CHAPTER 11

Advanced Energetic Binder Propellants

RENÉ COUTURIER

1. Background

1.1. DEFINITION OF ADVANCED ENERGETIC BINDER PROPELLANTS FAMILY

This family includes all propellants composed of a nitrate ester-based energetic binder in which fillers (oxidizer and, if necessary, metallic fuel) are incorporated.

Due to their composition, these propellants are intermediate between the double-base propellant family (nitrocellulose + nitroglycerine or other liquid nitrate ester) and the composite propellant family (inert binder + charge). Two very different processes can be used to manufacture them.

- A casting solvent process which uses the manufacturing system for traditional double-base propellants. The products manufactured by that process are called composite modified cast double-base propellants (CMCDB) or elastomeric modified cast double-base if they include an isocyanate curable elastomer.
- A slurry cast process similar to the process used to produce composite propellants. These products are referred to as crosslinked double-base propellants (XLDB) or NEPE propellants (nitrate ester-polyether binder including high level of fillers) for specific high energy propellants.

1.2. ADVANTAGES OF ADVANCED ENERGETIC BINDER PROPELLANTS

The necessity to improve performance of conventional propellants for tactical and strategic missiles was at the origin of the development of this propellants family.

Chronologically, the CMCDB propellants were manufactured industrially before the XLDB. Production began in the United States in the 1950s [1,2]. They were a logical continuation of double-base propellants which had significantly evolved since World War Two. As a matter of fact, the transition from a single-base casting powder (nitrocellulose) to a double-base powder (nitrocellulose + nitroglycerine) had allowed a remarkable energetic improvement as well as the possibility of tailoring corresponding propellants to the production of case-bonded grains, due to the improvement of their mechanical properties.

The inclusion of fillers such as nitramines, ammonium perchlorate, and aluminum in double-base casting powder was an additional step toward improvement of the energetic characteristics.

The development of CMCDB propellants, however, ran rapidly into a number of limitations, particularly when applied to strategic missiles, due to the manufacturing process involved. These limitations include:

- impossibility of obtaining solids contents that were as high as those of composite propellants;
- difficulties tied to the production of large case-bonded grains with high fillers contents and increasingly complex geometries.

Because of the potential advantages of these propellants, the formulations were redesigned with the purpose of applying new manufacturing processes. By substituting a nitrocellulosic polymer with synthetic polymers capable of higher plasticizer amounts as well as a high solid content, a manufacturing process related to that for composite propellants could be used. With the advent of XLDB or NEPE propellants a new step had been taken toward the improvement of the performance of strategic and tactical missiles. This family of propellants led to the highest energetic levels that are in fact industrially feasible.

2. Raw Materials

2.1. BACKGROUND

The formulation of a propellant may seem, initially, to be a simple operation, consisting of mixing additives inside a binder. In reality it is a complex operation, requiring that the grain designer takes into account all constraints related to the design of a propellant grain with those of the manufacturing process; for example:

- meeting the performance requirements (ballistic, mechanical, reliability, and safety of handling);

- tailoring of the manufacturing process in order to produce good quality and reproducible propellants, at the lowest cost, and under the best possible safety conditions.

Empirical knowledge inherited from tradition on the one hand, and the emergence of better technical tools on the other hand (computer codes, for example), help determine the best possible solutions to the problems at hand. Nevertheless, before a goal can be successfully achieved it must be assumed that, within a well-established manufacturing process, the raw materials, i.e. the basic ingredients of the propellant, are perfectly known. This implies:

- on the one hand, an in-depth characterization of each of the raw materials;
- on the other hand, the knowledge of their behavior toward each other, i.e. the study of their chemical compatibility. Because propellants are constituted, in large part, of high-energy additives, there naturally exists a problem of reactivity from ingredients likely to be mixed.

Preliminary chemical compatibility analyses are therefore mandatory for any new system. Based on the results obtained, the grain designer may or may not decide to include these additives.

The principle of the chemical compatibility tests typically is based on measurements of the gaseous emissions of vacuum-tested specimens, versus time and temperature. Additional tests may be needed to support the verdict when difficulties are encountered:

- measurement of the enthalpy of decomposition;
- analysis of the decomposition gases;
- use of chemiluminescence for nitrated derivatives testing

2.2. BINDER INGREDIENTS

2.2.1. Composition of advanced energetic binders

2.2.1.1. CMCDB binder

The major ingredients of CMCDB binders are:

- Polymer: nitrocellulose;
- Energetic plasticizer: nitroglycerine;
- Desensitizing plasticizers: glycerol triacetate (or triacetin);
- Other inert plasticizers: (if necessary): aliphatic or aromatic esters,
- Stabilizers: centralite, 2-nitrodiphenylamine.

With the casting solvent process, binder final composition is acquired in two phases:

First phase: manufacture of a casting powder, with a binder consisting of the nitrocellulose and possibly a portion of the energetic plasticizer.

Second phase: the plasticizer complement is included during the operation where the solvent (nitrate ester + desensitizer) is cast in the mold loaded with the casting powder.

Depending on the plasticizer amount, it may be necessary to crosslink the nitrocellulosic network to obtain a good mechanical behavior of the propellant.

2.2.1.2. *XLDB (or NEPE) binder*

The major ingredients of XLDB (or NEPE) binders are:

- Polymers: nitrocellulose, polyesters, polyethers, polycaprolactones and others;
- Energetic plasticizers: nitroglycerine, butanetriol trinitrate, triethyleneglycol dinitrate, and others;
- Non-energetic plasticizers: if necessary;
- Curing agents: polyisocyanates;
- Chemical stabilizers

With the slurry process the binders are always highly plasticized, and therefore crosslinked.

To be of any advantage, the prepolymers must exhibit specific properties:

- They must be liquid during the premix elaboration (prepolymer and energetic plasticizer).
- They must be capable of handling high plastification ratios without exhibiting any exudation phenomena after crosslinking.
- These prepolymer-plasticizer premixes must be capable of accepting high solids contents (approximately 77-80%) and still be cast into complex shapes. In this regard, the rheology theory of the flow of composite propellant slurries is applicable.
- After crosslinking, they must keep their elastomeric-type properties so as to be more capable of withstanding significant elongations over more or less wide ranges of temperature. This is due to the fact that XLDB propellants are used mainly in case-bonded grains.

2.2.2. *Polymers*

2.2.2.1. *Nitrocelluloses*

Nitrocelluloses, discussed in Chapter 9 on double-base propellants, are primarily characterized by their nitrogen content. The physicochemical and energetic properties of the polymer derive from that characteristic.

Nitrocelluloses used in rocket propulsion have nitrogen contents ranging between 11.5% (Q_v = 800 cal/g) and 13% (calorimetric value = 1010 cal/g). In the case of the CMCDB, however, nitrogen contents close to 12.5% are particularly well suited because the corresponding nitrocellulosic polymers allow one to meet specific requirements such as:

- inclusion of solid charges (such as oxidizers, fuels);
- introduction of high percentages of plasticizers.

However, nitrocelluloses are semi-crystalline polymers that, unlike polyesters or polybutadienes, do not have the chain flexibility that facilitates the incorporation of high contents of charges (70-80%). With CMCDB, whose basic polymer is nitrocellulose, the solids content compatible with satisfactory mechanical performance is limited to approximately 45%.

2.2.2.2. *Non-energetic prepolymers*

The prepolymers, which must be liquid at the temperature of the manufacturing process, and which are capable, after crosslinking, of both high plasticizer and high solids contents, are recruited essentially from hydroxy terminated polyesters and polyethers. Combined with isocyanates, they will give polyurethane networks.

Some prepolymers that are particularly interesting for XLDB or NEPE propellant are listed in Table 1.

So far, the most widely used prepolymers are the ethylene or diethyleneglycol polyadipates and the polyoxyethyleneglycols (PEG). At ambient temperature, PEG are usually found in a solid state, with a crystalline structure. They are, however, easily melted at temperature compatible with the use of energetic plasticizer (50-60°C). When exposed to high levels of plasticizers the PEG lose their crystalline structure.

The molecular mass of prepolymers ranges from approximately 1500 to 5000. In practice they are adjusted as a function of the propellant specific characteristics (mechanical properties, especially).

2.2.2.3. *Future developments* [3]

The performance improvement of XLDB propellants could conceivably be made by replacing today's inert polymers with energetic products, keeping, if

TABLE 1 *Some common inert prepolymers*

Prepolymer	Formula	Density ρ (g/cm^3) at 25°C
Polycaprolactone	$HO-[-(CH_2)_5-\overset{O}{\overset{\|}{C}}-O-]_n$	1.15
1.4 Butanediol polyadipate	$HO-[-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-]_n$	1.18
Ethyleneglycol polyadipate	$HO-[-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-]_n$	1.12 (solid) 1.19 (melted)
Diethyleneglycol polyadipate	$HO-[-(CH_2)_2-O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-]_n$	1.19
Polyoxypropyleneglycol (PPG)	$HO-[-CH_2-\underset{CH_3}{\underset{\|}{C}}H-O-]_n$	1.03
Polyoxypropyleneglycol (PEG)	$HO-[-CH_2-CH_2-O-]_n$	1.21 (solid) 1.11 (melted)

possible, the same properties. The synthesis process consists generally of grafting chemical groups with energetic characteristics on the polyester or polyether chains, such as: azide, nitro, nitrate, nitramine, fluoronitrate, etc.

2.2.3. *Energetic plasticizers*

Energetic plasticizers used in mass production are, for the most part, polyalcohol nitrates (Table 2).

Among these nitrate esters, nitroglycerine is still the most widely used, because of the high values of its calorimetric value (Q_v) and its density. Its drawbacks (vapor pressures, which are rather significant over 50°C, sensitivity to mechanical stimuli, and lower thermal stability over 100°C) are fully appreciated due to the experience acquired, for several tens of years, with double-base propellants.

The development of XLDB or NEPE propellants, with high plasticizers ratios, and whose composition is becoming increasingly different from that of double-base propellants, requires that a choice be made of the nitrate ester best suited to the requirements other than the energetic aspect. These criteria include:

- chemical and thermal stability;
- volatility;
- propensity to migrate;
- manufacturing cost;
- explosive behavior (mechanical stimuli, for example);
- physical and chemical compatibility with the various propellant additives.

Finally, a major effort is being devoted to the synthesis of new energetic plasticizers in order to correct some undesirable characteristics of today's nitrate esters. For example, molecules carrying nitrated groups ($R-NO_2$), azides ($R-N_3$) and fluoronitrated groups are being tested.

2.2.4. *Inert plasticizers*

The plasticizers incorporated in the advanced energetic propellants are similar to those used in the cast double-base propellants (see Chapter 9). They fulfill, in particular, the same functions: improvement of the manufacturing conditions, and/or of some functional properties of the propellant (ballistic, mechanical, safety).

The most common plasticizers carry ester functions:

TABLE 2 *Characteristics of nitrate esters widely used in rocket propulsion**

Composite	Abbreviation	Chemical Formula	ρ (g/cm³)	ΔHF (cal/g) p constant	Qa (cal/g)	Melting Point (°C)	Vacuum Stability at 200 h (cm³/g) 80°C	100°C
Nitroglycerine	NGL	$CH_2(ONO_2)-CH(ONO_2)-CH_2(ONO_2)$	1.600 (25°C)	−405	+1750	+13 (stable) +3 (instable)	1.6	23
Triethyleneglycol dinitrate	TEGDN	$CH_2(ONO_2)-CH_2-O-(CH_2)_2-O-CH_2-CH_2(ONO_2)$	1.327 (22°C)	−626	+616	−25	0.2	1.6
Butanetriol trinitrate	BTTN	$CH_2(ONO_2)-CH(ONO_2)-CH2-CH_2(ONO_2)$	1.520 (20°C)	−283	+1570	−11	1.7	16
Trimethylolethane trinitrate	TMETN	$CH_3-C(CH_2ONO_2)_3$	1.4568	−364	+1220	+15 +2	0.9	8.7

* The values indicated in this table have been measured at SNPE.

Glycerol triacetate (or triacetin):

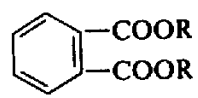
$$CH_2(OCOCH_3)-CH(OCOCH_3)-CH_2(OCOCH_3)$$

n-alkyl adipates:

$$RO-C(=O)-(CH_2)_n-C(=O)-OR$$

$(R = CH_3, C_2H_5, \ldots, C_8H_{17})$

n-alkyl phthalates:



$(R = C_2H_5, C_4H_9, \ldots, C_8H_{17})$

2.2.5. *Curing agents*

Crosslinking is necessary:

- For propellants using highly plasticized nitrocellulose, in order to strengthen the existing three-dimensional polymeric network whose chains, held by low-energy links (Van der Waals or hydrogen type), are stretched by an excess of plasticizer.
- When using hydroxy-terminated prepolymers, also in a highly plasticized environment; these prepolymers are usually liquid during the mixing (global process).

The curing agents are designed to react with some functions of the polymers or prepolymers so as to create a three-dimensional network that will ensure the cohesion of the cured propellant and, as a result, determine its mechanical properties.

The polyisocyanates are the most used with the energetic binder propellants. Diisocyanate may be enough to ensure the spatial cohesion of nitrocellulose. With diol prepolymers this cohesion can be ensured either with a system of triol/diisocyanate or with a polyisocyanate having a functionality greater than 2. Some of the polyisocyanates widely used in the field of crosslinked propellants are listed in Table 3.

The crosslinking density, which influences the mechanical properties of the final propellant, is controlled by:

- the NCO/OH ratio, which expresses the relationship between the number of available isocyanate functions and the number of alcohol functions;

TABLE 3 *Some common isocyanates*

Type	NCO/kg
Diisocyanates	
Hexamethylene diisocyanate (HMDI)	11.7
Toluene diisocyanate (TDI)	11.4
Isophorone diisocyanate (IPDI)	8.9
Functionality polyisocyanates > 2	
Tri(isocyanato-6 hexyl)-1.3.5 biuret	5.2

- the ratio: (OH of the triol)/(OH of the diol) with diol prepolymers involving a diisocyanate-triol system;
- the nature and the amount of crosslinking catalyst.

For a given composition, in a well-defined environment (temperature, agitation speed), the crosslinking kinetics depends on the nature of the polyisocyanate. It may, however, be regulated by adding catalysts. Very basic amines such as triethanolamine, frequently used for the manufacture of polyurethanes, are prohibited with energetic binders because of their great chemical incompatibility with nitrate esters.

The burning rate modifiers, particularly lead-base, also have a crosslinking catalyst effect, more or less pronounced according to their nature (Example: PbO, PbO_2).

2.3. FILLERS

Performance improvement of energetic binder propellant requires the incorporation of fillers (oxidizers or mixture of oxidizers and fuels).

The maximum of the solids content, compatible with good feasibility and acceptable mechanical properties, is determined by:

- manufacturing process (casting solvent or slurry cast);
- binder composition (nature of the polymer, plasticizing ratio);
- shape and size of the solid particles. The use of several particles sizes — whose average diameter ratios range between 5 and 10 — facilitates high fillers contents;
- use of bonding agents facilitates higher solid level as well as particles greater than 10 microns.

2.3.1. Oxidizers

The most common oxidizers used in the advanced energetic propellants are:

- Ammonium perchlorate (NH_4ClO_4)
- Nitramines:
  RDX ($C_3H_6N_6O_6$)
  HMX ($C_4H_8N_8O_8$)

Their main characteristics are discussed in Chapter 10.

2.3.1.1. Ammonium perchlorate

Incorporated in energetic binders, this oxidizer decreases the self-ignition temperature. Compatibility tests performed on ammonium perchlorate-nitrate ester mixtures reveal a special behavior, which is expressed by a first phase devoid of any noteworthy production of gas, followed by a sudden emission accompanied by a fairly violent decomposition phenomenon.

2.3.1.2. Nitramines

The nitramines are:

- *RDX* or cyclomethylenetrinitramine,
- *HMX* or cyclomethylenetetranitramine

RDX crystallizes in an orthorhombic form. HMX, on the other hand, may present four crystalline varieties (α, β, γ and δ). Only the form β, thermodynamically stable and the least sensitive to mechanical stimuli, is used for industrial manufacture. Both varieties α and γ may occur, however, based on the nature of the recrystallization solvent that is used. As for form δ, it is found only beyond 160°C.

As a result it is necessary, during the manufacture of energetic binder propellants, to prevent any possibility of solubilization of HMX (in the cleaning solvent of the tools, for example), to avoid being faced with the risk of later recrystallization in α or γ varieties, which are more sensitive.

Nitramines are powerful explosives, sensitive to shock and to friction. They must therefore be handled with all precautions inherent in high explosives: avoid the creation of dusts and friction areas; use remote handling during the most delicate operations.

RDX and HMX have similar thermodynamic characteristics, but because HMX has a higher density it results in more energetic propellants (if the volumetric specific impulse is considered).

Finally, it must be noted that the manufacturing costs of HMX are much higher than that of RDX.

2.3.1.3. *New oxidizers*

The synthesis research is essentially devoted to the development of dense, high energy molecules [3]. New specifications have been emerging, however:

- reduction of the sensitivity (related to the development of propellant with lower vulnerability);
- possibility of controlling the burning rates.

2.3.2. *Fuels*

Aluminum is widely used in advanced energetic binder propellants as a solid fuel. It is a metal with a high combustion heat, allowing an increase in the burning temperature of propellants. However, for its combustion, a sufficient quantity of available oxygen is necessary. As a result, in the case of high-energy propellants the oxidizer/fuel ratio must be adjusted in order to optimize the specific impulse.

2.4. VARIOUS ADDITIVES

2.4.1. *Chemical stabilizers*

Advanced energetic binder propellants, like all other double-base propellants, present a problem of chemical stability, inherent in the slow decomposition of the nitrate esters.

To delay this self-decomposition phenomenon, additives with a slightly basic nature are incorporated in the propellants, so as to block the nitrogen oxides that are released. The most widely used stabilizers have been described in the chapter on double-base propellants (Chapter 9).

Use of very energetic crosslinked propellants, that sometimes include the combination of products that are not very chemically compatible (nitroglycerine-ammonium perchlorate, for example), requires the development of ever more efficient new stabilizing systems. The criteria for selection are usually based on the following factors:

- the highest possible nitrosation kinetics;
- good solubility of the stabilizer in the propellant;
- good thermal stability of the nitrosated derivatives.

2.4.2. *Ballistic modifiers*

Energetic binder propellants without ammonium perchlorate can be characterized, in a first approximation, by a burning law of the type $r_b = a\,p^n$

where n, the pressure exponent, is generally high ($n > 0.8$). For these propellants to hold any interest it is necessary to decrease their pressure exponent and to be able to regulate their burning rate.

Burning rate modifiers incorporated in advanced energetic propellants usually come from the classic double-base propellants [3].

2.4.3. *Other additives*

Specific additives may be included in propellants to take into account the operating characteristics of the grain or its type of application, e.g. instability and/or flash suppressor additives.

3. Manufacturing Processes

3.1. MANUFACTURING PRINCIPLES OF ADVANCED ENERGETIC BINDER PROPELLANTS

The manufacture of these advanced propellants may be done according to two techniques with very different principles:

- A casting solvent process consisting of two major steps:
  - manufacture of a casting powder, made of the nitrocellulosic binder containing all solid additives, and if necessary, a portion of the energetic plasticizer;
  - manufacture of the propellant by injection of a casting solvent into a mold loaded with the casting powders defined for the preceding process; this casting solvent is composed of a nitrate ester and desensitizer mixture. The cohesion of the whole is obtained by curing.
- A slurry cast process is related to the manufacturing process of composite propellants. Its principle is based on the preparation of a slurry, containing all constituent elements of the propellant, which can be poured into the mold either by gravity or by injection. The cohesion of the whole is obtained during curing by the crosslinking of the polymer.

3.2. MANUFACTURING PROCESS OF CMCDB PROPELLANTS

CMCDB propellants are in fact an extension of the cast double-base propellants. Consequently, their manufacturing process is similar to that described in Chapter 8. Therefore, some adjustments are necessary by the presence of fillers, or of necessity of crosslinking.

3.2.1. *Influence of solid fillers (e.g. nitramines, ammonium perchlorate)*

In the manufacturing process of casting powders the charges are introduced during the kneading of the dough. The solvents composition must be optimized to promote the coating of these charges by the nitrocellulosic binder in order to obtain densities that are as high as possible in the finished granules.

In addition, the presence of the fillers is likely to modify the surface of the casting powder (creation of roughness, for example), which has the direct consequence of altering the packing density.

3.2.1.1. *Remarks on the screen loading density (SLD) and the packing density*

To evaluate the packing density, measurements of the screen loading density (defined by the powder weight in a determined volume) are done on the casting powder. These gravimetric densities depend on several parameters:

- density of the granules;
- their geometry: size, length/diameter ratio;
- imperfections of their surface, which affects the flow (importance of the glazing cycle);
- filling method.

According to the theoretical analyses [5] that have been done on casting powders, the screen loading densities are at their maximum when the L/D ratios are close to 1 (Fig. 1). Experimentally, it is preferable to use a L/D ratio

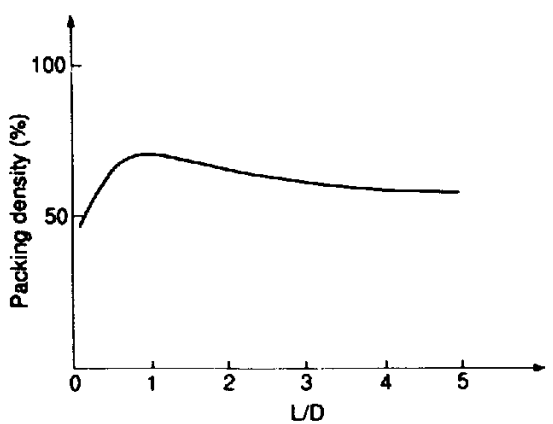


FIG. 11.1. Evolution of the packing density of the molds versus the L/D ratio of casting powders.

close to 1.2 to be in an area of the diagram capable of tolerating some scattering of the dimensions, without necessarily having a significant influence on the packing densities.

The presence of solid charges in the casting powders influences noticeably the values of SLD. Increasing the particle size for a constant filler content or increasing the filler content for a constant particle size leads systematically to a decrease of SLD. The aspect of the surface alone is responsible: more or less granular aspect, which inhibits the sliding of the grains against each other. Figure 2 shows the evolution of SLD of the casting powders loaded with 60% fillers when the particle size changes from 90 μm to 15 μm. The volumic packing density of the mold follows the same tendency. As for the role played by the fillers contents, it is made quite clear in Table 4.

To increase the packing density one may:

- work with the size of the casting powder (Table 5);
- adapt the industrial process for filling the molds; for example, there are

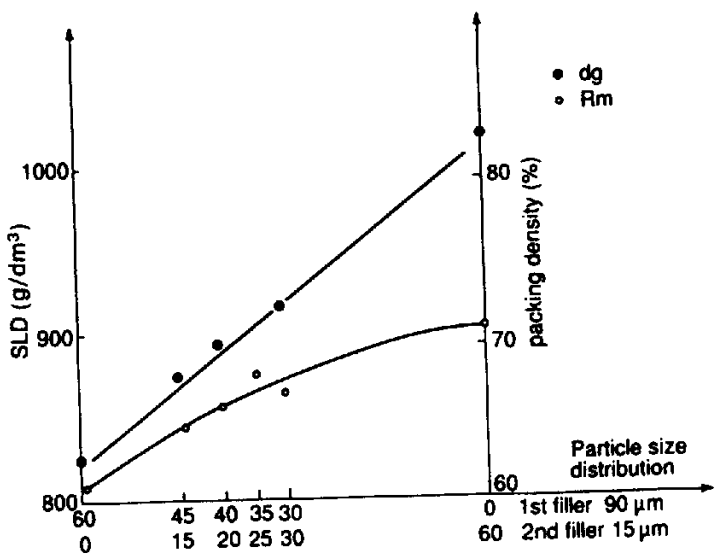


FIG. 11.2. Comparative evolution of screen loading densities (SLD) and of packing densities versus the particle size distribution (casting powder with 60% solid charges).

TABLE 4 *Influence of the fillers content on the screen loading density (SLD) and the packing density of the molds*

Fillers content (%)	45	60	45	60
Particle size (μm) of fillers	90	90	15	15
SLD (g/l)	970	825	1035	1010
Volumetric packing density (%)	66.0	60.5	71.0	68.0

TABLE 5 *Influence of the size of casting powders on screen loading density (SLD) and packing density of the molds*

Filler			
Content (%)		60	
Particle size (μm)		90	
Diameter of casting powders (mm)	0.9	1.5	2.0
SLD (g/l)	810	945	985
Volumetric packing density (%)	60.5	67.0	67.5

specially designed hoppers which allow both a regular flow rate of the granules, and a good distribution of the granules in the molds.

3.2.2. *Incidence from crosslinking*

The curing agents used to reinforce the highly plasticized nitrocellulosic networks are usually isocyanates which will react with residual alcohol groups of the nitrocellulose (combined if necessary to a hydroxy-terminated prepolymer). The isocyanates, slightly agitated, are introduced in the casting solvent just before the casting operation.

To ensure optimal crosslinking conditions, the humidity content of the various constituents must be as low as possible (a few hundred ppm). Therefore, particular attention must be used when degassing the casting powders and the casting solvent, which is done before the casting.

During the curing phase the casting solvent, which diffuses in the granules, serves also as a vector for the crosslinking agents, which usually have a high steric arrangement. At that time a competition takes place between the diffusion and the crosslinking kinetics, which requires the identification of a curing cycle designed to provide strengthening, as uniform as possible, of the nitrocellulosic network. Should the temperature conditions not be correctly adjusted, a superficial crosslinking of the casting grains may occur, hindering any further diffusion of the casting solvents.

3.3. MANUFACTURING PROCESS OF HIGH-ENERGY PROPELLANTS (XLDB–NEPE)

3.3.1. *Background*

XLDB propellants consist of an energetic binder with a high level of plasticization, in which solid charges are incorporated (oxidizers, fuel, various additives).

The following are the main reasons for the development of this family of propellants:

- possibility of obtaining high total solid contents (up to 75% approximately), allowing an improvement of both the specific impulse and the density;
- manufacture of propellant grains similar to composite propellants, making it possible to benefit from all technologies developed so far.

3.3.2. *Manufacturing flow sheet*

Although the manufacture of XLDB propellants is related to that of composite propellants, the processes and equipment had to be adapted to take into account the presence of liquid nitrate esters. This is due to the fact that the energetic plasticizers involved (nitroglycerine or others) are mixtures that are sensitive to mechanical stimuli (shock, friction), and that also often have vapor pressures which cannot be ignored beyond 50°C. The different steps of manufacture of a case bonded grain are described in Fig. 3.

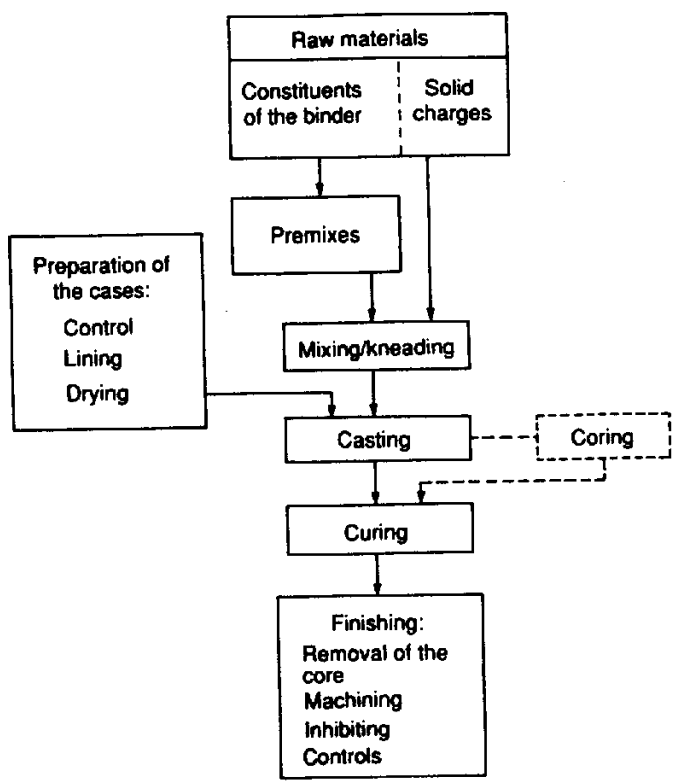


FIG. 11.3. Diagram of the manufacture of high energy propellants.

3.3.3. Cases preparation

3.3.3.1. Background

Two types of cases are currently used with this type of propellant:

- metallic cases made of steel, especially designed to handle significant pressures;
- composite cases which are increasingly used for high-performance applications.

These cases are, of course equipped with thermal protections and coated with a liner, a material for binding with the propellant.

3.3.3.2. Installation of the inert materials

Because the installation process of the various inert materials is described in detail in Chapter 13, this section will provide only a succinct list of the operations sequence necessary to prepare a metallic-type case to receive the propellant slurry. These operations include:

- surface treatment of the cases;
- bonding of the thermal protections;
- coating of the entire surface with a liner.

The process selected for the coating depends both on the nature of the liner and on the shape of the case. Spraying techniques, however, are most widely used.

The quality of these coatings is fundamental for a good adhesion of the liner to the propellant, and of capital importance for the reliability of the propellant grain.

To improve the bonding characteristics (tensile, shear, and peeling strength) between the liner and the propellant, we may have to resort to the use of embedding agents of very specific shapes inside the liner (for example, granules with a cellulosic derivative base), that will function as so many mechanical embedment points for the propellant.

3.3.4. Raw materials preparation

With the exception of energetic binders (nitroglycerine, butanetriol trinitrate, etc.) which require special handling, the other raw materials do not have to be treated or transformed before use. After acceptance according to a determined procedure, the raw materials are stored by homogeneous manufacture batches in the environmental conditions — temperature, humidity — required for their specific nature.

As for the energetic plasticizers, there are several possibilities, according to

the manufacturing processes selected for the propellants and the availability of the mass production of nitrate esters:

- Use of pure nitrate ester, which is possible when a production facility or dynamite extraction facility are located close to the propellant plant. This allows a rapid mixing of the energetic plasticizer with the prepolymer to form a desensitized premixture which can then be stored, i.e., from the time it contains a chemical stabilizer.
- Use of nitrate ester diluted with a volatile solvent (acetone or methylene chloride type) or an inert plasticizer (triacetin type). These solutions are used if the nitrate esters production facilities are located far from the propellant production facilities, or when the manufacturing process requires it.

3.3.5. Manufacture of propellant slurries

The principle of propellant slurry manufacture is based almost exclusively on the preparation of a binder with low viscosity in which the fillers are incorporated. After its homogenization in the suitable mixer, the slurry must maintain a certain level of viscosity to allow its casting by pouring or injection, for as long as the industrial process requires it.

The sequence of incorporation of the propellants ingredients is the result of a trade-off that takes into account, for example:

- evolution of the slurry's viscosity;
- safety problems, related to the use of liquid nitrate esters and/or the use of powerful oxidizers/fuel mixtures such as ammonium perchlorate and aluminum.

Furthermore, it is necessary during this particular phase to maintain very low levels of humidity to facilitate the development of urethane linkages (reaction of isocyanates with alcohols), thereby ensuring good propellant mechanical properties.

For the purpose of illustrating one of the possible manufacture plans, we will use a propellant that contains the following constituents:

Binder

Prepolymer with a tailored molecular weight, polyester or polyether type;
Nitrocellulose (used in low ratios as a crosslinker);
Nitroglycerine;
Stabilizer.

Charges

Nitramine (HMX or RDX);
Ammonium perchlorate.

Curing agents
Polyisocyanate;
Cosslinking catalyst.

The sequence of the operations necessary to obtain a homogeneous slurry can be summarized as follows:

- First, a premix is prepared, containing the prepolymer in which the stabilizer and the nitrocellulose are solubilized.
  This operation takes place at atmospheric pressure and at a specific temperature which must take the melting temperature of the prepolymer into consideration.
- Pure nitroglycerine or nitroglycerine in solution is added to this premix. This operation takes place under slight agitation, and at a moderate temperature. Once the energetic plasticizer is completely incorporated, the whole is placed under vacuum, still at a moderate temperature, and is subjected to a degassing, under slight agitation, to ensure both the homogenization and the dwelling of the premix. When the nitroglycerine is introduced as a solution, the degassing operation also permits the removal of the solvent.
- At the end of this operation the curing agent is added. The binder is then ready to receive the solid charges.
- In this particular case the nitramine (RDX or HMX) and the ammonium perchlorate may be introduced in the mixer, either consecutively or in sequenced phases. The tailoring of the incorporation procedure must take into account the various particle sizes that are used in order to avoid problems of unwanted increase of the viscosity of the slurry.

At the industrial level, it is preferable to have a system permitting a continuous introduction of the charges. Such a facility includes one or several hoppers, located above the mixer, containing the various fillers; the charges are fed to the mixer through a vibrating band.

- After the various charges have been incorporated, the mixing of the whole continues at moderate temperature — usually between 40 and 60°C — (under dynamic vacuum pressure below 50 mmHg), with the same goal, i.e. to maintain a humidity level on the slurry that is as low as possible. Approximately 1 hour before the completion of the mixing, the crosslinking agent is introduced into the slurry. From that moment on the polymerization has been started, and the viscosity of the slurry will keep evolving

Vertical mixers are particularly well suited for the manufacture of XLDB slurries because they allow:

- from a quality point of view, a good homogenization of the fillers in the binders;

- from a safety handling point of view, a significant decrease in the risks of diffusion of nitrated oils in the bearings.

3.3.6. *Production of propellant grains (casting, curing, finishing and quality controls)*

Casting, curing and finishing operations leading to the production of the propellant grains are comparable to those described in Chapter 10 on composite propellants. However, some adjustments were necessary to accommodate the presence of explosive charges (nitramines) and, particularly, of energetic plasticizers (nitroglycerine, for example), which are sensitive to mechanical stimuli, have a limited thermal stability, and are likely to migrate. Among the specific adjustments carried out, we may mention:

- use of specific valves preventing shocks and frictions;
- design of fluid-tight equipment, which keeps handling to a minimum — in this regard, integral molding is recommended because it cuts out all finishing operations;
- a greater control of the temperature of the curing facilities, to avoid any change likely to cause a decomposition of the nitrate esters.

Finally, the quality controls include those done on composite propellants, complemented by specific tests, such as chemical stability, and thermal behavior (cook-off tests).

4. Characterization of Advanced Energetic Binder Propellants

4.1. PHYSICAL AND PHYSICOCHEMICAL CHARACTERISTICS

4.1.1. *Density*

Depending on the nature and the fillers content, advanced energetic propellants present a wide range of densities (Table 6).

XLDB, because they accept a higher total solid content than CMCDB, naturally have higher densities.

The introduction of aluminum ($\rho = 2.7$ g/cm^3) in a propellant that already contains an oxidizer (HMX + ammonium perchlorate, for instance) is another determinant for the evolution of the densities.

4.1.2. *Glass transition temperature (T_g)*

The mechanical behavior of propellants may be be altered at low temperatures because of structural changes in the binder (glass transition, or of the

TABLE 6 *Densities (ρ) available in advanced energetic propellants*

Propellant type	CMCDB	XLDB		NEPE
Nature of fillers	nitramine	nitramine	nitramine + ammonium perchlorate	nitramine + ammonium perchlorate + aluminum
g/cm³	<1.70	<1.76	<1.80	<1.88

second order). The temperatures at which these transitions occur depend primarily, for a specific polymer, on the content level and the nature of the plasticizer (Fig. 4). In fact, in the case of nitrocellulosic binders, they tend toward the second-order transition temperature of the plasticizer when the plasticizing ratio increases [6]. We must remember that the second-order transition temperature of nitroglycerine, when it remains at superfusion, is close to − 65°C.

In the case of XLDB binders, which are highly plasticized, the glass transition temperatures typically range between − 55°C and − 60°C, which

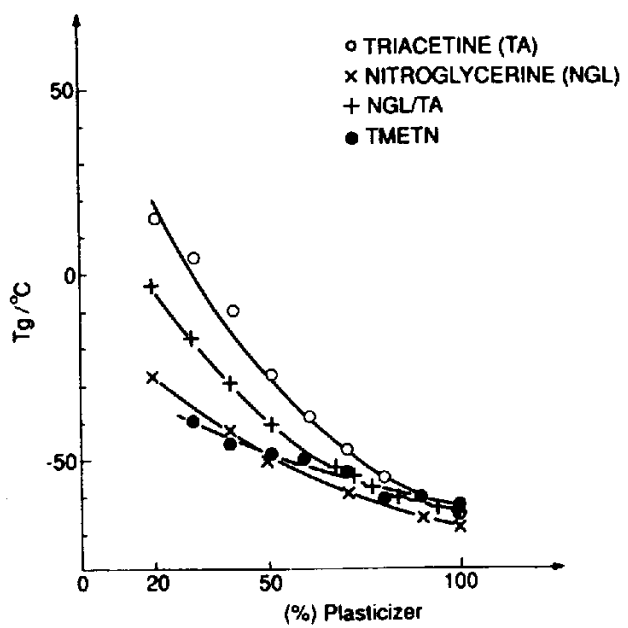


FIG. 11.4. Evolution of the glass transition temperature (Tg) of nitrocellulosic binders versus the amount and the nature of the plasticizer.

explains the good levels of elasticity of this propellant family as far as − 40°C to − 50°C.

4.1.3. *Thermal expansion coefficient (α)*

The binders of propellants have thermal expansion coefficients (α) that are greater than those of the charges. Therefore, the higher the fillers content, the more α will have a tendency to decrease.

Additionally, in the case of energetic binder propellants, the plasticizer usually shows the greatest variations of volume versus temperature. Consequently, the more the binder is plasticized, the more α will have a tendency to increase.

Based on these observations, the thermal expansion coefficients of XLDB propellants, measured above the glass transition point, usually range from 1.00×10^{-4} to $1.30 \times 10^{-4}\ K^{-1}$.

4.1.4. *Crystallization of energetic plasticizers*

In some cycles of low temperature conditioning, XLDB propellants with nitroglycerine base and crosslinked CMCDB (or EMCDB) with high plasticizing ratio may exhibit an embrittlement phenomenon, detrimental to the operational reliability of the propellant grains. Such embrittlement, which is manifested by a total or partial loss of the elastic properties of the material, is the result of the crystallization of the energetic plasticizer inside the propellant [7,8].

Research done on the crystallization of liquid nitrate esters has provided the following information [7]:

- pure nitrate esters do not crystallize easily;
- crystallization is facilitated through seeding with foreign matter that may be present in the propellant;
- once it has been initiated, the kinetics of crystallization depend on the temperature — with nitroglycerine, for example, the kinetics of crystalline growth has its highest value at around − 5°C (Fig. 5).

Energetic plasticizers may be differentiated through their ability to crystallize; nitroglycerine, for example, crystallizes faster than triethyleneglycol dinitrate or butanetriol trinitrate:

- use of specially designed nitrated oils delays or suppresses the crystallization phenomena [7-9].

As far as quality controls are concerned, energetic binder propellants are subject to isothermal conditioning at low temperatures (between 0 and − 50°C) or are exposed to daily arctic cycles, for example − 12°C ⇄ − 40°C,

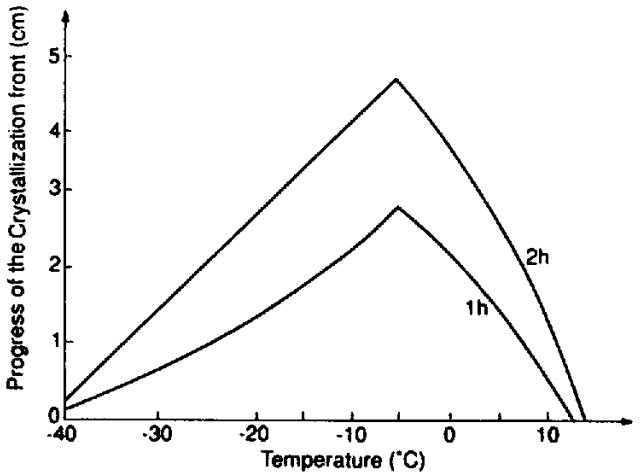


FIG. 11.5. Progress of the crystallization front on nitroglycerin specimens at varying temperatures (readings made one hour and two hours after conditioning).

which are more severe because they facilitate the crystalline germination-growth sequences.

Table 7 gives a description of the behavior at low temperature of two XLDB propellants, one plasticized with nitroglycerine and the other with a mixture of nitrate esters. The propellant containing the nitrate esters resists crystallization, i.e. its mechanical properties are not affected at low temperature, while the propellant containing nitroglycerine becomes embrittled within 10–15 days, depending on the type of conditions selected.

4.2. MECHANICAL PROPERTIES

Depending on the type of grain selected (free-standing or case-bonded), the mechanical characteristics required of the propellant are different:

- Free-standing grains: the propellant is free to deform. The mechanical strains involved mainly concern storage and firing. As far as the material is concerned, sufficient elastic modulus values must be ensured, particularly at high temperatures in the case of tactical missiles.
- Case-bonded grains: the propellant is bound to the case. Its mechanical properties must be tailored to the thermal stress/strains that occur at cooling, right after curing, and for the remainder of the life of the rocket motor. The strain resulting from deformation occurring at firing must also be taken into account.

To be suitable, the propellants must be capable of handling a good level of strain in the entire range of temperatures met during operational conditions

TABLE 7 *Low temperature cycling of XLDB propellants (fillers = 70%) evolution of the strain at maximum stress (ε_m)*

	XLDB	
Nature of the propellant	Nitroglycerine	Nitrate ester mixtures
Cycling conditions:		
Isotherm:		
−15°C	Crystallization after 15 days	No crystallization after 6 months
−30°C	Crystallization after 15 days	No crystallization after 6 months
Daily arctic cycle −12 ⇐ −40°C	Crystallization after 10 days	No crystallization after 6 months
ε_m (%) at −40°C	Crystallized propellant ~ 2%	Non-crystallized propellant ~ 22%

of the grain. In the case of tactical missiles it is particularly important to maintain a good trade-off between the strains at cold temperatures and the values of maximum stress (σ_m), and of the Young's modulus at high temperatures.

These mechanical considerations, related to the design of the grains, determine largely the areas of application of CMCDB/EMCDB propellants and XLDB/NEPE propellants:

- Non-crosslinked CMCDB propellants exhibit a good stress level under high temperatures, but the level of strain at cold temperatures is not suitable for use in case-bonded grains. As a result they are mainly used for the production of free-standing grains.

For these propellants, however, there is a possibility of extending their use to case-bonded grains, in as much as it is possible to increase the plasticizing of the nitrocellulosic binder, involving a strengthening of its network through crosslinking (EMCDB):

- XLDB propellants all exhibit good levels of elongation (including under low temperatures) and satisfactory stress at high temperatures. Consequently, they are well-suited for the production of case-bonded grains.

Mechanical characterizations performed on propellants

A systematic control of mechanical tensile properties is done on all propellants manufactured, first at ambient temperature, and if necessary at low temperature (−40°C, −50°C) and high temperature (approximately +60°C) for propellants intended for tactical applications. For a more detailed characterization, other tests are performed:

- Uniaxial tensile test, at various rates (from 0.5 to 500 mm/min, for example) and various temperatures. Experimental data permit the plotting of master curves necessary during the design of the propellant grain.

- Behaviour at creeping, and at relaxation.
- Simultaneous measurements of the volume variations during a tensile test, recorded with a gas dilatometer. This technique is well suited for the determination of the characteristics of the adhesion between binder and fillers.

4.2.1. *Mechanical behavior of CMCDB propellants*

Mechanical properties of the different CDB propellants occur during the curing operation, at the time when the casting solvent diffuses into the powder granules, which swell and bond to each other. The more the casting powder is plasticized, the better this diffusion will be. With curing temperatures of the order of 50–65°C, the mechanical properties stabilize within 2–4 days.

4.2.1.1. *Influence of the plasticizing ratio*

The possibility, on the one hand, of introducing a plasticizer in the casting powder, and on the other hand, of adjusting the casting powder/casting solvent ratio during the filling of the mold, provides the capability of obtaining propellants with a wide range of mechanical properties.

Let us take the case of a casting powder containing 45% of solid charges: up to 30% of nitroglycerine can be introduced, in place of the nitrocellulose. This substitution causes a variation in the plasticizing level (plasticizer/plasticizer + polymer) of the propellant of approximately 50–80%. In terms of the mechanical properties, it is manifested by:

- a decrease of the values of the maximum stress σ_m at all temperatures;
- an increase of the strain values at low temperatures.

Figure 6 illustrates the evolutions of σ_m and ε_m for various plasticizing ratios. At 65–70% the level of maximum stress σ_m at +65°C usually drops to values lower than 0.5 MPa. This may mean that it is no longer acceptable for a propellant grain, and it becomes necessary to crosslink the nitrocellulosic network in order to strengthen the mechanical properties of the propellant.

4.2.1.2. *Influence of fillers*

The quality of coating by the nitrocellulosic binder is a critical element of the mechanical properties of the finished propellant. As with XLDB or composite propellants, it is necessary to optimize the rheological properties of the binder, and the particle size distribution of the fillers. In addition, the quality of the binder-charge adhesion depends also on the nature of the charge. Figure 7 illustrates the volume variations $\Delta V/V$ recorded with a

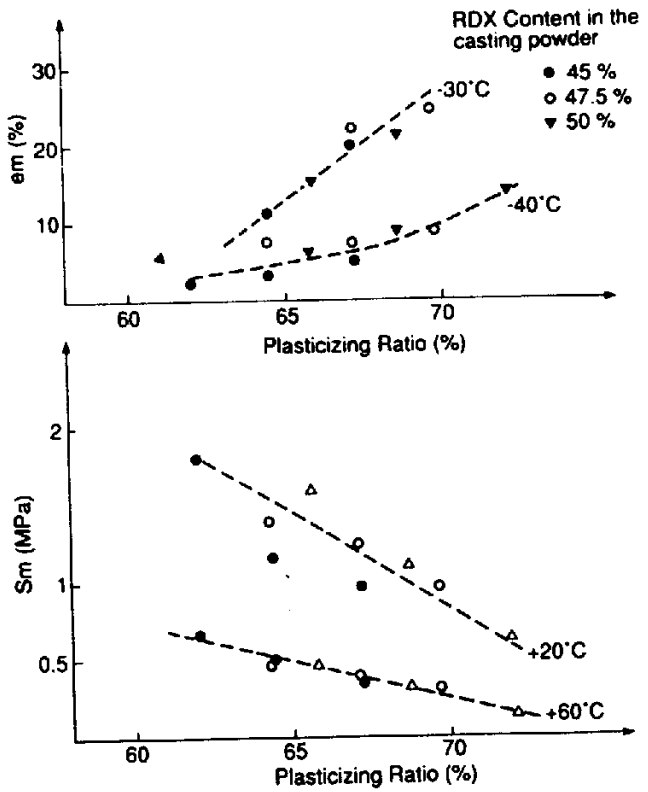


FIG. 11.6. CMCDB propellants. Evolution of σ_m and ε_m in function of the plasticizing ratios.

Farris gas dilatometer for two CMCDB propellants, one loaded at 30% with ammonium perchlorate, the other at 30% with RDX. It turns out that the ammonium perchlorate compositions exhibit a better binder-charge adhesion than those loaded with nitramines with identical particle sizes; dewetting occurs only at higher strains, and the total volume variation $\Delta V/V$ is clearly smaller.

4.2.1.3. *A special case: EMCDB propellants*

With plasticizing ratios greater than 65–70% it is necessary to crosslink the nitrocellulose to strengthen the maximum stress (σ_m) of these advanced CDB propellants at high temperatures. The strain values at low temperature of the resulting propellants are improved, and they may be used in case-bonded grains.

Reinforcement of the polymeric network may be obtained:

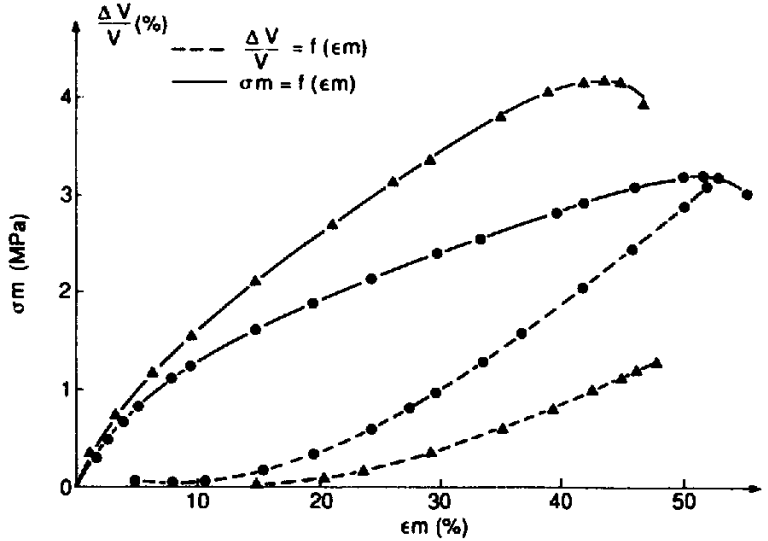


FIG. 11.7. Farris ga. ilatometer behavior of CMCDB propellants loaded with 30% ammonium perchlorate (▲) or 30% RDX (●).

- either by direct crosslinking of the nitrocellulose;
- or by crosslinking the nitrocellulose with small percentages of hydroxy-terminated prepolymer (preferably polyester) — this prepolymer is introduced in the casting powder or dissolved in the casting solvent before casting.

Small percentages of bi-functional isocyanates are sufficient to obtain an increase in the strain capabilities at high temperatures. Optimization is obtained with NCO/OH ratios lower than 0.1.

The values indicated in Table 8 for the mechanical properties of EMCDB

TABLE 8 *Influence of crosslinking on the mechanical properties of EMCDB propellants containing 30% RDX*

Plasticizing ratio	76%			81%
	No crosslinking of NC*	Direct crosslinking of NC	NC crosslinked with prepolymer	Direct crosslinking of NC
σ_m (MPa) at + 60°C	0.12	0.70	0.60	0.45
ε_m (%) at − 40°C	25	20	28-30	40

* NC = Nitrocellulose

propellants with 30% RDX demonstrate the advantage of crosslinking for increasing the σ_m stress capabilities at 60°C and the advantage of the prepolymer for the improvement on strains at − 40°C.

4.2.2. *Mechanical behavior of XLDB and NEPE propellants*

Mechanical properties of these propellants are also obtained after curing, since this phase is designed to activate the crosslinking process of the binder.

The final mechanical properties depend on the composition of the binder, on the fillers incorporated in that binder, and on the manufacturing conditions. Special attention had to be given to the characteristics of the binders of XLDB propellants due to their high contents of plasticizer (up to 70–75%).

4.2.2.1. *Characterization of XLDB binders*

Studies of the elaboration of XLDB binders have demonstrated the influence of formulation parameters such as: nature of the plasticizer and of the prepolymer, and nature of the isocyanates and of the crosslinking catalysts.

On the basis of crosslinking density measurements, the following tendencies can be observed:

- an increase of the plasticizing level contributes to a decrease in the crosslinking density, which tends to drop significantly when the plasticizer/polymer ratio is close to 3;
- a decrease is also recorded when the molecular weight of the prepolymer increases;
- the incorporation, as crosslinker agents, of polyols with high molecular weights (nitrocellulose and cellulose acetobutyrate, for example) improve the crosslinking density;
- the crosslinking density is optimal when the ratios NCO/OH are slightly greater than the stoichiometry;
- There is a fairly good concordance between the crosslinking densities of the binders and their mechanical properties. It has been possible to establish a linear relationship between these two parameters for simple systems with a polyoxyethyleneglycol or glycol polyadipate base [10].

4.2.2.2. *Influence of fillers*

As with all composite structures, the mechanical properties are tied to the interaction between the binder and the charge. When there is a transfer of stresses from the binder to the fillers, these function as a physical reinforcement, causing an increase of the modulus, and at the same time a decrease in

TABLE 9 *Mechanical properties evolution of XLDB propellants as a function of the total solid content*

Solid content (%)		65	70	70
Plasticizer content (%) (binder)		71	71	74
σ_m (MPa)	+20°C	1.0	0.8	0.7
	+60°C	0.8	0.6	0.6
ε_m (%)	+20°C	180	130	130
	−30°C	150	100	110
	−54°C	23	16	18

the elongations. The loading capability of binders is limited, however, and these limits particularly depend on the nature of the polymer, the plasticizer content and the nature of the fillers. Table 9 indicates some typical, σ_m stress and ε_m strain values for XLDB propellants with a polyester binder with various total solid contents.

As with composite propellants with a polyurethane binder, the optimization of the mechanical properties requires:

- the adaptation of the particle size of the various selected solid fillers;
- the control of the humidity levels, which must remain as low as possible.

Some fillers may have an influence on the elaboration of the polyurethane networks plasticized with nitrate esters. This occurs in particular with ammonium perchlorate, which has a low solubility in the prepolymers rich in ether links such as polyoxyethyleneglycols (PEG). The result in the corresponding propellants is a decrease in the maximum stresses (σ_m) at ambient temperature.

4.2.2.3. Conditions for propellant curing

The curing conditions (time, temperature) are determined by the stabilization of the mechanical properties. For case-bonded grains the lowest possible curing temperatures are always sought in order to reduce the thermal stresses due to cooling. Based on the type of propellant, the curing temperatures range from 40 to 60°C and the curing times necessary for the stabilization of the mechanical properties range from approximately 10 to 12 days.

4.3. BURNING RATE OF ADVANCED ENERGETIC BINDER PROPELLANTS

4.3.1. Burning rate of CMCDB propellants

CMCDB propellants need to be considered as an extension of the double-case propellant family. Therefore, the adaptation of their characteristics is done by modifying the characteristics of the binder, using the ballistic modifiers available for these DB propellants.

The introduction of nitramines in these binders compensates more or less for the effects of the "super-rate" caused by the presence of burning rate modifiers. K. Sumi and N. Kubota [11] describe the negative effect of increasing amounts of HMX in a propellant catalyzed with lead salicylate/ethyl-2 lead hexanoate; the plateau effect disappears for amounts higher than about 27%.

In general, less spectacular effects are recorded, which are manifested particularly by a decrease in the level of the burning rate; the plateau effects, although less marked, are nevertheless quite correct for fillers contents up to 40%. There are even ballistic modifiers based on lead or copper salts that remain virtually insensitive to the amount of nitramine [12]: retention of the plateau effect, a very small decrease of burning rate at the plateau (Fig. 8), retention of good temperature coefficient (< 0.15% per °C), and possibility of regulating the burning rate with well-known additives such as carbon blacks.

4.3.1.1. RDX–HMX comparison

Slightly less good burning characteristics have often been observed, experimentally, when HMX replaces RDX: lower burning rate, less marked plateau effect, and a temperature coefficient which is not quite as low.

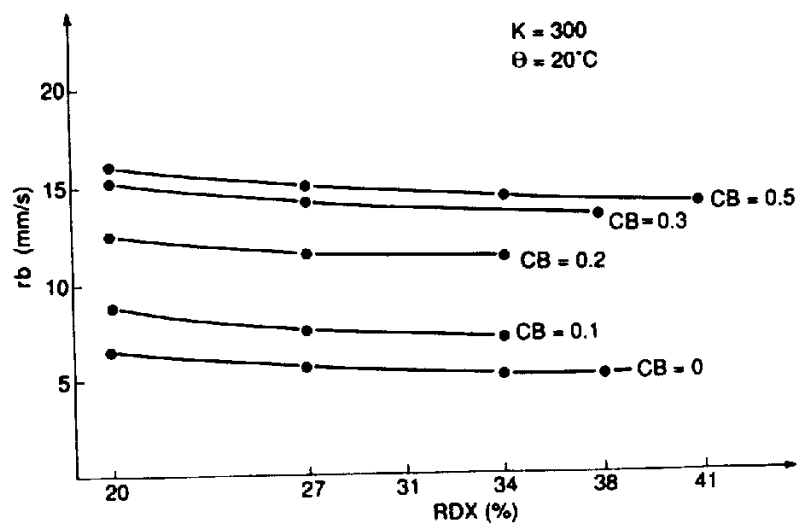


FIG. 11.8. Burning rate of CMCDB propellants as a function of RDX percentage for different content of carbon black (CB).

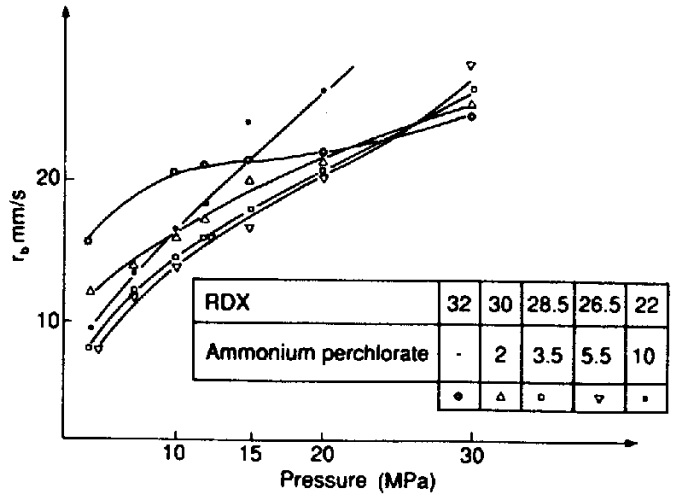


FIG. 11.9. Influence of ammonium perchlorate content on the burning rates of CMCDB propellants catalyzed with lead aromatic ballistic modifier.

4.3.1.2. *Influence of ammonium perchlorate*

Introduced in catalyzed CMCDB or EMCDB propellants, ammonium perchlorate causes the destruction of the plateau effect, even in very small amounts (Fig. 9).

4.3.2. *Burning rate of XLDB and NEPE propellants*

4.3.2.1. *Nitramine based XLDB propellants*

In his synthesis paper, R. A. Fifer points out the difficulties and the few solutions available to affect the burning rate of a propellant with a high content of nitramine [13]. As for the rare catalysts mentioned in the literature, they are not particularly efficient [3,14-16].

Although it is possible to modify the burning behavior of the most widely used binders based on prepolymers of the polyether or polyester type, highly plasticized with nitrate esters, the range of burning rates available remains fairly limited because of the presence of a high amount of nitramine (greater than 50%) [17].

Measures designed to modify the decomposition mechanism of nitramines (RDX or HMX) have not yet succeeded in providing solutions that are applicable industrially.

To sum up, the burning rates of XLDB propellants range from 2 to 15 mm/s at 7 MPa. The pressure exponents are situated between 0.35 and 0.60 and the temperature coefficients are very similar to those of composite propellants (π_k from 0.15 to 0.35% per °C).

Remark

Research for any new ballistic modifiers implies that a propellant feasibility study be done at the same time. This is due to the fact that some additives, particularly those with a lead base, turn out to be efficient crosslinking catalysts, which may make their use incompatible with mass production.

4.3.2.2. *XLDB propellants with nitramine and ammonium perchlorate*

Ammonium perchlorate acts as a very efficient ballistic modifier. It is possible to regulate the burning rate over a wide range by varying both the content and the particle size of the oxidizer. Figure 10 gives an idea of the evolution of the burning rate as a function of the evolution of the ammonium perchlorate-octogen proportions in a propellant with a 70% total fillers content.

In addition to the usual role played by the particle size and the amount of ammonium perchlorate, we may also note that:

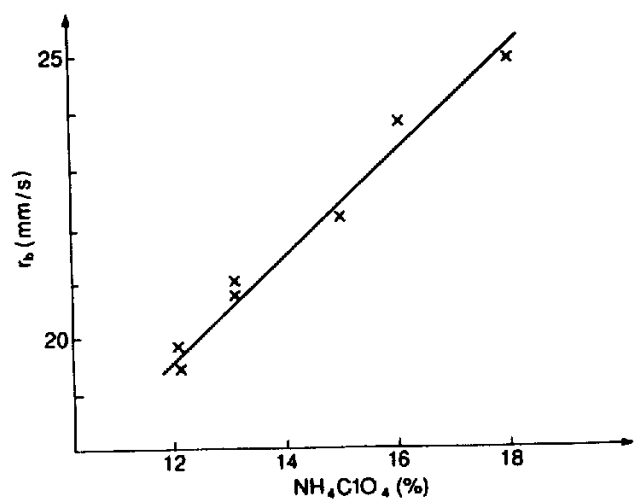


FIG. 11.10. XLDB propellant loaded with 70% fillers (HMX-Ammonium perchlorate). Evolution of the burning rate as a function of ammonium perchlorate content (particle size = 10 μm).

- Polyether binders tend to lead to burning rates that are higher than those obtained with polyester binders.
- Pressure exponents have a tendency to decrease when the ammonium perchlorate content increases. They decrease more rapidly when the particle size of the oxidizer is smaller, reaching minimum values which also depend on the size of the ammonium perchlorate particles. With fine ammonium perchlorate (3 μm), the exponent is around 0.50-0.55, while with somewhat larger perchlorate (10 μm), the exponent may drop to as low as 0.45.

4.4. ENERGETIC CHARACTERISTICS

4.4.1. *Recapitulation of theoretical performances*

Specific impulse (I_s) and volumetric specific impulse ($I_s.\rho$) theoretically attainable with these propellants are shown in Table 10.

I_s and $I_s.\rho$ evolve differently according to the nature of the solid charges incorporated in the binders:

- If the filler is a nitramine, I_s and $I_s.\rho$ increase in a virtually linear manner when the amount of RDX or HMX increases. Because RDX and HMX have closely related thermodynamic characteristics, the substitution of one by the other has little incidence on the values of I_s. But the difference shows up in the value of the volumetric specific impulse, due to the fact that the density of RDX is lower than that of HMX: respectively 1.818 and 1.903 g/cm^3.
- A combination of ammonium perchlorate with a nitramine allows a gain in performance provided, however, that the proportions are optimized as a function of the nature of the binders used (Figure 11).

Incorporation of metallic fuel, such as aluminum, combined with an oxidizer (perchlorate ammonium + nitramine) allows to obtain high I_s and

TABLE 10 *Theoretical performance obtainable with advanced energetic binder propellants*

Nature of fillers	Nature of the propellant	I_s (s)	$I_s.\rho$ (s.g.cm^{-3})
Nitramine	XLDB	250	440
	CMCDB*	245-250	415-425
	EMCDB		
Nitramine + ammonium perchlorate	XLDB	260	465
Nitramine + ammonium perchlorate + aluminum	NEPE	275	515

* The values of I_s and $I_s.\rho$ increase when the propellants are crosslinked, due to the presence of high amounts of nitrate esters in the nitrocellulosic binder.

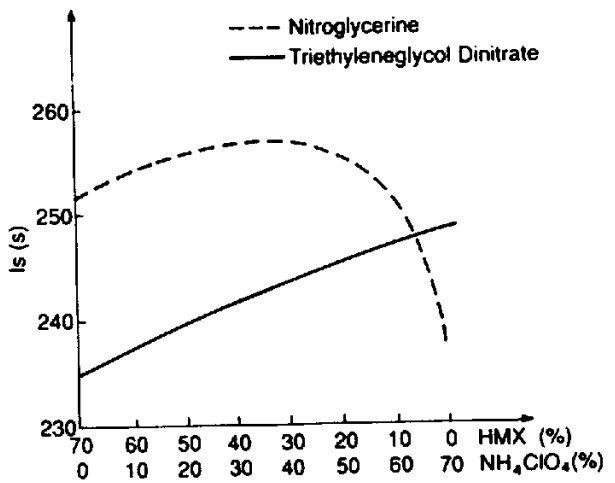


FIG. 11.11. Evolution of I_s as a function of the HMX/Ammonium perchlorate ratios for XLDB propellants with 70% solid fillers whose binder is plasticized either with nitroglycerine, or triethyleneglycol dinitrate.

$I_s.\rho$ values. As in the case with composite propellant, it is necessary, however, to optimize the proportions of the various charges to obtain the maximum performance. The optimum content of aluminum for NEPE propellants ranges between 15 and 20%.

4.4.2. *Measured performance*

The experimental measurements of specific impulse are done on standardized reference grains during a bench firing test. The propellant grains used have a radial combustion.

The specific impulses measured reveal a shortfall in comparison with the computer predictions, which do not take into account the various losses resulting from the nature of the grain and the firing conditions.

Furthermore, the presence of a metal such as aluminum creates a problem of combustion efficiency (due to the influence of the particle size, of the amount of fuel, the influence of the firing conditions and the size of the grains). Table 11 shows clearly that the shortfalls between theoretical I_s and measured I_s are greater with aluminized propellants.

4.5. FUNCTIONAL CHARACTERISTICS

4.5.1. *Signature*

Grain signature is assessed on its ability to produce smoke (primary or secondary) or afterburning phenomena (re-ignition of the combustion gases).

TABLE 11 *Theoretical and measured performances of several typical advanced energetic binder propellants*

Propellant	CMCDB	XLDB	NEPE
Nature of fillers	RDX	HMX + ammonium perchlorate	HMX + ammonium perchlorate + aluminum
Theoretical I_s(s) (expansion 70/1)	241	257	270
Measured I_s(s)	229	245	249
ΔI_s(s)	12	12	21
Standard motor	Mimosa diam. = 203 mm L = 1000 mm	Bates 12" diam. = 305 mm L = 508 mm	Bates 12" diam. = 305 mm L = 508 mm

Such phenomena, which may affect either the guidance or the detection of the missile, or of the combat platform, are discussed in detail in Chapter 5.

The importance of the signature of advanced energetic binder propellants depends primarily on the nature of the fillers incorporated in the propellant (Table 12).

The ability of these propellants to generate smoke and flashes is examined in the following sections.

4.5.1.1. *Primary smoke*

Usual energetic binders consisting of atoms C, H, O and N, do not generate primary smoke. This is also true for the oxidizers contained in these binders (RDX, HMX, or ammonium perchlorate). As a result, the release of primary smoke by CMCDB or XLDB propellants is mainly tied to the presence of additives carrying metallic atoms which are incorporated in the propellant to

TABLE 12 *Classification of advanced energetic binder propellants as a function of their ability to generate smoke*

	CMCDB EMCDB	XLDB		NEPE
Fillers	Nitramine	Nitramine	Nitramine +ammonium perchlorate (< 20%)	Nitramine +ammonium perchlorate +aluminum
Classification	Smokeless	Smokeless	Minimum smoke	Smoky

respond to a specific operational requirement. These additives, of which only small amounts are incorporated, include:

- ballistic modifier (lead and copper salts, for example);
- damping particles, sometimes required in some radial burning grains;
- afterburning suppressants including an alkaline ion (most often potassium) which decompose during combustion but may give rise to recombinations in the gaseous phase, which is detrimental to the signature.

4.5.1.2. *Secondary smoke*

Secondary smoke is characteristic of propellants that contain ammonium perchlorate. The formation of H_2O/HCl aerosols depends, on one hand, on the atmospheric conditions (temperature and relative humidity), and on the other hand, on the amount of NH_4ClO_4 in the propellant.

4.5.1.3. *Afterburning*

Afterburning phenomena can be suppressed by the introduction of additives with alkaline metals base (sodium and particularly potassium: K_2SO_4, KNO_3, K_3AlF_6 and others).

When developing new propellant compositions, however, the choice of an additive must take into account not only its specific afterburning suppressant function, but also such criteria as: influence on the feasibility, ballistic properties, chemical and thermal stability of the propellant, as well as the possible effects on the exhaust plume (primary smoke).

4.5.2. *Combustion instabilities*

Instabilities, longitudinal as well as transverse, which are typically observed in radial burning grains, are the subject of theoretical research so that computer codes may be developed for predictive analyses (Chapter 4).

This is an interesting approach, in as much as it should allow the reduction of the number of lengthy and expensive tests that need to be performed, particularly in the case of large rocket motors. For modest-size grains destined for tactical purposes, on the other hand, it is possible and even useful to define experimentally the stable combustion zones.

4.5.2.1. *Conditions for occurrence of transverse instabilities*

In a given propellant, the occurrence of combustion instabilities is tied, on one hand, for the firing conditions, and on the other, to the design of the propellant grains.

(a) Firing conditions

Pressure is a dominant factor. Instabilities usually occur at low pressures, the oscillations increase as the pressure decreases. For a given pressure, the firing temperature may also affect the triggering of instabilities.

(b) Geometry of propellant grains

Starting from free-standing grains with a constant diameter (D), there is a grain length (L) above which combustion instabilities occur. Conversely, starting from grains with a constant length (L), it is possible to determine an initial central port diameter (D) above which the combustion will be stable.

Finally, the combining of these different experimental firing tests allows one to obtain a more accurate definition of the grains size (Fig. 12).

4.5.2.2. *Function of damping particles*

Damping of the pressure oscillations in the combustion chamber can be obtained through the presence of solid particles in the combustion gases. For each specific vibration, there is a proper particle size.

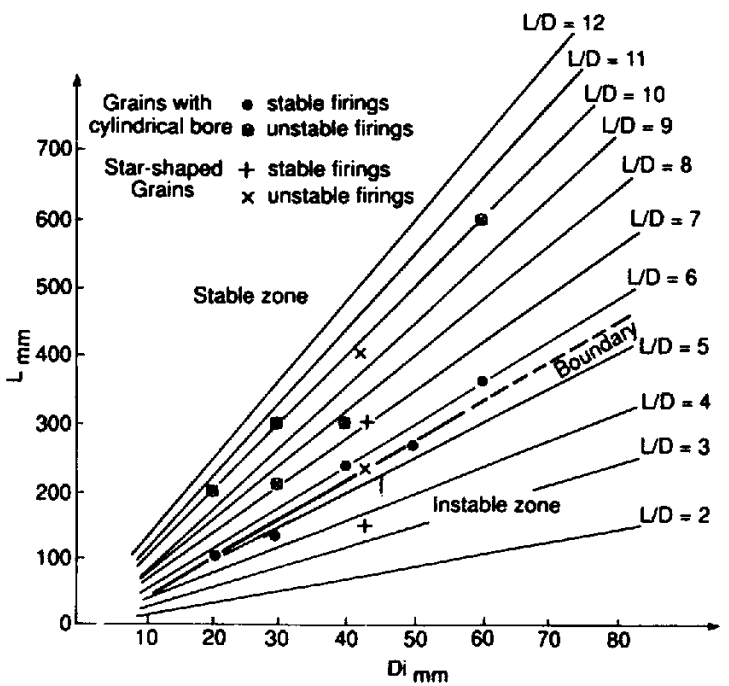


FIG. 11.12. Identification of a stable combustion zone as a function of the dimensional characteristics of the propellant grain. CMCDB propellant with 30% RDX.

When the grain is being designed, there are two ways of proceeding:

- By introducing metallic additives (aluminum or tungsten, for example) which, when they burn, generate oxidation condensed products (Al_2O_3, W_2O_3, etc.). This is the most widely used solution, but it does not afford the possibility of controlling the size of the particles that are generated.
- By introducing refractory additives with melting points that are higher than the combustion temperature of the propellants. This allows a better optimization of the size of the damping particles, provided that the vibration frequencies of the grain are known. The damping particles that can be added to CMCDB or XLDB propellants belong to the families of oxides (SiO_2-ZrO_2-Al_2O_3 for example), carbides (SiC-ZrC-BC), or nitrides.

When it becomes necessary to have recourse to the introduction of an additive to stabilize the combustion of a grain, the consequences on the other properties must be ascertained, such as:

- *Performance*: the metals (aluminum, for instance) contribute to raising the specific impulse; refractory products, on the other hand, are rather detrimental.
- *Burning rate*: these additives may cause perturbations of the burning rate-pressure law, particularly with CMCDB and XLDB propellants which contain catalysts common in double-base propellants.
- *Signature*: the solid particles released in the exhaust plume are responsible for primary smoke.

4.6. AGING

Aging behavior of propellant grains depends not only on the nature of the propellant, but also on the environmental conditions (temperature, and relative humidity, for example). For the propellant, this aging translates into an evolution of the chemical and/or physicochemical characteristics, which may in turn alter its mechanical and ballistic properties, as well as its safety behavior. Table 13 enumerates the major consequences related to these evolutions.

4.6.1. *Chemical stability*

The presence of nitrate esters in advanced energetic binder propellants requires, as with all double-base propellants, the incorporation of stabilizers whose function is to trap the nitrogen oxides resulting from the decomposition of the nitrates.

The stabilizers used for CMCDB and XLDB propellants that contain no ammonium perchlorate are often the same ones used for homogeneous

TABLE 13 *Consequences of aging on the properties of advanced energetic binder propellants*

Type of evolution	Nature of the evolution	Consequences and properties affected
Chemical	Decomposition of nitrate esters	●Chemical stability (consumption of stabilizer) └→Explosive behavior (risk of ignition) ●Physical integrity (cracks) └→Operational safety
	Evolution of the polymer network: rupture of chains, creation of links	Crosslinking density └→Mechanical properties
Physicochemical	Mobility of the energetic plasticizer: migration, exudation, volatilization	Composition of the material ●Mechanical properties └→●Ballistic properties ●Explosive properties
	Binder-charge adhesion	Mechanical properties
	Crystallization of the plasticizer (cycling at low temperatures)	Mechanical properties └→Explosive properties

propellants: 2-nitro diphenylamine (2NDPA), and *N*-methyl *p*-nitroaniline (MNA), for example. When they contain ammonium perchlorate, resorcinol (or resorcinol derivatives) combined with 2NDPA is also efficient.

The mechanisms of nitrate esters decomposition, and of the oxides interaction with the stabilizers, are described in depth in Chapter 9.

The chemical stability of advanced energetic binder propellants may be affected by some ingredients of the binder and the nature of the fillers, as well as by the various additives necessary for the functional characteristics of the propellant grain.

4.6.1.1. Influence of the binders

- Increase of energetic plasticizer content in the binder is generally manifested by a faster consumption of the stabilizer.
- The polyurethane binders plasticized with energetic nitrate esters usually exhibit a chemical stability that is lower than those of nitrocellulosic binders. Among the parameters that influence this stability are:
  - nature of the polyisocyanates: in general, the aromatic polyisocyanates give a slightly better chemical stability;
  - nature of the prepolymer: prepolymers rich in ether functions lead to less chemical stability.

4.6.1.2. Influence of the fillers

- Nitramines (RDX and HMX) are chemically stable. They do not participate in a significant manner in the degradation of the advanced energetic binder propellants.
- Ammonium perchlorate, on the other hand, plays a particular role by modifying the decomposition mechanisms of the nitrate esters and the interaction mechanisms of the nitrogen oxides with the stabilizers. Under standard aging conditions (50–70°C), this is expressed by a lower consumption of the stabilizer and lower gaseous emissions.

4.6.1.3. Influence of the additives

Incorporation of additives in even small amounts may cause significant modifications in the decomposition kinetics of nitrate esters. This is true in the case of ballistic modifiers.

4.6.2. Cracks caused by aging

The propensity of a grain of a specific size to crack is a function, on one hand, of its chemical and physicochemical behavior, and on the other hand, of its mechanical properties (refer to Chapter 9).

For propellants with similar compositions and mechanical properties, resistance to cracks caused by aging depends mostly on the nature and the proportion of stabilizer(s) included. It has been demonstrated, for example, that centralite is clearly less efficient than 2-nitro diphenylamine (2NDPA). With CMCDB or XLDB propellants it might be interesting to combine two stabilizers that have very different nitrosation kinetics to improve resistance to cracking.

Included among the other propellant constituents that may affect this type of aging are:

- presence of ballistic modifiers;
- cure agents (nature, content);
- nature of the fillers. The presence of ammonium perchlorate slows down the gases generation, leading as a result to critical sizes much larger than those of double-base propellants or CMCDB or XLDB propellants loaded with nitramines.

4.6.3. Mechanical aging

The main causes of the evolution of the mechanical properties of the advanced energetic binder propellants are the presence of nitrate esters, the crosslinking systems, mobility of the plasticizers, and environmental factors.

4.6.3.1. *Presence of nitrate esters*

Nitrogen oxides issued from the decomposition of the nitrate esters have the capability of reacting directly with the polymeric chains, or of combining with traces of humidity present in the propellant to produce chemical species (HNO_3 for example) which are particularly aggressive toward the polymers (cutting by acid hydrolysis). The result is a depolymerization causing a decrease of the Young's modulus of the material. However, this mechanical aging can be minimized through the presence of chemical stabilizers performing efficiently inside propellant.

4.6.3.2. *Curing agents*

Circumstances may occur where crosslinking is not entirely completed at the end of the curing phase. During storage the mechanical properties of the propellants may evolve toward a slight hardening, caused by the continuation of the polymerization.

In addition, the eventual formation of secondary products during crosslinking — due to the presence of traces of humidity, for example — may have an influence on the kinetics of self-decomposition of the nitrate esters.

4.6.3.3. *Mobility of the plasticizers*

In the course of aging, the plasticizer may migrate into the materials that are in contact with the propellant (inhibitor, liner, etc.). The localized depletion of plasticizer causes a hardening of the propellant. The development of bonding materials for advanced energetic binder propellants does not completely exclude the risks of diffusion, but does limit them to such low levels that they do not compromise mechanical integrity near the interfaces.

4.6.3.4. *Environment factors*

- *Humidity*: the humidity associated with the decomposition products of nitrate esters accelerates the acid hydrolysis of the nitrocelluloses and polyesters, for example. Humidity most probably also has some effect on the quality of the binder-charge adhesion.
- *Air (oxygen)*: aging in an oxidizing atmosphere (exposed to air, for example) may facilitate a degradation of the mechanical properties. To prevent this process, propellant grains may be stored in inert atmosphere, such as nitrogen.
- *Temperature*: it is quite obvious that the mechanical aging processes in ambient temperature are very slow; however, their kinetics is accelerated whenever the storage temperatures increase.

In practical terms we must remember that non-crosslinked CMCDB propellants have very few problems of mechanical aging. But propellants whose mechanical characteristics are obtained by crosslinking — mainly XLDB propellants — are more sensitive to this type of aging.

4.6.4. *Ballistic aging*

Advanced energetic binder propellants show no significant modification of their ballistic characteristics over time.

The factors that could have any influence are related to modifications in the composition of the propellant are:

- loss of plasticizer (diffusion to the inhibitors, or volatilization);
- chemical evolution of the burning rate modifiers.

4.7. SAFETY CHARACTERISTICS

4.7.1. *Background*

Propellants are, above all, materials for which combustion is the major risk. However, the development of new high energetic propellant families has contributed to the identification of techniques and methodologies to study the safety in order to take into account:

- various manufacturing phases;
- various situations in the operational life of the propellant (such as storage, transport, firing).

These methods provide the capability of defining the major risks that must be considered in a given situation: combustion (hazard class 1.3) or detonation (hazard class 1.1). The resulting analyses allow us to deduce information on the nature of the future design of facilities, or on the protective measures needed for personnel and the environment.

4.7.2. *Safety behavior during the manufacture of advanced energetic binder propellants*

4.7.2.1. *CMCDB propellants*

(a) Behavior of the casting powders

The risks involved with casting powders are similar to those from granular products:

- Starting in deflagration in a limited space, they may, under the effect of a sudden increase in the gaseous pressure, lead to a mechanical explosion of the containers, or worse, to a detonation. This is known as the deflagration-detonation transition phenomenon (DDT).

Consequently, it is important to know these mechanisms very well in order to design suitable storage facilities and to determine the conditions of usage that minimize the risks.

Standardized tests allow us to measure the critical explosion heights (CEH) and detonation height (CDH).

Generally, the CEH and CDH decrease when:

- The burning rate of the powder increases. This tendency is clearly demonstrated in the case of casting powders containing mixtures of HMX and ammonium perchlorate. As a matter of fact, when the perchlorate amount increases at the cost of the nitramine, the burning rates increase while the CDH values drop (Fig. 13).
- The proportion of explosive materials (nitroglycerine + nitramine) increases. In fact the CEH and CDH values are more sensitive to a variation in the amount of nitrate ester than that of nitramine.
- The size of the casting powder grains decreases.

- The French Card Gap Test also evolves with the size of the granules in a given composition. When the diameter changes from 0.8 to 2.0 mm, the

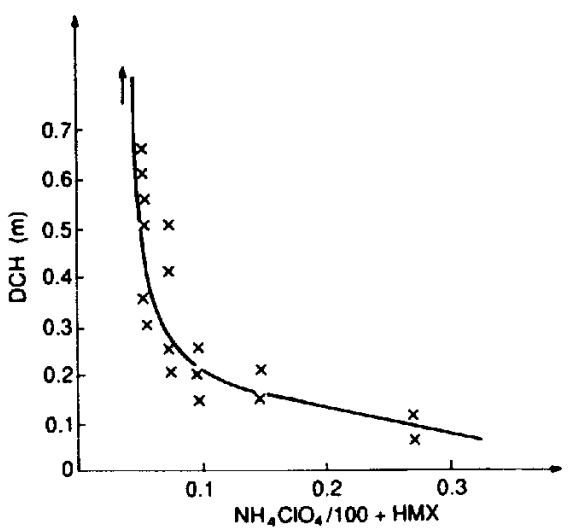


FIG. 11.13. Evolution of the detonation critical height of casting powders as a function of the ammonium perchlorate-HMX ratio.

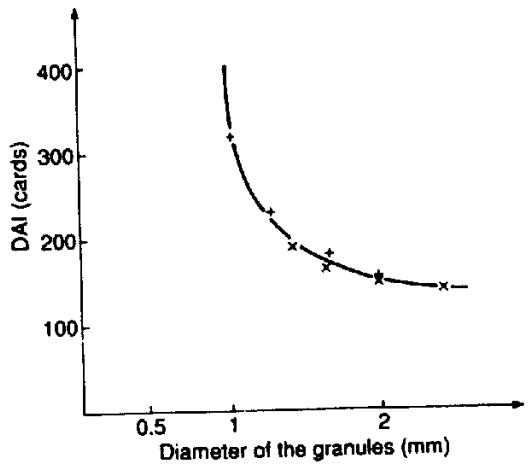


FIG. 11.14. Behavior of french card gap test of casting powders containing 10% nitroglycerin and 15% RDX.

gap drops from 300 to approximately 150 cards (Fig. 14). With granular products the high values of gap may be the result of a deflagration to detonation transition and not the result of a shock to detonation transition, which is the normal case. Indeed, for a weak shock wave, there is no detonation initiation, but only in deflagration; it is this deflagration which later takes on a detonation regime.

- The sensitivity of casting powders loaded with nitramines to mechanical stimuli such as shock or friction does not evolve much with the total solid contents.
- Casting powders may be sensitive to electrostatic discharge if they are not graphitized. To make them perfectly conductive, however, the glazing must be perfect.

A poor distribution of the graphite, often due to a poor surface aspect of the granules, may result in the electric conductivity having virtually no effect.

4.7.2.2. XLDB and NEPE propellants

(a) Premixes behavior

Premixes based on polymers and nitrate esters are sensitive to mechanical stimuli, and in particular to shocks. Their behavior is closely related to that of casting solvents, which is to say that they may manifest two detonation regimes (low and high speed), according to the type of stimulus.

(b) Slurries behavior

The behavior of homogenized slurries at the end of the mixing phase is fairly close to that of finished propellants after curing, as far as mechanical stimuli and propensity to detonate are concerned.

For propellant slurries with solid contents adapted to mass production, it can be observed that:

- these slurries generally exhibit no violent reaction to a 30 kg drop hammer test, below 4 m;
- use of ammonium perchlorate results in an increase in the sensitivity of the slurries to friction — moreover, depending on the nature and the amount of oxidizer, the same behaviour as the most sensitive composite propellants can be found;
- gap of slurries after mixing, measured with the French gap test, is below 240 cards.

4.7.3. *Safety behavior of propellant grains*

- The gap values, at the French gap test, of advanced energetic binder propellants, are less than 180 cards. These non-confined propellants can be given in the 1.3 hazard classification — the major hazard being combustion — of the French law. Double-base propellants which, we should remember, have been used around the world for over tens of years without any problems, have gap values of around 100 cards. The increase of gap values compared with those of double-base propellants results from the incorporation of explosive fillers, and more precisely nitramines.

As for the conditions of detonation triggering of propellant grains, they have been discussed in detail in Chapter 7. Transition phenomena such as deflagration to detonation or shock to detonation generally imply a prior fragmentation of the propellants. Propellants with good mechanical properties are therefore necessary to allow a minimization of these hazards. In this regard, XLDB propellants, which are designed for use as case-bonded grains, have an excellent mechanical behavior and naturally have a good resistance to fragmentation.

- CMCDB and XLDB propellants, loaded with moderate amounts of nitramines, are not sensitive to friction (behavior identical to that of double-base propellants). The somewhat more greater sensitivity of XLDB propellants comes for the most part from the higher content of nitramines ($> 60\%$). Ammonium perchlorate is a sensitizing element for the propellant in the form of slurry or crosslinked (Fig. 15).
- The shock sensibility behavior (30 kg drop hammer test) of CMCDB or XLDB propellants is not any different from the other current propellant families.

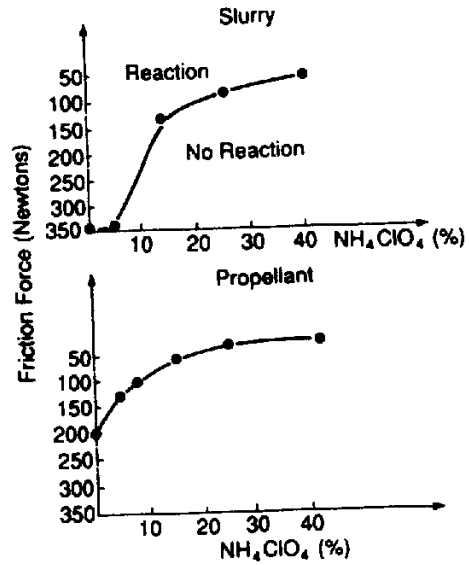


FIG. 11.15. Evolution of the friction sensitivity coefficient of XLDB propellants with 70% fillers (slurry and propellant) as a function of fine ammonium perchlorate content.

- XLDB propellants do not appear to be sensitive to electrostatic discharge test. But some compositions of CMCDB propellants react to capacitative discharges. However, the normal reaction of the propellant to this type of sollicitation is a non-violent combustion (the propellant grain generally does not present any fragmentation).
- In terms of behavior to thermal stimuli (self-ignition or the cook-off test) a distinction needs to be made between compositions with or without ammonium perchlorate. CMCDB and XLDB propellants without ammonium perchlorate always have critical thermoinitiation temperatures higher than 100°C; these temperatures tend to decrease when the size of the grain increases. On the other hand, propellants containing ammonium perchlorate usually exhibit thermoinitiation temperatures below 100°C, but they are not affected by the size of the grain.

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