CHAPTER 13

Thermal Insulations, Liners and Inhibitors

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1. Inhibiting Materials and Thermal Insulation in Solid Propulsion

The function of a rocket motor is to deliver a thrust according to a predetermined program.

With solid propellant rocket motors, theory allows us to relate the thrust law required by the designer to the evolution versus time of the burning propellant surface [1,2].

The evolution of that surface depends heavily on the presence of organic materials adhering strongly to the propellant. These materials, called combustion inhibitors, limit the initial combustion surface so that the combination of the grain geometry and the combustion law of the propellant results at any instant in the desired thrust.

To completely fulfill their role the inhibitors must present a whole set of characteristics which will be described in detail later in this chapter. The most important is an excellent bonding to the propellant. This property is essential for the reliability of the rocket motor, because any debonding between the inhibitor and the propellant results almost invariably in a failure of the rocket motor due to an uncontrolled pressure rise.

Other inert materials are often present in the combustion chamber, ensuring such functions as the bonding of the propellant with the wall of the motor case (liner), or the thermal insulation of case surfaces exposed to the hot gases (thermal protection).

In the following pages we will use the term "insulating matérials" for these various materials (inhibitors, restrictors, liners, thermal protections) illustrated at figure 1.

Very strong interactions take place between the design of the grain, the propellant and the various insulating materials. Consequently, the properties of the latter have a significant influence on performance, service life and cost of rocket motors.

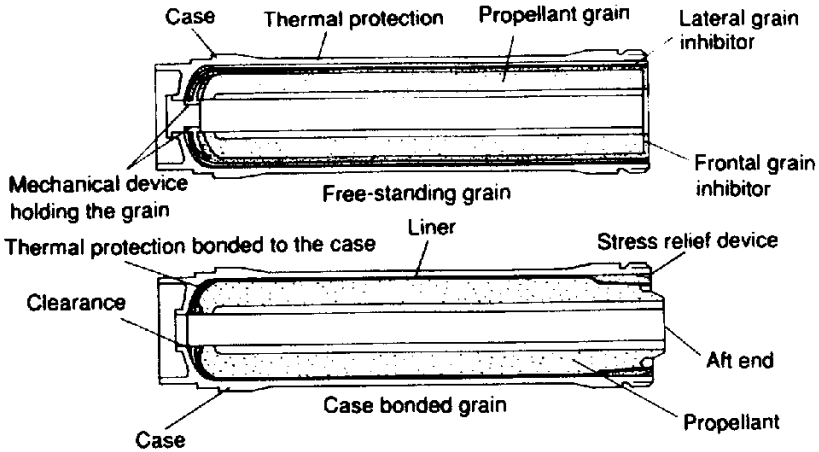

FIG. 13.1. Configuration of a solid propellant rocket motor (without nozzle).

2. Background

2.1. SPECIFICATIONS OF INSULATING MATERIALS

The insulating materials must satisfy many specifications difficult to quantify. They include, but are not limited to:

- Sufficient bonding within the entire range of working temperatures of the motor.
- Low ablation rate, to minimize the inert mass on board. At the same time the resulting "char" must remain porous: the decomposition gases must exhibit a low molecular mass, the pyrolysis of the material must not lead to emission of smoke or flashes.
- Low thermal conductivity.
- High specific heat.
- Low density.
- Mechanical strength compatible at all temperatures with the deformation of the grain during the various manufacturing and storage phases, or with those deformations resulting from various thermal and mechanical stress to which the rocket motor is subjected in the course of its life including, of course, firing.
- Pyrotechnic compatibility with the live constituents of the motor (propellant, ignition powder).
- Sufficient electric conductivity to avoid electric charge build-up.
- Chemical compatibility with the components of the motor: the insulating materials must not upset the chemistry of propellant but maintain the nominal characteristics of the latter.
- Good gas permeability.

- Low humidity absorption.
- Good aging characteristics.

2.2. THEORETICAL DATA REQUIRED FOR THE DESIGN OF INSULATING MATERIALS

The development of insulating materials for rocket motors calls for deep knowledge in multiple fields of studies, such as chemistry, thermodynamics, mechanics, optics and many other branches of physics.

Because of their particular importance for the work of the rocket motor only some aspects, related to the mechanisms of the adhesion, ablation and emission of smokes, are discussed in the following sections.

2.2.1. Fundamentals of the mechanisms of adhesion

In spite of the large number of studies dealing with the phenomenon of adhesion during the past 40 years, the basic laws are relatively poorly known and there is no unified theory capable of explaining the entire set of phenomena [3,4].

One of the major difficulties is that adhesion is a multidisciplinary subject requiring the collaboration of experts in the field of chemistry of polymers, the physical chemistry of surfaces, the strength of materials, the mechanics of fracture, and more. In addition, the number of parameters involved in a theoretical modeling exceeds by far the analyses and computation capabilities.

In spite of these somewhat pessimistic premises, bonding theories have emerged. However, we must not forget that their scope is limited and that their capability of prediction does not extend beyond a few typical and particular fields.

2.2.1.1. Mechanical model

MacBain was the promoter of a mechanical model where the adhesion is due to a fixing of the bonding agent to the roughness of the substratum. MacBain's research was done more specifically for the bonding of wood, and although his model is in general no longer used, it is regaining interest because of the recent research of Wake.

Broadly speaking, the roughness of the substratum is only a favorable factor inasmuch as the wetting is sufficient. When that is not the case, the portions that have not been wetted form the start of a break themselves. In terms of adhesion between the liner and the propellant, mechanical linking is used when adhesion is difficult, such as with propellants with low chemical reactivity (cast double-base) or those which are highly plasticized (CMDB).

2.2.1.2. *Electrical model*

In 1948, Deriyagin and Krotova proposed a theory of adhesion based on electrostatic phenomena observed during plucking tests on adhesives. Skinner developed a similar theory in 1953. According to his theory, the system constituted by the bonding agent and the substratum is compared to a capacitator. For example, with an organic bonding agent and a metallic substratum the metal can play the role of the electron donor and the polymer that of the receiver, leading to the formation of a double electric layer.

The difficulties in developing a theory explaining the origin of the electric charges are due to a lack of information about the levels of energy and about the process of conduction in the polymers.

Although experimental work seems to confirm the validity of this model, it is seriously criticized, and many authors agree in their opinion that the electric effects observed are the consequence rather than the cause of a high level of adhesion.

2.2.1.3. *The diffusion model*

The Russian researcher, Voyustkï, originated a theory according to which the adhesion results from the diffusion of the molecules of the surfaces in contact, creating a transition layer between the substratum and the bonding agent. The plane interface is replaced by a spatial interphase. The reciprocal solubility of the materials constituting the assembly is a primary condition for obtaining a good bonding. Voyustkï suggests, in addition, use of the adhesion as a criterion for the thermodynamic compatibility of the polymers, the best example of perfect compatibility being the self-adhesion of crude rubber to itself, where the interface is quickly impossible to distinguish.

With this model the classic parameters of diffusion influence bonding strength, including time, pressure, temperature, steric configuration of the diffusing products and the crosslinking density of the substratum and, in the case of polymers, they are the structural characteristics such as molecular mass, morphology and crystallinity.

While the diffusion phenomenon is certainly important in the case of self-adhesion, and for the bonding of polymers, it is difficult to imagine its contribution in the case of bonding polymers to glass or metal. Schonborn and Juntsberger, without refuting the existence of diffusion phenomena, feel that they are subordinated to the process of putting in close contact, at the molecular level, the materials to be bonded.

2.2.1.4. *Wetting model*

In 1963, based on thermodynamic considerations and on the research done by Zisman on the critical tension of the wetting of solids, Good, Fowkes and Dann, and Sharp and Schonborn, developed and proposed a new model.

Since the bonding forces have a field of action on the order of the molecular distances, a good bonding is created by an intimate contact between the adhesive and the substratum, such a contact allowing the development of these forces. This is in the occurrence, a criterion of proximity, involving the cleanliness of the surfaces and a perfect wetting.

In this model the bonding energy can be determined, based on the surface energies of the solids to be bonded and considering the wetting to be ideal. Calculated in this manner, the bonding energy corresponds to the energy of formation of the assembly. Experimentally, the debonding energy is often considerably greater.

2.2.1.5. *Chemical model*

Chemical adhesion involves chemical valence bondings between the adhesives and the substratum. In spite of the obvious interest offered by this type of mechanism, few studies have been done. It is true that demonstrating the chemical reactions at the interface is particularly difficult.

As far as the bonding to propellant is concerned, it is noteworthy that theories of chemical bonding are widely used to create specific molecules known commonly as bonding promoters. These reactive products, exhibiting low molecular mass, are carefully selected and introduced into the inhibitor. They diffuse towards the interface where they react with the polymer of the propellant to create stable chemical bondings, provided the wetting has been done correctly.

2.2.1.6. *Model of the interfacial layer with weak cohesion*

Bikerman, the author of this model, assumes that the probability of seeing a rupture propagate itself exactly at the interface between the adhesive and the bonded material is extremely low. From this premise it can be deduced that the debonding occurs either in the adhesive or in the bonded material. In fact, according to Bikerman, and more recently also to Sharpe, there is another possibility: that of a debonding propagating itself in an interfacial layer with weak cohesion. These authors distinguish several layers with weak cohesion:

- a first layer consisting of air continues to exist at the interface (imperfect wetting);
- other layers formed when foreign substances with low molecular mass, contained in the adhesive or the bonded material, migrate to the interface;
- yet other layers coming from a reaction between the atmosphere of the ambient medium (humidity for instance) and the bonded material, or the adhesive.

Although Bikerman's analysis is also contested, it allows an explanation of a number of observations made in the field of bonding. In particular it clarifies greatly the role of water vapor absorbed by most of the surfaces.

As for the bonding of propellants on to combustion inhibitors, when combined with the theories of the diffusion and chemical bonding, Bikerman's analysis allows the establishment of a conceptual frame within which the technology used to perform the different bondings in rocket motors can be developed.

2.2.2. Fundamentals of the thermal protection process through ablation

If the combustion chamber were to be directly exposed to the propellant combustion gases, the weakening of the structure would lead unavoidably to a rupture by bursting.

Should the inhibitors not play their role, the rapid heating of the propellant would bring on an uncontrollable increase of the burning surface, with consequences similar to those mentioned above.

In practice, the combustion chambers and the propellant grains must be thermally protected against all excessive heating during the operation of the motor. To provide this protection, organic materials coming into contact with hot gases (2000–4000 K) protect the underlying areas through a complex endothermic decomposition mechanism generally known as protection by ablation [5-8].

The temperature of the thermal protection rises by conduction until it reaches its decomposition temperature by pyrolysis. This initiates highly endothermic chemical reactions leading to the creation of gas and leaving a sooty deposit, more or less porous, called "char".

A steady state establishes itself between the combustion gases and the material in the process of pyrolysing. The pyrolysis front regresses. Once this regression is finished, the heat absorption mechanism by thermal decomposition ceases. Only the char, inasmuch as there is any, continues to participate, by conduction and radiation, in the protection of the underlying material.

It is important to note that these materials have a low thermal conductivity which, combined with the short firing times, decreases the heating by conduction of the protected parts.

2.2.2.1. *Examples of experimental test used to evaluate the thermal characteristic of insulating materials*

Several experimental systems are commonly used to compare the materials among themselves or to measure the physical values necessary for modeling the rate of ablation by computer analysis, using specially developed numerical programs.

"*Extension firing*" (using an "exhaust pipe"). The tested materials are placed in a pattern of a hexagonal base cone. They are mounted in pairs in order to limit the dispersions caused by variations of the flow (Fig. 2).

Analysis of these results allows us to plot the ablation curves for a given propellant, linking the ablation rate to the average speed of the flow of the gases. These curves can be plotted for specific chamber temperatures, nature of gases and time of exposure.

Firing of end-burning grains. With the end-burning grain system the ablation can be measured on very low gas flow rates and for long firing times, which is not feasible with exhaust pipe firing. Analysis of the tests results in a curve linking the ablated thickness to the firing time.

The plasma torch. The plasma torch is also used. It allows us to know the behavior of different materials.

Finally, conventional differential thermal analysis (determination of the ablation enthalpy) and thermogravimetric analysis permit the completion of the data used to predict the ablation rate, thanks to numerical programs.

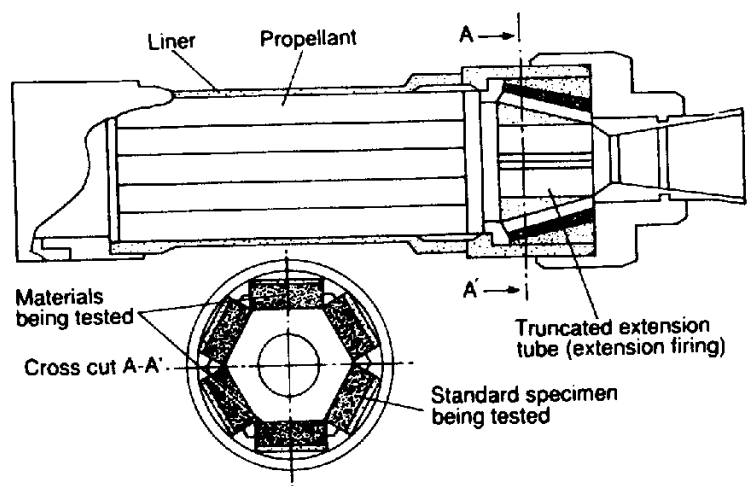

FIG. 13.2. Firing test designed to evaluate the ablation rate of thermal insulations.

2.2.3. Fundamentals of optical phenomena related to the operation of a rocket motor

The emission of smoke or flashes by rocket motors is a critical factor for many missile systems [9,10]. The release of smoke reveals the location of the launcher. A smoke trail makes the trajectory of the missile visible at great distances, giving the target the possibility of escape. For wire-guided missiles the plume greatly reduces visibility conditions. The presence of solid particles in the plume may hinder the functioning of the guiding device. The presence of flashes may interfere with tracking systems located on the firing pad.

2.2.3.1. *Fundamentals of the smoke phenomena*

Smoke may be defined as a condensed liquid or solid phase, in suspension in air. There are, usually, two categories:

- condensation smoke;
- dispersion smoke, formed by the subdivision of very fine particles.

In rocket propulsion the dispersion smoke composed mainly by metallic or refractory particles results from the combustion of the propellant and the pyrolysis of the insulating materials, while condensation smoke comes from low-mass organic molecules existing as vapor in the plume that condenses during the rapid cooling following expansion of the gases in the nozzle.

2.2.3.2. *Visibility of an object as a function of the contrast*

The visibility threshold of an object is usually expressed in terms of contrast. When an object moves away from the observer, the contrast decreases because of atmospheric absorption. At a fixed distance between the observer and the target, when the luminosity increases, the contrast also increases because the target is more luminous than its background and the opposite occurs when the target is less luminous. Consequently, the plume of a missile is more or less visible whether the missile flies over grassy ground, the sea, or toward the sky.

2.2.3.3. *Opacity of the smoke*

Visibility of an object through a smoke plume varies according to the manner in which the particles reflect, diffuse or absorb light. The main parameters are morphology, size and density of particles, refraction index and wavelength of incident light.

The opacity of the smoke can be reduced by decreasing the number of particles released, as well as their size, until reaching a diameter much lower than the wavelength of the incident light.

2.2.3.4. *Duration of the smoke*

Experiments, full-size, have demonstrated that losing sight of a target for 1-2 s is sufficient for the launcher to lose control of the missile. Conversely, a rapid dispersion of the smoke — in less than 1 s — may be compatible with efficient tracking systems.

2.2.3.5. *Development of smokeless motors*

Insulating materials must be considered as potential sources of smoke which are particularly inconvenient when the propellant has been selected on

the basis of its low signature. There are, however, two categories of inert materials with low or no signature:

- Low or no signature materials due to the fact that no particles are ejected: the "particles" released during their pyrolysis are mainly gaseous, or non-condensable, or very small. This goal can be achieved by using organic materials without refractory fillers.
- The highly refractory materials for which solid particles formed during the pyrolysis are few in number and stay in the combustion chamber.

2.2.3.6. *Flashes emitted by the rocket motors*

These flashes come from the plume made of heated gases released by the nozzle or from reignition (postcombustion), caused by recombination with the oxygen of reducers contained in the gases. Attenuation of the flashes is usually obtained by introducing appropriate ions in the combustion gases, capable of blocking the recombination reactions that involve free radicals (Chapter 5).

These ions may be contained in the propellant itself, or if the design of the motor allows it, in the inert material subjected to a controlled pyrolysis during the operation of the motor.

2.2.3.7. *Experimental methods for the measurement of smoke*

Because of the complexity of the phenomena involved, experiments have been conducted during the firing of motors consisting of a cylindrical end burning grain, inhibited laterally and on the front-end surface with the material being tested and for which the grain has been carefully selected, based on its own very low signature, previously measured by firing of non-inhibited grains.

The observations deal primarily with the opacity of the smoke. An experimental device, called an opacimeter, allows us to measure the attenuation in the axis of the jet as well as perpendicular to it, while a film is being taken using a luminous background made of selected color patterns.

2.2.4. *Combustion of the propellant along the inhibitor*

In the vicinity of the bonding of the propellant and the inhibitor a large number of physicochemical phenomena may occur, which influence the burning rate of the propellant. This alteration is felt particularly for end-burning grains where the existence of a local increase of the burning rate

along the inhibitor may have a strong effect on the pressure and thrust curves [1,2]. This burning rate increase may be the result of:

- heating of the propellant under the inhibitor, due to the circulation of heated gases in the clearance between the chamber and the grain;
- segregation of the fine oxidizer particles in the vicinity of the inhibitor, caused by decanting-type mechanisms — this possibility exists only in the case of grains cast in their inhibitors;
- existence in the liner of compounds which are ballistic modifiers (iron oxide);
- existence of vacuums or microscopic cracks;
- alteration of the local composition of the propellant through the migration of mobile molecules towards and from the inhibitor (plasticizers, crosslinking agents, liquid combustion catalysts and others);
- local variations in the radiation density of the flame in the vicinity of the inhibitor.

For instance, if the plasticizer of a propellant can migrate to the inhibitor, the propellant close to the inhibitor appears, locally, richer in oxidizing species. This results in an increase in the burning rate as well as in the pressure exponent, so that the burning rate enhancement grows with propellant temperature and operating pressure of the motor.

To minimize this phenomenon the grain designer selects materials that are impermeable to the mobile components of the propellants and balances, *a priori*, the chemical potentials on each side of the bonding surface. When equilibrium cannot be obtained, he may, on the other hand, introduce into the inhibitor a plasticizer moderating the burning rate of the propellant.

2.2.5. *Method of prediction of the aging of the bonding*

As with all other components of the rocket motors, the insulating materials must ensure complete operation for the duration of the service life of the motor. Among these, the "bonding" function is certainly the most sensitive to aging.

The aging of the bonding is caused by the development of chemical reactions, complicated by diffusion phenomena. Each of these reactions exhibits an activation energy which, lacking a more precise theoretical model, can be idealized by an Arrhenius-type law. The aging is evaluated by comparisons of results recorded at ambient temperature at various stages with results recorded at moderate temperatures ranging from 40 to 50°C. The raw materials themselves need to be perfectly stable during the period of time considered.

Accelerated aging experiments on complex materials need to be performed with the greatest circumspection because they usually tend to overestimate.

2.2.6. *Pyrotechnical compatibility — selection of the raw materials*

The raw materials of the insulating materials for combustion chambers must be chemically compatible with the energetic ingredients of the propellants (mineral oxides, nitrated plasticizers, explosives, nitramines and others). Two tests are currently performed for this purpose:

- Differential thermal analysis, where the research worker subjects the energetic ingredient, in powder form and in the presence of the material being tested, to a regular increase of temperature. The verdict is made on the basis of the modification of the decomposition temperature of the live ingredient.
- The "vacuum test", where the tester puts together, in powder form under heat and vacuum, the live ingredient and the inert materials for testing. The verdict is made on the basis of the volume of gas produced as well as on its rate of production.

2.2.7. *Criteria for the selection of raw materials used in the formulation of insulating materials*

There are many considerations that are principal factors in the development of insulating materials to obtain satisfactory mechanical properties, bonding and other design goals, while other data limit the choice of the designer (for example, pyrotechnical compatibility). In particular, the raw materials must satisfy the following conditions:

- guaranteed availability over a sufficient period of time;
- stability over time;
- reproducibility of the production, process including the control of the impurities coming from the raw materials.

2.3. DETERMINATION OF THE CHARACTERISTICS OF THE BONDING PERFORMANCE OF INSULATING MATERIALS

Once the formulation of an inhibitor has been selected, based on the general rules discussed above, it is necessary to determine its performance.

The mechanical characteristics of inert materials are measured: For a rapid determination of these characteristics the tests are performed at ambient temperature, with tensile loading rates of 50 mm/min, while a complete characterization requires the tests to be performed with several loading rates (from 1 to 1000 mm/min) and several temperatures (−40°C, +40°C, +60°C).

The bonding characteristics are determined by carrying out tensile, shearing and peel tests.

We should note here that the bondings between the insulating material and the propellant behave more or less like their constitutive components, and that, as a result, bonding master curves can be plotted.

The methods selected to design a rocket motor are based on results from tensile and shear tests, since all types of loading involved can be reduced into these two basic stress/strain modes. The peel test, on the other hand, although not used in the determination of the stress and strains of the grain, is widely used for two main reasons:

- peeling is a test of resistance to tearing that simulates very well what occurs at the ends of the grain;
- peeling can be considered as an indication of the quality of the bonding.

2.4. OPTIMIZATION OF INSULATING MATERIALS

The formulation's analysis is done by taking into account the rules of the art and previous experience, and also by performing, during the initial phase, various tests using a wide range of parameters likely to provide the desired performance in order to select the most promising results.

This phase may require a long time. It is also the most difficult one because intuition plays an important role. It leads to selection of a family of formulations that is the first approximation of the composition desired.

Two distinct activities will then take place in close relation to each other; one involving the formulation itself and the other the manufacturing processes. When this work is completed, the formulator is able to define the limits of the composition and the acceptable variations of the raw materials and production processes that can be used to maintain constant properties of the material.

A third phase consists in testing the reproducibility and the aging, after which the industrial documentation is completed.

2.5. MOST COMMONLY EXPERIENCED FAILURES

The type of failure most often observed on a rocket motor involves the bonding between the inhibitor or the liner and the propellant. This may be attributed to the significant variability of the materials used and, to an even greater extent, to the variability of the bondings. The latter problem may be accentuated by anomalies occurring during manufacture:

- insufficient prevention against the environment at the time of preparation of the materials and the actual bonding;
- insufficient knowledge of the raw materials, which may contain impurities such as adhesion poisons;

- insufficient knowledge of the solubility and diffusion properties which cause undesirable chemicals (from a bonding point of view) to migrate and localize at the interfaces (live or inert plasticizers);
- insufficient knowledge of the rates at which the bonding develops resulting in premature stresses and strains in the bonding.

To take precautions against such anomalies it is important to perform, at the commencement of the development of an insulating material, full-size experiments, accelerated aging and overtests, complemented by surveys, so that the real results obtained may be compared to the laboratory tests.

2.6. QUALITY INSPECTION OF BONDINGS

The techniques used to create the bondings today are even more similar to an art that has reached a certain level of maturity than they are to an exact science. Consequently, it is not always sufficient to select the raw materials carefully, and to combine them using a strictly defined process to guarantee that all required specifications are met.

The manufacturer must therefore be able to evaluate by non-destructive means the quality of the work done, in order to discover anomalies such as voids, debonding and porosities. There are numerous non-destructive tests that can be applied to bondings, although only two are widely used for industrial applications. These are described below.

2.6.1. Quality inspection of bondings by X-ray

X-rays, using mainly the usually small differences in the density of the various materials, are able to detect debonding only when there is some separation between the materials. However, since X-ray systems generally use powerful generators, sensitive emulsions and highly trained operators, a very high proportion of failures are identified. In addition, it is possible to improve the global resolution power of the method by varying the stress condition of the area examined (moderate cooling of the suspect area, for example).

New technology such as image processing or new analysis tools, such as tomography and Compton scattering, may improve the sensitivity and reliability of this quality inspection technique which, in any case, is not capable of differentiating between a good bonding and a poor one. Finally, video radioscopy, also slightly less sensitive, allows us to increase significantly the productivity of non-destructive inspection operations.

2.6.2. Control of bondings by ultrasound

The propagation of ultrasounds inside materials is disturbed when the beam meets an interface or a heterogeneity. Analysis of the signals received

allows us to perform insurance quality of the bondings. This is a fairly complex task and requires both favorable testing conditions, such as the possibility of using a coupling liquid, and experienced operators.

This method is used mostly with small free-standing grains, in addition to X-rays.

3. Processing Insulating Materials

3.1. INHIBITING PROCESS OF FREE-STANDING GRAINS

The most simple process to inhibit free-standing grains is coating them by casting into a mold.

One method widely used with long pot-life materials consists of mixing all the ingredients in a vertical mixer with a bowl fitted out to allow the injection of the uncured insulator into several molds assembled on a plate distributing the inhibitor.

Another method involves casting the grain inside an inhibiting material (inhibiting tube or restrictor) previously shaped, either through the extrusion process (in the case of a thermoplastic material) or by pressure molding, either with a press or in an autoclave (in the case of a rubber material).

Other basic processes are sometimes used, their selection being often dictated by technical or economical constraints:

- Wrapping ethylcellulose tapes on extruded or cast grain of double-base propellant.
- Soaking of propellant grain in an inhibiting solution. This technique is acceptable only for small objects such as the strands used in the strand-burner test.
- Pushing the propellant grain into a mold containing at the bottom an appropriate quantity of uncured inhibitor.
- Spraying on the propellant grain with a material exhibiting appropriate rheological characteristics.

Except for the first process mentioned, these principles have not been widely developed in the industry.

3.2. PROCESS OF PREPARATION OF THE CASES FOR CASE-BONDED GRAINS

A case-bonded grain includes, in addition to the case, thermal protection, liner and devices designed to accommodate the nozzle.

The application of the liner will be described in detail, while only brief indications will be given concerning the thermal protection.

3.2.1. Fitting the thermal protection into the case

For metallic motor cases the thermal protection components, consisting of polymers reinforced with cooling or refractory fillers, are molded in their final form and then bonded inside the case. The adhesives used must give the bonding characteristics required and also be easy and foolproof to apply.

When the cases are obtained through filament winding, the composite is frequently wound around a destructible mandrel coated with the uncured thermal protection. The entire assembly is placed in an oven, both to polymerize the composite and to cure the thermal rubber.

The thermal insulation is often provided with stress relief devices designed to reduce the stresses in the bonding surfaces of case-bonded grains. These features are also known as relief flaps.

3.2.2. Preparation of the case and the liner

3.2.2.1. Inspection of the cleanliness and dryness of the thermal insulation

It is necessary, to obtain a good bonding, to proceed to the coating on a clean surface.

Wetting tests reveal possible pollution of the surface. In such a case, cleaning (grease removal) operations must be performed again, involving if necessary a mechanical sandblasting before continuing the equipment of the case.

Another important point is the complete absence of humidity. The presence of water may hinder the bonding of the liner to the thermal protection, and later on, also of the propellant to the liner.

3.2.2.2. Preparation of the liner

The preparation of the liner can be made in one step (one shot) in a mixer of a type similar to those used for the mixing of the propellant. Such a technique is possible only when the pot-life of the liner is sufficient to allow all sequences of the laying process to be completed. For this purpose, the use of "blocked catalysts" is particularly well-indicated [13,14], or better yet, the use of a blocked curing agent which is thermally activated [15].

The use of liners diluted in a solvent artificially increases the pot-life and facilitates the spraying. Attractive in principle, this process allows only the spraying of thin layers.

The liner may also be prepared in the form of a material with two components which are mixed at the last moment at the site of coating, using precision automatic feeding equipment. The control of the flow rate of the components requires a high and instantaneous precision. Although many

quantity measuring and mixing machines exist on the market, few of them offer the required characteristics and they need to be adapted to meet specific requirements: flow control with the required level of precision, for limited rates of throughput of the order of 50 g/min, while keeping track of the data of operations already performed. The combined use of sufficiently sensitive gages and computer controls allows these requirements to be satisfied [16,17].

3.2.3. *Application of the liner to the cases*

3.2.3.1. *Coating the liner by centrifugation*

The principle of the centrifugation process consists of introducing the liner in a liquid state at the bottom of the case and proceeding to polymerization by subjecting the case to a rapid spinning, which plates the liner against the wall of the motor. The operation, thanks to specially designed machines, can be performed for the cylindrical motor case and the front- and aft-ends. Today, this process is being replaced by spraying, which allows reduction of the inert mass involved, and improvement of the propellant mass fraction of the motor.

3.2.3.2. *Coating the liner by spraying*

The "spraying process" involves spraying the liner in a liquid state in fine droplets onto the inner surface of the case before the crosslinking reaction has taken place. The spraying system, and if necessary the case, must be activated to be moved in relation to each other to ensure that the required thickness of layers of liner is deposited at the right places.

Many systems are used in the industry for the spraying of liquids:

- blowing by compressed air of a liquid jet: pneumatic spraying (Fig. 3);
- sudden expansion of liquid under pressure: airless spraying;
- blowing by centrifugal force with a device such as a disk or a bowl spinning at high speed (Fig. 4).

The blowing of the product can be facilited with the use of a device generating electrostatic charges: "electrostatic spraying heads".

The liner spraying systems are derived from commercial equipment. However, it was necessary to redesign them completely to adapt them to using uncured liners exhibiting extremely high viscosities. At the same time they were miniaturized, so that today it is possible to coat cases with an insides diameter of 40 mm.

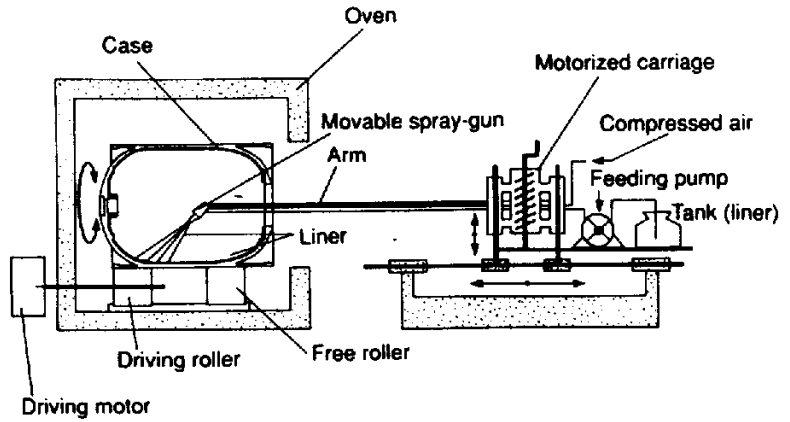

FIG. 13.3. Device used to spray the uncured liner into the case (pneumatic spraying).

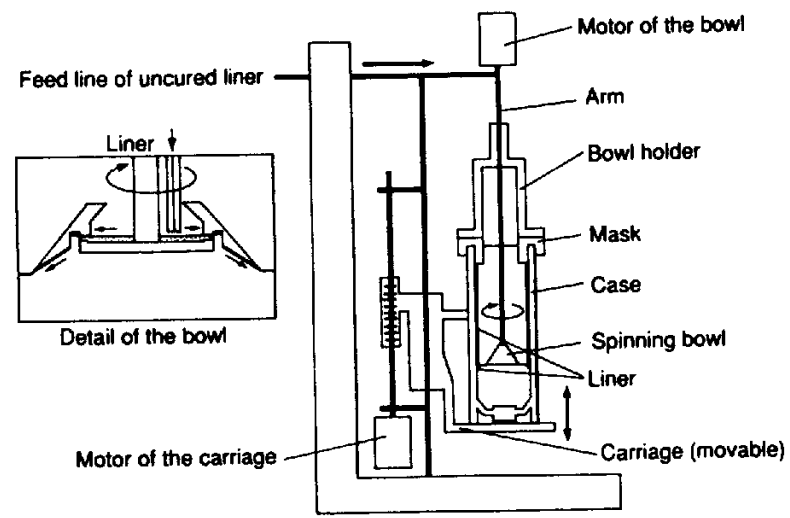

FIG. 13.4. Vertical spraying machine (Mechanical spraying of the liner).

3.2.4. *Application of a liner with mechanical embedment*

When faced with difficult bondings, as might be the case with highly plasticized propellants, an improvement consists in embedding the liner with particles — typically cylindrical particles — which permit a mechanical embedment between the liner and the propellant [18]. This incrustation can be done by pneumatic spraying of particles on the liner while it is still uncured.

The peel test value of the embedded liner in peel tests is multiplied by a factor of 2 to 3. The incrustations constitute some sort of obstacle to the propagation of tear caused by peeling.

3.2.5. *Recycling of the coated cases with a cured liner out of specifications*

Defects may be present in the materials or the bondings in a case, and they must be detected before proceeding to the casting of the propellant. When the defect cannot be corrected it is desirable to be able to recycle the case. Several techniques are available:

- Prolonged soaking in a solvent, causing a swelling of the materials, which can later be removed by mechanical brushing.
- Removal of the material with a high-pressure water jet. This technique cannot be used with composite materials because it would cause irreversible damage to the case.
- Removal of the material with a heating device locally weakening the mechanical properties of the material to be removed.
- Dissolving the liner to be removed with a solvent selected not to attack the other inert materials present in the case.

4. Examples of Insulating Materials Used In Rocket Propulsion

While the compositions of propellants developed in various countries have a pronounced similarity, due as much to energetic considerations as to the availability of raw materials, the diversity of insulating materials (e.g. polyurethanes, epoxides, silicones, synthetic rubbers and phenolic resins), precludes trying to be exhaustive or even provide detailed descriptions of each type.

For the several examples dealt with in the following sections, reference is made whenever possible to patents and papers listed in the bibliography, particularly when it concerns the chemical aspect of the materials [19].

4.1. INHIBITING MATERIALS FOR FREE-STANDING GRAINS

4.1.1. *Cast inhibitors*

Inhibiting by casting over a propellant grain is interesting in particular for small grains. Nevertheless, some large grains are still produced using this technique.

4.1.1.1. *Cast inhibitors for composite propellants*

This technique is not much used in actual production. The materials used have been prepared based on propellant binders — particularly when it involves polyurethane — correctly adjusted in terms of the crosslinking rate and final mechanical properties.

Polyurethanes, although exhibiting good bonding characteristics — particularly with the peel test — are expensive to produce due to their sensitivity to humidity, and epoxide-based inhibitors are being preferred whenever their mechanical and bonding properties are deemed sufficient for the selected application.

4.1.1.2. *Cast inhibitors for extruded or cast double-base propellants (Table 1)*

Most elastomers which can be crosslinked at low temperature are potential materials for the formulation of cast inhibitors: unsaturated polyesters and silicones curing at ambient temperature, polyurethanes, polysulfides and epoxides can be used. In fact, the selection of one over the other is based on constraints related to the operational mode of the motor and the exact composition of the propellant used.

Table 1 lists the major characteristics of various cast inhibitors belonging to the three most commonly used families, which are briefly described in the following sections.

4.1.1.3. *Unsaturated polyester*

Polyesters are made of unsaturated polymer chains diluted in styrene and capable of crosslinking by free-radical-type reactions with the assistance of appropriate catalysts and accelerators.

The polymer is usually blended with refractionary fillers designed to improve the thermal resistance. At the manufacturing level their low initial viscosity makes them ideal for casting, but they can also just as easily be injected with precision automatic feeding equipment.

This family of inhibitors was developed very early, in the 1950s [20], and is still widely used. Its known limitations are related to a high smoke emission, attributable to high amounts of aromatic products contained in the formulation, as well as a propensity — that could be high depending on the type of propellant used — to swell in contact with nitrated plasticizers. The swelling alters the mechanical properties of the material and shortens its service life. Improvements have been obtained by:

- using a primer of the triisocyanate type which, by reducing the rate of migration of nitroglycerine, reduces the swelling;

TABLE 1 *Major characteristics of cast inhibitors for extruded or cast double-base propellants*

1	2 Inhibitors mechanical properties			3 Physicochemistry			4	5 Behavior at firing		
Inhibitors[a]	*Sm* (MPa)	*E* (MPa)	*er* (%)	Test temperature	[b]	*cp*[c]	Density	Propensity to enhance the burning rate	Ablation rate[d] (%)	Smoke signature[d,e] (%)
EPE 01	0.9	540	10	−40°C +20°C +60°C	0.44 1.07 1.67	1.13 1.58 1.76	1.50	yes	15	88
EPE 02	4.5	530	17	−40°C +20°C +60°C	0.55 1.20 1.44	1.17 1.53 1.71	1.50	yes	20	85
SI 111	4.5	1.90	45	−40°C +20°C +60°C	4.1 3.2 4.4	1.54 1.36 1.43	1.32	no	5	88
SI 113	5.5	2.35	37	−40°C +20°C +60°C	1.0 1.0 0.9	1.45 1.33 1.42	1.50	no	5	90
SI 119	2.5	1.92	132	−40°C +20°C +60°C	7.4 5.2 5.3	1.52 1.44 1.51	1.34	no	10	80
SI 117 A	5.3	6.70	15	−40°C +20°C +60°C	4.5 2.9 3.6	1.65 1.27 1.35	1.45	no	2	88
SI 120 A	3.8	3.70	15	−40°C +20°C +60°C	1.0 0.9 0.9	1.42 1.31 1.39	1.43	yes*	2	90
PU 003	7.3	596	30	−40°C +20°C +60°C	0.40 1.30 1.82	1.10 1.68 1.96	1.30	yes	40	90-92

TABLE 1 (*continued*)

PU 004	8.5	523	35	−40°C +20°C +60°C	0.54 1.25 1.40	1.28 1.76 1.83	1.33	yes	30	90-92
PU 005	7.5	450	50	−40°C +20°C +60°C	0.46 1.30 1.10	1.44 1.73 2.15	1.35	yes	35	90-92
PU 11 C	7.5	517	60	−40°C +20°C +60°C	0.44 1.0 1.58	1.59 1.87 2.29	1.36	no	30	90
PU 51 G	15.0	316	100	−40°C +20°C +60°C	0.44 1.41 1.68	1.17 1.69 1.90	1.54	no	15	85

* Yes, in some cases.
[a] EPE = Polyester based inhibitor; SI = silicon-based inhibitor; PU: urethane-based inhibitor.
[b] Coefficient of thermal expansion ($10^{-4}.K^{-1}$).
[c] *cp* = Specific heat coefficient ($J \times G^{-1} \times K^{-1}$).
[d] Loss of weight of the inhibitor measured after completion of a static firing test.
[e] Light attenuation through the plume.

- introducing polymer chains with halogen atoms [2] and also reducing and even removing the aromatic diluents which increase the smoke signature.

4.1.1.4. *Silicone inhibitors: an excellent inhibiting material once the bonding problems are under control*

Silicone inhibitors are produced from polydimethylsiloxane-reactive oils, crosslinking through a condensation mechanism under the influence of the appropriate catalysts. They contain refractory fillers and fibers which lead to the formation, during firing, of a solid char which retains the particles in the combustion chamber of the motor. This factor, combined with the absence of tar formation by condensation, imparts a very low signature to silicone inhibitors.

This family of inhibitors has other specific characteristics such as the absence of any absorption of nitrated plasticizers, giving it a good stability for all of its physical characteristics, such as mechanical properties, shape, etc.

Unfortunately, silicones have a low natural propensity to adhesion on the propellant. The remedy consists usually in using a primer based on a functional silane. The use of such a primer, however, is not economical or desirable in terms of reliability of the bonding.

In France, self-adhesives, particularly high-performing polydimethylsiloxanes, were developed. The process that permits self-adherence is a direct application of the theory of chemical bonding at the interface.

All relevant details on this family of inhibitors are contained in references [10] and [22], which provide a complete review of the chemistry, the performance and the characteristics of production of silicone-based inhibitors.

4.1.1.5. *Polyurethane inhibitors; generaling only gases during a thermal decomposition (organic inhibitors)*

In this class of inhibitors are grouped materials that are made from polymers with a saturated and oxygenized chain without mineral refractory fillers (or with submicron particle sizes). These materials decompose by pyrolysis, preferably in a gaseous form with a minimum formation of soots and tars.

From the binders currently available for elastomers able to crosslink at low temperature, polyethers or hydroxylated polyesters are the best candidates to fullfill the required criteria.

In the case of crosslinking by isocyanates, a first study points to hydroxylated resins with polyoxyethylenic and polyoxypropylenic chains, with a carbon versus oxygen ratio of 2 and 3, respectively. In practice, however, the best compromise between a low signature and thermal resistance is obtained with polymers made by opening C4 or C5 rings including oxygen [23] and further progress is still being made.

The possibilities for choice of refractory fillers are more limited, inasmuch as there is not a great number of highly oxygenized thermostable organic products. Oxamide appears to be the best one; but in the case where the thermal resistance would prove to be insufficient, a dense mineral filler, with appropriate particle size and capable of providing oxygen, can be added.

Another means consists of incorporating into the formulations a low quantity of fibrous mineral or organic filler. The ablation ratios are improved by 20–25% and the signature properties are not altered [24]. The viscosity of the mixtures continues to be compatible with injection casting.

Injection with precision automatic feeding equipment at high or low pressure makes it possible to reduce the cost of inhibiting, particularly for high rates of production. However, this manufacturing process requires a formulation of inhibiting composition based on two components preferably exhibiting similar viscosities and equivalent masses.

4.1.1.6. *Future cast inhibitors*

It seems that some applications, such as rocket motors for antitank missiles, will continue to use free-standing grains inhibited by cast inhibitors for a long time. The future ideal inhibitor should combine the simplicity of the polyester, the stability of the silicone and the low signature and excellent bonding of the polyurethane. A compromise of this sort is not easy to come by, although the epoxide systems cured at low temperature, handicapped for a very long time by the low pyrotechnic compatibility of the amine curing agent, may hold the key to future progress. Methods have been recently found that are both easy and may be industrially feasible, allowing the use of curing agents in the presence of double-base propellants, which offers prospects of development attractive in terms of cost and performance.

4.1.2. Restrictors for free-standing grains

Restrictors are made from elastomeric material presenting sufficient thermal resistance (polyvinyl chloride, thermoplastic rubber or synthetic rubber) molded in advance with the external shape of the grain into which the propellant in its slurry form is cast before curing. This process results in a particularly economic manufacture. It requires the use of elastomers selected for their adhesive properties with the propellant (such as EPDM rubber or butyl in the case of composite propellant with polyurethane binder) or their low signature, for cast double-base propellants. A reader interested in this particular area will find numerous details on the composition of restrictors for composite propellants in reference [25] or double-base propellants in [26] and [27].

4.2. LINERS FOR CASE-BONDED GRAINS

Free-standing grains do not permit the construction of motors with large diameters. The development of case-bonded technology provided an answer to this need.

This is not the place for an historical review of the development of this process. Interested readers may refer to articles listed in the bibliography [28–30]. But the emergence of this motor design led to the development of a new elastomer material, called binding material or liner, designed to ensure the mechanical bond between the case and the propellant or between the thermal protection and the propellant. In the beginning, the adhesion between the liner and propellant was obtained by keeping the same binder for both materials. Without a doubt this was done to have the best thermodynamic compatibility possible, as well as sufficient wetting of the interface. Later, research demonstrated that the optimum binding was often obtained with a chemical composition of the liner that was different from that of the propellant binder.

The following factors play an important role in the creation of the binding:

- curing level of the liner at the moment when the propellant is cast: presence or not of reactive chemical functions;
- presence in the liner of chemical species capable of diffusing and of chemically binding with the propellant binder: presence of adhesion promoters;
- crosslinking density of the liner: allowing sterically the thermodynamically possible diffusion.

4.2.1. Detailed formulation of a liner for a propellant with a CTPB binder (Table 2)

The base polymer will be a polybutadiene in order to ensure good thermodynamic compatibility. For reasons of reactivity and low viscosity, a hydroxytelechelic (HTPB)-type polybutadiene was selected; and to be able to tailor the mechanical properties, a hydroxylated chain extensor with low mass was added to the prepolymer.

A mineral filler (carbon black, titanium oxide) also regulates the mechanical characteristics, increases mechanical resistance and controls the rheology of the material before polymerization. The stoichiometric ratio allows adjustment of the level of the mechanical properties with great precision.

In order to ensure a high level of adhesion between the liner and the propellant, the liner will include an adhesion promoter capable of creating linkage through covalent bonds at the interfaces.

Finally, a catalytic system will not only allow control of the rate of crosslinking but also, in some cases, will control the nature of the chemical reactions at the interfaces.

TABLE 2 *Composition and characteristics of a liner designed for an aluminized composite propellant using a CTPB binder*

Physical properties of the liner	
Density at 20°C	1.14
Electrical resistivity	10^{12} Ωm
Linear thermal expansion coefficient	120 10^{-6}/°C
Specific heat	0.4 Cal/g
Composition of the liner	
HTPB	66.0%
Chain extender	8.0
Antioxidizer	0.3
Bonding promoter	3.6
Filler	13.0
Crosslinking agent	8.6
Catalyst	0.5
Pot-life—20 min at 20°C	
Mechanical properties of the liner[a]	
Temperature	+20°C
S_m (MPa)	2.2
(%)	250
E (MPa)	0.8
e_m (%)	800
e_r (%)	800
Bonding properties	
C = shear strength (MPa)	0.65
T = tensile strength (MPa)	0.65
P = peeling strength (daN/cm)	2.5

[a] Tensile loading rate 20 mm/min.
[b] Test rate 10 mm/min.
Test temperature 20°C.

Of course, the propellant will be cast on a liner that is not completely cured, to facilitate the adhesion, and that is free of poisons such as absorbed water, tensio-active agents, etc.

The selection of the set-point is made by using a methodology that allows us to localize rationally the optimum of a function of several variables (experimental design factorial studies).

Table 2 provides the composition and the major characteristics of a liner for composite propellant (CTPB binder).

4.2.2. Other examples of liner development in response to specific situations

For the most part, the general ideas proposed in relation to the development of a liner for CTPB liner propellant are also true for the other types of

binders. However, particular situations arise where special requirements are needed.

For instance, a propellant may, because of its composition, be sensitive to electrostatic discharges. In this case appropriate precautions must be taken to eliminate the risks during the manufacture or handling of the grains. Such precautions include, for example, devices to eliminate the charges and equipotentiality of all elements. A specific means of protection consists, for instance, of building a Faraday cage around the grain, thereby eliminating all outside influences. A family of conductive lines has been developed for this purpose. Their extreme viscosity in the uncured state required the development of highly original spraying systems.

4.2.3. *Liners designed for tactical case-bonded grains manufactured at high rates of production*

The development of case-bonded propellant grains in tactical missiles was a consequence of requirements for high propulsion performances.

A review of possible concepts has been published by E. Gonzales and F. Marks [31], which demonstrates the usefulness of taking into account, in particular, the inert components of the motor.

Similarly, R. T. Davis and J. D. Byrd pointed out the economic advantages expected from the use of a liner with a blocked isocyanate as a crosslinking agent [15].

These types of liners have been developed in France during recent years. They have a pseudo-plastic behavior which eliminates all risks of dripping during manufacture, and crosslink through the use of a blocked isocyanate linked to an appropriate catalytic system.

The selection of the blocked isocyanate was made in such a way that it not only contributes to a very long pot-life at ambient temperature, but also provides (during the deblocking through thermal activation at 60°C — in particular during the curing of the propellant) the isocyanate functions allowing an improvement of the cohesion at the interface between liner and propellant. In addition, the blocking agent acts as a plasticizer for the propellant, improving the binding behavior at low temperature.

In terms of mass production, the very long pot-life results in a great flexibility of use, significantly reducing manufacturing cost.

4.2.4. *Liners designed for grains using propellant with high levels of nitrated plasticizers (XLDB)*

In terms of their compositions these propellants resemble the conventional composite propellants already discussed in this chapter, with several additional particularities (undesirable in terms of bonding) linked essentially to the presence of a significant quantity of nitrated plasticizer.

The liners are similar in their composition, as well as in the quality control methods, to those we just examined. However, in order to improve peel behavior a form of mechanical linking, known as mechanical embedment [18], was used in the past. Recently, with the purpose of simplifying the process, improving the reliability of the bonds between the liner and the propellant and reducing the costs, a family of liners with direct bonding has been developed.

4.3. THERMAL PROTECTION DESIGNED FOR THE INSULATION OF COMBUSTION CHAMBERS

Excellent descriptions of these materials are available in the bibliography [32,33] or in commercial brochures [34]. Protection through the ablation mechanism was described earlier. We will therefore limit ourselves here to pointing out that the elastomers used to manufacture flexible thermal protection are most often made of rubber (NBR, NR, EPDM and Hypalon) with cooling fillers (oxalate, carbonate and hydrate) and refractory charges such as carbon, silica or asbestos fibers. In contrast, the majority of the rigid thermal protections are made of phenolic resins (or derivatives) reinforced with refractory fibers such as asbestos, silica, carbon, alumina or even nylon. The selection is always guided by the particular characteristics required for good operation of the motor.

However, the thermal protection for integral boosters located in the propulsion chamber of a missile powered by a ramjet calls for special attention in this section.

The reader may find in this book, as well as in the bibliography, pertinent information about the functioning of these ramjets [35].

The point that needs to be emphasized here has to be with the fact that the material ensuring the bonding of the propellant to the case during the boost phase of the missile must also later work as the thermal protection of the combustion chamber of the ramjet. Consequently, this thermal protection must have the usual performance characteristics of a liner. In particular, it must be sufficiently elastic to withstand, without breaking, the deformation induced by the operation at high pressure of the booster grain. This virtually forbids the use of phenolic compounds reinforced with silica. Of course, the elastomer selected must withstand the oxidizing atmosphere of the ramjet combustion chamber without burning.

Because of these two requirements, the number of choices is drastically limited. Only polysiloxanes (or derivative materials) are capable of satisfying all of these specifications. Table 3 gives the composition and main characteristics of such a thermal protection.

However, the siloxanic materials due to their very low critical wetting tension (the second lowest after PFTE) have a very poor natural adhesion with the propellant. This resulted, in the United States in particular, in the

TABLE 3 *Major characteristics of a thermal protection for integral booster for a ramjet missile*

Physical characteristics, at 20°C	
Density at 20°C	1.45
Electrical resistivity	10^6 Ωm
Linear Thermal expansion coefficient	$4.7 \times 10^{-4}.K^{-1}$
Thermal conducitivty	0.40 W/°C m
Specific heat	1.13 J/°C
Composition	
Bicomponent silicone elastomer	
RTV type	46%
Granular refractory charge	23%
Fibrous refractory charge	18%
Catalyst	7.0%

Mechanical characteristics[a]

Temperature	S_m (MPa)	(%)	E (MPa)	e_m (%)	e_r (%)
−40°C	5.6	4.6	122.0	55	55
+20°C	4.7	3.8	138.0	51	51
+60°C	4.5	4.6	96.0	52	52

Bonding characteristics[b]

	Shear strength (MPa)	Tensile strength (MPa)	Peeling strength (daN/cm)
HTPB Composite propellant with liquid burning rate modifier	6.5	7.5	1.5
Aluminized HTPB composite propellant	5.0	7.0	2.0

[a] Tensile loading rate 50 mm/min.
[b] Test rate 10 mm/min.
Test temperature 20°C.

development of complex solutions to ensure the bonding of the booster grain to the chamber [36].

In France, the research was oriented in two directions:

- improvement and simplification of the bonding techniques of the integral booster in the combustion chamber of the ramjet;
- improvement of the thermal performance of the material in terms of a decrease in thermal conductivity and a rise of mechanical strengthening of the residual char, to make it capable of withstanding flow instabilities in the combustion chamber of the ramjet.

To improve the bonding of the propellant to the thermal insulation much attention has been paid to the chemistry of the propellant binder.

HTPB, which is used to manufacture the propellant of the booster, crosslinks through a reaction of the isocyanate functions on mobile hydrogens. Advantage has been taken of this reaction in the selection of polydimethylsiloxane as a binder for the thermal protection, and to introduce in the latter adhesion promoters, such as functional silane or blocked isocyanates. These chemicals improve the bonding by creating strong chemical links at the interfaces with the propellants. The result is that the propellant may be directly bonded onto the thermal protection. Among other things, this solves the problem of combustion of residues at the transition between the boost phase and the operation of the ramjet chamber.

Simultaneously, an improvement of the mechanical strength of the pyrolyzed portion is attempted by using polymers leading to a higher amount of ceramic-like residues than with polydimethylsiloxanes, and by increasing the efficiency of the endothermic reactions during the exposure of the thermal protection to a high heat flux. Significant progress has been made in the following areas:

- use of fibrous refractory reinforcements to improve the thermomechanical resistance of the char;
- use of polymers similar in type to those used as precursor for the production of silicium carbide fibers;
- use of polysilarylene-polysiloxane as a replacement for polydimethylsiloxane as a binder for the thermal protection material, leading to a significantly higher amount of refractory residues [37].

5. Conclusion

This chapter, devoted to insulating materials for propellant motors, shows that the preparation of a case or the inhibition of a grain are very complex tasks, because they must reach a fine compromise between a large number of often contradictory requirements.

The reader will have noted that making the appropriate materials available to the designer of the motor is a crucial factor, for the following characteristics:

- access to complex design, permitting adjustment of the internal ballistics;
- decrease of the inert mass in the motor;
- reliability and safety of operation;
- wide range of firing temperatures;
- industrial costs.

In the end, it turns out that for the reasons previously mentioned, the development of insulation materials is one of the most difficult and time-consuming of the tasks involved in the development of solid rocket motors.

Here more than in any other area, it may be true that the predominantly experimental nature of the techniques used must rest on the best-known theories and a very rigorous experimental research, while leaving a large place to the intuition and the experience of the designers.

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