophorone diisocyanate

FIG. 10.7. Reaction of MAPO with IPDI and HTPB.

A number of additives featuring nitrile groups are also fairly widely used [8].

2.1.4.3. *Catalysts*

Catalysts are often necessary to reduce the curing time of the propellant.

Besides the kinetic aspect they may have a significant impact on the mechanical properties by facilitating some favorable reactions, thereby giving direction to the formation of the polymer network.

They are usually organic salts of transition metals (iron, chromium, tin). Several examples are provided in Table 8. Very detailed research is being performed because their nature and the amounts used must result in a trade-off between the workability of the mixture (viscosity of the slurry, pot life), curing time, and mechanical properties.

Complex systems with two or three chemical products such as triphenylbismuth, maleic anhydride, and magnesium oxide have emerged, and allow excellent compromises between pot life and curing time [9].

TABLE 8 *Catalysts for polyurethane binder propellants*

Iron acetyl acetonate	$Fe(C_5H_7O_2)_3$
Copper acetyl acetonate	$Cu(C_5H_7O_2)_2$
Lead octoate	$[CH_3-(CH_2)_3-CH(C_2H_5)-COO]_2Pb$
Ditubyl tin dilaurate	$CH_3-(CH_2)_{10}-COO-Sn(C_4H_9)_2-OOC-(CH_2)_{10}-CH_3$
Lead chromate	$PbCrO_4$

2.1.5. *Various additives*

Based on the various properties required from the propellants, specific additives are included. These usually are solids and their amount rarely exceeds a few percent of the binder.

2.1.5.1. *Antioxidant*

These are essential to ensure satisfactory aging of the propellant in various ambient conditions.

The binder, an organic material, is subject to degradations that are reflected by changes in the network and consequently, in the mechanical properties of the propellant. Generally, the combustion properties are little affected.

The aging may be:

- Oxidizing: this occurs with either the oxygen in the surroundings of the propellant grain, or gases occluded inside the propellant. Antioxidants are added, usually phenols or aromatic amines. This occurs particularly in the case of propellants with polybutadiene binder, whose C=C links are particularly sensitive to oxidation, in accordance with mechanisms that have been extensively studied for high molecular mass rubber. Antioxidants, well known in the rubber industry, are used, phenols in particular (di tertiary butyl paracresol, diamino *n*-phenyl-*n*'cyclohexyl-paraphenylene, 2.2. methylene bis (4-methyl-6-tertiary-butyl phenol), among others).
- Hydrolytic: this occurs with polyesters, where the ester links may hydrolyze and lead to a depolymerization of the binder.

2.1.5.2. *Burning rate stabilizing agents*

The pressure-time curve of a propellant grain may be considerably disturbed by inopportune local variations in the burning rate of the propellant. This is often the case with non-metallized propellants.

Based on the origin of these disturbances, the grain designer uses stabilizing additives of a varying chemical nature:

- Opacifiers (carbon black): these are found to be necessary in non-metallized propellants to block the radiation of the burning front, which has a tendency to heat the propellant below the burning surface, accelerating its combustion and creating low pressure fluctuations.
- Anti-instabilities and damping additives: these additives are discussed in Chapters 4 and 5. Their use may eventually adversely affect the polymerization of the propellant.

2.2. SOLIDS

There are two types:

- Oxidizers: the primary ingredient of the propellant (60–80%).
- Fuels: generally used in amounts not exceeding 25%.

These are powder solids whose shape and particle size determine the maximum amounts that can be included in the binder [11]. Figure 8 shows the influence on the relative viscosity (ratio of the viscosity of the suspension versus the viscosity of the interstitial liquids) of several particle size distributions of spherical particles whose diameters range between a 5 to 10 ratio. For a given viscosity limit (imposed by manufacturing capabilities), the accept-

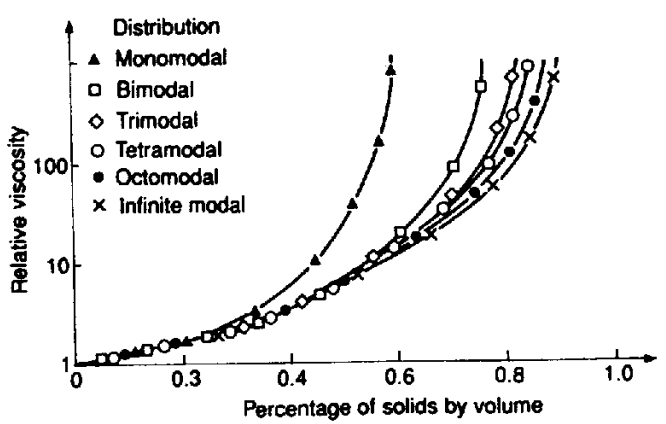


FIG. 10.8. Comparison of relative viscosities calculated for multimodal optimum systems.

able amount of charges by volume increases with the number of particle sizes, each particle size settling in the gaps formed by the larger sizes.

Three or four particle sizes are commonly used in propellants; it is sufficient to come close to a viscosity optimum for a specific solid loading. However, it is not always possible to use the particle size distribution best suited to obtain a high solid loading. This is due to the fact that particle size has a considerable effect on the burning rate of the propellant, and often it is this parameter which predetermines the size of the particles that will be used.

The nature of these solids is, of course, the major parameter influencing the energy of the system, although it also affects the burning rate, as already discussed.

In Chapter 1 we saw that the specific impulse can be expressed in a very simple manner:

$$I_s = K\sqrt{\frac{T_c}{M}}$$

where:

T_c = combustion temperature in the chamber;
M = average molecular weight of the exhaust gases.

The selection of an oxidizer-fuel couple is consequently a compromise between seeking to obtain a high burning temperature (related, in preliminary analysis, to the enthalpy of the formation H_{f_0} of the propellant), a low molecular weight for the combustion products, a high propellant density and, naturally, the required burning rate.

2.2.1. Oxidizers

The characteristics of a good oxidizer are:

- The capability of supplying oxygen (or fluorine) to burn the binder and the other fuel, with the maximum heat of combustion.
- The highest possible formation enthalpy. Figure 9 shows the formation enthalpies of the major kinds of oxidizer products that include the groups: ClO_3, ClO_4 NO_3 in the solid products.

The advantage of using NF_2 and NO_2 is revealed by the good location in the graph of CH_3NO_2, N_2F_4:

- The highest possible density.
- A sufficient thermal stability. Decomposition temperatures exceeding 100°C are required to permit the manufacturing operations and to safeguard the propellant.
- A good chemical compatibility with the other ingredients contained in the propellant, in order to avoid any undesirable exothermic reaction.

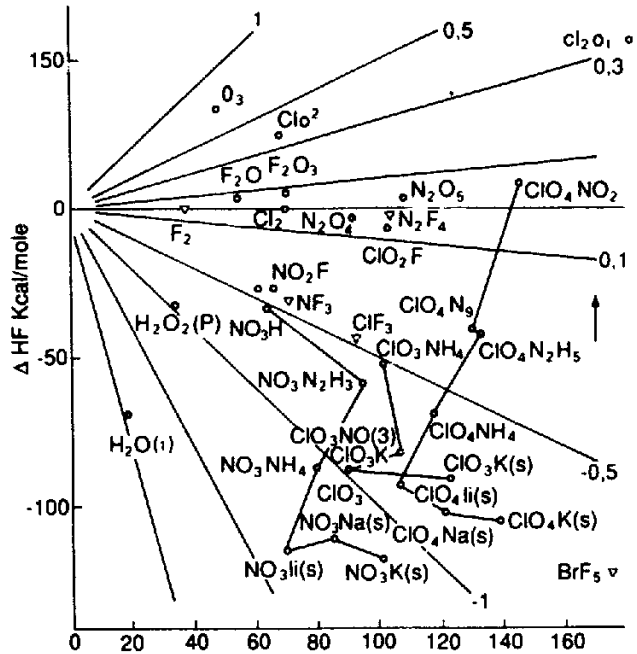


FIG. 10.9. Enthalpy of formation for major oxidizers as a function of the molecular weight.

- The availability of different particle sizes in order to obtain high solid loading and required burning rates.

In practice, the number of oxidizers used in composite propellant is rather small: ammonium perchlorate (AP) covers most of the cases. Next, ammonium nitrate, HMX and nitroguanidine are used the most. The characteristics of these products are given in Table 9.

2.2.1.1. NH_4ClO_4

By looking at Table 9 one easily understands why the use of this compound is so prevalent: it is dense, thermally stable (much more so than the chlorates) and its decomposition produces only gases of which a large proportion is oxygen.

SNPE uses, for example, six industrial particle sizes that permit the tailoring of burning rates from a few mm/s to 70 mm/s at 7 MPa with burning rate modifiers. They are as follows:

TABLE 9 *Some characteristics of the major oxidizers*

Oxidizer	"Free" oxygen by weight	Density	Decomposition temperature (°C)	ΔH_{f_0} (kcal/kg)	Remarks
Ammonium perchlorate, NH_4ClO_4	34	1.95	> 270	−601	In various particle sizes
Potassium perchlorate, $KClO_4$	46.2	2.53	> 500	−748	Presence of condensed KCl in the combustion gases
Ammonium nitrate, NH_4NO_3	20	1.72	Very stable	−1098	Numerous allotropic varieties if not stabilized
HMX $(CH_2N_2O_2)_4$	0	1.91	> 200	+68	Strictly speaking this is not an oxidizer
Nitroguanidine	15	1.76	Very stable	+217	Same as above
$NH_2-\underset{\underset{NH}{\|}}{C}-NO_2$					

Type	Average diameter (microns)
B	400
b	200
D	100
F	10
M3	3
M1	1

The first two varieties are obtained directly by crystallization, the others by grinding.

2.2.1.2. $KClO_4$

Very dense and oxygen-rich, this oxidizer has the drawback of giving to the propellant limited energetic characteristics. In addition, it also leads to high pressure exponents.

2.2.1.3. NH_4NO_3

This oxidizer, with very low ΔH_{f_0} and with little oxygen available, leads to specific impulses that are much lower than those obtained with the perchlorates. Its use is generally limited to gas generator propellants, where low burning temperatures (below 2000K) and slow burning rates (1-2 mm/s) are often sought. In addition, it exhibits a change of allotropic form at +32°C, accompanied by variations of volume causing significant variations in the properties of the propellants, including deterioration. So-called "stabilized" varieties have been obtained through cocrystallization with various salts (such as NiO). This has the drawback of introducing condensable in the propellant [12]. They are, however, more and more used.

2.2.1.4. $(CH_2N_2O_2)_4$: HMX

HMX is not an oxidizer, but it is the only product in the table with a positive enthalpy of formation. As a result, it is used as a supplementary energetic solid in propellants already having a high level of oxygen.

2.2.1.5. Nitroguanidine

Nitroguanidine is not an oxidizer either; but the relatively high value of ΔH_{f_0} make it useful as a supplementary charge, like HMX, although at a lesser degree (because of its low density and its deficit in oxygen), particularly as a moderator of the burning rate of ammonium perchlorate propellants.

2.2.2. *Fuels*

The diagram in Fig. 10 permits classification of fuels based on the energy available for the formation of the fluorides and the oxides. It illustrates:

- The small difference between fluorides and oxides, with an energy higher than the chlorides;
- The following decreasing order of energetic interest of the fuels, Be > Li > B > Al > H and C.

However:

- Beryllium is difficult to use, except for very specific applications, because of the toxicity of its combustion products.
- Lithium is not dense enough.
- With boron, B_2O_3 is not obtainable. In reality, sub-oxides are formed due to the thermodynamic conditions in the combustion chamber. Accordingly, this fuel loses its theoretical energetic advantage, except under specific environments very rich in oxygen, in the combustion chamber of ramjets and ramrockets (Chapter 12).

Magnesium is an interesting fuel, although much less dense (1.7) than aluminum (2.7).

Aluminum is virtually the universal fuel for composite propellants. It is available in spherical powders, with small diameters (a few microns to a few tens of microns), and it is well suited for high solid loading. The fine layer of aluminum oxide, which inactivates the grains in humidity, makes it easy to handle.

Carbon and hydrogen, which are always present in a propellant because

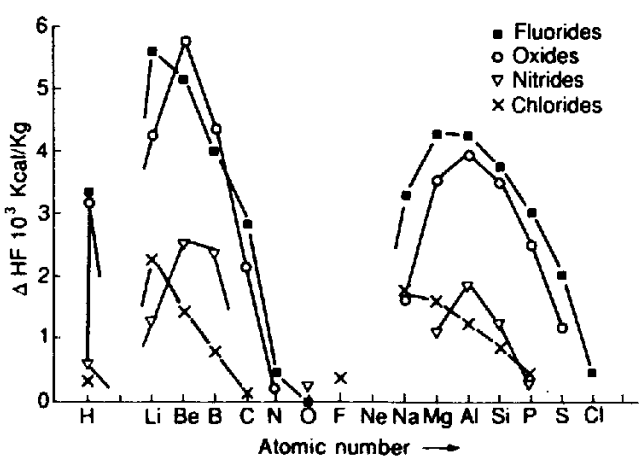


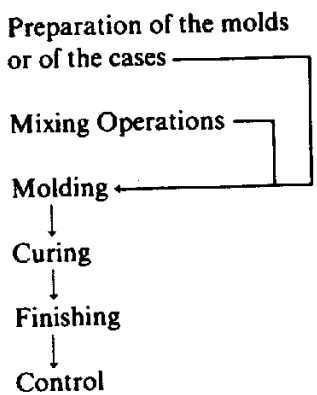
Fig. 10.10. Energies available through formation of exhaust products.

they are essential ingredients of the binder, play a major role in the exothermicity of the combustion,, and have a significant advantage over aluminum by producing gaseous combustion products.

Other fuels such as heavy metals have been tried, including Ti, Zr and Pb. None of them is being used, except for zirconium, whose cost remains very high. Its very high density (6.5) and its good combustibility may lend it a certain interest for applications where the amount of space available for the propellant is limited (integral booster for instance).

3. Manufacturing and Quality Control Methods

A complete manufacturing cycle of composite propellants could be represented by the following diagram:



Any of these operations is delicate, and conditions the quality of the propellant grains (microscopic and macroscopic homogeneity, effect on the operational properties). The preparation of the molds and cases is described in Chapter 13.

3.1. MIXING OPERATIONS

The mixing operation consists of the kneading of a solid phase (primarily oxidizer and fuel) and a liquid (the ingredients of the binder). It is designed to produce an homogeneous slurry that can be molded, with a good level of reproducibility of the characteristics of the propellant.

Because of the high investment costs of a mixing facility, all mixing operations that are non-pyrotechnic, and can be done outside of the mixing facility, are done with conventional mixers.

The more important preliminary mixing operations are shown in Fig. 11.

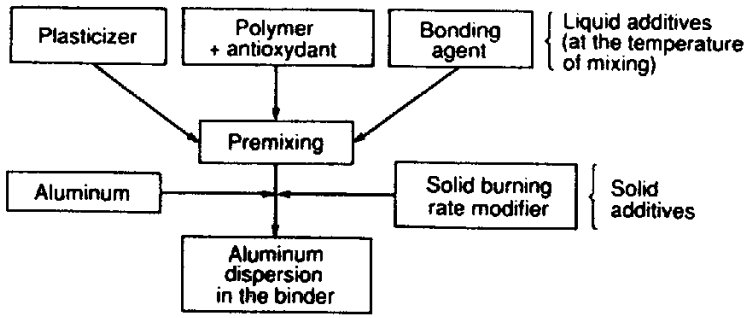


FIG. 10.11. Premixing operations.

3.1.1. *Preparation of the binder (Premix)*

A typical operation will now be described.

The premixing is done in a container equipped with a mixer. After they have been weighed, the ingredients are put in the container, as follows: the polymer, the plasticizer and the bonding agent. The mixture is heated to 60°C.

The aluminum is poured into the container with the binder, while continuously agitating to ensure a good mixing (this is the case at SNPE; other companies can incorporate aluminum in the propellant mixer).

The kneading is the most important operation in the manufacture of the propellant. It must last long enough to create a homogeneous slurry, suitable for casting. It is also an expensive operation, because of the energy and manpower requirements, and its duration should be as short as possible without affecting the quality.

In the past, the first mixers used for the manufacture of propellants were horizontal mixers. The drum was made of stainless steel to avoid corrosion from the perchlorate. Two rotating Z-shaped blades would knead and cut the slurry. The clearance between the wall of the drum and the edge of the blades was very small — a few millimeters — to minimize the amount of dead space where the blades could not reach, and the intense shearing action was designed to ensure a good level of homogeneity in the slurry.

Some kneading phases require the slurry to be heated; others that it be cooled. This was achieved through a mixer with a double-wall system, where a circulating liquid could be either heated or cooled at will.

Humidity is bad for all propellant compositions. All facilities where there are mixers are air-conditioned, and the mixers themselves are closed with a tight-fitting lid. This lid is equipped with a vacuum device, used to obtain a low residual pressure of about 10 mm of mercury. Volatile components, water, and air trapped in the slurry are easily removed in the course of the kneading phase.

Over the past 15 years the horizontal mixers have been gradually replaced with vertical mixers with two or three blades, and an orbital motion.

The process for the mixing operations on these vertical mixers has remained virtually unchanged from the horizontal mixers; but flexibility and production rates have greatly increased, due to the possibility of exchanging the drums. The time required to load and unload the mixers has been cut down to a minimum.

The vertical position of the blades completely prevents the bearings and seals from having any direct contact with the propellant mixture, thus avoiding contamination of the gearbox: cleaning of the mixer is easier and a higher level of safety is attained.

The sequence of mixing operations is as follows:

The binder is first freed from any gases, after which the oxidizer is introduced. This may be done manually, repeating the operation several times (in the case of a small mixer), or remotely, using a hopper equipped with a vibrating chute or an Archimedes' screw, in a dry environment.

This is a very important phase because the order of introduction of the various oxidizer particle sizes, as well as the timing of the introduction, determine the viscosity of the slurry.

Both the various parameters of the process, as well as the formulation (wetting agents, bonding agents, particle size distribution of the oxidizing solids and the type of aluminum and its particle size), are optimized to obtain a slurry which is as fluid as possible. Better filling of the mixer is possible, and the mixing times are shorter.

In Fig. 12 is an example of the evolution of the torque of the mixer for two

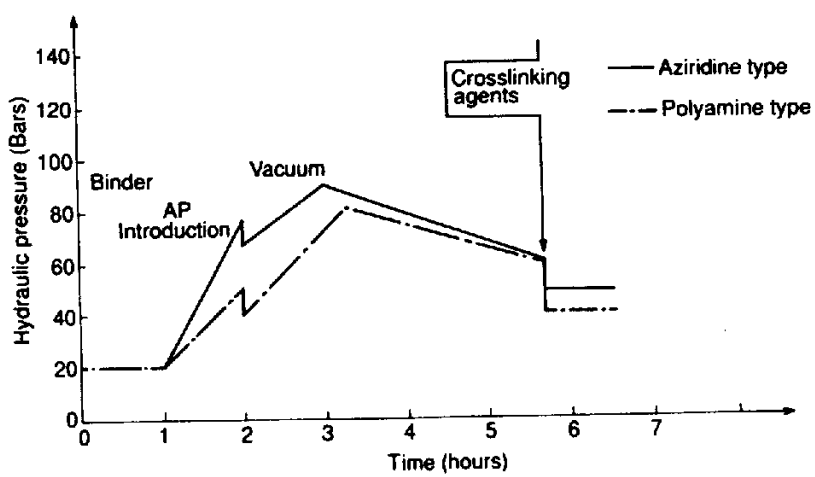


FIG. 10.12. Torque build-up during mixing.

propellant compositions both containing 90% solids, but differing by the bonding agent used.

The introduction of the oxidizer is the most critical phase in terms of safety. The propellant is not a homogeneous slurry yet, and ammonium perchlorate in contact with fuel is sensitive to mechanical stimuli. If this inhomogeneous and porous slurry ignites, the combustion to detonation transition phenomenon may take place.

This phase is followed by a homogenization designed to improve the wetting of the solids by the binder and to decrease the viscosity to the point where casting can be performed under good conditions. Specimens may be taken during this phase to check on the oxidizer content and on the burning rate.

The crosslinking agent and the polymerization catalysts are usually introduced last, a few tens of minutes before the end of the mixing operation.

The propellant slurry is transferred to an isothermic container, when horizontal mixers are used, to be transported to their casting facilities. In the case of a vertical mixer, transport is done by moving the entire drum.

3.1.2. *Continuous mixing processes*

For a long time, research work has been devoted to processes that could lead to continuous mixing as a substitute to the batch mixing process. Since this evolution has an important effect on the whole process of production of the propellant grains it will be described at the end of this book in the chapter devoted to the future of solid rocket propulsion.

3.2. CASTING OF THE GRAINS

3.2.1. *Sequence of operations*

There are three major phases involved in the molding of composite propellant grains:

- First, the filling of the structures and the molding of the central port of the grains, or of the aft face of the grain.
- Second, the polymerization or crosslinking of the propellant. This is the "curing" phase which takes place in an oven, or directly in the casting pit if the grain is very large.
- Third, demolding, machining of the central port and faces when necessary, and finishing operations to give the propellant grain its final aspect.

Typically, the process followed is:

To start, the mold, usually the body of the rocket motor with the inside surface completely coated with the liner, is filled with the propellant slurry, coming directly from the mixer.

This is a delicate operation. There is a wide range of propellants and various types of behaviors can be characterized: some propellants flow well, some propellants stick to the walls, some are very viscous; there is also a great variety of products manufactured, from the small propellant grains for rockets to the grains for space or ballistic missiles. They must, every one of them, be perfectly molded, and devoid of any casting defects.

The most widely used technique is "vacuum casting"; an alternative technique is injection under pressure, called die-casting. Both are described below.

When manufacturing propellant grains that have a central port, conformation is ensured by casting with a mandrel, either as a monoblock or in several parts. The mandrel is placed inside the case before the propellant is cured.

This operation is a simple one when the core can be easily put in place and extracted from one of the end faces of the propellant grain. Furthermore, if the space between the walls of the structure and the mandrel is large enough to allow the propellant to flow well, and for a progressive casting to be done, the mandrel is installed in the case before the casting operation begins. When this is not the case, the molding of the central port is done after the casting has taken place: the mandrel, guided from the outside, is driven progressively into the propellant by applying pressure.

An intermediate solution consists of using a two-part core. The grain is cast with the first, lower part already in place. The top part is placed on the bottom part after the casting has been completed.

3.2.2. *Rheologic characteristics and casting processes*

The choice of casting process, of the size of the casting devices and the definition of the casting conditions, depends, in addition to the size and the shape of the future grain, on the flowing ability of the non-polymerized propellant slurry.

Data on the behavior of the propellant during vacuum or injection casting is provided by its rheologic behavior law. It is specific to each formulation, and ties the shear stress τ, a function of the load imposed on the material (such as pressure, gravity, and others) to the resulting rate of deformation $\dot{\gamma}$.

This law is determined by using a rheometer, an instrument with a revolving cylinder body placed inside a cylindrical container. A rotation speed Ω is imposed, and the value of the resulting torque $\mathcal{M}$ is recorded.

The law is determined based on the curve $\mathcal{M}$ as a function of Ω, converted into the shear stress τ as a function of the stress rate (τ is expressed in Pascals and $\dot{\gamma}$ in s^{-1}): $\tau = f(\dot{\gamma})$.

Precise plotting is necessary for low levels of shearing ($\dot{\gamma} < 1\ s^{-1}$), corresponding to the conditions that are typical during gravity casting.

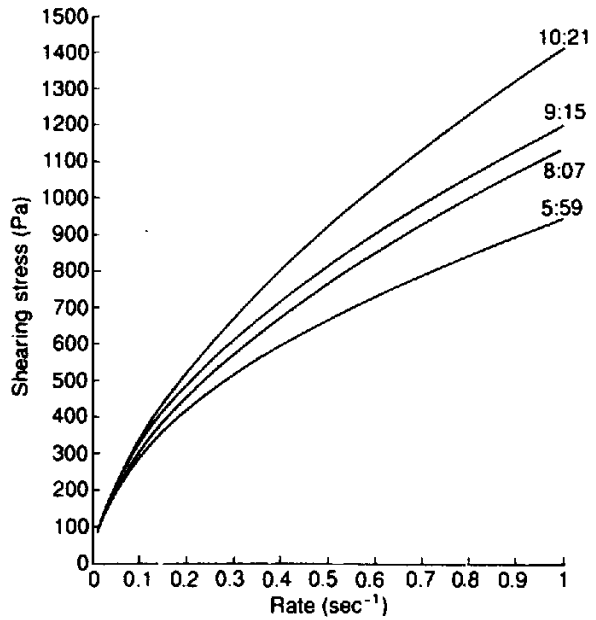


FIG. 10.13. Typical rheograms, as a function of time after introduction of the crosslinking agent (hours-minutes).

The viscosity is determined, for a given shear rate, by the ratio $\tau/\dot{\gamma}$. Typical examples of rheograms are given in Fig. 13.

There are three major types of behavior:

- Compositions exhibiting a Newtonian behavior: their viscosity is constant, therefore independent from the casting conditions.
- Compositions exhibiting a pseudo-plastic behavior: their viscosity diminishes when the shear stress is increased. This particularity occurs regularly, although it is more or less pronounced.

  Such a slurry does not spread well, but is well suited for die-casting.
- Compositions exhibiting an expanding behavior: contrary to pseudo-plastic compositions, their viscosity increases with the shear rate. This is fairly rare. Such a propellant would present great difficulties if it had to be injected.

Knowledge of the behavior law provides information that is useful to select the casting process for the propellant and the conditions under which it should take place. It allows the prediction of the flow rate of the slurry in the existing casting facilities and the calculation of the number of grains that can be cast within a period of time compatible with the pot life of the propellant.

3.2.3. *Description of the major grain casting processes*

3.2.3.1. *Vacuum casting process, by gravity*

The oldest process is the vacuum casting process, illustrated in Fig. 14.

The mold, which most of the time is a thermally protected case covered inside with a liner, is placed in an enclosure that can be heated, and its pressure lowered between 10 mm and 30 mm of mercury. The purpose is to obtain a complete degassing of the slurry, a necessity for the manufacture of grain without voids.

According to the size of the object manufactured, the enclosure is shaped like a "closet" or a "bell" for small to mid-size grains, or a casting pit for large grains for space launchers or ballistic missiles.

The casting bowl which contains the propellant is placed above the enclosure. It is linked to the top of the enclosure by a duct, called the casting pipe. The end of this pipe opens into the casting enclosure, above the case to be filled. It is equipped with a slit plate.

This slit plate divides the slurry into strips during the casting to ensure efficient degassing of the propellant.

It also organizes the flow of propellant so that it falls directly and is fairly well distributed between the mandrel and the case in grains with a central

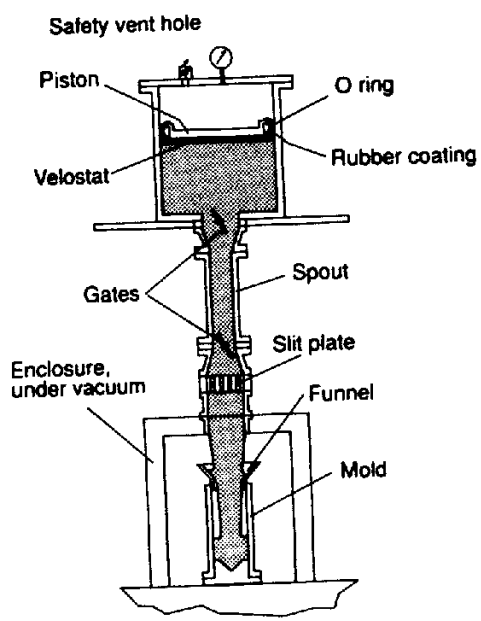


FIG. 10.14. Casting.

port. Because of the difference of pressure between the casting bowl and the enclosure, the propellant flows continuously from the drum to the casting matrix. Coming out of the slit plate, and according to the design of the slit plate, the flow takes the shape of fillets or ribbons of slurry which pile up inside the structure and settle under the effect of their own weight.

The selection of the casting flow rate is the result of a trade-off between:

- The need to have a rapid flow to accommodate time-saving industrial requirements and to avoid a significant increase of the viscosity due to the progress of curing.
- The need for a fairly slow flow to permit sufficient degassing of the slurry after it has gone through the slit plate, and spreading inside the case necessary for a high quality casting.

The selected flow rates are a function of the geometry of the grains, and vary from several kilograms per minute for small grains to flow rates of several hundreds of kilograms per minute for large grains.

The gravity casting process continues to be most widely used today, because it sufficiently satisfies the needs of propellant casting.

It is a simple process, well suited to the use of large quantities of material. In contrast to other casting and molding industries (plastics, loaded polymers and others), large quantities of material are involved for each object.

This process affords all necessary guarantees of safety, considering the sensitivity of the materials used, and ensures good overall quality.

It is well suited for the low production rates most often used in this industry.

3.2.3.3. Die-casting process

The characteristics described above also point out the limitations of the process. The design of higher-performance motors, which are highly specialized in terms of their missions and require the lowest possible cost, implies the manufacture of objects with more complex shapes: for example, bi-composition grains, long grains, and grains with small diameter and little space available between the case and the mandrel.

High-performance propellants may also exhibit high viscosity in the casting phase, which is due to the use, for example, of very fine perchlorates or high solid loading ratios.

Finally, the manufacture of certain small objects requires high production rates to allow significant cost reductions.

This led to the study and development of casting processes by injection under pressure: die-casting. This process involves forcing the slurry to move by subjecting it to pressure, and using that pressure to fill the molds rather than simply relying on gravity.

The various methods used to apply pressure have led to the development of several specific processes:

(a) Pressure applied using a gas (Fig. 15)

The propellant is placed in a flexible and deformable pouch. This pouch, located in an air-tight enclosure, is linked to the mold through a suitable linking system. The enclosure is filled with a gas under pressure which presses upon the outside surface of the pouch. The propellant is pushed into the mold.

This process is well suited to the manufacture of small objects with complex shapes, and produced in small series.

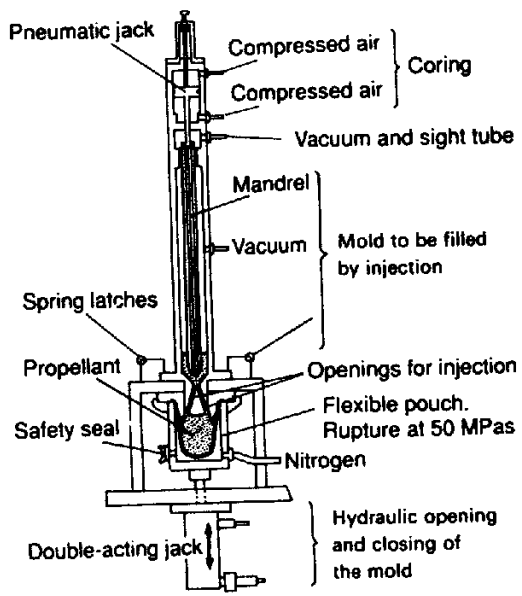


FIG. 10.15. Illustration of injection casting.

(b) Pressure exerted mechanically, using a hydraulic piston

This is the most simple of systems. The propellant is placed in a drum similar to the casting bowls described above. The drum is linked to the bottom of the mold by a pipe. Pressure is exerted on the slurry with a scraping piston placed on top of the propellant.

The propellant, under the pressure of the piston, continuously without any interruption into the mold, and fills it. The level of propellant increases inside the mold. This type of casting is known as spring casting.

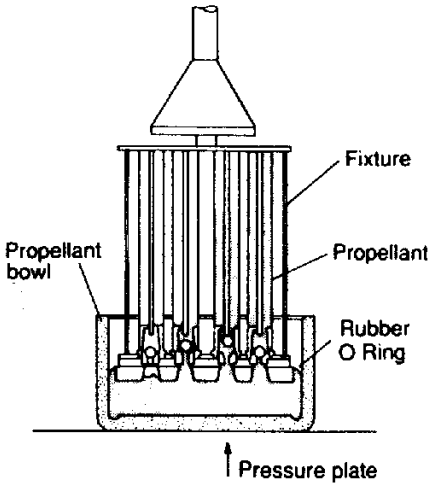


FIG. 10.16. Casting of a propellant in a case under pressure.

One interesting evolution of this classic process has led to the casting process by "stamping" [14]; it is illustrated in Fig. 16.

In order to minimize the waste of slurry inside the pipes linking the drum to the mold, and to allow the casting of a large number of cases in one single operation, the cases are placed directly on the piston, which has been perforated with a specific number of holes, to allow a direct connection between the propellant in the drum and the cases. This setup is mounted on the drum containing the propellant, and is pushed in by applying pressure.

When the pressure is exerted, the propellant goes up and fills the cases. A valve system closes each case when it is filled. The entire setup, piston and cases, is located in an oven. Each propellant-filled case is removed from the piston after cure of the propellant.

This process permits casting of a very large number of case-bonded grains, in one single operation.

(c) Pressure exerted mechanically, using an Archimedes' screw

This process is developed from a special type of mixer: the mixer-extruder (Fig. 17).

The mixing is done in the usual way, in a drum equipped with Z-shaped blades. This mixer, however, has at the bottom an Archimedes' screw used to extrude the product through a threaded-cylinder type of opening at a pressure calculated as a function of the rate of rotation and the rheologic characteristics of the propellant.

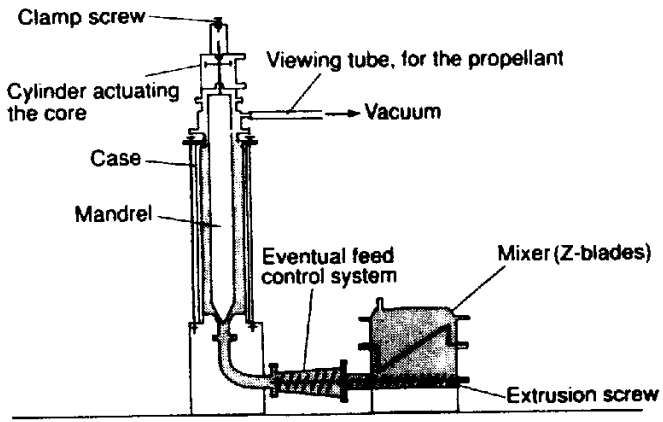


FIG. 10.17. Direct transfer through mixer/extruder.

By linking this opening to the bottom of a case or set of cases, the propellant can be transferred directed from the drum, where it is kneaded under vacuum into the cases without being exposed to atmosphere.

Many grains require central port profiles that cannot be obtained simply by casting. Several techniques are available:

- Machining of the deep axisymmetric slots using an especially designed tool at speeds tailored to the material [15].
- Using segmented mandrels. This technique, although simple in principle, requires in practice the use of complex machinery with safety handling problems that need to be resolved: the mandrel must be kept tight, and there is the issue of safety when removing the pieces of the mandrel. Consequently, this method is used only when central port configurations cannot be obtained through casting with removable monoblock core, or through machining, as with fynocyl grains, for instance. It is also used for maximum loading ratio grains which must be manufactured by integral molding, and for which mechanical finishing operations are not permissible.
- Using mandrels that are destructible after curing of the propellant, or at the time of ignition.

The technological and implementation difficulties involved with multiple-segment mandrels led to research on simpler concepts, and resulted in the creation of mandrels made of a material, either braided or in strips, wrapped in a very specific pattern, compressed and coated with an elastomer or a polyurethane foam. The easiest cases can be handled with a simple foam with sufficient rigidity and capable of disintegrating at ignition. With this process, grain configurations can be obtained that would be completely impossible

using either the machining process or the mechanical removable mandrel. This process places no limitations on configurations or geometry.

This description of casting principles may convey the impression that these technologies are simple. In reality, however, numerous issues have to be checked and eventually resolved to arrive at a qualified and reliable process, such as: air-tightness of the toolings; safety in regard to sensitivity to friction and static electricity of the propellant; compatibility between the inert materials involved and the propellant; and temperature and internal pressure stresses during cure. Without any doubt, most of the knowledge necessary for the manufacture of performing, reliable propellant grains, at an attractive production cost, is applied to this area rather than to the more spectacular area of propellant tailoring.

3.3. TEMPERATURE CURING AND FINISHING

Temperature curing is designed to accelerate the crosslinking reactions, i.e. harden the propellant rapidly. This is done by raising the propellant to a moderate temperature while in the casting pit or in an oven.

Changes in the curing process made to improve the properties of the propellant grains are further described below.

3.3.1. Curing under pressure

The 1960s saw the emergence of composite cases, which offer the significant advantage of being lighter than metallic cases but are also more able to deform when subjected to internal pressure.

Benefit can be derived from the latter characteristics to minimize residual stresses/strains occurring in the grain caused by thermal shrinkage when cooling after cure.

The leading concept of this process consists in subjecting the case loaded with the propellant to a pressure during cure such that, when depressurized, the movement of the case will follow, almost perfectly, the predicted contraction of the propellant grain when cooling [16].

By decreasing residual stresses/strains, the mechanical safety coefficient is improved. Curing under pressure is also reflected by an increase of the volumetric loading ratio of the case and higher quality of the propellant.

3.3.2. Integral molding

For productivity reasons, or for production of specific grain configurations, as well as for safety reasons (avoiding trimming the grain by machining it with a cutting instrument), the integral casting or molding technology is increasingly being used.

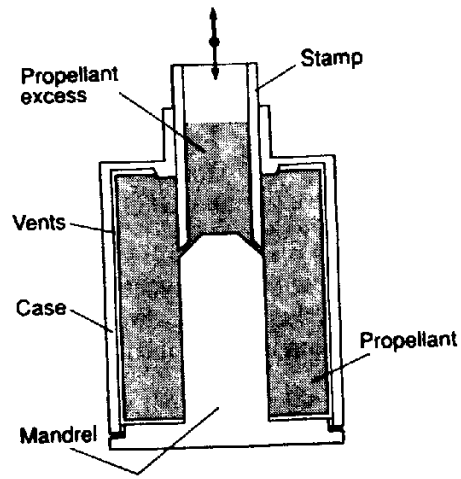


FIG. 10.18. Principle of integral molding.

With this process, which can be coupled with curing under pressure if need be, the propellant grain is obtained directly by casting, as shown in Fig. 18.

The implementation of the integral molding process involves the following considerations:

- An absolute thermal control of the casting-curing cycle — which must be isothermal — only very small temperature changes (positive) are permissible, and after the final tool has been applied to ensure complete confinement, negative temperature changes are forbidden, for risk of creating cavities.
- The viscosity build-up of the slurry and the development of mechanical properties during cure, as well as the thermal characteristics of the grain, determine the curing cycle.

3.4. INFLUENCE OF THE MANUFACTURING PROCESSES OF PROPELLANT GRAINS ON THEIR FUTURE COMBUSTION CHARACTERISTICS AND MECHANICAL AND STRUCTURAL INTEGRITY

3.4.1. Anisotropy of the combustion characteristics

Analysis of the pressure and thrust-versus-time curves at firing of the grain demonstrates that the manufacturing processes influence the burning rate of the propellant.

For example, pressure curves recorded during the firing of MIMOSA grains of composite propellant exhibited differences when the propellant was cast with the mandrel already placed in the mold or if the mandrel was introduced after casting.

The pressure-time curve shown in Fig. 19 for the first process shows a characteristic hump occurring approximately halfway through the web burned, while the pressure curve for the second process is flat.

The most important known findings are:

- Halfway through, calculations demonstrate that the burning rate of grains cast with the mandrel in place is always higher by 3–7%.
- The size of the pressure hump is not a function of the burning rate of the propellant.

Other experiments performed on BATES grains confirm these findings. Because experiments where grains of this type manufactured using both processes were extinguished, revealing that the burning surface halfway through the burned web is very similar to the theoretical surface, the pressure hump effect must be attributed to a burning rate variation as a function of web to be burned.

In the United States, AFRPL fired 2500 motors with 7–900 kg of propellants manufactured with 250 formulations for the BATES program. These firings served to reveal the hump effect [17].

Several explanations have been suggested. At the time of casting, binder-rich zones are created, in strata, at contact with the walls of the mandrel and of the case. The binder-rich zones burn slower, which would explain why the burning rate is a function of the web burned [18]; on the other hand, these strata are destroyed when the mandrel is inserted.

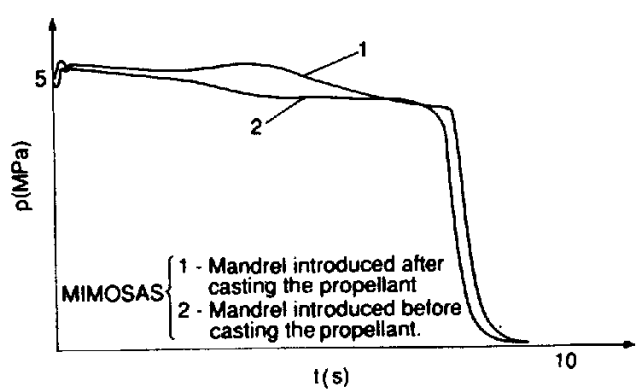


FIG. 10.19. Pressure curves for the same propellant.

3.4.2. *Anisotropy of the mechanical characteristics*

Systematic measurements made on propellant specimens removed from propellant grains tend to demonstrate that these orientation effects, tied to the casting process, may also have an impact on the mechanical characteristics and, consequently, on the effective safety factor of the propellant grains.

The more pronounced the orientation of the successive layers of propellant from the casting operation of the slurry into the case, resulting in significant shearing stresses in the slurry, the greater these effects will be. The viscosity of the propellant, in particular, plays an important role.

- On large case-bonded grains, manufactured with the classic gravity casting process through the base of the aft end of the rocket motor, dissections have shown that the propellant is homogeneous inside the grain but that the structural integrity deteriorates in the "raised collar" usually added to allow casting slightly more slurry than necessary to fill the case of the rocket motor exactly. But this area, considering the local geometrical narrowing, and because it is subjected to the effects of the volume variations of virtually the entire propellant mass during temperature changes, is the most mechanically stressed and strained area at a time when the propellant is already partially crosslinked. In some sense the propellant is "damaged". Variations of 40% have been recorded between the values of the modulus and the elongation capability of this area and the rest of the propellant grain.
- Die-casting processes involving a high degree of oriented injection coupled with high-level viscosity slurries may lead to variations in the elasticity modulus, ranging from 30% to 40% between the direction of the casting and the perpendicular direction.

This influence resulting from the casting process of the slurry and the geometry of the mold may very well have a considerable impact on the comparisons of characteristics between manufactured grains and grain specimens designed for quality control, cast from the same slurry. Constraints resulting from the manufacturing process require that the specimen designed to control the structural integrity of the grains be an object tailored to industrial production, easily machined, and with the smallest possible size.

Systematic analyses have led to the following conclusions: the mechanical characteristics of the control specimen (parallelepiped obtained through simple casting by gravity) have been found to be representative of the grain in a great number of propellant grains.

On the contrary, in a specific finocyl grain, the mechanical characteristics of the specimen have been shown to be inconsistent with those of the propellant grain. Elastic elongations systematically lower in the propellant grain than in the specimen have been observed. A general analysis of

all test data enabled us to discover that this phenomenon was specific to a particular kind of composite propellant. Further research succeeded in defining a more closely representative although simple specimen, obtained by casting with a star-shaped mandrel.

A number of assumptions or observations were made in the course of analyzing this phenomenon:

- The propellant grain and the specimen must have identical thermal histories. The case of the grain and the core may play a thermal role and influence the final level of the mechanical characteristics.
- The size of the specimen must be sufficiently large to be representative of the propellant grain.
- The liners, and thermal insulations may have some effect (such as migration, for example).
- In the case of significant shearing of the slurry (die-cast or gravity-cast grain), the phenomenon may be intensified.

3.5. QUALITY CONTROL

The mission of the quality control services is to ensure the quality of the product, particularly by controlling the following areas: raw materials, manufacturing operations, finished product.

3.5.1. Overview

Quality control operations on finished products can be divided in two major categories:

Destructive tests performed on specimens made with identical propellant: measurement of ballistic and mechanical properties using methods described in Chapters 4 and 6, and comparison with the specifications established for the propellant grain.

Non-destructive tests performed on the propellant grains. The non-destructive quality control tests, although not specific to composite propellants, are described below.

3.5.2. Non-destructive testing or inspection

In opposition to destructive tests that may include testing until failure of the specimen, non-destructive tests are designed to ensure the quality and integrity of the material or of their complex assemblies by "inspecting" them without altering them. These tests commonly fall into three categories:

- Inspection of the mass to identify cracks, cavities or heterogeneities.
- Examination of the bonds to identify debondings, cracks or inclusions.
- Control of the geometry to verify the dimensions.

With case-bonded grains, it is very important to inspect the most critical bonding zones which are located, usually at the aft or head ends.

Simple methods, such as visual or dimensional controls, are widely used, either to observe any surface anomalies, or to check the functional dimensions of the finished object.

Generally, these methods do not call for sophisticated principles. But they may very well use very intricate methods, such as endoscopy, surface control devices, television, stereoscopy, laser proximetry, and others.

These methods are useless for the control of the interfaces or the mass of the propellant grain. It is therefore necessary to have recourse to advanced technologies that allow us to traverse the material regardless of the nature of the material encountered.

The most widely used of these techniques are based essentially on the analysis or the detection of a wave or a radiation after its absorption, reflection, or emission. The oldest and most prevalent of these techniques call for ultrasound and X-rays. The most recent ones apply newly discovered principles, and make use of powerful automatic computer methods that facilitate the analysis of the information.

The implementation of these techniques usually requires large infrastructures and costly investments. The selection must therefore be very carefully made to ensure that the testing facilities will allow performance of quality control easily, at the best possible price.

The major difficulty encountered comes from the fact that in every case, there are superimposed interfaces, sometimes located behind a zone normally not bonded.

This means that one area can hide another and make the methods suitable for the analysis of the first interface completely useless on the other. The methods used fall into two categories:

- So-called "global" methods, which generally provide qualitative information, over a large area, at one time.
- "Spot" methods, which provide qualitative and quantitative information over a limited area.

It is desirable for one technique to be capable of providing these two types of investigations.

3.5.2.1. Inner control

The oldest and still yet most widely used methods are based on X-rays and ultrasonic waves.

(a) X-ray testing (Fig. 20)

This technique allows us to assess the inner homogeneity of the propellant grain (lack of cracks, bubbles, porosities, foreign matter, for example), the

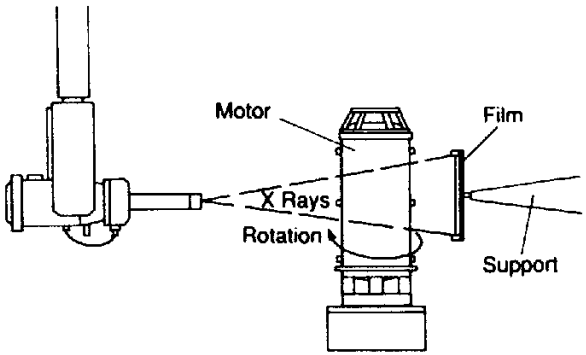


FIG. 10.20. Diagram of an X-ray facility.

quality of the bonds between the various elements of the propellant grain (liner-case or thermal insulation, liner-propellant, propellant-propellant), and also to determine the thickness of the various components. This test is based on the variations in the absorption of X-rays by the elements constituting the grain, which is translated by contrast differences on the various materials used to receive the radiant image. On film, negative film usually, cavities and debonding, which have a low absorption, will show as dark areas; metallic foreign matter, more absorbing, is paler.

X-rays are produced by bombarding fast electrons on a heavy metal target. The resulting energies may range from 50 keV to a few tens of MeV.

An energy of approximately 2 MeV is produced with a Van de Graaf electrostatic generator, while a greater energy will be produced with an electromagnetic linear accelerator.

Analysis of the radiating image, usually captured on photographic film, is a delicate operation, which requires highly qualified personnel regardless of the imaging method used: naked eye or microdensitometer.

This is equally true for the radiologist, who must have knowledge of a collection of parameters which greatly influence the quality, and therefore the analysis, of the final image. These parameters include:

- intensity of the X-ray;
- type of film used;
- distance of the source to the grain;
- positioning of the film in relation to the grain;
- number of angles of exposure;
- exposure time.

The determination of these parameters is often the result of a trade-off: for instance, an increase of the intensity of the X-ray results in a shorter exposure

time, although it increases the graininess of the image on the film. Similarly, increasing the distance to the grain results in a trade-off between a longer exposure time and the depth of field.

The optical density obtained on the film varies significantly according to the area under observation. An average density is necessary to correctly reveal defects, often requiring the use of films with different speeds. For instance, the image of the inhibitor-propellant bonds is done with a slow film, while the central areas will be done with a fast film.

The precision of the measurement of thickness and of the size of the defects is affected by:

- out-of-focus areas, dependent on the focal length of the radiographic camera;
- graininess of the film;
- intensity of the radiation, which affects the contrast.

X-ray radiography, followed by analysis of the image on the film, is a slow and expensive technique for extensive testing; but is a highly precise method for the observation of the inhibitor-propellant bondings and is widely used for large propellant grain.

(b) Ultrasonic testing

This technique is based on the observation of the variations experienced by an ultrasonic wave traversing an object. It is therefore possible to detect the transmission or the reflection of an ultrasonic wave or to analyze the nature of the signal (amplitude, frequency, phase).

This type of control is rarely used for mass exploration because propellant is highly absorbing. It is not very useful in determining the size of a defect. Still, it is frequently used to check the propellant-inhibitor bonding, though limited to the first interface only. It may present some interest for the assessment of the boundaries of bonded areas, and is therefore used as a method to analyze small areas, using portable equipment.

Other techniques, similar to the one just described, may also be used sometimes:

- γ absorption: this is of limited use because of the pyrotechnic threat tied to radioactive sources;
- neutrons: cannot be used for high thicknesses hydrocarbon materials;
- acoustic emission: difficult because of the low emissive power of propellants;
- infrared thermography: this is not suitable for superimposed bondings such as are found in propellants;
- optical holographic interferometry.

New techniques are currently being developed with the help of better-performing and more modern techniques for the recording and analyses of the image.

(c) New investigation methods

The purpose of these new techniques is to:

- remedy the shortcomings of classic radiography by, for instance, aiming for rapidly available information, in real time;
- provide a reception level tailored to the requirements;
- respond to the need for spatial observation;
- answer the necessity of recording the information obtained;
- find a high level of cost-effectiveness.

They include:

Televised radioscopy. This technique, which is increasingly used [19] and is perfectly suited for industrial production, provides the ability for continuous and dynamic observation (Fig. 21). It combines the use of television, video-taping and computers. Total observation in real time of a moving object is

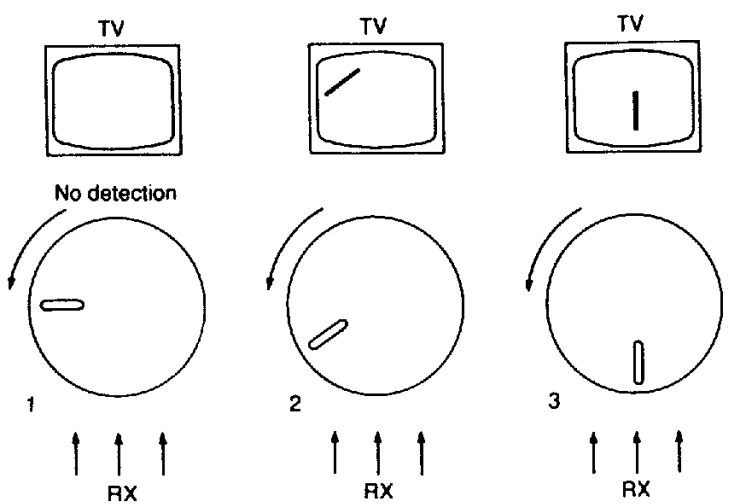


FIG. 10.21. Televised radioscopy: dynamic observation.

possible from a completely automatic observation post. This observation post is divided into three sectors:

- information gathering sector;
- analysis sector;
- memory sector.

Through its new design, this technique offers many advantages and contributes to significant savings in testing operations.

Observation with this new technique of, for example, 64 mm diameter propellant grains, allows us to guarantee the detection of 0.8 by 8 mm cavities, and of foreign objects with an average diameter above 0.5 mm.

Tomodensitometry. In the medical field, this technology is known as "scanning." It is the result of a logical evolution of tomography (Fig. 22), itself derived from radiography. It permits, using a computer, the reconstruction of images of successive slices of the object, providing a record on film of information that is not accessible with the classic X-ray method, in particular, the observation of the inner configuration of a specimen. Through a reconstruction of a succession of sections it reproduces the three-dimensional aspect of all areas of the object examined. As with televised radioscopy, the completely automatic control is an important advantage, permitting us to acquire, analyze and decide in real time, at a minimum cost (Fig. 23).

This imaging method, used until recently mainly for small objects, is now being applied to stages of ballistic missiles.

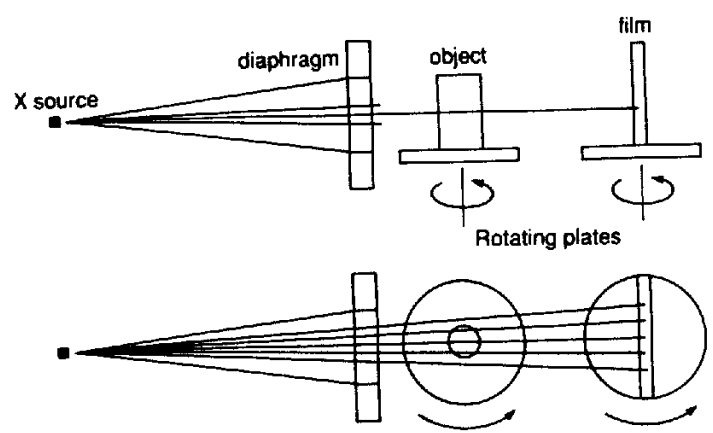


FIG. 10.22. Diagram of the tomography inspection.

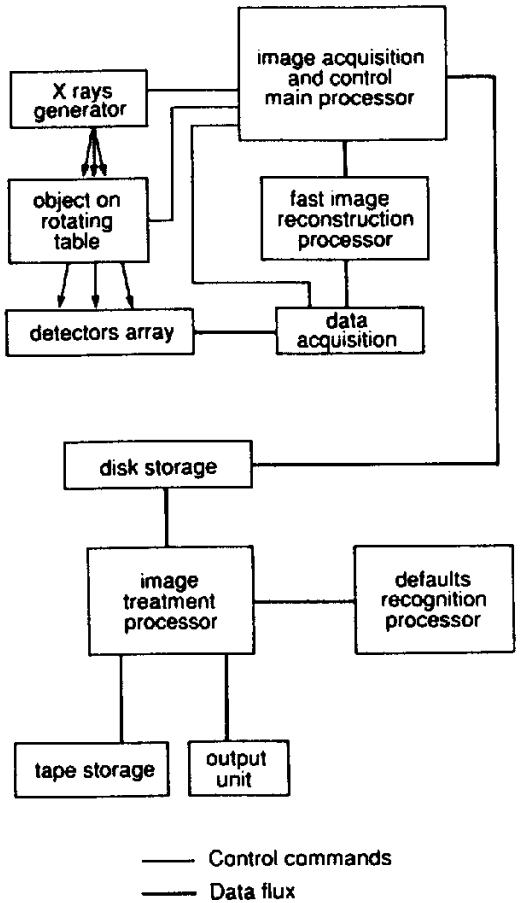
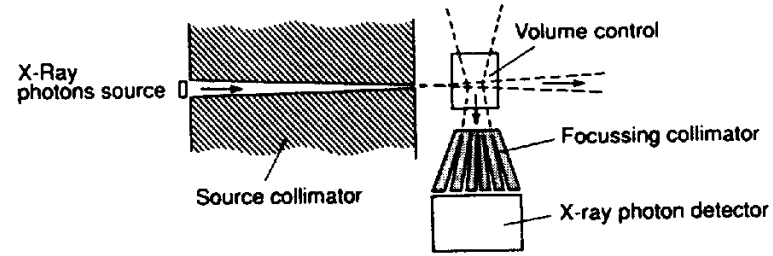


FIG. 10.23. Organization of a tomodensitometry set up.

Compton Scattering. This technique allows the reproduction of images by computers resulting from the observation of the Compton effect, the scattering of an X-ray or gamma-ray upon impact with the object examined. One of the advantages consists of having the source and the detector on the same side of the object (Fig. 24).

When only the periphery of a very thick object is being checked, this technique permits the use of less powerful X-ray generators than would be necessary with the tomodensitometry X-scanning.



Compton scattering technique for the detection and location of density anomalies in the material

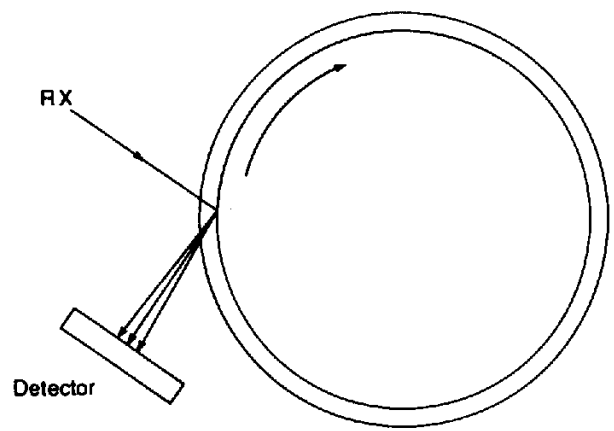


FIG. 10.24. Diagram of the principle of quality control with Compton scattering.

4. Properties of Composite Propellants

4.1. ENERGETIC AND COMBUSTION CHARACTERISTICS (STANDARD DELIVERED PRACTICAL SPECIFIC IMPULSE IS USED)

4.1.1. Isolites (polyurethane–polyether binder, ammonium perchlorate)

These non-metallized propellants are used essentially for gas generators, or as "sustainer" compositions for missiles where a low signature (absence of solid particles) is required.

The specific impulse, like the density, is low: some compositions where a portion of perchlorate has been replaced with nitroguanidine to adjust the burning rate at approximately 1-3 mm/s at 7 MPa do not exceed 180-190 s.

4.1.2. Butalites (polybutadiene binder, ammonium perchlorate)

The burning rate range of these "reduced smoke propellants" is much wider. They are used for the same purposes, and the tendency is to use them instead of Isolites. The reduced smoke propellants with the highest specific impulse attain I_s ranging from 235 to 239 s, with burning rates at 7 MPa which may exceed 60 mm/s if very fine ammonium perchlorate and a high percentage of ferrocene catalysts are used.

At lower burning rates, on the other hand, the impulses are comparable to those of non-metallized polyurethane propellants, because the ammonium perchlorate has to be replaced, in part, by a cooling charge.

4.1.3. Aluminized composite polyurethane propellants or Isolanes (polyurethane, ammonium perchlorate, aluminum)

The standard specific impulse rarely exceeds 240 s, and they are currently replaced by polybutadiene propellants.

4.1.4. Aluminized composite polybutadiene propellants or Butalanes (polybutadiene, ammonium perchlorate, aluminum)

The conventional aluminized composite propellants with the highest specific impulse, they are currently manufactured in very large quantities. They contribute an increase of 5 s over the best polyuretanes, with a density capable of reaching 1.86. They are used in the most powerful version of ballistic missiles, as well as in tactical missiles where the range of the burning rate (more than 60 mm/s at 7 MPa) and excellent mechanical properties are very valuable qualities.

4.1.5. Composites with HMX (Butalanes X)

These propellants, with some HMX added, offer a gain of 3-4 s in specific impulse over the best Butalanes, including, however, a small loss of density.

4.1.6. Solid post-boost system propellants: Butamites (polybutadiene binder, nitramine), and nitramine-based propellants

These propellants, which contain a hydrocarbon binder and a nitramine, are not used in main rocket motors because of their limitations in terms of specific impulse and burning rate. However, their kinetic characteristics, their "cleanliness" and the non-corrosive nature of their gases, and their specific impulse superior to that of AP propellants make them a better choice when severe temperature limitations (2000-2500 K) are placed on the combustion gases in gas generators, or for warhead dispersion systems of ballistic missiles [20]. An illustration is provided in Fig. 25.

The same types of binders are used as in typical propellants: polyesters, polybutadienes, and the nitramines are usually HMX or RDX.

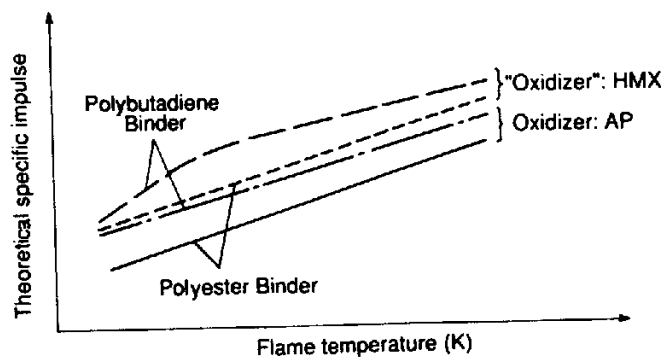


FIG. 10.25. Effect of substitution of AP by HMX for two types of propellants.

Their combustion is rather peculiar: low burning rates, a few millimeters per second; at low pressure, this burning rate increases with the solid loading ratio and decreases with the particle size of the nitramine. The pressure exponents, ranging between 0.5 and 0.7 at low pressure, tend toward 1 above 150 bars, and the burning rate becomes the same as that of pure nitramine [21,22]. This high exponent makes them particularly suitable for the modulation of the flow rate by varying the pressure.

4.1.7. Gas generator propellants: Butanites and Ammonium nitrate propellants

Also reserved for use with gas generators, these are the "coldest" of the industrially used propellants ($T_c < 1400$ K). Their burning rates are a few millimeters per second and their specific impulse is low [23,24].

4.2. MECHANICAL CHARACTERISTICS

These are discussed in Chapter 6; consequently, this section describes only certain aspects relating to the chemical composition: capability curves and the kinetic of the development of mechanical properties.

4.2.1. *Capability curve*

By plotting on a diagram (Fig. 26) the values of the maximum stress S_m versus the maximum strain for various values of the crosslinking or cure ratio — ratio of the reactive functions of the crosslinking agent and the polymer — we see that the corresponding point follows a curve characteristic of the given composition, called the capability curve. For small values of the crosslinking ratio the mechanical capability is very weak, and S_m and e_m decrease simultaneously. For high values of that ratio the elongation capabilities are very small. For values that are overall close to the stoichiometry, the aspect of the curve allows us to determine the best trade-off between S_m and e_m, i.e. determining the mechanical properties of the propellant. Changes resulting from different lots of raw materials — reflected by slight variations in the reactive function concentrations — must be such that, to be acceptable, an identical capability curve is obtained.

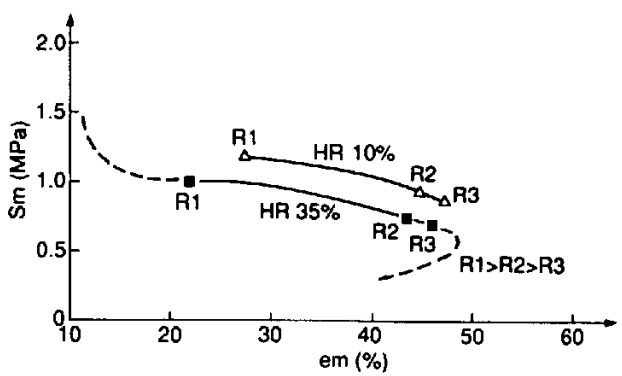


FIG. 10.26. Stress at maximum strain versus maximum strain as a function of the curing ratio (HTPB, AP, Al propellant).

4.2.2. *Cure kinetics and development of the mechanical properties*

The propellant grains that are being manufactured to be handled without being damaged must have mechanical properties that are virtually stabilized at the end of curing. This explains why the kinetics of the crosslinking must be well determined for each material developed, by measuring the cure state and the mechanical characteristics during the curing operation at various temperatures.

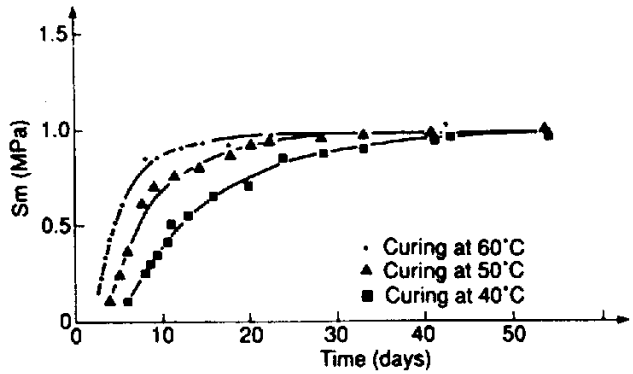


FIG. 10.27. Example of the build-up of maximum stress as a function of the curing temperature.

Figure 27 illustrates the evolution of the maximum stress over time for three cure temperatures. We note that:

- The energy that activates the crosslinking reaction is independent from the temperature, but slightly dependent on the progress of these reactions. The value of energy E which allows the best reproduction of the curve at different temperatures is close to 10 to 15 kcal/mole for propellants formulations based on carboxy or hydroxytelechelic polybutadiene.
- Since generally the cure temperature does not affect the final level of mechanical properties, we may assume that the state of the propellant mechanical properties after complete crosslinking is not dependent, at least within the useful range (40–60°C), on the cure cycle that is being used.
- A simple model can be used to predict the effect of a cure cycle. The development of the mechanical properties — maximum stress, for example — versus time is expressed by formula of the type: S_m/S_m stabilized = $f(Q)$ where Q, called "cure quantity," is related to the cure cycle.
- Having determined the relations S_m/S_m stabilized = $f(Q)$ allows us to predict the effect of a given cure cycle on the mechanical properties.

4.3. AGING OF COMPOSITE PROPELLANTS

Experience has shown that it is the mechanical properties that can be the most seriously affected by aging. The thermodynamic and kinetic properties are rarely modified.

There are numerous factors influencing aging, and their incidence varies according to the propellant considered.

4.3.1. Temperature

Temperature accelerates the multiple aging reactions, in various ways, depending on their activation energy.

In practice this means that the determination of the aging characteristics needs to be done at a temperature as close as possible to the temperature that will be really encountered, considering the diversity of the possible reactions, which the temperature does not all accelerate in the same manner.

4.3.2. The environment

Generally, air and humidity are aging factors by initiating oxidation and/or hydrolysis reactions:

- Oxidations of the double bonds of the binder causing an over-crosslinking, followed by a break of the chains through depolymerization.
- Hydrolysis of certain sensitive functions such as the esters bonds, and also the action of the water on the binder-oxidizer bond. Beyond a certain threshold of relative humidity (70-80%), AP absorbs the water, resulting in the destruction of the binder-oxidizer adhesion, eventually surface dissolution, and the acceleration of the oxidizing attack through the formation of perchloric acid.

4.3.3. Mechanical stresses

When the mechanical stresses exceed a certain threshold they may result in a degradation of the material by causing, for example, binder-solid separations.

An accumulation of the degradations (fatigue) may make the propellant useless, as is clearly demonstrated by the previously mentioned case of unstabilized ammonium nitrate propellant (Fig. 28).

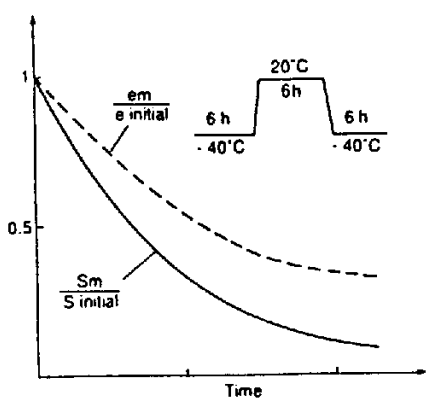


FIG. 10.28. Evolution of the properties of an AN-HTPB propellant during thermal cycles.

4.3.4. Contact with other organic materials

The propellant is bonded to a liner or a combustion inhibitor. Some of the elements which are not tied chemically may migrate from the propellant to the rubber; others may migrate in the other direction and significantly modify the composition at the interface with consequences which will naturally not only affect the mechanical properties and the characteristics of the bonding, but also the burning rate, through the migration of catalysts or plasticizers. This issue takes on a great importance for end-burning grains where the burning rate may be greatly disturbed alongside the inhibitor, and cause a modification in the combustion parameters.

4.4 SAFETY CHARACTERISTICS AND PYROTECHNIC BEHAVIOR

The composite propellant types Isolite, Isolane, Butalite, and Butalane generally exhibit high critical detonation diameters, over 1 m, and a low sensitivity. The introduction of oxidizers likely to detonate such as RDX and HMX will of course decrease the critical diameter, but composite propellants may generally be considered not to be very sensitive, thus fulfilling rather well the specifications for low vulnerability or lower risk. The major mode of decomposition from stimuli such as friction, shock, impact, or fire, is combustion. Ammonium perchlorate composite propellants may, however, exhibit a violent reaction (thermal explosion) at slow cook-off, i.e. a few degrees per hour temperature increase.

In terms of the manufacture, an analysis of the history of accidents that have occurred in the composite propellant industry certainly shows that, outside of special cases where the cause is foreign to the product itself (presence of foreign bodies, external stimuli, or equipment malfunction for example), and until the development of high burning rate propellants and HTPB binders, the major causes of accidents were linked to the handling of the wastes, more or less inhomogeneous, of perchlorates and other oxidizers contaminated with grease or organic matters, or to mixtures (dust, for example) of solid oxidizers and fuels. This explains why, in the manufacture of propellants, very rigorous attention must be paid to keeping oxidizers apart from fuels, to the cleanliness of the facilities, and to the handling of wastes or objects contaminated with propellants. Explosions, even detonations, have occurred during the destruction of wastes by burning. Their origin is a transition of combustion to detonation in this sometimes porous and inhomogeneous medium.

Experience, coupled with a systematic characterization of the sensitivity of all products at every stage of the manufacture, has permitted the establishment of concrete measures, reflecting the safety margins of operations carried out during production, that towards the end of the 1960s have generally become the standards for this industry. These measures have had to be

drastically amended, however, with the development in industrial manufacture of two new products: high burning rate propellant with ferrocene additives and HTPB binders which, by making the propellant a very poor conductor, have caused ignitions of electrostatic origin.

4.4.1. High burning rate propellants

High burning rate aluminized composite propellants containing high levels of ferrocene derivatives have been at the origin of many accidents that have occurred in the industry during recent years [25]. This does not mean that they should be rejected because, as we saw, they have unique operational characteristics. However, their greater sensitivity, associated with more violent effects, demands that the production, handling and quality control methods be thoroughly reassessed.

Table 10 lists a certain number of sensitivity characteristics of typical polybutadiene-AP-Al propellants and of propellants with a ferrocene derivative. The sensitivity tests were performed in accordance with the codified standards of SNPE (Chapter 7).

The reactivity of the mixture of ammonium perchlorate with a ferrocene derivative determines the pyrotechnic behavior of the propellant.

Indeed, mixtures of pure products are sensitive to mechanical stimuli, with a sensitivity level identical to that of granular explosives or of a pyrotechnic ignition powder. These characteristics, listed in Table 11, determine the behavior of the finished product, and require that special precautions be

TABLE 10 *Sensitivity characteristics of aluminized polybutadiene composites (Butalanes) with a ferrocene derivative*

	Stimuli				Mode of decomposition		
	Thermal		Mechanical		Detonation		
Test	*AI*[a] (°C)	Cook-off (°C)	CSF (N)	Shock[b] (m)	*CGT*[c]	*CDD*[d] (mm)	Combustion *V*[e] (mm/s)
With ferrocene derivative							
20-30 mm/s	220	155	50-70	1.75	<1	60	4-3
30-50 mm/s	196		50-70	1.25	<1	60	4-5
50 mm/s	190		30-50	0.50	<1		>6
Without ferrocene derivative							
7-9 mm/s	320	175	140	2-3	<1		1
12-15 mm/s	265	175	90	1.75	<1		1

[a] *AI* = Autoignition temperature, heating at 5°C/mm.
[b] Shock = 30 kg drop hammer test, no-reaction height.
[c] *CGT* = Detonation aptitude index, number of cards (French).
[d] *CDD* = Critical detonation diameter.
[e] *V* = Burning rate at atmospheric pressure.

TABLE 11 *Sensitivity of mixtures of ammonium perchlorate/ferrocene derivatives compared with explosives*

Test	Pure AP	50/50	72/25	90/10	95/5	HMX	PETN	MIRA*
CSF (Newtons) (friction Julius Peters)	>360	37	20	22	35	100-200	40	34
CSI (Joules) (impact Julius Peters)	13	5	3	3	2	4-5	3	6
Autoignition (5°C/mm)°C	~400	275	260	260	295	256	184	300

* Pyrotechnic ignition composition.

observed for the production. In addition, the ferrocene derivative facilitates the decomposition of perchlorate. Analyses have shown a decrease of the order of 150°C in the exothermic decomposition peak of the ammonium perchlorate decomposition. Consequently:

- the higher the content of ferrocene derivative,
- the higher the content of perchlorate,
- the smaller the particle size of the AP,

the greater the reactivity will be.

4.4.1.2. Decomposition modes

(a) Detonation

The critical diameter of these propellants is much smaller, in some cases as small as 60 mm, setting them clearly apart from those other types of composite propellants, although their response is measured by less than one card at the card gap test.

(b) Combustion

The thermal effects of these formulations present a major threat during manufacturing operations. This is due to the fact that the combustion propagates very rapidly to the surface of the specimen following an accidental ignition.

The regression rate measured during a strand burner test, at atmospheric pressure, is greater than 3 mm/s, and increases with the amount of ferrocene catalyst. A test done on a small star-shaped grain shows that a flame 1 m long appears in a few tenths of a second. This vigorous ignition capability must be taken into account in the determination of the protective zones for the personnel during manufacture, and can require remote operations.

4.4.1.3. *Sensitivity to mechanical stimuli*

(a) Shock

In a 30 kg drop hammer test, a 4 m fall does not lead to a detonation, and the effects are hardly more violent than the effects obtained with typical compositions. The non-reaction height, however, is much lower than with typical propellants, which show no reaction below a drop of 2 m: the results varied between 0.50 m and 1.75 m.

(b) Friction

These compositions are sensitive to friction, in the conditions created by the Julius Peters testing device (0.4 mm thick blades). Strong reactions were observed, and the higher the content of ferrocene derivative, the more sensitive the compositions are (Fig. 29).

While typical propellants have CSF values greater than 70 N, these propellants exhibit values ranging between 50 and 70 N, lower values can be recorded for formulations whose burning rate at 7 MPa is greater than 50 mm/s.

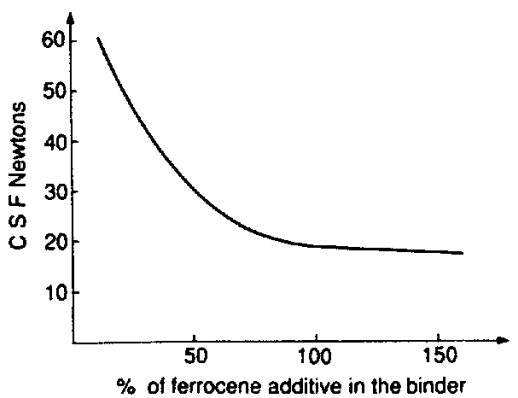


FIG. 10.29. Friction sensitivity.

4.4.1.4. *Sensitivity to thermal stimuli*

(a) Autoignition temperature

The presence of ferrocene accelerator lowers the autoignition temperature to approximately 200°C, and triggers violent decomposition phenomena in specimens that are not observed with typical propellants, whose reaction temperature is close to 300°C.

(b) Cook-off

The thermal stability of compositions accelerated by a ferrocene derivative is lower than that of typical propellants, and this is more so when the particle size of AP decreases and the amount of ballistic catalyst increases. Cook-off tests performed with a specimen 50 mm in diameter and 50 mm in height have demonstrated a 50°C decrease of critical temperature, which, however, continues to be higher than 125°C.

4.4.1.5. *Sensitivity to static electricity*

These propellants are sensitive to capacitive discharges only above a certain amount of aluminum (SNPE Test No. 37). Although above that particular amount, the aluminum quality (shape and size of particles) plays a fairly significant role in this type of stimuli, mechanical characteristics and temperature may also be important factors.

4.4.1.6. *Production safety measures*

While thermal effects are the acknowledged major threat from these compositions when polymerized, it is nonetheless necessary, because of the reactivity of the ferrocene derivative with ammonium perchlorate, to adopt preventive measures for mixing these components.

Ferrocene derivative, for example, may contain volatile ingredients (pure ferrocene), which by condensing on the cold parts of the mixer, may lead to mixtures with AP dust that are particularly sensitive to mechanical stimuli.

In general, these manufacturing operations are done under the highest safety conditions practiced by the industry.

The sensitivity of the various composite propellant families can be illustrated with the diagram of autoignition temperature versus sensitivity to friction shown in Fig. 30.

4.4.2. *Detailed presentation of the problems related to sensitivity to static electricity*

Table 12, where the resistivities at 20°C of various binders are given, shows that the historical development of these binders was accompanied by an increase of their insulating nature. It is therefore logical that during the manufacturing process that necessarily includes handling, friction, and movement of insulating and conductive materials, we would see an increasing number of occurrences with an electrostatic origin, such as electrostatic discharges that not only are an impressive sight, but also may lead to mechanical rupture of the materials.

The development of these propellants was combined with a development of

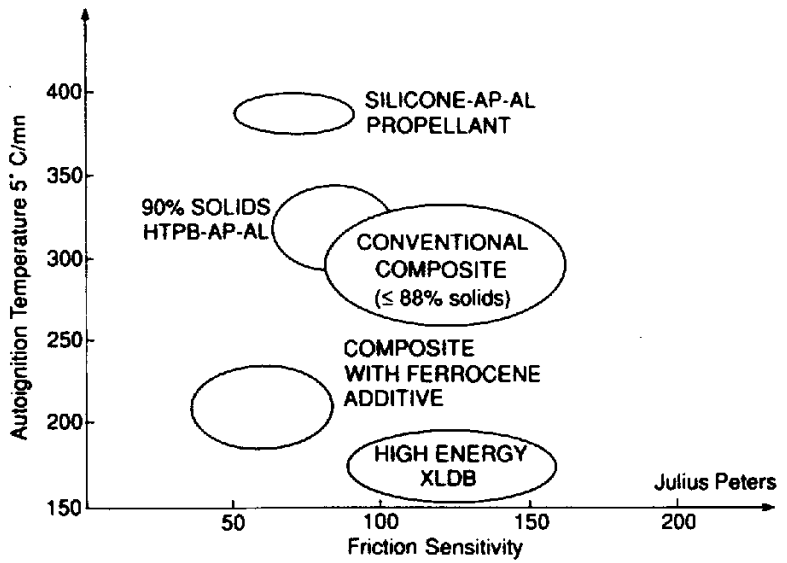


FIG. 10.30. Propellant families sensitivities.

TABLE 12 *Volumetric resistivity at 20°C of the major binders of composite propellants, and of several materials*

Nature	Resistivity (Ω m)
PU binder (polyurethane based on polyoxypropylene glycol)	6×10^8
CTPB binder	7×10^9
HTPB binder	2×10^{12}
PVC inhibitor	10^{12}
Thermal insulation rubber	10^{12}
Thermal insulation rubber, treated for conductivity	10^4

the insulation and case materials. Metallic cases, for example, were replaced by highly insulating composite cases that could only aggravate the problems: the Faraday cage effect of the case disappeared, and the propellant became sensitive to outer electric fields.

Traditional tests to determine sensitivity to electrostatic discharge, typically adapted from tests used for pyrotechnic powders, classified the composite propellants as insensitive but at the same time, accidental ignitions were happening during their manufacture. Little by little the origin of these ignitions was traced back to static electricity. It was SNPE researchers who identified the phenomenon [27,28], created a model reproducing the incidents observed during manufacture, recommended practical measures to minimize these phenomena and, finally, partially clarified the mechanisms involved.

The so-called capacitive discharge test was described in Chapter 7.

For propellants identified as sensitive to capacitive discharges, the analysis of the phenomena observed, such as the occurrence of the cracking phenomenon before the ignition phenomenon, suggests that the reaction mechanism can be broken down into two essential phases:

1st phase Emergence of a cracking phenomenon, related to a critical potential,

2nd phase Emergence of an ignition phenomenon, related to a specific critical energy.

All observations tend to demonstrate that the reaction begins inside the propellant. The existence of a critical potential shows that cracking is caused by one or several electric phenomena.

Among those electric phenomena that have been identified, discharges between aluminum particles may be considered as the most likely one:

- Aluminized compositions alone were found to be sensitive.
- The volumetric resistivity of pure aluminum powder shows that for a given critical potential, the value of resistivity changes from 10^7 to 10^3 Ω m. This corresponds to a puncture, for a certain number of particles of the aluminum oxide layer that covers the pure aluminum.

A factor analysis of the active ingredients of propellants essentially revealed the influence of:

- ratio, particle size and shape of aluminium particles;
- particle size of ammonium perchlorate;
- resistivity of the binder.

Temperature must also be taken into consideration. Some propellants that are insensitive may become sensitive when the temperature is lowered. When the aluminum ratio is constant, the decrease in diameter of the aluminum particles, i.e. their increase in number, leads to compositions that are more sensitive to capacitive discharges.

A model based on percolation theories was suggested. A "percolation" coefficient P was identified, such that:

$$P = \frac{N_c/N_i}{\sigma_L/V_L}$$

$P > 10^{10}$ Ω m for sensitive propellants;
σ_L = conductivity of the binder;
V_L = unit volume of the binder;
N_c = number of conductive particles (aluminum);
N_i = number of insulating particles (ammonium perchlorate, HMX).

With ammonium perchlorate we note that the influence of the particle size plays a role inverse to that of aluminum.

In addition, the volumetric resistivity measurements of binders have demonstrated that the polyurethane binder with a polyether prepolymer base is the least resistive. Both polybutadiene binders, on the contrary, are much more resistive (HTPB binder resistivity at 20°C: $7 \times 10^9\ \Omega$ m; HTPB binder resistivity: $2 \times 10^{12}\ \Omega$ m).

This classification, based on resistivities, also works well for the sensitivity scale of propellants. For instance, polyurethanes are not sensitive at 20°C, and among the polybutadiene HTPBs are the most sensitive.

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