CHAPTER 9

Double-base Propellants

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1. Introduction

Propellants in which the binder consists of an energetic polymer plasticized with a nitric ester, more particularly nitrocellulose plasticized with nitroglycerine, are commonly called double-base propellants. The oxidizing and reducing elements that are involved in the release of energy through combustion are combined in the same molecule. In fact, nitrocellulose and nitroglycerine bring together the carbon, hydrogen and oxygen necessary for the chemical reaction. As a result these are known as homogeneous propellants, in contrast to the composite propellants. And depending on whether the manufacturing process is by extrusion or casting, they are also known in France either as "SD" (solventless or extruded double-base propellants or EDB), or as "Epictetes" (cast double-base propellants or CDB).

Double-base propellants are one of the oldest propellant families. Their development is connected to the development of propulsion. At the end of World War One, gun propellants were essentially colloidal powders with a nitrocellulose base. The incorporation of nitroglycerine made it possible to increase the energy level, and although the simultaneous increase of combustion temperature limited their use as gun propellants, they became usable for rocket motor propellants.

The applications for such rocket motors require tailoring of the combustion pressure, burning time, over a wide operating temperature range, which is activated by means of additives to the propellant. For the past 40 years, propellant compositions have continued to evolve. The number of additives has increased, and in some compositions where they represent 5-10% of the total weight there are as many as 10 additives. These developments have allowed a considerable increase in the quality, performance and reliability of motors using double-base propellants.

Today, their development and use are linked to the economics of their production and to some of their inherent charateristics such as:

- good mechanical properties including stiffness which is particularly well suited for free-standing grains and for the manufacture of various geometries with close dimensional tolerances;
- good aging capabilities, particularly under humid conditions;
- operational characteristics that are well suited to some specific applications such as:
  - little or no solid particles in the gas jet, i.e. little or no primary smoke,
  - little or no chemical elements likely to recombine with the atmosphere to create secondary smoke,
  - burning rates that are well under control and generally show little sensitivity to the operational temperature.

2. Compositions and Raw Materials

2.1. FUNCTIONS OF THE CONSTITUENTS

The constituents of double-base propellants can be classified in five large groups of products, based on their functions:

- energetic base constituents,
- additives for easier manufacture,
- chemical stability additives,
- burning rate additives,
- other additives for specific operations.

2.1.1. The energetic base

The energetic base of double-base propellants is mainly composed by nitrocellulose (40–70%) and nitroglycerine (15–41%). Other nitrated products are also sometimes used, such as nitroguanidine.

The manufacture of these propellants involves combining these two products homogeneously, using a gelatinization process [1] which is based on the mechanism of interaction between the nitroglycerine molecules introduced in the network of the nitrocellulose macromolecules, and the atoms or groups of atoms of these polymers. These mechanisms are numerous, complex and governed, at a microscopic scale, by means of attractive forces, ranging from Van der Waals forces (relatively weak attractive forces), to hydrogen bonds whose energy may reach 12 kcal per bond, and including dispersion forces, interaction forces between dipoles and others.

The behavior of nitrocellulose in relation to solvents with a basic nature has been the object of many studies [2]. These solvents include ketones, esters and alcohols. The oxygen (basic) of carboxyl groups can interact with the hydrogen (acid) of the secondary nitrated groups ($CH\text{-}O\text{-}NO_2$). This

phenomenon is a function of a large number of parameters such as the degree of nitration of the cellulose (referred to as percentage nitrogen in the NC), the crystallinity, and the degreee of polymerization.

As far as nitroglycerine is concerned it is to be considered as a poor solvent which does not form a true solution with the polymer. It does not penetrate the organized zones of the polymer and swells only the amorphous interstitial spaces according to a solvation process. One of the explanations is considered to be the presence of oxygen links in the nitrocellulose molecule. Because of the rigidity of the chains and their spatial organization, these oxygens have a weak interaction with the nitrated groups of the nitrocellulose molecules.

The introduction of mobile solvents such as nitroglycerine permits bringing nitrate groups closer to the vicinity of the oxygen links. This allows an interaction to occur between the oxygens of the nitrocellulose and the acid hydrogen of the $CH\text{-}O\text{-}NO_2$ group of the nitroglycerine. As a result a portion of the nitroglycerine (30%) is used to solvate the nitrocellulose, the remainder being more or less mobile within the network. At the macroscopic level the beginning of the gelatinization process is often marked by a swelling of the nitrocellulose fibers. The continuation of the process must be promoted by a mechanical, thermal or chemical intervention, such as the addition of another volatile solvent.

2.1.2. Additives for easier manufacture

These additives are necessary to facilitate the manufacture of the material. These are essentially inert plasticizers designed to promote the gelatinization phenomenon. They represent typically 0–10% of the propellant, and phthalates or triacetate types are commonly used to desensitize the nitroglycerine for safer handling. Mechanical properties may also be modified.

Other additives, such as graphite, are used in very small amounts (below 0.1%) to facilitate some operations; for example, the flowing of the casting powders (Xenon powders) used for the production of CDB propellants.

2.1.3. Stability additives

The nitric esters of double-base propellants decompose at rates dependent on time and temperature. This decomposition corresponds to the rupture of the $O\text{-}NO_2$ bonds, and releases nitrogen oxides. Without a stabilizer, the products resulting from the decomposition have a catalytic effect on the decomposition reaction rate. The reaction is controlled when stabilizers are included, which usually have a benzene nucleus capable of fixing the nitrogen oxides by substitution.

An uncontrolled decomposition of the nitric esters could have serious disadvantages:

- From a safety point of view: since the decomposition is exothermic, there could be a risk of ignition of the propellant when the energy released becomes greater than the heat loss through exchange with the environment.
- From a quality point of view: there could be a risk of gas cracking of the propellant when the decomposition kinetics of gas generation is faster than the gas diffusion. This phenomenon is observed beyond a certain thickness of the material. The critical size corresponds to the dimensions where cracks appear at a given storage temperature.
- From a performance point of view: because the decomposition is exothermic, the propellant energy — that is, the energy available for use — would decrease with time.

The above emphasizes the importance of the selection of stabilizers in the formulation of double-base propellants.

2.1.4. *Ballistic additives*

The burning rate of double-base propellants varies greatly with pressure, so that during their combustion in a rocket motor, small fluctuations in the combustion are translated into significant pressure variations. As a consequence, an accidental increase of the burning surface may result in an overpressure that could lead to the explosion of the rocket motor.

Ballistic additives are added to the propellant to reduce the sensitivity of the burning to pressure fluctuation, as well as to catalyze burning rates to the higher regimes.

Some of these additives permit a burning rate independent of the pressure, within a given range of pressures (the plateau effect). The plateau effect was given its name because the burning-rate-versus-pressure curve has the shape of a plateau. When the burning rate decreases with increased pressure the phenomenon is called mesa effect. In the absence of such additives the burning rate increases with pressure according to an exponential law. Accordingly such additives are commonly referred to as ballistic modifiers or burning rate catalysts, or sometimes as platonization agents.

The advantage of propellants with such plateau curves is obvious. Random fluctuations of the burning area to throat area ratio result only in minimal variations of the burning rates, and in very weak pressure variations. This in turn enhances control, predictability and reliability of the motor performance.

Furthermore these burning rate additives usually reduce the temperature coefficient of variation of burning rate, enabling reduced motor performance variability over a wide temperature range.

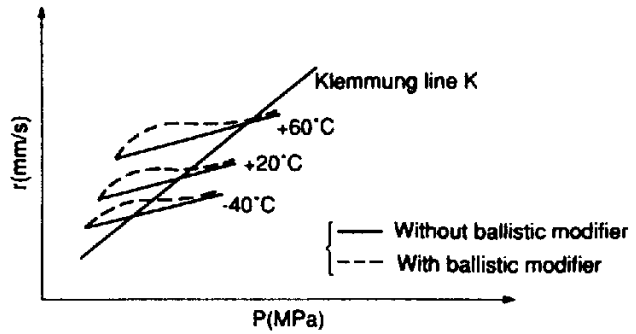


FIG. 9.1. Diagram burning rate-pressure of a double-base composition.

2.1.5. *Operational additives*

Some characteristics peculiar to the use of a specific rocket motor or its design may need some other additives.

Regardless of the configuration of the combustion chamber, the burning rate must be stable, and this may require the presence in the combustion gases of solid particles, such as refractory products to attenuate acoustic combustion instability effects.

Special needs in terms of guidance or plume signature may require the absence of re-ignition of the gaseous jet; flash suppressant additives may be used to satisfy such requirements.

2.2. RAW MATERIALS CHARACTERISTICS

This section describes some of the characteristics of the principal ingredients of double-base propellants with respect to their influence on processing and final properties.

2.2.1. *Energetic raw materials*

2.2.1.1. *Nitrocellulose*

Cellulose nitrate, commonly called nitrocellulose, is obtained by action of sulfonitric mixture (sulfuric and nitric acids) on cellulose. Such nitrate esterification is in a heterogeneous phase reaction of mixed sulfuric and nitric acids on cellulose fibers, in the course of which all three hydroxyl functions of the cellulose may be nitrated to a greater or lesser degree.

The nitrogen content of the nitrocellulose represents the degree of nitration of the available hydroxyls in the cellulose chains. Accordingly it indicates the energetic level of the product.

In France the nitrocelluloses are classified following a nomenclature connected to the nitrogen content (in mass percentage). The more usually used in a double-base production, are the following grades: CP_1D, CP_2L and CP_2U (13.1 N-12.6 N-11.7 N).

(a) Solubility

The nitrocellulose solubility in polar solvents varies in accordance with the nitrogen content.

The nitrocellulose grades insoluble in a given mixture of ether and alcohol at 56° Baume are called type I (CP_1). The soluble grades are called CP_2.

(b) Viscosity

An important characteristic of the nitrocelluloses is the degree of polymerization or molecular weight, which is equal to the number of anhydroglucose structural units forming the cellulose chain. This parameter principally determines the viscosity of the nitrocellulose in a given solvent.

(c) Calorimetric value in calories per gram

The energetic properties of the nitrocelluloses are a function of their percentage of nitrogen. Table 1 lists the major characteristics of nitrocellulose, based on the French nomenclature.

2.2.1.2. *Nitroglycerine*

Nitroglycerine or glycerol trinitrate resembles a colorless oil. It is obtained through nitration of glycerine by a sulfonitric mixture. Its very high calorimetric value (1750 cal/g) has led to its generalized use in double-base propellants [4].

2.2.1.3. *Other energetic ingredients*

Beside nitrocellulose and nitroglycerine, other energetic products may be used when special applications are involved. Nitroguanidine, for instance, is used as a cooling agent or as a combustion moderator.

Other nitrate esters may be used either wholly or in part in substitution for nitroglycerine. In particular the use of triethylene glycol dinitrate or butanetriol trinitrate is noteworthy.

TABLE I *Major characteristics of different nitrocellose qualities*

Type	N%	Calometric value (cal/g)
CP_1D	$\geqslant$ 13.35	1060
CP_1E	13 to 13.35	1040
CP_2L	12.60 to 12.80	970
CP_2P	12.40 to 12.59	940
CP_2S	12.20 to 12.39	910
CP_2T	11.80 to 12.19	870
CP_2U	11.60 to 11.79	830

2.2.2. *Process additives*

2.2.2.1. *Plasticizers*

The most commonly used are:

- diethyl phthalate, a phthalic ester employed as a plasticizer for EDB propellants;
- dioctyl phthalate, a plasticizer for CDB propellants;
- and particularly, in the CDB process glycerol triacetate or triacetin, as an inert liquid mainly used in association with nitroglycerine in the casting solvent. In this way the impact and friction sensitivity are reduced and the gelatinizing behavior reinforced.

Other plasticizers sometimes used are:

- saccharose acetoisobutyrate, also acts as a burning rate modifier;
- ethyl phenyl urethanne, a plasticizer for EDB propellants;
- sucrose octoacetate;
- adipates such as ethyl, octyl, etc.

2.2.2.2. *Other additives*

Graphite is often used as a coating agent for the casting powder in the cast double-base process. In low quantities (less than 0.1%) it reduces electrostatic charges and facilitates the powder flow into the casting molds.

Waxes (Candellila, Montant) in very small amounts, on the order of 0.5%, facilitate the extrusion process of solventless propellants. Some stearates, magnesium stearate for example, have a similar role to the waxes.

2.2.3. Stabilizers

The molecular structure of stabilizers consists of aromatic benzene rings suitable for reaction with nitro groups NO_2 arising from the decomposition of the NC/NG nitric esters. The most common stabilizers are:

- Diethyl diphenyl urea or centralite acts as a stabilizer and also a plasticizer for nitrocellulose. It is not suitable in charge grains of large web thickness because the products of its stabilization reaction are gases of poor solubility and diffusivity in the propellant. This can result in gas cracking or fissures in the propellant.
- 2-Nitrodiphenylamine, which can act on the ballistic properties of the propellant by increasing the burning rate and temperature coefficient. On the other hand, diphenyl amine, a basic stabilizer for single-base powders, cannot be used because of its reaction with nitroglycerine.
- *N*-methyl-*para*-nitro-aniline, with its very high capability of fixing the nitrogen oxides, has an efficient stabilizing action, but also a more rapid consumption and, consequently, quicker utilization of the stabilizer. Its use is recommended for applications with high thermal stresses, or for large size-grains. It is generally associated with one of the other stabilizers, which ensures a longer lasting complementary effect.
- Resorcinol, which has a weaker stabilizing effect.

A certain number of other substances with aromatic cores compatible with nitroglyerine can also be used, including, for example, 2-methoxynaphthalene and trimethoxybenzene.

2.2.4. Ballistic additives

For double-base propellants the ballistic catalyst effect is obtained by using metallic compositions [5,6], in particular lead salts or oxides.

The most widely used ballistic modifiers are lead salts such as dibasic stearate, neutral stearate, salicylate, octoate, resorcylate, basic oxide (PbO), and saline oxide (Pb_3O_4).

These products affect the energetic level of the propellant, its burning rate, the operational pressure range, and the manufacturing process. Consequently their use and amount are dependent on the properties required, and vary from one composition to another.

Copper-based products can be added to the propellant to strengthen the effect of the other catalysts. Salicylate, octoate, oxides, and chromite are among the most common copper compounds used.

Finally, although alone it has a non-catalytic action, acetylene black is widely used, because its efficiency becomes very high when associated with other catalysts such as lead or copper salts.

2.2.5. Operational additives

The major particulate damping agents are zirconium oxide, zirconium silicate, and silicium carbide. Various other products may also be used, including tungsten and boron carbide.

After burning flash suppressants additives are potassium-based; they are selected based upon:

- their efficiency in flash suppression;
- their chemical compatibility with the propellant;
- their influence on the propellant properties, in particular, the ballistic properties.

Among the potassium salts used are, for example, cryolite, sulfate (the oldest), bitartratre, and oxalate.

3. The Manufacturing Process

3.1. REMINDER OF THE FUNCTIONAL ROLE OF THE PROCESS

The role of the manufacturing process is to ensure the transformation of the raw materials into a finished product which is as close as possible to the desired grain shape and size. Therefore, the manufacturing process provides for a number of essential functions, such as the homogenization of the product, its gelatinization, and its shape.

3.1.1. Homogenization

The various ingredients exist in very different physical states: floss for nitrocellulose, liquid for nitroglycerine, and amorphous powder or crystalline state for the ballistic catalysts. An intimate mixture must be ensured. There are various techniques to be used, including kneading, screw extrusion, and laminating between rollers.

All three of these techniques are used with solventless propellants. Solvent kneading is used for the first phase of the production of CDB propellants.

3.1.2. Gelatinization

Nitrocellulose gelatinization by nitroglycerine results in the swelling and partial solution of the fibrous structure of the nitrocellulose.

A temperature increase facilitates the gelatinization. The rolling of EDB propellants, for instance, is done at high temperature (100°C); the kneading of casting powders at a temperature between 30 and 40°C; CDB propellants are cured at a temperature close to 60°C.

Gelatinization is also facilitated by mechanical action during the mixing of the casting powders and particularly, during the rolling of EDB propellant. Finally, it is further facilitated by the use of the solvent system with an acetone and alcohol base, or ether and alcohol, during the preparation of the casting powders. These will modify the state of the nitrocellulose and the absorption kinetics of the nitroglycerine by the nitrocellulose.

3.2. MANUFACTURING PROCESS OF EXTRUDED DOUBLE-BASE PROPELLANTS (EDB)

3.2.1. The conventional process

3.2.1.1. Manufacture of the paste: impregnation of the nitrocellulose with nitroglycerine

Since the transport of nitroglycerine was forbidden, the mixing of nitrocellulose and nitroglycerine has been done at the facility where the nitroglycerine is manufactured. The process used, called "impregnation", consists of placing nitrocellulose in suspension in water agitated by compressed air, and of pouring nitroglycerine, which disperses itself into droplets suspended in the water medium under the effect of the agitation. These droplets are absorbed by the nitrocellulose fibers with which they come in contact. The resulting product, called a paste, is then homogenized and drained of excess water, leaving a water content of 30% as required by law for transportation.

3.2.1.2. Drying of the paste

Too wet to be used in the manufacturing process, the paste is dewatered by spin centrifuge for several minutes, reducing the water content to approximately 20%.

3.2.1.3. Kneading

The water content of the paste is neither accurately known, nor is it perfectly constant throughout the entire mass. A further mixing operation is necessary to obtain a homogenized product. The water content is also measured, which allows calculation of the weight of dry nitrocellulose, and therefore deduction of the amounts of constituents that need to be added during the kneading operation. These other ingredients are added successively during the kneading, in small amounts for the solids and by spraying for the liquids. At the end of approximately 30 min, the premixed paste obtained is unloaded from the kneading machine. This paste constitutes a homogeneous unit, identified and used as such for the remainder of the manufacturing process.

3.2.1.4. Gelatinization: rolling operations

The removal of water from the paste and the gelatinization of the nitrocellulose by the nitroglycerine is obtained by the dual effect of pressure and heating, in two rolling phases.

During approximately 6 min, the agglomeration rolling is an essential step for the gelatinization of the propellant and for the creation of the ballistic properties. Because the rollers are rotating at various speeds, this operation is also called differential lamination.

The sheets produced by differential rolling still contain too much water. A further rolling, during approximately 15–20 min, perfects the gelatinization and eliminates the residual amount of water. It is done with rollers rotating at identical speeds, called a finish rolling.

3.2.1.5. Carpet rolling of milled sheets

Before they can be put into the barrel of the extrusion press the laminated sheets must be rolled up to have a diameter slightly smaller than the diameter of the barrel of the press involved. It is very important during this operation to prevent heat losses.

3.2.1.6. Extrusion

Whether horizontal or vertical, an extrusion press for double-base propellants always includes a barrel with a heating jacket, where very hot water is circulated (70–80°C) and a piston moving inside the barrel. This is fitted with annular air outlets. It is absolutely necessary to avoid blocking air into the propellant rolls being compressed, because the air could become heated through adiabatic compression, and cause ignition.

The press barrels have various sizes; they may measure up to 380 mm diameter and hold up to 90 kg of propellant. The bottom of the barrel consists of a sort of filter with holes, the "sieve plate" through which the material is forced into a second barrel located just before the extrusion device. The extrusion device consists of a die that determines the outside shape of the free-standing grain or the propellant (cylinder, star, square, rectangle, etc.)

and of one or several needles to create perforations within the required shape.

When manufacturing large grains there is only one die per extrusion press; but for small or mid-size diameters the extrusion press may be equipped with up to 12 dies. The operations are performed in the following order:

- introduction of the roll into the press barrel;
- the piston is lowered to the surface of the propellant (approach of the piston);
- vacuum process takes place to remove occluded air;
- the piston is set in motion, at a specific speed to effect the extrusion process.

To guarantee a good stability of the dimensions of the sections extruded, precise heat control is necessary to maintain the die at a uniform temperature. Manufacturing quality depends on strict control of the extrusion operations. Rheology studies have been done to determine the thermal and mechanical mechanisms involved in the extrusion process [7]. A model reproducing the thermomechanics of the flow inside the die has been developed that takes into account the variations of viscosity as a function of the temperature and the shear stress to which the propellant is subjected. The thermal phenomenon, however, does not occur inside of the product, but at its surface. A boundary layer is created, and its characteristics govern the flow and/or defects caused by ripping. The conventional laws applied to molten polymers are not capable of taking this boundary layer into consideration. Consequently, even if its modeling is rather complex, the knowledge of the boundary layer occurrence guides the choice of the geometry of the dies. For example, profiles that have a propensity to break or disturb this boundary layer should be avoided.

On exit from the extrusion press the strand or section of propellant swells, because of the release of pressure. The higher the extrusion pressure, the greater the swelling will be. To ensure the reproducibility of the swelling, the extrusion pressure is set for the specific compositions, and the rate curve of the descending piston is also controlled.

Typically the hydraulic pressures that are being exerted are approximately 18 MPa, resulting in a pressure on the material that may reach 70–100 MPa.

Safety rings limit the exerted pressure, and can be cut in case of fire.

3.2.1.7. Cutting

The extruded sections are roughly cut to be somewhat longer than the final dimension.

3.2.1.8. Machining

The propellant strands or sections, which undergo swelling to a larger or smaller extent depending on the extrusion conditions, shrink during cooling.

This phenomenon makes it difficult to obtain dimensions of close tolerances without including a final machining.

Cutting to the final length is done after cooling has been completed, sometimes even after an aging period. The cutting is usually done with a milling saw. With the use of lathes, mills and drills, the outside and the inside of the grain can be precisely shaped, according to requirements.

For the most part the cutting tool is cooled with fluid during the machining operation, and the propellant machining swarf is removed from the vicinity by vacuum exhaust.

3.2.1.9. Inhibiting

Most of the grains for rocket propulsion must be inhibited on their outside surface, as well as inside, in some cases. There are various techniques available that depend on the size and the shape of the grains. They also depend on the nature of the inhibition material. Typical materials are:

- filled or unfilled polyester cast inhibitors from prepolymers, with low viscosity, and applied by a casting process;
- silicone polymer resins, applied by injection into molds surrounding the propellant grain;
- polyurethane inhibitors, currently becoming increasingly popular, which are injected around the propellant grain whose surface has been coated with a primer.

3.2.2. Other processes

The process described above is the process most widely employed for the manufacture of solventless propellant grains. A significant amount of energy is put into the material, giving propellants manufactured in this manner excellent ballistic and mechanical properties. However,

- there are some variations in the manufacture of the propellant material (calendering and stamping);
- new technologies, such as screw extrusion, already widely used for the production of plastic materials, are replacing the conventional processes.

3.2.2.1. Calendering

Calendering permits the production of sheets or strips with a very regular thickness, varying from 0.075 to 2 mm, and a textured surface, including ribs, ridges, barbs, grids, and others variations.

The propellant sheets from the finishing extrusion rollers previously described are passed through calender rolls. The latter is a powerful rolling machine in which the rolls have a surface tailored to the propellant manufacture. The rolls are also heated and have variable rotation speeds.

3.2.2.2. *Stamping (or hot forming)*

Stamping is a hot forming process, or thermoforming, of propellant pieces obtained by press or screw extrusion. These pieces are first cut to have approximately the weight and size of the future grain [8]. The operation is carried out in several phases:

- the propellant piece is placed in the mold, which consists of a die with the desired outside profile and a stamp with the complementary geometric profile required;
- the mold is closed, the temperature is raised to 80–90°C, the forming temperature, and limited pressure is applied (3 kPa);
- the stamp is moved inside the die cavity to compress and force the softened propellant to obtain the final shape desired;
- the stamp is removed from the die.

The advantage of this process resides mainly in the fact that it allows the production of geometrical shapes that cannot be obtained by extrusion, such as full head-end grains (where the central bore opens at only one end) and elaborate and complex patterns which are difficult to obtain by extrusion.

3.2.2.3. *Screw extrusion*

The production process for EDB propellants involves a large number of successive phases, which are an economic handicap for the production of a large number of parts.

Various attempts have been made to replace the EDB process with a more continuous and economically more advantageous process (using solvents and production in a non-solvent–liquid phase [9,10]).

The most complex attempts have sought to use the technology widely employed for the production of plastic materials, i.e. the screw extrusion process [11,12]. After a considerable period of adaptation this process is currently used for the industrial mass production of EDB propellant grains [13].

Two extruders are used successively; they are designed to perform the following operations: agglomeration rolling, final rolling, and extrusion. Kneading is the only separate operation that is retained, owing to the critical importance of precise measurement of the quantities of the various ingredients in the propellant composition. These screw extruders include:

- a variable-rate feeding system;
- a temperature control system for the screw and the die;
- a set of exhaust ducts to allow removal of water and gases;
- a die placed at the end of the extruder, used to shape the material.

The first extruder is fitted with an adjustable screw; this ensures the gelatinization of the wet mixture. The mixture, transformed into granules, is fed continuously to the second extruder. These granules can also be obtained through a continuous rolling process. The second extruder, which is fitted with two parallel screws, completes the homogenization of the mixture and ensures the shaping of the material.

In addition to the economic advantages, this process is also a safer one, inasmuch as the work can be done at a certain distance, does not require any contact between the operator and the material, and reduces the amount of handling and transfers.

3.2.3. *Current products*

There is a very wide selection of double-base extruded propellants. The size range extends from very thin sticks (outside diameter 1.5–5 mm) to very large diameter grains (around 500 mm).

Many extrusion profiles have been created, including end-burning grains, multiperforated, and external star grains with cylindrical or star-shaped central bores.

The weight of the grains varies from several grams, in the case of ignition increments, for example, to a few tens of kilograms for ground-to-air missile boosters.

The propellant manufacturing cycle is relatively short. The mixing, rolling and extrusion operations can be done in just 1 day. This rapid production feature of the solventless process makes it attractive for large-scale industrial production.

3.3. MANUFACTURING PROCESS OF CAST DOUBLE-BASE PROPELLANTS (CDB)

This process involves two main phases:

- Manufacture of the casting powder, which contains all of the nitrocellulose and the solid ingredients, as well as a portion of the inert plasticizers and, sometimes, nitroglycerine. This powder comes in the shape of small cylinders with a diameter and length close to 1 mm.
- The casting and curing phase. The casting powder is placed in a mold. A casting solvent — consisting mainly of desensitized nitroglycerine — fills the interstices between the grains. Heating at moderate temperature leads to a penetration of the casting solvent into the grains, resulting in the creation of a homogeneous propellant grain [14].

3.3.1. Manufacture of the casting powder

3.3.1.1. Preparation of the raw materials

The raw materials are generally used without any special treatment. The nitrocellulose, however, stored in a wet condition, undergoes a dehydration by ethyl alcohol before it is used.

When the casting powder contains nitroglycerine, a premixing operation is necessary. This consists of impregnating the dehydrated nitrocellulose with a nitroglycerine solution in acetone. This operation is carried out in a mixer equipped with one vertical blade slowly rotating.

3.3.1.2. Kneading

All ingredients are mixed together with the suitable solvents in order to obtain an extrudable dough. Although various solvents can be used for this operation, the most common ones selected are mixtures of ether and alcohol or acetone and alcohol.

The kneading, which takes place in a horizontal mixer with Z blades, produces a uniform mixture of all of the powder ingredients and allows the beginning of the gelatinization of the nitrocellulose in the presence of volatile solvents and plasticizers. Various parameters govern this gelatinization:

- The amount of solvent is adjusted according to the compositions used and, in particular, to the quality of nitrocellulose. The solvent to dough ratio or percentage has a significant influence on the solvation/gelation of the nitrocellulose and, as a result, on the ballistic and mechanical properties of the final propellant.
- The composition of the gelating solvent, i.e. the relative proportions of ether and alcohol, or acetone and alcohol.
- The introduction order of the ingredients. The nitrocellulose, if necessary premixed with the nitroglycerine, is introduced first, and the mixing operation is begun with the solvent so as to prepare a dough which will be ready for the subsequent homogenization of the various ingredients: plasticizers and ballistic catalysts.
- The temperature, generally maintained below the boiling point of the solvent, at approximately 30-40°C.
- The duration of the mixing operation, usually less than 4 h.

3.3.1.3. Extrusion

After the mixing, the dough is compacted into the barrel of an extrusion press which, unlike the presses for the solventless propellants, does not require a fine heat control or vacuum system. The operation is controlled to ensure a constant extrusion speed, because this speed has a direct effect on the size of the extruded sticks (diameter close to 1 mm). The behavior of the dough at extrusion is largely a function of its composition and of its gelatinization state [15].

3.3.1.4. Removal of solvents

The cords produced by the extrusion press are placed in an oven in order to remove most of the residual solvents. As a result the sticks get a certain hardness, which makes them easier to cut.

3.3.1.5. Cutting

The quality of the cutting, typically using a guillotine technique, is important, because it directly influences the bulk or packing density of the powder. Typically, the length of cut is equivalent to the diameter of the sticks, i.e. 1 mm.

3.3.1.6. Final drying

Most of the solvents have been removed in the course of the previous operations; however, residual solvents are caught in the nitrocellulose fibers, and a simple heat conditioning may not be sufficient to remove them completely. Consequently, the next step may involve soaking the product for several days in hot water (60-80°C). This hot water medium facilitates removal of the solvents. Water has little chemical affinity with nitrocellulose, and can easily be removed by hot air drying (60°C). The proportion of volatile material in the powder is reduced to a value close to 1%.

3.3.1.7. Finishing

After the drying phase, the casting powder is often coated with graphite. This reduces the powder electrostatic charges and facilitates its flow properties. This operation also permits a deburring of the grains, i.e. a removal of the surface roughness, increasing the bulk or packing density of the powder. This operation is carried out either in a batch process in a mixing tower or a coating machine, or in a continuous process in a hopper with an endless screw.

The powder sub-batches obtained are mixed together to form a large homogeneous blended lot of casting powder. This operation is an essential one, because the uniformity of the properties of the cast propellant are largely determined by the properties of the casting powder.

3.3.1.8. *Control of properties*

A certain number of the characteristics of the casting powder are systematically controlled:

- the water and volatile material contents in the finished powder are limited respectively to 0.7% for water and 1.8% for the volatile materials;
- the apparent density or gravimetric density, which determines the packing or volume loading of the grains in a column of powder, and is consequently directly related to the final composition of the propellant;
- the chemical composition and, in particular, the amount of stabilizers, ballistic catalysts and graphite;
- the thermal stability, which is monitored by a sample heat test, where the temperature is raised up to 108.5°C or 120°C — the time required for the emission of nitrogen oxides is determined;
- the heat of explosion, which determines the final energetic properties of the propellant.

3.3.2. *Manufacture of the casting solvent*

The casting solvent is a mixture of nitrate esters and inert plasticizers. The latter are called desensitizers because they decrease the sensitivity to shock and friction of the nitrate esters.

The most commonly used solvents are obtained by mixing nitroglycerine and triacetin, which is a good desensitizer of nitroglycerine (Fig. 2).

Values for the following parameters are chosen to meet the requirements of particular applications and the desired performance:

- percentage of desensitizer (between 21% and 27% in most cases),
- percentage and the nature of the stabilizer (between 0.5% and 1%).

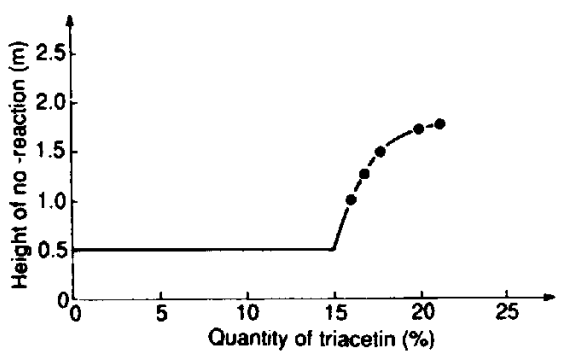


FIG. 9.2. Sensitivity to 30 kg fall-hammer test of casting solvent as a function of the quantity of triacetin.

The casting solvent is produced by introducing the nitroglycerine into a premix containing triacetin and the stabilizer. A dehydration process is carried out by heat treatment — under vacuum accompanied by pappling or bubbling dry air through the mix. A water content of less than 500 ppm is attained.

3.3.3. *Manufacture of the cast double-base propellants*

The objective is to obtain a homogeneous product by gelatinizing the casting powder with the casting solvent.

3.3.3.1. *Filling of the molds*

The casting powder is loaded into a casting mold that consists of the following parts:

- a base to allow the positioning of the casting corset and ensure a good distribution of the casting solvent;
- a metal casting corset or tube which will give the propellant blank grain its outside shape;
- a metal core to shape the central bore of radial burning grains;
- a top assembly to seal the mold, which includes a vacuum system and a sighting system allowing a check on the casting solvent injection.

The powder packing density generally reached is around 65%. This is a function of:

- the size of the casting powder grains — theoretical calculations reveal that the grain arrangement is optimum when the length versus diameer ratio is close to 1.
- the method by which the casting powder is introduced — various methods have been used to best fill the molds: vibrations, successive sieves with cross mesh and bars set in a spiral along the filling funnel;
- the characteristics of the casting powder itself: apparent density and also the surface condition, which in turn depends on manufacturing conditions, quality of the nitrocellulose, and powder nitroglycerine content.

Once the mold has been filled with powder a degassing phase, carried out under reduced pressure at ambient or moderate temperature and lasting a few hours, removes the residual volatile solvents and the air contained in the mold.

3.3.3.2. *Casting*

The casting consists of injecting the casting solvent into the base portion of the mold serving as a distribution chamber, and subsequent passage through the powder bed.

The interstices between the casting powders are filled with the casting solvent or gelatinizing liquid. Modeling studies of this phase [16,17] have revealed significant behavior variations, depending on the state of gelatinization and the nature of the casting powders.

3.3.3.3. *Curing*

Following casting the mold contents are subject to a curing process. This accelerates the gelatinization of the nitrocellulose by the casting solvent. The diffusion of the solvent is assisted by the presence of the triacetin molecules, which have a significant affinity for nitrocellulose. This phenomenon corresponds to more or less active interactions between the plasticizer and the nitrocellulose polymer, and causes a slight exothermic effect [18].

The curing process varies within different countries; it includes either one curing phase or two distinct steps:

- A precuring of 24–72 h, at a temperature of approximately 40–45°C, letting the grains absorb the maximum quantity of solvent necessary to make them swell. During this precuring phase the casting powders are already sufficiently gelated and coalesced to each other to allow the removal of excess casting solvent. This is necessary to avoid a risk of decomposition of the nitroglycerine in the surplus liquid during the second curing operation.
- The curing itself, which completes the migration of the solvent to the core of the nitrocellulose fibers.

As the curing progresses, the core of the granules becomes increasingly translucent and, after a few days, the entire grain is transformed into a homogeneous substance. The propellant has then attained its finished mechanical and ballistic properties. The entire operation requires periods of more than 72 h and temperatures ranging from 50 to 65°C (Fig. 3).

During the curing phase the propellant undergoes variations of volume whose magnitude depends on the degassing conditions of the powder and the solvent. These variations correspond mainly to the filling of the microporosities of the granules of the casting powder (Fig. 4).

3.3.3.4. *Mold disassembly*

Disassembly consists of removing the core from the propellant grain and drawing the grain from the casting tube.

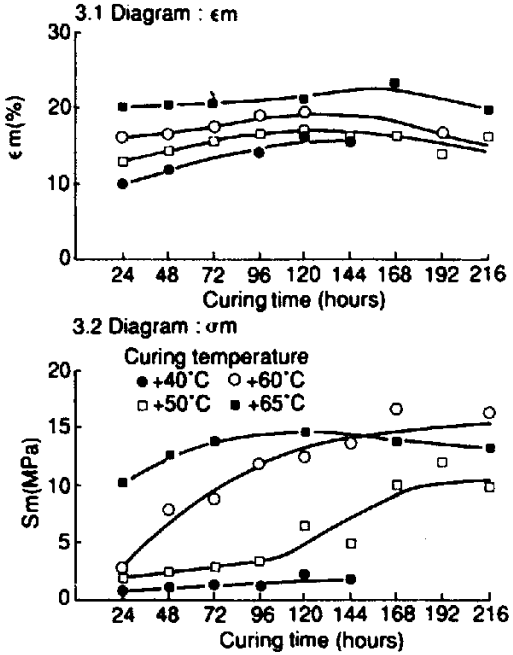
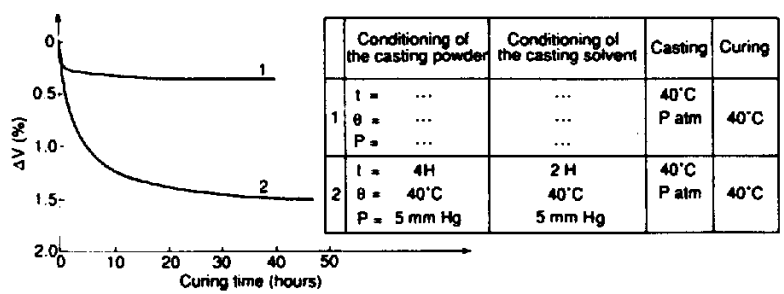


FIG. 9.3. Diagram of mechanical properties set up of a cast double-base propellant as a function of the curing conditions (time-temperature).



	Conditioning of the casting powder	Conditioning of the casting solvent	Casting	Curing
1	t = ... θ = ... P = ...	... ...	40°C P atm	40°C
2	t = 4H θ = 40°C P = 5 mm Hg	2 H 40°C 5 mm Hg	40°C P atm	40°C

FIG. 9.4. Diagram of the volume variations of a cast double-base propellant as a function of the conditioning of the casting powder and of the casting solvent.

3.3.3.5. *Machining*

The ends of the propellant grain must be removed because their composition is slightly different due to the fact they were in proximity to the excess solvent during the precuring operation.

The grain is then cut to the proper dimensions using the same techniques as for extruded propellant grains (Section 3.2.).

3.3.3.6. *Inhibiting*

The process used to inhibit double-base cast propellants is the same as the process described for extruded propellants (Section 3.2.).

In some instances there are advantages for other techniques when application allows it (small or medium-size grains with fairly regular external profile). These techniques involve casting the propellant into the inhibitor by using a insulator as a casting mold. This operation offers the two following advantages:

- the machining operation is no longer necessary because the grains are cast directly in the dimensions required (except for the length of the grain);
- the final inhibiting operation is not necessary.

3.3.4. Other processes

The evolution of double-base cast composition toward increasingly energetic propellants has imposed some modifications to the process. For instance, the search for high contents of nitrate esters (nitroglycerine, for example) led to partly incorporating them into the casting powder, requiring, as a result, two modifications:

- the addition, already mentioned, of nitroglycerine to the nitrocellulose in a premixing phase;
- the exclusion of the water steeping phase, since the presence of high amounts of plasticizers facilitates the elimination of the volatile solvents.

The screw extrusion technique can simplify the process of obtaining casting powder. The performance characteristics of propellants made from such a casting powder are similar to that of propellants obtained by the conventional process.

3.3.5. Current products

The casting technique permits the production of propellant grains with virtually no limitations as far as shape is concerned, except for the height of product cast, although these can be as high as 2 m.

Many varied types of propellant grains are produced, such as end-burning grains, grains with cylindrical or star-shaped center bore, with variable profile such as partially slotted tubes, or dual propellant grains.

Their size may vary from a few grams to several hundreds of kilograms.

Because the cast double-base propellant technique has been thoroughly mastered, it allows the production of large industrial quantitites; for example, sustainer propellant grains for anti-tank missiles.

4. Characteristics of Double-base Propellants

4.1. PHYSICOCHEMICAL CHARACTERISTICS

4.1.1. Density

The density of double-base propellants results from the density of their raw materials: nitroglycerine (1.60), nitrocellulose (1.650–1.662). However, it is also influenced by the density of the additives: lower-density non-energetic plasticizers and higher-density ballistic modifiers. Typically:

- 1.55 to 1.66 for EDB propellants;
- 1.50 to 1.58 for CDB propellants.

4.1.2. Linear thermal expansion coefficient

The coefficient determines the geometrical changes to the grains as a function of temperature, and consequently, permits assessment of the tolerances required inside the combustion chambers. This coefficient is characteristic of the nitrocellulose, nitroglycerine and plasticizer mixture, and is approximately 1.2×10^{-4}.

4.1.3. Specific heat capacity

Characteristic of the nitrocellulose–nitroglycerine matrix, the specific heat capacity is approximately 0.350 calorie per gram per degree for all double-base propellants.

4.1.4. Thermal capacity

Derived from the previous characteristics (specific heat, density) this is in the range of 0.570 calorie per gram per cubic centimeter.

4.1.5. Thermal conductivity

This property governs the heat exchanges inside a grain subjected to varying thermal environmental conditions. The reference value of 10×10^{-4} watt per centimeter per degree means that these propellants are a relatively insulating material.

4.1.6. Heat of explosion

The heat of explosion of the propellant is directly tied to its energetic level. Based on the respective ratios of the various ingredients, the two double-base propellants cover the following ranges:

- from 700 to 1100 cal/g for EDB propellants;
- from 500 to 900 cal/g for CDB propellants. The low values correspond to compositions with high contents of inert plasticizers, used as gas generators.

The heat of explosion of a propellant is equal to an additive value characteristic of each of its constituents. Table 2 gives the theoretical values for the major constituants of double-base propellants.

TABLE 2 *Heat of explosion of the main ingredients of double-base propellants*

	Potential (cal/g)
Slabs	
Nitrocellulose	+800 to 1080
Nitroglycerine	+1750
Nitrocellulose/nitroglycerine paste: 74/26	+1070
66/34	+1180
62/38	+1250
60/40	+1190
59/41	+1270
58/42	+1280
50/50	+1350
Additives	
Centralite	−2440
2 Nitrodiphenyl amine (2NDPA)	−1548
Diethylphthalate	−1765
Dibutylphthalate	−2070
Triacetin	−1253
Neutral lead stearate	−2103
Basic lead stearate	−1264
Lead salicylate	− 915
Lead octoate	−1331
Pb_3O_4 minium	+ 139
Lead oxide (PbO)	+ 68
Copper octoate	−1941
Copper chromite	+ 245
Potassium cryolite	− 14
Potassium sulfate	+ 222
Potassium nitrate	+1428
Acetylene black	−3395
Magnesium stearate	−2806
Aluminum	+3656
Candelilla wax	−3277
Magnesium	+3214
Copper oxide (CuO)	+ 367
Dinitrotoluene 2-4	− 150
Dinitrotoluene 2-6	− 72
Ethylphenylurea	−2236

4.2. MECHANICAL CHARACTERISTICS

Over the course of their service life, solid rocket motors are subjected to various stress factors (such as acceleration, vibration, shock, thermal effect, and others) which need to be compared with the mechanical capability of the propellant. A certain number of characteristics determines the propellant mechanical capability, including those discussed in the following paragraphs.

4.2.1. Hardness

Hardness is a quick and simple way of assessing the mechanical properties of a material. The values usually obtained at 20°C are about 55 shore A.

4.2.2. Tensile and compression behavior

Double-base propellants are characterized by high elastic moduli and mechanical properties suited to use in free-standing grains, sometimes with a very thin web.

These characteristics are most commonly determined by performing uniaxial tensile tests. The JANNAF specimen, dumbbell type, is most widely used. A complete mechanical characterization of the properties of a propellant needs the performance of a large number of tensile tests in order to test the behavior of the material within a wide range of times and temperatures. A sample of the master curve (Sm, E, ε, em) of an EDB propellant is given in Fig. 5. Table 3 is a mechanical characteristics example of an extruded and cast composition.

TABLE 3 *Comparison of the mechanical properties of an EDB propellant and a CDB propellant*

	−40°C	+20°C	+60°C
EDB Propellant			
Sm (MPa)	51	11	2
ε (%)	2.8	2.5	8.0
E (Mpa)	1835	439	21
e_r (%)	3.4	15.7	31.8
CDB Propellant			
Sm (MPa)	33	11	3
ε (%)	1.0	2.0	10.7
E (MPa)	3279	555	27
e_r (%)	1.2	24.5	66.8

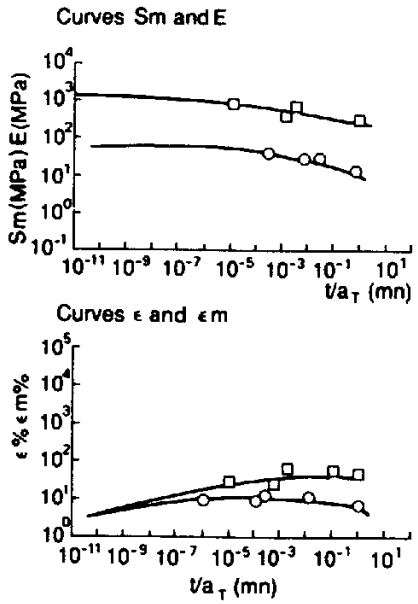


FIG. 9.5. Master curves for an E.D.B. propellant.

4.3. KINETIC CHARACTERISTICS

4.3.1. *Burning rate*

The burning rate of homogeneous propellants depends primarily on the ballistic modifiers in the composition.

Figure 6 and 7 show the performance currently available. The range of burning rates of EDB propellants, at 20°C, is between 5 and 40 mm/s, while the range of CDB propellant is narrower, from 3 to 20 mm/s.

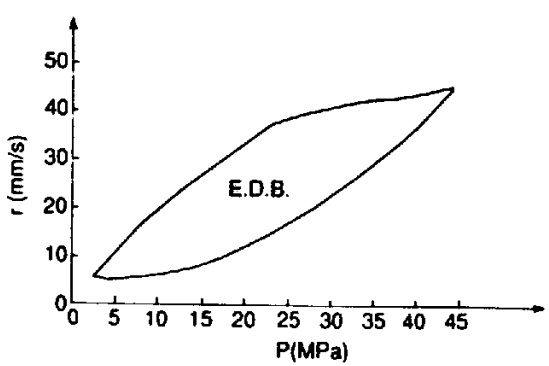


FIG. 9.6. Range of burning rate-pressure available to E.D.B. propellant.

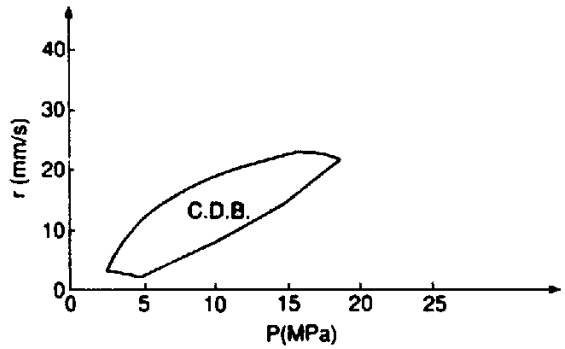


FIG. 9.7. Range of burning rate-pressure available to C.D.B. propellant.

The plateau effect is found in a pressure range which depends on the burning rate. Consequently, at 5 mm/s the plateau pressure is around 5 MPa, while at 40 mm/s it is approximately 30 MPa.

4.3.2. *Temperature coefficient*

The temperature coefficient expresses the sensitivity of the propellant burning rate to its temperature before combustion. Where homogeneous propellants are concerned the values obtained vary greatly, depending on the composition:

- $-\pi_k = 0$. The burning rate is independent of the temperature. This phenomenon is observed, in particular, for EDB propellants with low energetic levels (lower than 900 cal/g).
- $-\pi_k < 0$. As the temperature before combustion goes up, the burning rate decreases. This type of value if found mainly wih CDB propellants with low energetic levels (of the order of 700 cal/g).
- $-\pi_k > 0$. This is the most frequent case with these propellant families. The values obtained are in the range of 0–0.3% per degree; a few higher values can be found with highly energetic propellants (higher than 1100 cal/g).

4.3.3. *Parameters affecting the burning rate*

The burning rate depends mainly on the nature of the catalytic system. Besides this major factor, there are other parameters worthy of notice.

4.3.3.1. *Adjustment*

Certain elements such as acetylene black, by varying very slightly the amounts used, can significantly change the burning rate. This property is

used to guarantee a perfect reproducibility of a specific composition, regardless of the various raw materials lots.

4.3.3.2. *Ballistic modifiers particle size*

Some of the catalysts can influence the burning rate with their particle size. This effect is of relatively modest importance; it has been seen with certain oxides (CuO, for instance). The particle size of the catalysts typically is of the order of a few microns.

4.3.3. *Manufacturing process*

The processing may also have an impact on the ballistic properties of double-base propellants, inasmuch as they influence the homogeneity of the catalysts' distribution and the gelatinization of the product. This effect was demonstrated with both propellant families.

(a) Extruded double-base propellants

The duration of the agglomeration rolling operation (done in the presence of humidity) can be significant in some cases to the level of the final ballistic performance. There is a decrease in the pressure exponent and the creation of a plateau effect by prolonging the duration of this rolling operation [19].

(b) Cast double-base propellants

The gelatinization phenomenon is, for this family, mostly due to the chemical action of the solvent used to manufacture the casting powder. As such, the amount of solvent introduced in the mixer and, in particular, the quantity of acetone, are likely to have an influence on the characteristics of the final propellant. A large quantity of acetone promotes the gelatinization and makes the fibrous structure of the nitrocellulose disappear. Casting powder, in an advanced state of gelatinization, has less affinity for the casting solvent, which will have more difficulty in penetrating inside the casting powders. The final propellant, as a result, will be more heterogeneous and the ballistic properties, which are related to the homogeneity and the state of gelatinization, will therefore be modified.

(c) Comparison of EDB and CDB processing techniques

Both processing techniques have been tested for the manufacture of double-base propellants. The EDB process leads to a better-gelatinized and more homogeneous product, because of the efficiency of the mechanical and

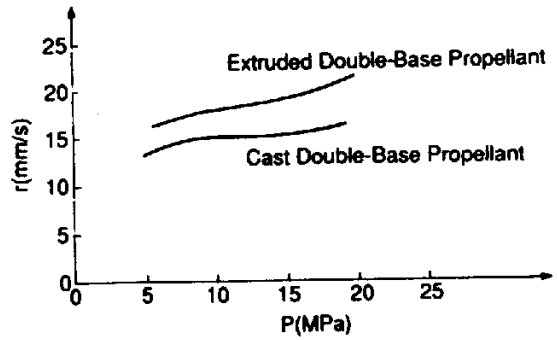


FIG. 9.8. Influence of the manufacturing process on the ballistic characteristics of a double-base propellant.

thermal actions of rolling. A comparison of the ballistic properties (Fig. 8) reveals a higher burning rate for the EDB propellants.

4.3.3.4. *Energetic level*

The plateau effect of the double-base compositions is obtained by using catalytic systems tailored to the energetic level of the composition.

The plateau burning rate is related to the super-rate effect caused by the ballistic modifiers. The result is that a high energetic level leads naturally to a high burning rate.

The energetic level also has a significant impact on the temperature coefficient, which generally increases with the energy of the compositions.

4.4. ENERGETIC CHARACTERISTICS

The energetic characteristics are usually expressed in terms of specific impulse (in seconds). As an alternative to the necessity of systematic experimental measurements on standard grain, various simplified approaches have been used to determine the energy characteristics of a propellant:

- the theoretical specific impulse, derived from thermodynamic calculations;
- the heat of explosion, corresponding to the measurement of the calorie value during the combustion of the propellant.

4.4.1. *Theoretical performance*

The theoretical performance of a given composition may be calculated by taking various parameters into account, such as:

- atomic composition of the propellant (C, H, O, N and others);
- chemical equilibrium in the combustion chamber;
- combustion conditions (gas expansion).

4.4.2. Heat of explosion

The heat of explosion, expressed in calories per gram, permits a simple measurement of the energetic level. The operation is carried out in a calorimetric closed vessel, and consists of measuring the rise in temperature of a specific quantity of water during the combustion of a specific amount of propellant.

The value of the heat of explosion of a composition may also be determined through calculations. It is the result of the weighted algebraic sum of the calorimetric values of its constituents (Section 4.1.).

4.4.3. Available range

This is primarily a function of the amounts of the major constituents (nitroglycerine: 1750 cal/g, nitrocellulose: 920 cal/g, inert plasticizer: −1300 cal/g), as well as of the possibility of having a plateau effect. An increase in the energetic level leads, in fact, to a decrease of the plateau effect, because of a loss of efficiency of the combustion catalysts.

Today, the highest performances with acceptable ballistic characteristics are approximately 1100 cal/g for EDB propellants and 900 cal/g for CDB propellants.

An increase of the energetic level, significantly higher than these values, may be obtained by adding nitramines (Chapter 11).

4.4.4. Correlation between the specific impulse and the heat of explosion

There exists a linear relationship between the specific impulse and the calorimetric value (Fig. 9). The difference between the theoretical specific impulse and the delivered specific impulse for a reference rocket motor weighing approximately 2 kg is about 15 s.

The weight of the reference grain is also an important parameter in terms of influence. For instance, a difference of 2 s in specific impulse is found depending on whether the measurement is made on a standard motor equipped with a star-shaped central bore grain 203 mm in diameter, 500 mm long, and weighing 19 kg; or with a grain measuring 90 mm in diameter, 300 mm in length, and weighing 2 kg.

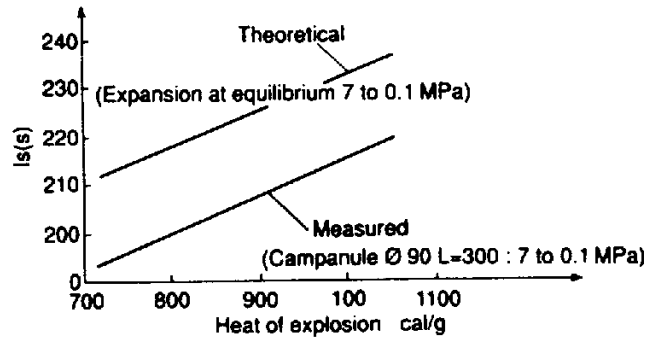


FIG. 9.9. Correlation diagram between the measured specific impulse, the theoretical specific impulse, and the heat of explosion of double-base propellants.

5. Operating Characteristics

5.1. SIGNATURE

5.1.1. Smoke

Propellant combustion and the decomposition through pyrolysis of the inert materials of the rocket motor (inhibitors and thermal insulation, for example) generate smoke in the rocket exhaust which may have a detrimental consequence, either by interference with the missile guidance or by permitting the missile or its firing location to be revealed. A distinction must be made between:

- primary smoke, which is generally the result of metallic particles contained in the propellant; and
- secondary smoke, which may result from the condensation of the combustion gases (H_2O, for example) or of the combination of atmospheric water vapor with certain combustion products (HCl, HF, and others).

Various approaches, more or less quantitative, allow evaluation of the amount of smoke produced by a propellant:

- thermodynamic calculation, used to determine the chemical products resulting from the combustion;
- visual assessment; and
- optical measurements taken in the visible or the infrared wavelengths.

Homogeneous propellants produce no secondary smoke and little primary smoke, since they contain no reducers and have only a small amount of metallic particles from their additives [20] such as:

- ballistic modifiers, generally consisting of organic salts and copper or lead minerals;
- particulate damping, generally consisting of refractory oxides, limited to the necessary amount because they remain as solids in the jet and their particle size can be optimized to reduce their interaction with light;
- Flash suppressant additives, which as alkaline-ion-based products (usually potassium) may also include other metallic-type elements (aluminum, for instance).

5.1.2. *Secondary flame*

Besides smoke, another element considered when assessing the signature is the presence of flames in the exhaust. The combustion gases may re-ignite downstream from the exit plane of the nozzle. This is known as the afterburning phenomenon, which corresponds to an oxidation by the air of the reducer products (H_2 and CO) produced by combustion of the propellant.

Similar to the smoke, the measurement of the exhaust during propellant combustion gives an indication of the intensity of the flash produced. The signature is not limited to the visible spectrum, but occurs also in the infrared region.

Many studies in this field have determined that the principal parameters are:

- composition of the propellant (energetic level, combustion temperature, nature of the gases, amount of reducing products, and presence of flash suppressants);
- combustion conditions;
- performance of the missile.

To prevent secondary afterburning it is necessary to seed the exhaust with particles likely to block the reactive mechanisms of re-ignition [22].

Many studies have been made to identify the additives that would be effective and the best manufacturing processes. Among the products most often mentioned in publications, and most widely used industrially, we find products with an alkaline metal base (usually potassium), such as nitrate, cryolite, sulfate, and potassium hydrogenotartrate, but also barium-based and tungsten-based products. The selection of an additive is made by taking into account not only its efficiency, but also the consequences resulting from its introduction on the propellant performance, in particular:

- energetic level,
- chemical stability,
- aging properties,
- creation of primary smoke and
- ballistic performance.

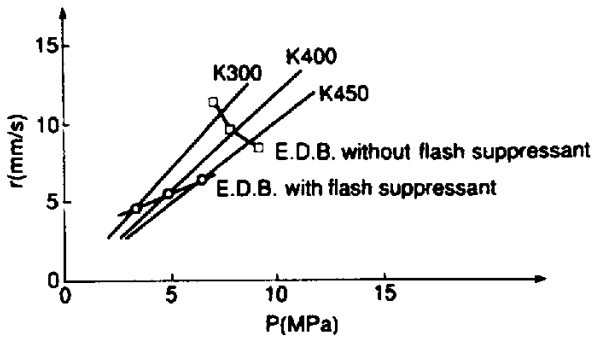


FIG. 9.10. Diagram of burning rate-pressure of an E.D.B. propellant with and without flash suppressant.

The direct introduction in manufacture during mixing of a flash suppressant is likely to significantly modify the ballistic performance of EDB or CDB propellants (Fig. 10); it is therefore necessary to modify the propellant manufacturing process to avoid this problem.

In the case of EDB propellant it suffices to incorporate the flash suppressant late in the process. This prevents it from mixing intimately with the ballistic catalysts. By introducing the suppressant at the time of the final rolling operation it is possible to obtain propellants with ballistic performances which are not adversely affected by the presence of this additive.

In the case of cast double-base propellant the process modification consists of separating the flash suppressant from the ballistic modifiers by using two casting powders, only one of which contains the suppressant additive. This allows the content of suppressant to be adjusted to the relative amounts of the casting powders. The best trade-off needs to be determined between the amount of additive in the special casting powder, and the amount of that casting powder to be used in the composition.

5.2. COMBUSTION INSTABILITIES

5.2.1. *Theoretical data*

Under certain internal configurations and firing conditions, radial burning grains may exhibit combustion instabilities that will translate into pressure fluctuations. These instabilities may belong to two types:

- longitudinal instabilities, whose frequency is a function of the geometrical dimensions of the grain (a few hundred hertz);
- high-frequency transverse instabilities, which may have two different modes, radial or tangential, or possibly a mixture of the two.

These instabilities cause:

- perturbations in the nominal pressure, triggering oscillations of the thrust delivered by the propellant grain;
- a possible pressure shift that may, in some cases, result in the extinction of the grain;
- the risk of re-igniting the gas jet, leading to an afterburning phenomenon.

These instabilities are more frequently tiggered in propellants with a high energy level or a fast burning rate.

5.2.2. *Effect of the configuration of the propellant grain and of the firing conditions*

The frequencies of the instabilities are related to the geometrical dimensions of the central bore of the grain. For instance, there usually is, for a given diameter, a length above which combustion instabilities will occur (Fig. 11). This length depends on the nature of the propellant. Conversely, for a specific grain length these instabilities appear at a diameter smaller than a certain limit value. We must also consider that, in addition to the length and the diameter values, certain geometrical configurations of the central bore may also be more prone to trigger instabilities. In the case of a star-shaped central bore, for example, an even number of branches is a factor likely to trigger instabilities (perfect symmetry of the grain).

While the firing conditions are a significant triggering factor, pressure is still the essential parameter. While they do not occur at high operating pressures, instabilities appear toward the lower pressure, generally corresponding to the lower limit of the plateau effect. It is, as a matter of fact, possible to identify a threshold pressure below which instabilities are started.

Similarly, low temperatures are more likely to trigger instabilities [22]. The

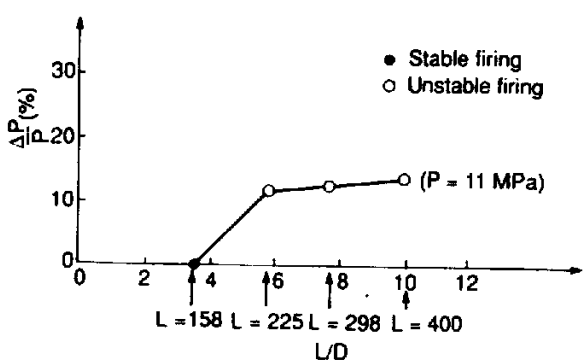


FIG. 9.11. Influence of the length of a 90 mm diameter star grain on the severity of the combustion instabilities.

combination of a low pressure and low temperature (– 40°C) creates a high likelihood of instabilities.

Finally, this phenomenon does not appear to be related to the chemical nature of the propellant but rather to its ballistic characteristics (such as burning rate), and its energetic characteristics (such as heat of explosion).

5.2.3. *Function of the refractory additives*

The presence of solid particles in the gas exhaust from the combustion chamber permits damping of the pressure oscillations. A judicious selection of their quality and quantity allows complete suppression of the combustion instabilities (Fig. 12). There are several possibilities:

- a source, outside of the propellant, such as the inhibitor or the thermal insulations, which, through degradation caused by the combustion, seeds the gas exhaust with particles;
- the inclusion in the propellant of aluminum, zirconium, or tungsten particles which, during combustion, produce liquid or solid products (Al_2O_3, W_2O_3, for example);
- the presence of refractory additives in the propellant, which is the most widely used technique.

The products used are selected on the basis of the smallest possible needed quantity. Among the selection criteria are:

- The melting temperature, which must be greater than the flame temperature; the most widely used compositions are oxides (ZrO_2, SiO_2, B_2O_3), carbides (Si, Zr, Ti) and silicates ($ZrSiO_4$) [23].

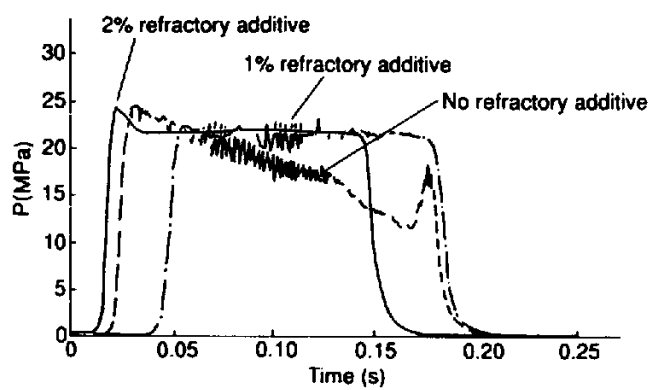


FIG. 9.12. Evolution of the combustion instabilities recorded on an E.D.B. standard ballistic grain (32 × 16 Type) as a function of the quantity of refractory additive.

- The particle size, selected in accordance with the formula:

$$R = \frac{3}{2}\left(\frac{\mu}{\rho \pi F}\right)^{1/2}$$

where:

R = optimal radius of the particles,
μ = viscosity of the combustion gases,
ρ = density of the particles,
F = frequency of the instabilities.

In practice, the optimal radius is smaller than a micron.

- Finally, since these additives may have a detrimental effect on the other characteristics of the propellant, they are chosen for the minimum negative impact on:
  - the chemical stability of the propellant and its energetic performance,
  - the burning rate and the temperature coefficient, and
  - the signature.

5.3. EROSIVE COMBUSTION

Erosive combustion occurs when a solid propellant grain is exposed to a gas flow, parallel to its surface and with a high flow rate (Q). We see a significantly increased burning rate for the propellant (V) compared with the normal burning rate (V_o), related by a formula of the type:

$$V = V_o[1 + k(Q - Q_s)]$$

where k is the erosivity coefficient of the composition (which depends on the burning rate, the catalytic system used, etc.) and Q_s the threshold of the flow above which the erosive phenomenon occurs.

Firing of the propellant grain, followed by quenching, permits the analysis of the contours, and determination of the erosivity coefficient. The erosivity coefficient of EDB propellants is of the order of 4×10^{-4} and the threshold flow rate varies from 500 to 100 g per second per square centimeter.

6. Chemical Stability

6.1. BACKGROUND

The nitrate esters used with double-base propellants are molecules that are not very chemically stable. In the usual ambient conditions of temperature, pressure and hygrometry their decomposition is slow. However, in more severe environments (high temperatures, acid chemical environment), the

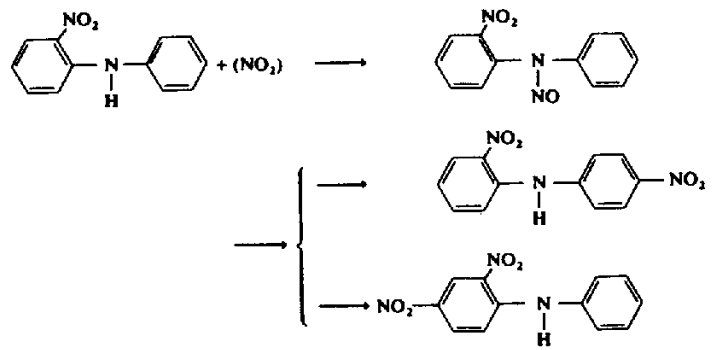
decomposition of nitric esters becomes autocatalytic. These reactions give rise to radical thus:

$$RONO_2 \dashrightarrow RO_2^{\cdot} + NO_2^{\cdot}$$

The free radicals attack the nitrate esters not yet decomposed; this is followed by a complex succession of secondary reactions producing gaseous products such as CO, N_2, and mainly, nitrogen oxides NO and NO_2.

The function of stabilizers introduced into the propellant is to remove a portion of the nitrogen oxides by fixing them chemically. The autocatalytic procedure is thereby slowed down.

The stabilizer reactions involved correspond to a succession of nitrosation and nitration reactions. In the case of 2-nitrodiphenylamine, it is of the type:



In these conditions the use of a double-base propellant is based on knowledge of:

- the intrinsic chemical stability of the composition, assessed at the time of its development and controlled during its manufacture;
- the preservation of sufficient stability for the entire service life of the propellant, which is generally determined through the performance of accelerated aging tests.

Consequently, the manufacturing controls are based mainly on two principles:

- the inclusion of stabilizer in the propellant;
- the kinetics of emission of nitrogen oxides.

6.2. TESTS

6.2.1. Stabilizer quantity

The inclusion of stabilizers is checked on standard samples that are representative of the various batches. In the case of CDB propellants this control is also made, on the casting powder.

The analyses are done using chromatographic techniques (chromatography during the gaseous phase, or high-performance liquid chromatography).

The values obtained usually correspond to a theoretical percentage, ranging from 1% to 3%. A drop in this percentage reveals a variation in the manufacturing process such as, for example, a rolling temperature that is too high.

6.2.2. Stability test at 120°C

The high-temperature stability tests measure the rate of nitrogen oxide output of a propellant standard specimen (2.5 g) placed in a test tube inside a temperature-regulated enclosure. A methyl purple reactive paper is placed in the tube. The color of the paper changes in the presence of nitrogen oxides. This change of color marks the first release of nitrous vapors that are not trapped by the stabilizer. The test usually takes place at 120°C in order to accelerate the decomposition phenomenon and shorten the time necessary for the paper to change color (a few tens of minutes). This type of test is also done for CDB propellants, on the casting powder at 108.5°C.

The results obtained from these tests are a function of the compostion and may vary for the double-base propellant family from 30 to more than 100 min. However, when testing a given propellant composition, industrially manufactured, the values obtained are highly reproducible.

The results of these tests may not be directly related to the service life of the propellant, but yet they allow us to assign each manufactured propellant a reference value which is characteristic of the composition, thereby giving a basis for detecting possible changes caused by foreign bodies in the propellant, variation in manufacturing conditions, or quality of the raw material.

A significant difference in comparison to an average value indicates a manufacturing deviation.

6.2.3. Chemiluminescence

This technique has been recently developed to assess the chemical stability of propellants and to avoid some of the drawbacks of the test done at 120°C, i.e.:

- 120°C is a very high temperature that is not related to the normal storage temperature of propellant;
- the 120°C test is a global analysis of the phenomenon of the generation of nitrogen oxides, without any distinction between the various types: NO, NO_2 and others.

The chemiluminescence technique relates the amounts of NO and NO_x to the intensity of a luminous radiation that accompanies the chemical reaction

(NO_x: mixture of NO and NO_2) of NO in the presence of ozone.

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

The quantity of light given out is directly proportional to the number of nitrogen molecules contained in the gas being analyzed.

The propellant sample, when heated, gives off an amount of gaseous nitrogen oxides. This gaseous sample is separated into two parts, one which goes directly into a chamber containing ozone where the reaction takes place, in front of a photomultiplicator, and the other first going through a catalytic convertor that reduces NO_x to NO.

The analysis of the data obtained in this manner allows us to measure by deduction the amounts of NO, NO_x and NO_2. With this method the emission of the various nitrogen oxides can be continually recorded.

A quantitative interpretation of this test for manufacturing control may be done by specifying:

- the shape and weight of the reference sample;
- the temperature of the test;
- the duration of the test.

Finally, by comparing the NO and NO_2 levels, an indication of the degree of the material alteration is obtained; the degree increases with the level of NO.

6.2.4. Other tests

The stability of propellants can also be measured by performing a number of other gaseous evolution tests. These are generally done when there is a need to determine the characteristics in a special environment. There is, for example, the vacuum test designed to quantitatively measure the gaseous volume released after a 200 h exposure to a specified temperature.

6.3. PARAMETERS AFFECTING THE CHEMICAL STABILITY [24]

Much work has been done to determine the parameters that have an influence on the chemical stability of propellants. As a result, the following parameters were identified:

- *The heat of explosion*: the increase in the energetic level results in an acceleration of the kinetics of nitrogen oxide generation.

Heat of explostion	*CDB Composition*	*Stability a 120°C (mn)*
900 cal/g	Paste 1 + 2 NDPA	100
1100 cal/g	Paste 2 + 2 NDPA	80

- *The nature of the stabilizers*:

Stabilizer level 2%	Centra-lite	2 NDPA	MNA	Resor-cinol	2 NDBA 1% MNA 1%	2 NDPA 1% Resorcinol 1%
Stability at 120°C (mn)	60	80	100	80	90	65

- *The amount of stabilizers*: with a 1100 cal/g composition the stabilizer does not have much effect at an amount above 2%.
- *The nature of the additives*:
  - potassium salts are usually detrimental to chemical stability;
  - refractory additives have no influence;
  - the effect of burning rate additives (Pb and Cu salts) depends on the nature of the salt. Aromatic salts have the capability of fixing nitrogen oxides, and are therefore generally favorable to chemical stability.

7. Aging

The decomposition of the nitrate esters described above leads to an aging of the propellant, depending on environmental conditions (temperature, humidity, presence of inhibitor, etc.), resulting in the progressive consumption of the stabilizer, which can culminate in a cracking of the propellant, an alteration of the mechanical properties, and a change in the ballistic properties.

7.1. CONSUMPTION OF THE STABILIZER

In order to assess the service life of a propellant in terms of its chemical stability, samples are subjected to accelerated aging at temperatures ranging between 60 and 80°C. The amount of stabilizer is measured over time. Based on usual kinetic laws (Arrhenius or Berthelot), a stabilizer consumption law can be deduced for the storage temperatures of the propellants.

With EDB and CDB propellants the service life that corresponds to a consumption of less than 50% of the stabilizer is on the order of several tens of years at ambient temperature.

7.2. AGING-RELATED CRACKING

The gaseous products from the decomposition of the nitrate esters are soluble in the propellant through which they diffuse to atmosphere. When the kinetics of gaseous generation exceeds the rate of diffusion, the gases created exert a pressure which may cause a physical breakdown of the material (cracks, vacuum holes), particularly in the case of thick propellant grains.

Several formulas have been proposed to determine the critical pressure in terms of the mechanical properties (S_m, e_m) of the propellant [25].

The cracking phenomenon can be modeled, based on the laws:

- of Arrhenius for gas generation;
- of Henry for solubility of gases in propellant;
- and of Fick for gas diffusion.

The experimental studies may be done with propellant cubes, of different sizes, subjected to high temperatures (on the order of 60–80°C). X-rays of the cubes can detect the occurrence of defects such as vacuum holes and cracks. This is known as the cube test. It can be used to determine the critical edge length: the largest cube which, when subjected to a test of specified duration at a specified temperature, exhibits no degradation [26].

The analysis of these results, extrapolated to normal temperatures, makes it possible to determine the critical diameters of the grains of a given propellant composition.

7.3. MECHANICAL AND BALLISTIC AGING

Providing that the environmental conditions are such that the chemical stability of the propellant is preserved, double-base propellants do not have any significant change of their mechanical or ballistic properties. However, a substantial loss of nitroglycerine could lead to a hardening of the propellant.

8. Safety Characteristics

Propellant grains for rocket motors are designed and manufactured to be used according to a well-defined decomposition mode: combustion burning. This is a slow phenomenon that propagates itself through parallel layers. The initiation of the phenomenon can be obtained through various types of induced stress: thermal, mechanical, or electric.

However, propellant may, under certain conditions best avoided, adopt a different mode of decomposition, even a different regime of decomposition.

8.1. SAFETY AND TOXICITY OF THE INGREDIENTS

The various ingredients used in propellants are indexed in toxicity lists which indicate the various and particular precautions that must be observed during the manufacture.

As far as the pyrotechnic safety characteristics are concerned, the nitrocellulose is usually desensitized through the addition of water — manufacture of pastes — or alcohol. (A propellant conditioned with alcohol belongs in the hazard class 1.4.)

On the other hand, taking into account its characteristics (Table 4) nitroglycerine is never used pure, but in association with nitrocellulose (EDB propellant pastes) or with triacetin, a casting solvent for CDB propellants.

The crystallization of nitroglycerine, likely to occur at temperatures below 12°C, must be prevented, although the crystallized product is no more sensitive than the liquid product. The hazard lies in the fact that the crystallization is likely to produce frictions between the crystals, and thus in turn may lead to a decomposition by detonation.

In addition to the pyrotechnic risk, nitroglycerine is also toxic. Its vapors cause migraines and nausea because it is a cardiac hypotensor.

TABLE 4 *Comparison of safety characteristics between nitroglycerine and casting solvent*

Test	Results expressed in	Nitroglycerine	Casting solvent (78% Nitroglycerine)
Card gap test	Number of cards	>340	75
Sensitivity to 30 kg fall hammer	Height of no reaction (m)	0.5	>4
Critical thickness	mm	<0.1	4
Steel tube-drop test	Height of no reaction (m)	<0.25	1

8.2. APTITUDE TO IGNITION

8.2.1. *Heat sensitivity*

The heat sensitivity tests are designed to determine the temperatures at which a propellant specimen ignites. These tests may be performed with specimens broken into small pieces (autoignition test) or compact (cook-off test).

8.2.1.1. *Autoignition test*

This test is used to measure the temperature of spontaneous ignition of the propellant:

- either by progressive heating, regularly increasing the temperature by 5°C every minute;
- or by sudden heating.

These tests tell us exactly the maximum temperatures to which the propellant can be subjected during its manufacture or its use.

In the progressive heating test, 180°C is a reference temperature used for all double-base propellants.

8.2.1.2. *Cook-off test*

This test is used to determine the lowest temperature of spontaneous ignition after extended exposure to that temperature.

This temperature is around 110°C for all double-base propellants.

8.2.2. *Mechanical sensitivity*

The combustion of the propellant may also be triggered by the mechanical stimuli of impact or friction. Various tests have been devised to quantify the level of stimulus necessary to cause ignition, including:

- friction sensitivity: the average recorded value is of the order of 20 Newton;
- impact sensitivity.

Several tests have been developed to characterize the impact behavior of propellants. Two of these are most widely used:

- the 30 kg fall hammer test: the principle involves dropping a 30 kg weight onto a plate of propellant; the height of the drop determines the amount of energy involved;
- the impact sensitivity test: steel fall hammers of various weights are dropped from varying heights onto a propellant sample held between two steel clamps.

The values obtained in these tests identify the level of impact that are prohibited for the propellant (dropping propellant grains, shocks, etc.).

8.2.3. *Electric sensitivity*

Double-base propellants have been found insensitive to electric energy up to about 600 mJ.

8.3. DETONABILITY

Detonation is an exothermic chemical decomposition reaction which, coupled to a shock wave, propagates itself through the material. This

accidental rate of decomposition is a risk for all solid propellants, and in particular for double-base propellants. A certain number of criteria exists that permits us to characterize the detonability:

- the detonability index. When compared to the results obtained with composite propellants — one card — the values corresponding to double-base reveal a significantly increased aptitude for detonation: 90-100 cards.
- the critical diameter. They are significantly smaller than those of composite propellants.

Table 5 provides an overview of the major safety characteristics of double-base propellants.

TABLE 5 *Main safety characteristics of double base propellants (typical cases)*

Tests	1000 cal/g EDB	800 cal/g CDB
Ignition		
Autoignition through progressive heating	173°C	176°C
Autoignition through sudden heating	268°C	277°C
Cook-off	110°C	
Friction sensitivity	210 N	210 N
30 kg hammer fall sensitivity (no reaction)	greater than 4 m	greater than 4 m
Impact sensitivity	4.9 J	5.9 J
Static electricity sensitivity	600 mJ	600 mJ
Detonability		
Card gap test	100 cards	90 cards
Critical diameter	2 mm	14 mm

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