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Development of Modern Solid Propellants

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Introduction: Chemical Propellants, Solids and Liquids

BECAUSE of their relative simplicity, solid-propellant rockets came into use long before liquid-propellant rockets. Even if the initial uses of solid propellants in the form of blackpowder might have been in peaceful fireworks, history quickly mentioned them in connection with guns, fire arrows, and other types of armaments. This characteristic of being an "old technology" and the connection with military devices probably partially explains why, centuries later, the visionaries of space travel tended to look to liquid systems, leaving the solid rocket in the role of an ordnance device. In fact their strong orientation toward liquids was probably a consequence of a lack of vision of the future technology. And, in fact, during the first thousand years there was very limited progress in solid propellants, and this, of course, led to small hopes of achieving the high impulses of big rocket motors. The invention of composite propellants removed the impulse limitations in the middle of the 20th century.

Ed Price[1] wrote that "the history of solid rockets is very special for its spirit of people making things to happen." We will see how the key people in the development of modern solid propellants had more than any other quality that of entrepreneurs. (Typical examples like the creation of Aerojet and the development of Thiokol will be described later.) Also, in many aspects the people dealing with solids have often been inventors and self-made men, whereas the people involved in liquids were or considered themselves to be scientists and members of the academia. Of course, science always followed, but this characteristic of being a sort of invention, and sometimes the characters of the inventors, might have contributed to some lower consideration for solid-propellant technology, which was sometimes considered a black art.

The initial development of contemporary solid propellants is more or less an American story, but the rest of the world followed, and some innovations in the technology came from outside the United States. Prehistory, inventions, inventors, science, technology, uses and applications, and development in the world should be covered in this paper. We hope that the reader will excuse the author for all of the imperfections and omissions: lack of information—mainly related to confidentiality, either for security reasons or for proprietary reasons, extension of the task, limitation of space, loss of historical traces and archives, should be generally responsible.[2] Finally, it might be useful to remember a few points that are often forgotten by people not directly involved in solid-propellants technology and which justifies a high level of consideration for it. In a solid rocket motor (SRM) the propellant is not only a commodity, an energetic fuel with which to fill the tank, it is also the tank, the pumps, and the injection system, and the largest part of the combustion chamber.

All of these points will become more apparent after a thorough reading of the companion article by Caveny et al.[3] on the U.S. solid-rocket program in this issue.

Powder Rockets: from Black Powder to Double-Base Propellants

Black powder was probably the discovery, at the end of the first millenium, of some Chinese alchemists who were experimenting with various flame-producing materials. Their studies involved the mixing and heating of various substances including sulfur, charcoal, and eventually saltpeter (potassium nitrate). Depending upon the proportions of these ingredients, they obtained explosive or propelling properties that they learned to apply to various pyrotechnic devices, mostly fireworks but also rockets called fire arrows. From China this knowledge spread to India, to the Arab countries, and finally to Europe, but for centuries, to make war, the gun was favored in Europe; the rocket was used in recreational pyrotechnic or signal devices.

The 19th century is sometimes called "the first golden age of rocketry."[4] During this period, there was in Europe a transfer from a relatively developed technology of fireworks towards military rockets, especially in England under the influence of William Congreve. These rockets were aimed at explosive or incendiary goals, but also psychological effects. At this time, after loading and ramming the powder in the rocket case, a cone shape cavity was formed throughout two-thirds of the propellant. The pyrotechnists called the cavity of the propellant grain—our modern bore—"the soul of the rocket" because they discovered that it helped to get the high thrust needed to make the rocket fly.[4] However, Congreve rockets had many limitations: they were not entirely safe, and their precision was very bad. An important improvement was brought about by an Englishman, William Hale who modified the design in order to make the rocket spin and thereby stabilize its trajectory, but the great progress in the design of Hale rockets was not paralleled in propellant progress.

Nobel and Vieille, Smokeless Powder

There had been experiments on new powder formulations since the beginning of the 19th century without much success and with big accidents occuring, so that the use of variations of the basic black

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powder stayed the rule. The elimination of smoke and solid residues were required to solve many technical, strategic and tactical problems in guns and rockets. The first breakthrough in making a truly workable smokeless powder came in France in 1886. Paul Vieille found ways to nitrate cotton so that it was possible to dissolve it in solvents, which led to gelatinized masses of nitrocellulose that could be formed into gunpowder grains. This enabled the quick development of totally new propellant charges for guns with much higher performance. In 1887, Alfred Nobel patented Ballistite, based on nitrocellulose plasticized by nitroglycerine under a process similar to the celluloïd process invented by J. W. Hyatt in 1870. It was a first step in the direction of extruded double-base (EDB) propellant grains. The two types, called single-base and double-base powders, have been in competition for applications to guns until today. The double base is more adapted to rockets because of better combustion at lower pressures, but single-base powders can be used in gas generators, ejectors, etc.

These powders were better defined chemically and physically and more favorable for physical measurements and modeling of combustion. The hypothesis of combustion in parallel layers that had been proposed by Piobert[5] in 1836 could be perfectly applied. This enabled Vieille to establish the law of dependence of the rate of combustion with pressure $r = ap^n$, which bears his name, through measurements of the evolution of pressure during the combustion of samples in a closed vessel, where n is called the pressure index or exponent. Low values of this index correspond to a reduced sensitivity of the chamber pressure to variations of ambient temperature and to variations in burning surface area or nozzle throat area during operation of a rocket motor.

Finally, the 19th century might have been a golden age for rockets not so much because of their revival in battles with Congreve and Hale, but because Nobel and Vieille established the bases of the modern solid propellants.

Propellants and Rocketry in the First Part of the 20th Century

Rocket propulsion evolved in two very different directions in the first part of the 20th century. The first direction was focused upon access to space and astronautics for which the visionaries of space travel, Tsiokolsky in Russia, Goddard in the United States, Esnault-Pelterie (who coined the word "astronautique") in France, and Oberth in Germany very quickly understood that rocket propulsion was the key. In that direction maximum performance was the most important and liquid propulsion was to be preferred. The second direction was more or less the prolongation of the 19th century developments in weapon systems, with rockets of higher performance, but also satisfying requirements of compactness, long shelf life, and immediate readiness. In that direction solid propulsion was better adapted and was applied to a number of unguided air to ground rockets, to the bazooka antitank weapon, to artillery rockets, etc. All of these applications were described as ordnance rockets.

By the end of the century, both types of propulsion would be used on numerous spacecrafts and launchers.

World War II

As everybody knows, World War II saw the development of modern liquid propulsion in Nazi Germany and its application on the V2. In the field of solid rockets, the most advanced state of the art, all over the world, in 1939, was based on EDB, with a high pressure index leading to enormous variations in chamber pressure and thrust with variations of ambient temperature. The propellant charges were produced by press extrusion with rigid limitations in geometries (only cylindrical grains are possible) and sizes. The charges of propellant often used an internal-external burning tube design and burned on all surfaces. All designers recognized that radial internal burning grains would be better. This could be obtained by using externally inhibited propellant grains or propellants bonded to the motor case. The latter design would of course provide higher propellant loading in the motor case. Case-bonded propellant grains able to withstand the stresses and strains generated by ambient temperature variation were accomplished by the end of the 1940s using composite propellants based on polysulfide binders.

In the United States the main actors in propellants were probably the California Institute of Technology, where EDBs were produced at a place called Eaton Canyon (a production moved by 1944 to China Lake[6]), Section H at the Naval Propellant Factory Indian Head,[7] the Explosives Research Laboratory in Bruceton, Pennsylvania, and last, but not least, the Guggenheim Aeronautical Laboratory, California Institute of Technology (GALCIT), where cast composite propellant was invented and Aerojet created.

Invention of Composite Propellants

Composite propellants are the base of all modern developments of solid rocket propulsion systems. The origin of the space shuttle boosters and other space launchers boosters, of all of the solid rocket motors of the ballistic strategic missiles of the Western countries, and of the great majority of the motors of tactical systems can be found in the invention in 1942 of the first cast composite propellant by John W. Parsons. The somewhat legendary story of these beginnings is well documented in pictures and written accounts.[1,2,8,9]

The story began in 1936 at GALCIT (GALCIT later gave birth to the Jet Propulsion Laboratory), under the direction of professor Theodore von Kármán. There, a very small group, including John Parsons (see Fig. 1),[10] a self-taught very talented chemist, and an excellent mechanic named Edward Forman, under the supervision of Frank Malina, experimented during the following years on liquid and solid rockets and established the bases of future developments. Martin Summerfield joined the group a little later.

Parsons wrote in 1937 a report titled "A Consideration of the Applicability of Various Substances as Fuels for Jet Propulsion," in which he reviewed in detail the properties and performances of chemical compounds in both solid and liquid rocket propulsion. In this paper Parsons clearly understands that liquids could achieve higher levels of performance compared to solids. However, other factors of consideration to Parsons and Malina were cost, availability, storage conditions, complexity of mixtures and delivery systems, handling, volume, etc.

Parsons' Propellants Development at GALCIT

At the end of 1938, the group focused on jet-assisted takeoff (JATO) rockets for assisting aircraft. At first Parsons tried black and smokeless powder mixtures, which resulted in a significant number of misfires and explosions, limited burn time, and low efficiency. After many unsuccessful tests he even wondered whether a stable sustained combustion process was possible. Von Kármán and Malina

Fig. 1 Inventor of composite propellant, John W. Parsons, circa 1940, at Guggenheim Aeronautical Laboratory, California Institute of Technology, Pasadena, California.

worked on a series of theoretical and mathematical analyses proving (in 1940) that the process was stable if the propellant were without defects[8]: "...calculations showed that as long as the ratio of the area of the throat of the exhaust nozzle to the burning area of the propellant charge remained constant the chamber pressure would remain constant." This established the basic equation of the steady-state operation of a solid rocket motor.

Parsons and Forman redesigned their rocket, which was static tested and flight tested in the first part of 1941. As a consequence, they were funded by the U.S. Navy for production of JATOs, even if there were still failures.

Founding of Aerojet and the First Composite Propellant

The production of solid JATOs from the GALCIT facilities was of course difficult. In March 1942 von Kármán, Parsons, Malina, Forman, and Summerfield founded the Aerojet Engineering Corporation for the production of rocket systems. Parsons was given the responsibility at Aerojet to overcome the exploding solid JATO problems. He found that most of the problems with the powder units were caused by poor chemical aging. Parsons pondered the issue for some time: how to make a propellant more stable and simpler to handle. Then, in late May or June 1942, while watching tar paper being applied to the roof of a building, he realized that asphalt mixed with the right solid oxidizer could make a good propellant. Easily poured and formed when hot, it would cool and dry without the brittleness and cracking that plagued the use of the black powder mixtures. It remained stable over a wide temperature range. He had the idea to use potassium perchlorate for the oxidizer. Tests with this propellant (called GALCIT 53) proved successful.

This was a fundamental breakthrough in solid-propellant rocketry. At first the Ordnance Department of the Navy objected strongly to the use of potassium perchlorate as an oxidizer because it had proved unsafe in the past. But Parsons proved that the objection was no longer valid if chlorate impurities were eliminated. Joseph Schumacher[11] has told how "in his office at WECCO (Western Electrical Company, which was already producing chlorates) in Los Angeles, on a quiet Saturday afternoon of december 1942, he received a telephone call from a man who identified himself as Jack Parsons of the GALCIT. This man went on to say that GALCIT was interested in developing a reliable domestic source of potassium and ammonium perchlorate"... and this started another piece of history.

Production of service-type units using GALCIT 53 began shortly therafter at the Aerojet plant that was installed in a former automobile dealership building (which is today an AIAA historic site) in Pasadena. The propellant was mixed and cast in another plant in Azusa. Extensive studies were conducted on asphalt-based propellants in the following years. Early on, Parsons used ammonium perchlorate (AP) as the oxidizer, and the result was a better performance and the suppression of condensed KCl in the chamber and at the nozzle throat. The exhausts were less smoky, but only if humidity was low.

Parsons left Aerojet, which had became Aerojet General, a subsidiaty of General Tire, in 1945. He worked then for various organizations, did consulting work, and invested a lot in his interest in occultism and in paganism.[12] Parsons died in 1952 in the explosion of some materials he had stored in his garage.

Frank Malina became the first director of the Jet Propulsion Laboratory (JPL). Martin Summerfield headed for many years solid-propellant research at Princeton University, where he trained many graduate students who later became reknowned scientists and managers in rocket propulsion, like Len Caveny, Naminosuke Kubota, Kenneth Kuo, Luigi De Luca, Woodward Waesche, and several others.

Three Glorious Decades of Solid Propulsion: 1945–1975

During the 30 years that followed World War II, the liquid propulsion development from the V2 to Saturn V brought access of man to the moon while the scaling up of solids went from the JATOs to the boosters of the space shuttle. For better understanding of the numerous achievements of the period, we will present first the main families of solid propellants. After that we will discuss their genealogy starting from where we left off in 1945.

Some General Considerations on Solid Propellant and Energetics of Propulsion

Before embarking on a descriptive presentation of compositions that might look tedious to newcomers, it is worth remembering the index of merit of a propellant, the specific impulse *Isp* that we have vaguely called until now "the performance," and the rationale of the research of improved propellants, from the energetic point of view. *Isp* measures the impulse provided per unit weight of propellant expended. It is also the ratio of the thrust to the mass flow rate expressed as weight per second, so that units of *Isp* are seconds. *Isp* allows a comparison of various rocket propulsion systems and different propellants. At the system level high-density propellants are also of interest; this is why solid rockets are the best way to obtain very high thrust and impulse.

In the case of chemical propellants, it is easy to express *Isp* as a function of parameters related to the propellants chemistry. *Isp* is proportional to $(T_c/M_w)^{1/2}$, where T_c is the chamber temperature of the gases and M_w is their effective mean molecular weight. This means that propellant compositions must be based on compounds with weakly chemically bound structures that will rearrange through highly exothermic chemical reactions into low molecular weight structures. Oxidizer–reducer reactions are used the most. In the oxidizer category we have fluorine derivatives, perchlorates, nitrates, and nitro compounds, etc. In the reducer category we have hydrocarbons, metals, etc. Compounds that combine in the same molecule the oxidizing and the reducing elements with a high enthalpy of formation (like nitrocellulose or nitroglycerine) are called energetic compounds. They can be used as monopropellants or introduced in a formulation.

Today the research of new propellant formulations is greatly helped by the use of thermochemical computer codes and the availabilty of thermodynamical functions of a great number of chemical species.[13] The quasi-international standard is derived from a code developed by Gordon and McBride[14] at NASA. We are still, however, dependent on the compounds that nature and the industry have to offer, or we will have to develop new ones; and this had a great influence on the development of the main propellant families. Also we have to remember the importance of the way the constituents of the formulation decompose, thereby dictating the combustion regime.

Main Propellant Families

The delivered specific impulses and densities of these families are summarized in Fig. 2. The values shown are measured in standard motors. In the United State, the standard motor is called the Ballistic Test and Evaluation System. It has been described by Geisler and Beckman.[15] To make comparisons, standard conditions of operation of the motor must also be defined. The most important are the chamber pressure and the expansion ratio. In Fig. 2 these values are

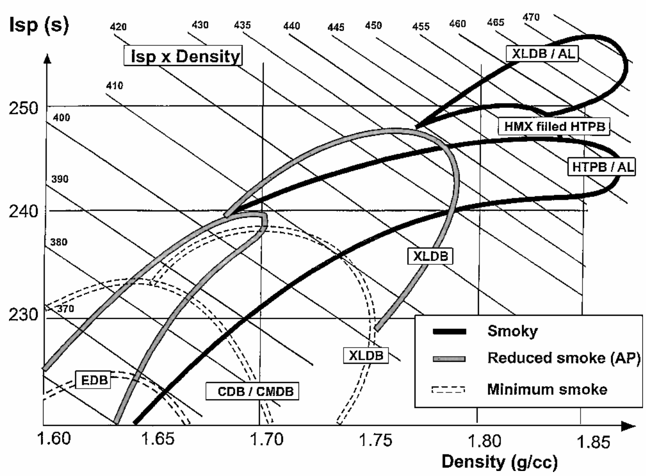

Fig. 2 Delivered *Isp* and densities of the main propellant families.

7 MPa and an expansion from 7 to 0.1 MPa, close to the values often used in the United States of 1000 psi and 1000 to 14.7 psi.

Different standard motors and conditions of operation can be found in the literature; sometimes calculated values neglecting all losses, especially two-phase flow losses (from 10 to 20 s) resulting from condensed solids like alumina, are offered without warning. It is then useful to give precise reference values for the conditions of Fig. 2 for typical propellants; 245 s are obtained for a composite propellant (polybutadiene binder, 68% AP, 20% A1); 236 s for a reduced smoke propellant (polybutadiene binder, 85% AP); and 254 s for a high-energy propellant (high-energy binder, 10% AP, 46% HMX, 19% A1). GALCIT 53 was probably close to 160 s.

Six families of propellants are today commonly manufactured and used. They are described in specialized references, for instance, Davenas[16] and Sutton.[17]

1) The more than one-century-old EDB is prepared by impregnation of nitrocellulose with nitroglycerine, generally in a water medium to get a paste as a first step. The most frequently employed nitrocellulose has a content in nitrogen (N) of 12.6%. Solubility and ability to plasticization is a function of this index. The final composition is obtained through kneading with additives and carpet rolling at some elevated temperature. The additives include stabilizers, ballistic modifiers, afterburning suppressants, etc. The final configuration is obtained by extrusion through a die having the desired shape. The outer diameter is limited to about 300 mm in western countries. Monodimensional cylindical shapes are obtained directly but additional grain machining may be performed.

2) The cast double-base propellants' (CDB) ingredients are similar or parents to those of EDB propellants. They are obtained by casting a mixture of nitroglycerine and an inert plasticizer, called casting solvent, into a mold (which can be the rocket motor case) containing a previously prepared nitrocellulose-based powder in which the various additives have been already incorporated. The casting solvent swells and dissolves the nitrocellulose through a curing of some days at elevated remperature (typically 60°C). CDBs have of course much less size limitations and allow the realization of three-dimensional shapes.

EDB and CDB propellants are generally stiff, with a high elastic modulus and low elongation capability, especially at low temperatures, and so their use is rather limited to free-standing grains. These properties might however be of interest in some applications, for instance, when very precise dimensions are required.

3) Composite modified cast double-base (CMDB) are derived from CDB propellants by addition of energetic solids and, generally, nitroglycerine in the casting powder, which increases the level of energy and the plasticization of the final formulation. When they include only a nitramine (HMX, RDX), their atomic omposition based on carbon (C), hydrogen (H), oxygen (O), nitrogen (N), gives them "minimum smoke," sometimes called smokeless characteristics because there are very few condensed species in the nozzle exhausts and no secondary condensation.

4) Elastomeric modified cast double-base (EMCDB) propellants, an improvement of CDB with better mechanical properties for case bonding, have been developed in the United Kingdom. They are produced by the same process as CDB and CMDB with the same type of basic formulations. A hydroxyl prepolymer (polyester, polycaprolactone) and an isocyanate cross-linking agent are introduced in the liquid casting solvent.

5) Composite propellants are based on a nonenergetic polymeric binder and high levels of AP. They might or might not contain aluminum powder as a fuel. They are obtained by mixing, generally under vacuum, the solids to the liquid ingredients of the binder, introducing a cross-linking agent in the mix, casting under vacuum, and curing to obtain a solid grain. The propellants without aluminum are called reduced smoke propellants because there is no primary smoke in the exhausts, but secondary smoke formation is possible in certain conditions of ambient temperature and humidity by condensation of water with hydrochloric gas resulting from the combustion of AP.

6) High-energy propellants is the name given to compositions based on a binder highly plasticized by a liquid nitric ester or a mixture of nitric esters and energetic solids like nitramines. They might also contain AP and aluminum. They are sometimes called cross-linked double base (XLDB) even if there is very little or no nitrocellulose in the binder. They have a physical behavior of the same type as composite propellants. Their production process is roughly the same, with of course a special preparation of the energetic binder elements. Composite and high-energy propellants are very well suited for case-bonded grain applications because of their mechanical behavior: low modulus and high-elongation capability in a wide temperature range.

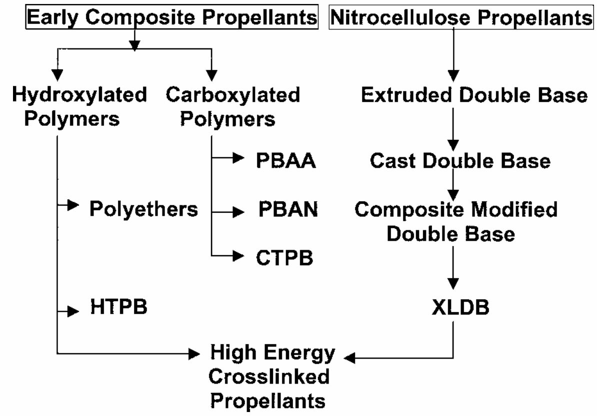

Fig. 3 Family tree of 20th century composite propellants merge with 19th century double-base family to achieve high-energy cross-linked propellants.

Besides the main ingredients, all propellants can contain additives, generally at low contents, used as stabilizers, afterburning suppressants, combustion instabilities suppressants, and burning-rate modifiers. One of the important tasks of propellants designers is to find a practical way (filler particle size, burning rate modifier, etc.) to control the burning rate and pressure index, which are key factors in designing SRMs.

Figure 3 presents the family tree of solid propellants with its two main branches. As we already know, the double-base branch originated in the second part of the 19th century, whereas the composite branch developed during the second half of the 20th. The two branches merged late in the 20th century in high-energy propellant formulations. All of these developments can be linked to the development of the chemical industry, which offered scientists during this period many new ingredients, particularly synthetic functional polymers.

Composite Branch

By 1950 polystyrene-polyester, PVC plastisol, and polysulfide binder systems had replaced the asphalt binder of Parsons because of the need for more reproducibility and better mechanical behavior over a wide range of temperature. The polyester system was developed by Aerojet. These propellants were suitable for JATOs, but not for case bonding because of high stiffness and low elongation. PVC binder composite propellants were developed by Atlantic Research Corporation (ARC),[18] which was founded in 1949. These propellants[19] used the same oxidizers and most of the additives of other propellants, but the binder was cured by solution of the plastisol of PVC at high temperature. Mixes of the ingredients can be prepared and kept for extended periods before molding through casting, pressing, or extrusion. The easy extrudability is an economic advantage. On the other hand, these propellants do not have the rubbery and high elongations characteristics needed for case bonding: they are adapted to small, free-standing grains. For the future it was then necessary to develop cross-linked binder systems based on the condensation of liquid functional prepolymers.

Aluminized Propellants

The discovery at ARC that large amounts of aluminum (16 to 20%) added to these compositions raised the specific impulse by about 10% and density by more than 5% is a breakthrough: it allowed, for instance, the design and development of the Polaris missile at the end of the 1950s. The history of that discovery was told by one of the authors, Charles Henderson, in a way that places it in the invention category. Historian Hunley[2] explains that Henderson and Keith Rumbel were aware that some calculations showed that the *Isp* could be raised only within a narrow range and should decrease beyond the 5% level. But they still made tests up to 21% and observed a continuous increase of *Isp*. They also established the initial rules for good combustion of aluminum.

During the mid-1950s, Rohm and Haas researched the important complimentory benefit of suppressing destructive acoustic instabilities by tailoring the aluminum type and particle size.[20] An insightful discussion on the subject of aluminized propellants has been recently presented by Geisler.[21]

Some Theory in Solid Loadings, Gelation, and Cross-Linked Binder Networks

The development of the composite branch has been parallel to progress in polymer science that brought new scientific support to the art of formulating propellants. Some simple and elegant theories provided the qualitative base for orienting the development of what is, after all, a composite material obtained by cross-linking highly filled polymers. Farris[22] established an extremely simple but illuminating model of viscosity when solid particles of different sizes are incorporated in a suspension. The model explains how to make the best packing of fillers in order to obtain the lower viscosity for casting and the lower final elastic modulus in the final propellant after crosslinking. Farris also showed the great importance of the bonding of the fillers with the binder. Improving this bonding increases the linear part of the stress–strain curve and the maximum stresses and elongations as a consequence.

Paul J. Flory, Nobel Prize 1974, developed a gelation theory of polymers by polycondensation and models of elasticity of polymer networks. This theory could be used to understand the formation of the binder of composite propellants. He determined the critical conditions for the formation of infinite networks starting from liquid functional polymers until gelation. (He also developed thermodynamic theories of elasticity which relate the mechanical properties to the characteristics of the network.)

Oberth and Bruenne[23] have made an excellent presentation of these subjects, focused on binder-filler interactions and bonding agents.

Polysulfide Binders

Polysulfides are important in history for at least two reasons: 1) they were the first liquid functional prepolymers to be used to elaborate semi-elastic binders crosslinked by chemical condensation with a multifunctional agent and 2) because they resulted in the development of a large solid propulsion company, Thiokol, today ATK Thiokol, the world's biggest company in solid propulsion. This history has been summarized in detail by Sutton.[24] It started in 1926 when Dr. Joseph C. Patrick, who owned a small chemical laboratory, discovered the properties of insolubility and elasticity of a nonexpected residue (one more case of "resin" formation in doing synthetic organic chemistry!), formed by condensation of ethylene dichloride with sodium polysulfide. Patrick took a patent, invented the name Thiokol for his product, and started a business and a company. In 1943 C. Bartley, a JPL engineer, searching for a better binder than asphalt, succesfully tested a Thiokol liquid polymer. A polysulfide-based propellant and a liner based on a layer of polysulfide polymer containing carbon black were developed. This was the first case bonding system, the essential breakthrough enabling large solid motors. Finally, because the existing propellant manufacturers were not interested, in order to expand, the tiny Thiokol entered the solid-propellant business with locations at Elkton in 1948, Redstone Arsenal in Huntsville in 1949, and later, in Utah, in 1956. The chemistry of liquid polysulfides, their curing, and the formulations of propellants using them have been described by Arendale.[25]

Early Polybutadiene Propellants

The polysulfide chain is much less favorable than an hydrocarbon chain for high *Isp* and elasticity. Chemical structures closer to synthetic rubber looked then more favorable. Research was conducted at Thiokol in the mid-1950s to investigate liquid polybutadiene polymers.[26] The replacement of styrene by acrylic acid in the free radical copolymerization in emulsion of butadiene-styrene rubber led to polybutadiene acrylic acid (PBAA), a polymer with carboxyl groups. A terpolymer of butadiene, acrylonitrile, and acrylic acid called PBAN was made by similar synthesis. Substitution of PBAA in propellant formulations resulted in higher tear resistance, and this polymer was finally adopted in the propellant of the Minuteman in 1960. The production was finally operated by the organization that is now The American Synthetic Rubber Corporation. PBAN is still used today and is by far the prepolymer produced in greater quantities.[27] It has a low viscosity and a low production cost. The curing systems are based on polyaziridines or polyepoxides compounds or a combination of both. It was later discovered that the aziridine compounds played the role of bonding agent with AP.

Based on theoretical considerations, terminated functional prepolymers should impart greater extensibility to the binder network. A carboxy terminated polymer (CTPB), based on a free radical polymerization starting from an azodicarboxyl initiator (azobis cyanopentanoic acid), was developed by Thiokol at the end of the 1950s and later produced by B. F. Goodrich. It gave significantly better mechanical properties making possible case bonded designs with motor mass fractions as high as 0.94. The propellant of the retromotor of Surveyor, which landed on our moon in 1966, was a CTPB (HC 434)-based propellant with 70% AP and 16% Al. Many CTPB propellants were formulated and produced in the United States and in the world before the general acceptance of hydroxy terminated polybutadiene (HTPB).

Polyurethane Propellants

The polysulfide/polybutadiene branch that we have described was a Thiokol branch. Aerojet developed a polyurethane branch.[28] In 1953 the JATO business was declining, and Aerojet was looking for a case bondable propellant in order to be more fully able to participate in the rapidly increasing missile business. Their action was to be based, as much as possible, on materials already available from the chemical industry. At this time of great development of polyurethanes in plastics and foams, the orientation was natural. A polyurethane binder having the qualities of a good polymer network could easily be developed based on linear polymer diols cross-linked by condensation with diisocyanates and triols. Of course many variations of these basic building elements are possible, all using the chemical reaction $RNCO + R'OH \rightarrow RNHCCOOR'$. As prepolymers, polyoxypropylene glycol (PPG), a polyether, and polyneopentylglycol azelate (NPGA), a polyester, were the most used. Other polyethers and esters could be considered and later found a new role with nitrate ester plasticizers in high energy propellants. TEA, triethanolamine, one of the polyols that was used in the second generation of binders at Aerojet must be remembered because it was part in the discovery of the important role of bonding agents in mechanical properties. Triethanolamine reacts superficially with AP forming a perchlorate of TEA with elimination of ammonia and bonds to the polyisocyanates in the binder through its hydroxy functions (see Oberth and Bruenner[23] for a very good presentation of the chemistry). Polyurethanes were used on the Polaris, the Minuteman Stage II, the Hawk ground-to-air system, etc. By the middle of the 1960s, polyurethane propellants were however outperformed by the CTPBs. Aerojet reacted by the development of nitro plasticized binders providing higher *Isp* and density to the propellant.

Both competitors and branches of the composite part of the family would in fact reconciliate at the middle of the 1970s with the qualification of HTPB-based propellants that are polyurethane-polybutadiene propellants.

Double-Base Branch

Double-base propellant had been used for nearly a century when two discoveries led to very important developments in their

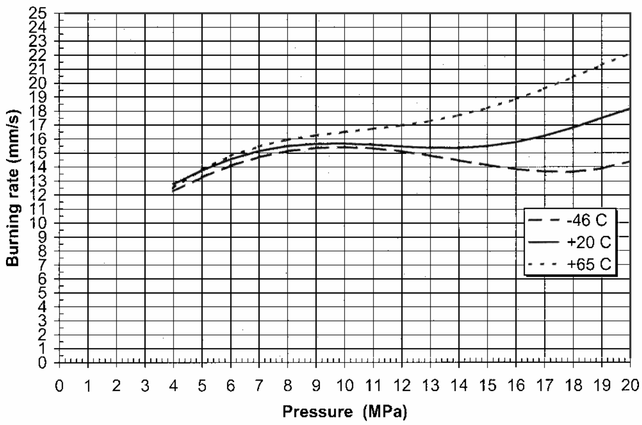

Fig. 4 Plateau effect showing pressure region of nearly constant burning rate and moderate temperature sensitivity (SNPE Propellant SD1171-6). An example of effect achieved by lead salts.

applications. The industrial organization responsible for the development and scale-up of these technologies was the Hercules Powder Company (today part of ATK). The double-base branch of the family tree is a Hercules branch!

"Platonic" Propellants

In 1946, bizarre, or at least unusual, ballistic properties were observed by W. H. Avery at Allegany Ballistics Laboratory (ABL), Cumberland, Maryland, on some extruded propellant grains. Early solventless EDB compositions had high nitroglycerine (NG) content for high energy but also for plasticizing to help extrusion. These propellants had high flame temperatures with detrimental effects on case and nozzle. After some time it was recognized that propellants with reduced NG content could provide a better compromise for the motor. Extrusion lubricants had to be added to help the production of massive charges. When that was applied to a relatively low energy composition with lead stearate as lubricant, the so-called plateau effect was discovered.[29] Figure 4 shows typical burning rate vs pressure curves. Through systematic study of lead compounds, plateaus were later obtained with higher energy compositions (until 1500 cal/g). In 1949, the so-called mesa effect was observed at ABL. By 1958, investigators in the United States, in England, and in France had developed families of EDBs (and CDBs) with extended plateau or mesa burning rate in pressure regions useful for rocket and gas generators. The highest burning rates were achieved by combinations of lead and copper salts of hydroxy substituted benzoic acids.[30] Lead stannate, lead oxide, and cupric oxide were also efficient. Carbon black in minute percentages was found very effective for enhancing burning rate and reducing temperature dependence and was used for lot to lot normalization of the burning rates.

Development of CDBs and CMDBs

The cast double-base process was developed by John Kincaid and Henry Shuey. This is indirectly recognized in some papers, but, probably for confidentiality reasons, there was no formal publication by the authors. They are generally mentioned as having conducted that work at the Explosives Research Laboratory, which had been created at the Bureau of Mines at Bruceton, Pennsylvania, to support the war effort. The process might have been inspired by the PVC plastisols developed at that time. After the war this technology was pursued and implemented by Hercules[31] at ABL. Casting powder and casting solvent were produced at Radford, Virginia, in a facility operated by Hercules on an Army plant and sometimes at the Naval Ordnance Station (NOS) Indian Head. The history of solid rocket development at ABL has been presented by Moore.[32] The processing of these propellants has been described in details by Steinberger and Drechsel,[33] Austruy,[34] and Couturier.[35]

The discovery of the plateau effect leading to low-temperature-sensitivity coefficient of the motor associated to a great range of burning rates in useful pressure domains had also a great effect on the success of CDBs and later CMDBs in tactical systems. The introduction of NG and later of nitramine fillers in the casting powder led to an increase in energy while excellent ballistic properties were maintained.[36] These more highly plasticized compositions could be case bonded. This type of composition, with AP and Al, was used in the late 1950s in U.S. ballistic missiles. The first one was the second stage of the Polaris A2, which was developed at ABL but produced in the larger plant of Magna, Utah.

During the 1960s, a castable slurry approach was studied to obtain the same final composition as CMDBs. The final evolution in the 1970s and 1980s was the quasi- or total suppression of nitrocellulose and the development of slurry cast XLDBs, which reconciliated the composite and the double base branches.

Solid Propellants in Applications

For years the best propellant for strategic systems was easy to characterize: it was the best propellant available in terms of *Isp*, density, and ability to obtain a high mass fraction in the motor. The development of the propellants that we have presented was totally correlated with the development of new or improved missiles. Umholtz[37] presents the solid-propellant performance history during the period 1960–1980. It is exactly the same as the history of development of strategic systems in the United States!

Solid-Propellants Applications to Space Systems

The safety characteristics and associated hazards of propellants during their entire life cycle are very important for applications. Energetic materials and, more specifically, propellants are classified according to United Nations recommendations. They define divisions 1.1 involving mass detonation hazard or 1.3 involving only combustion and thermal flux.

The space launch industry took advantage of the 1.3 strategic missile propellants for adding strap-on solid boosters to their launch vehicles. With the exception of the U.S. all-solid Scout and of the French Diamant space launch vehicles in the 1960s, most of the world's space launch vehicles evolved from liquid propulsion systems. However, nearly all of these liquid-core systems were later upgraded with strap-on solid propellant boosters to improve their performance at minimum cost.

Solid propellants, generally composites, were developed or adapted (the latter being the most general case by far) for numerous space applications involving launchers stages, pyrotechnics, auxiliary propulsion, satellites, and spacecrafts. Because of the size of some units and programs requiring a lot of handling and transportation and because of the design of the space launch facilities and of their environment, hazards must be reduced to a minimum. Class 1.1 propellants, which might be acceptable in a specifically designed and military managed environment, are unacceptable. On the other hand, compactness is less essential, and more propellant can be preferred to greater *Isp* if the tradeoffs are positive. The difference between propellants used in defense systems and in space systems must however not be overestimated. The use of already developed technologies, with the same basic raw materials (which is a guarantee for lower cost and continuity of procurement) and formulations derived from already qualified and flight-proven propellants has been the rule. As example, the development of the first big segmented motors by United Technology Center (UTC), a small startup company at the beginning, nowadays Pratt and Whitney Space Propulsion, started in 1962 for the Titan, used a 84% solid propellant based on PBAN.[38] Parallel to this development, technology demonstrations were conducted[39,40] and culminated with the test, by Aerojet, of two monumental 260-in.-diam monolithic motors[37] in 1966 and 1967. The propellant was also based on PBAN. It is also used in the space shuttle SRMs developed from 1974 to 1979, for which Thiokol applied also its experience with first stages Minuteman and Poseidon.

Solid Propellants in Tactical Systems

A great variety of architectures and a great variety of compositions are used in tactical systems. This is because of the variety of missions. Burning times can for instance vary from 40 ms (light antitank system) to more than 180 s (Exocet sustainer). Each propellant family can satisfy a specific requirement. This explains why today, to some extent, all families of propellants are still being produced. Different grain shapes and designs, case-bonded or free-standing grains, end burners, etc., are used. Considerations of absolute performance in *Isp* and density are important, but pressure–thrust laws requirements at various temperatures, environmental conditions in operation and firing, signature of the combustion products, aging, safety and vulnerability, and, last but not least, cost consideration must be taken into account for tradeoffs. Compromise between *Isp* and burning rates are often necessary, especially for low burning rates. Many burning-rate modifiers have been studied and developed. In the case of AP composite, iron compounds are mainly used for high burning rates. Ferrocene derivatives are favorable because, as liquids, they do not conflict with solids loading. Liquid carborane derivatives have also been used. Low burning rates with high *Isp* is a more difficult problem.

Many short-range ground launched missiles were developed by in France in the 1950s and 1960s using double-base propellants produced by Service des Poudres, which later became the company SNPE. All of these missiles of Aerospatiale were optically guided so smokeless propellants was a requirement. CMDBs with RDX fillers appeared during the 1970s on the improved Roland, on the improved Crotale of Matra, whereas the Rapier in the United Kingdom used an EMCDB. It could then be concluded that for short-range battlefield missiles smokeless propellants are preferred, but later, for the VT1, a new improvement of the Crotale system, a reduced smoke propellant, was used.

Among the numerous developments by ARC,[18] a specific achievement can be taken as example of the variety of designs in tactical systems: the wired end burner in which the conductivity of metal wires embedded in the propellant is used to enhance the burning rate. The big success of this concept and of ARC at the same time was the shoulder-launched Redeye surface to air missile using an ARCITE propellant. The Stinger, successor of the Redeye, used the same concept with a CTPB propellant, and the alternate Stinger fielded in 1998 uses the same concept with an HTPB propellant.

The technologies of aircraft, launched systems in the 1950s and 1960s were often directly derived from the strategic ballistic missiles. They used polyurethane-based and CTPB-based aluminized propellants. An original development was the short-range attack missile[41] in the United States, with a solid pulse motor. It used a 86% solids CTPB propellant with ultrafine AP and a liquid alkyl ferrocene catalyst for high burning rate. One of the many problems encountered was with the migration of the catalyst causing an increase in motor pressure progressivity.

For more details on tactical propellants, the reader can refer to Davenas[16,42] and on the very important subject of plumes to an AGARD publication[43] and to Victor.[44]

Exotic Propellants

This is the somewhat trivial name that was given to the numerous propellant formulations, based on more energetic combinations than those using hydrocarbons, AP, and Al, that were tried and sometimes tested during the 1960s. The corresponding research work was conducted in the United States under an important program called the ARPA Project Principia from 1958 to 1964. The U.S. Chemical Industry, and particularly Du Pont, Dow Chemical, ESSO, and 3M, was enrolled in the development of new energetic compounds and powerful oxidizers like hexanitroethane, nitronium perchlorate, hydrazinum mono- and diperchlorates, hydroxylamine perchlorate, hydrazinum nitroformate, difluoramino compounds, fuels like boron, metal hydrides, and metals like beryllium a zirconium. They were introduced into propellant formulations (whenever possible!) and tested by the propellant industry. Very few detailed results of this tremendous effort have been published, most of the material being probably still classified (thus newcomers can rediscover at their expense—or the expense of their sponsors and taxpayers—what has been done in the past and failed). The final results were quite limited. This effort has been summarized by Geisler,[45] who concludes that "the most resounding success and impact of the program was the development of Thermochemical Tables and related computer programs to permit the accurate determination of propellant performance." Sarner[46] gives properties and discusses some of the ingredient types considered as part of the Project Principia.

Energetic compounds are however used in many applications, from rocket propellants, high explosives, gun propellants to various pyrotechnic devices, military or commercial, like airbags. This probably explains why, after some disappointment in the research of the 1960s on high-energy propellants, work on new ingredient slowed down but never completely stopped and, as we will see, restarted in the 1980s.

To conclude this section, the important role of some organizations created at the beginning of that period must be underlined. The U.S. Chemical Propulsion Agency and JANNAF Interagency Propulsion Committee evolved from the 1948 Solid Propellant Information Agency. The propellant development reporting, archiving, standardization, and coordinating functions of these coupled organizations contributed directly to the U.S. successes and indirectly to the worldwide technology. This was also the role of AGARD of NATO, created by von Kármán in 1952 (another of his multiple achievements!), and, more specifically in our field, of its Propulsion and Energetics Panel.

The 1980s: Higher-Energy Propellants, Low Signatures, New Production Processes

By 1975 the main propellant families were established, and two very important developments were started in the United States: the Trident C4 missile using high-energy XLDB and the space shuttle SRMs using PBAN. In new compositions the 1975–1985 period could be summarized as the HTPB and the minimum smoke decade.

Advent of HTPB Propellants

According to Klager,[28] Aerojet demonstrated HTPB propellant in small rockets as early as 1961, but it was not really developed until the beginning of the 1970s. Several HTPB polymers were studied, based on anionic or free-radical process. Ionic polymerization gives a tighter polydispersity and purely difunctional polymers, which should mean according to the theory better mechanical properties. However, the R45 Polyoly BD resins made by ARCO Chemicals at the beginning of the 1970s gave better results in the final propellant, considering all characteristics, especially viscosity, even if they had a greater polydispersity and a functionality of the order of 2,4. They are HTPB polymers obtained by radical polymerization starting from hydrogen peroxide as a precursor. Adding the lower cost of these polymers, which are used in many commercial applications, made them a tremendous success and generated many imitations in various countries.

Finally, R45 polymers allow higher solid loadings, which means higher *Isp* and density and better rheology, which allows high burn rates using ultrafine AP with excellent mechanical properties at low temperature. Technically, one of the problems was to find adapted bonding agents. In the United States, the most widely used are called HX 752 or BIFA phenylenedicarbonyl bis (2-methyl aziridine) and HX 879 or TEPANOL, tetraethylene pentamine acrylonitrile. In France, a compound from the imine family named methyl BAPO, methylamino bis(methylaziridinyl) phosphine oxide, was developed.

After qualification during the 1970s HTPB propellants were quickly incorporated in many defense systems developed during the 1980s. They were also very much welcomed because of the strong push, for tactical reasons, towards reduced smoke propellants.

During the war in Vietnam, the high signature of aluminized propellants permitted quick detections of missile firings. HTPBs allowed a reduction of Al in the formulation or even its elimination, still keeping acceptable performances because of high levels of AP in this reduced smoke propellant. Small amounts of refractory particles (e.g., aluminum or zirconium oxide, zirconium carbide) were added to eliminate the combustion instabilities that resulted.

At the beginning of the 1990s, new segmented motors for space launchers were developed. The solid rocket motor upgrade (SRMU) was developed by ATK for the Titan, and an HTPB propellant developed by SNPE was chosen for the Ariane V SRMs. Aerojet started the development of the advanced SRM (ASRM) for the shuttle with an HTPB propellant using the continuous mixing process, but this development was cancelled by NASA in 1994. Various upper-stage motors using aluminized HTPB propellants, sometimes with limited amounts of HMX added for increased *Isp* and probably burning-rate considerations while keeping a 1.3 classification, were also developed,[47] for instance, the ORBUS family by UTC/CSD and the inertial upper stage, for the shuttle and for the Titan vehicles. Various strap-ons and motors for small launchers using HTPB propellants were also developed by ATK, Thiokol and Aerojet.

High-Energy Propellants

All three stages of the Trident C4 SLBM, which was deployed in 1979, were based on XLDBs made by Hercules. It was the first propellant in western countries having a standard delivered *Isp* higher than 250 s (270 theoretical). The propellant was based on a polyglycoladipate prepolymer-diisocyanate system, highly plasticized by NG, and 70% solids, AP, Al, and HMX. Ten years later in the D5 it was replaced by a propellant called NEPE 75, based on a polyether, polyoxyethylene glycol, and 75% solids reaching a delivered *Isp* close to 255 s and a density higher than 1.85 gm/cc. An example of composition is provided by Cleeton.[47]

High-Energy Minimum Smoke Propellants

Some of us think as Bob Geisler, who frequently says that AP is a miracle. Its only sin is the atom of Cl in its molecule. Ideally, even secondary smoke should be eliminated, but the performance penalty of using conventional CDBs might be too high. For that reason high-energy minimum smoke propellants were developed, first by Hercules, in the early 1970s, for tactical systems. They are based on polyurethane binders plasticized with nitrate esters similar to those used on ballistic missiles and with HMX or RDX. Lead compounds or other metal compounds are used as ballistic modifiers. Quite low pressure index and temperature coefficients could be achieved, which was a good surprise because of the high level of energetic plasticizers. The range of burning rates is however limited, approximately 2 to 15 mm/s at 7 MPa. Theoretical *Isp* near 250 s, delivered 238 s, is feasible. Refractory metals powders of the same kind used with reduced smoke propellants are added. The first use was on the Army Chaparral missile. These propellants were classified as 1.1. A loss of strain capabiliy of the propellant by thermal cycling at low temperatures ("arctic cycle") was however observed when pure NG or tri metylol ethane trinitrate (TMETN) were used. Systematic studies[48] of the crystallisation of nitrate esters and their combination lead to the use of another nitrate ester, butane triol trinitrate (BTTN) or of mixtures of plasticizers like NG/BTTN or TMETN/BTTN. The modified propellants were developed by Hercules, Thiokol, and ARC and used on numerous Army systems (Chaparral, Hellfire, Tow, ADATS, Javelin).

Evolution of Production Processes

Since its origin, the solid propellant industry has been based on discontinuous "batch" processes, but a shift can be noted during the last two decades towards continuous production lines as an answer to new economic constraints.

In the case of EDBs, the process that had been defined a century ago has long remained the basis for production. Since the 1960s, differents attempts were made to develop a continuous process, based on screw extruders. Their industrial development was limited to some niches. In France, a continuous line was implemented by SNPE during the 1970s. It was organized around a single screw followed by a twin-screw mixer extruder. The same type of development was carried out by Dynamit Nobel AG in Germany. This process was not a true continuous one because all raw materials were not mixed "in line." The continuous process started after the mixing of the composition; only the phases of deshydratation, gelatinization, and extrusion were conducted into the tandem of extruders. An original process was also developed in Sweden by Bofors. The main phases were conducted under water with the help of a limited quantity of solvent to produce small pellets that were extruded into grains by a continuous machine. The mass of propellant produced by continuous processes was limited because of the hazardous dehydrating phase in a closed extruder, but a drastic evolution took place in 1987 when Wasag in Germany selected an open continuous roll mill able to transform the wet paste into gelatinized pellets well suited to feed a twin-screw mixer extruder. For many observers this was the pertinent way to a simple and safe continuous process.

Besides the evolution of the extrusion process a stamping process, taking advantage from the thermoplastic behavior of double-base propellant was developed by SNPE. This is a compression-molding technology enabling the elaboration of noncylindrical grains.

In the case of CDBs, the principles of the casting process have not changed since the beginning.

Composite Propellants Processing

ARC had developed for the first time a continuous process through a single-screw extruder for ARCITE. In the case of castable composite propellants based on a thermosetting binder, the traditional manufacture of the propellant is generally done through a premix fabrication for blending together the polymer, the plasticizer and aluminum, dough or slurry elaboration by mixing the premix with the oxidizer, the curing agent and different ingredients in a heavy-duty mixer, under vacuum and at moderate temperature, casting into the mold or motor case, and curing in an oven or a casting pit. The phase of preparation of the slurry is extremely important to obtain a good homogeneity of the viscous dough and a complete deaeration. The initial equipment was derived from those in service for double-base propellants production (sigma blade mixers), remotely controlled, with a nominal capacity of 1000 liters, but some of them were able to handle 2500 liters per batch. These kind of mixers work well but exhibit a structural weakness: the bearings supporting the blades are immersed into the mix. In case of leakage, air entrances lead to undesired porosity and an heat rise unacceptable for safety. Specific vertical mixers able to meet the quality and safety requirements of the propellant industry were then designed. " Planetary" mixers were developed with two blades or three blades. The blades "explore" the totality of the bowl volume allowing a high-efficiency mixing. This type of vertical mixer has been extensively used since 1960 with a nominal capacity of 300 or 420 U.S. gallons. In the 1970s the needs for big SRMs and the need to reduce costs lead the U.S. company JD DAY to the design of a giant vertical mixer, with a nominal capacity of 1800 U.S. gallons, able to deliver 12 tons of propellant per batch (Fig. 5). Only a few specimens of these machines are in service, in Utah at ATK and at the Franco-Italian Regulus facility in French Guyana. These types of vertical mixers are probably close to the technological limits of the batch process. For increased capacities the efficiency of the heat transfer and the deaeration capability would become insufficient.

Alternatives to the Batch Process: Advent of Continuous Production Lines

The first real important attempt to composite propellant continuous production was carried out by Aerojet in 1960.[49] The heart of the process was a "continuous reciprocating interrupted screw mixer" (Swiss BUSS design for plastic masterbatching). The mixer was fed by loss-in-weight feeders and metering pumps. It was followed by a deaerator and a paste pump toward the casting pit. In line control systems were implemented. More than nine million pounds of propellant were succesfully produced for the Polaris program. This process was "cocooned" for many years and reactivated for the ASRM for the space shuttle in 1989. There is no doubt that in case of technical success this program would have led the continuous process to the status of industrial tool, but the program was cancelled—"ostensibly for funding reasons. To the more technology minded participants (this action) constituted a retreat to the existing technologies and organizational structures" writes Umholtz,[37] a consideration that might, at least partially, be true. The facility implemented at Yellow Creek (Missisipi) was then dismantled.

It was necessary to wait until 1994 to see the continuous process reach the rank of industrial tool under the pressure of the

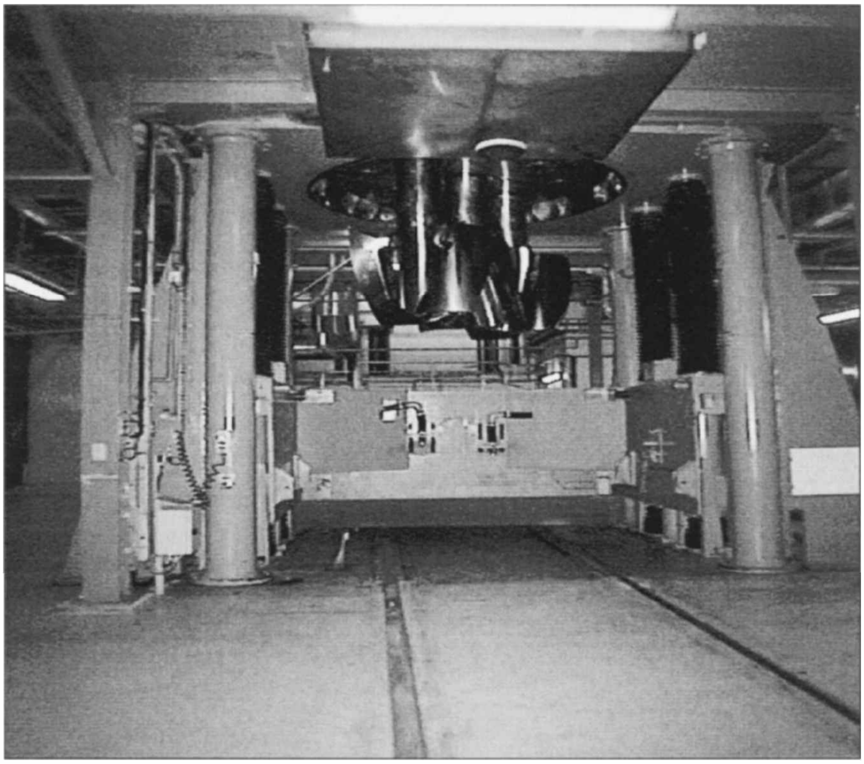

Fig. 5 Largest mixer, 1800 gallons, 12 tons of propellant per batch.

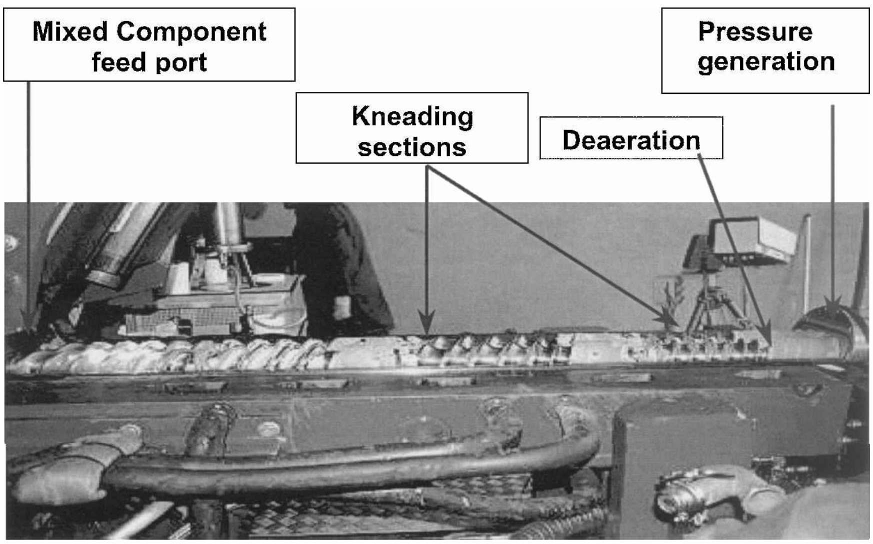

Fig. 6 Principles of a continuous twin-screw operation.

automobile industry looking for high-quality and low-cost propellants for the airbags applications.[50,51] It was necessary to build precise and stable loss-in-weight feeders and design appropriate screw and barrel elements for fully intermeshing corotating twin-screw extruders, self-wiping deaeration ports, and safety deconfinement devices. Since 1995, more than 1600 tons of composite propellant were manufactured using a SNPE operation (Fig. 6) for continuous production of millions of identical airbag inflators. This fact give a clear demonstration of the stability of the process. Compared to the conventional process, the costs of investment are drastically reduced and the hands-on time reduced by a factor of three. The safety is increased by the reduced quantity of propellant processed at a given time.

A joint program[52] between the United States and France on the continuous processing of composite propellant for rockets was conducted by SNPE and the Naval Surface Warfare Center Indian Head together with Stevens Institute of Technology. During 1997–1999, many cast motors (French side) or extruded motors (U.S. side) were successfully produced and tested. Also the capability of the process for production of the HTPB propellant of Ariane V was demonstrated.[53]

Rheology, Numerical Simulation

One on the most important points in the elaboration of solid propellant is the preparation of an homogeneous paste of high viscosity, able to be cast or extruded into net shape. To carry out this unit operation under predictable conditions it is necessary to be able to derive the rheological behavior law of the paste. It was only in the 1980s that specific rheometers were developed. Now data banks have been established giving the shear stress according to shear rate curve for the different families of propellants. In every case the rheogram obtained is of the pseudoplastic type. In the case of composites, investigation of the rheological behavior of the suspension led to a comprehensive knowledge of the segregation of fillers under casting conditions.

During the 1990s, the improvement of numerical simulation methods and the tremendous progress of computing power made possible the numerical simulation of the main phases of the process.[54] We are then better able to understand the physical phenomena involved in the industrial process, to select better equipement, and to evaluate the margin of safety (heat rise, friction, shearing, formation of dead spots), conditions that lead to segregation between the binder and solids, etc. It has became possible to simulate planetary mixing numerically, cast molding (single or multibatch), injection molding, and twin-screw operation. Numerical simulation was in fact an important part in the recent success of the continuous processing whose complexity is far beyond the ability of all intutive analysis.

Solid Propellants in Airbreathing Systems

The technologies of airbreathing propulsion of supersonic systems, as applied to tactical propulsion, have been described by Leingang and Petters,[55] Cazin and Laurent,[56] and Leisch.[57] Long-range surface-to-air missiles using liquid ramjets and jettisoned solid boosters were developed in the 1950s in the United Kingdom, United States, and former Soviet Union. These systems were not very mobile and could not be carried under aircrafts. During the 1960s and 1970s, advanced development programs related to integral rocket ramjets (liquid-fuel) and (solid-fuel) ducted rockets were conducted in the United States and in France (where the ramjet had been invented by René Lorin in 1913). In the second half of the 1960s, the Air Force Rocket Propulsion Laboratory sponsored several technology and flying demonstrations ducted-rocket programs centered around the use of a fuel with high loadings of boron. At the same time the Russian SAM 6 ducted rocket appeared on the battlefield in the Middle East. All of these concepts use an integral booster, that is, a first solid-propellant stage, integrated into the ramburner chamber, which burns first. Then air is admitted in the chamber, and gases generated by combustion of a fuel-rich propellant gas generator are injected and burned, heating the stream of air. The fuels tested were hydrocarbons and magnesium because they burn easily with a good heating value or boron because of its very high heating value. The only system finally developed, from 1975 to 1983, was the French ASMP air-to-ground nuclear missile developed by Aerospatiale with an integral booster designed by SNPE and Aerospatiale and a liquid ramjet designed by ONERA and Aerospatiale. The integral booster uses a high burning-rate HTPB propellant. For smaller missiles and shorter ranges a concept called "rustique" ducted rocket in which the generator grain is integrated in the ram chamber and burns at the chamber pressure was developed. A fuel-rich propellant with sophisticated ballistic characteristics was developed by SNPE and ONERA. In the United States an advanced development program called variable flow ducted rocket, which was preparing a new propulsion system for the air-to-air AMRAAM (advanced air to air missile), was conducted during the 1990s by ARC and Hercules McGregor Division. Today another air-to-air missile, the long-range METEOR, is developed in the United Kingdom using a Bayern Chemie Protac boron-fuel ducted rocket.

Gas Generators and Divert Propulsion

These are vast and diverse areas in which a great variety of unconventional or at least nonmainstream propellants are used. They range from gas generators used for ejection of missiles or for pressurization of liquid-propellants tanks, to small thrusters, to big postboost control systems used in strategic systems, to sophisticated systems used to deviate in a few milliseconds the trajectory of a surface-to-air tactical missile. Any kind of nonaluminized propellant can be found in these applications. Specifications for low exhaust temperatures, absence of condensed particles, and sometimes of chlorine are very often imposed. Composite propellants loaded with nitramines only in order to have high enough *Isp* and low temperatures of the order of 2000 K, low burning rates, and low erosion were developed; ammonium nitrate could be used to obtain even lower temperatures. On the other hand, small thrusters using HTPB composites with ultrafine AP and a liquid burning-rate catalyst, burning at high pressures (more than 20 MPa) during a few tens of milliseconds, have been developed. Examples of many divert and auxilliary propulsion systems developed by ARC are described by Sparks and Friedlander.[18] A typical XLDB formulation used in an hot-gas divert valve gas generator was presented by Cleeton.[47]

Science, Mechanisms, and Models

By 1950, the equations of internal ballistics and the analytic description of the steady-state operation of the rocket motor were clearly established, as testified for instance by the books of Wimpress[58] and Huggett et al.,[59] which presented already the modern theory. On the other hand, the knowledge of the physicochemical mechanisms involved was very crude and could not provide any understanding of what parameters were essential and how to manipulate them. In the field of mechanical integrity, the theoretical bases were ready, but a huge amount of work was needed to characterize the new materials and adapt the models. At this time some accidental modes of decomposition of solid propellants were unknown or not totally appreciated in their possible effects. These are three key areas on which we will focus to illustrate the development—and the limitations—of our knowledge of solid-propellant behavior. How this knowledge was put into practice is explained in the paper of Caveny et al.[3]

The industry and government laboratories like the the U.S. Navy laboratories at China Lake the Air Force Rocket Laboratory at Edwards Air Force Base, ONERA and Centre de Recherches du Bouchet in France, and equivalent organizations in various countries were very important in these developments.

Combustion Mechanisms and Models

Several outstanding books or reports have been published on solid-propellant combustion within the last 40 years of the 20th century by Summerfield,[61] Barrère et al.,[62] Williams et al.,[63] Kuo and Summerfield,[64] Zeller,[65] De Luca et al.,[66] and Yang et al.[67] These books demonstrate that during the second half of the 20th century the knowledge of the subject has considerably increased.

Solid-propellant combustion in fact includes many aspects: steady-state combustion, erosive burning, transient combustion (ignition, combustion instabilities), and metal particles combustion. This section will just focus on some general results.

In the 1960s most attention was given to AP composite propellants. Summerfield identified the critical mechanism that described its combustion behavior and proposed the granular-diffusion-flame model.[68] That model, based on the idea that fuel and oxidizer gasify at the burning surface and diffuse together, initiated the understanding of composite propellant burning. However, the great variations in AP propellant burning rate with pressure, particle size, and loading required more comprehensive models. In the early 1970s Beckstead et al.[69] published their multiple flame (BDP) model based on a complex interaction between the oxidizer monopropellant flame and two different diffusion flames above the oxidizer–binder interface. This phenomenological interpretation was able to explain most of the observed propellant behavior for many years. For AP-based propellant, composite or double base, AP primary diffusion flame is apparently the dominant mechanism, related to the increased temperature of the diffusion flame possibly enhanced by the reactivity of the chlorine-containing products. This assumption has been supported by Parr and Hanson-Parr[70] 25 years later in their study of diffusion. In contrast to AP propellants, Beckstead and McCarty[71] analysis of Cohen[72] data on HMX-based propellants led to a modification of the BDP model, adding that the burning rate was dependent on how individual particles burn through the binder to an adjacent one because a diffusion-related process seems to be absent in these propellants.

The combustion mechanisms of double-base propellants have been summarized in the 1980s by Lengellé et al.[73] In the 1950s basic studies had given a good understanding of the combustion, for example, see Heller and Gordon.[74] Work performed in the Soviet Union was reported in the 1960s, for instance, by Zenin[75] of the

Institute of Chemical Physics. The active part of the lead salt has been found to be the oxide of lead (PbO) that accumulates above the propellant surface after the salt has been trapped in the carbon residue layer. If the propellant or the active binder produces less carbon residue, then the lead salt effectiveness is reduced.

In the internal flow of gases in a solid rocket motor, solid-propellant combustion interacts with their aerodynamics. The most important effects often observed are erosive burning and combustion instabilities.

Erosive burning is a phenomenon of increase of the local propellant burning rate caused by high-velocity gas flow across the burning surface. Most propellants have a minimum crossflow velocity below which erosive burning is not observed, referred to as the threshold velocity. The erosive burning mechanism is believed to be caused by the increase in gas-to-solid heat feedback caused by the increase in transport coefficients and by the turbulence-enhanced mixing and chemical reaction of the oxidizer and fuel-rich gases pyrolized for AP-based composite propellants. Steady combustion is a complex mechanism including chemical and physical effects (nature and details of solids and additives, particle size distribution, operating conditions: pressure, initial temperature, radiation). In the erosive burning phenomenon the crossflow velocity (parallel to the solid-propellant burning surface) constitutes an additional operating condition of extreme importance. Many theoretical approaches have been developed, which were grouped in five categories discussed by Razdan and Kuo.[76] The first (and still widely used) model for the erosive burning is from Lenoir and Robillard[77] in 1957. They supposed that the heat transfer was able to modify the burning rate. This simple model is still used in current monodimensional analysis. Chemically reacting turbulent boundary-layer models are however mainly in use today because they are well suited to computational-fluid-dynamics analysis of erosive burning.

Combustion instabilities are the result of interactions among three classes of phenomena: chemistry and chemical dynamics, combustion dynamic, and combustor dynamics. There are many unacceptable instabilities in solid rockets (for instance, see a partial compilation by Blomshield[78]). Attention and support has been given to research in this area for more than 50 years, albeit usually not in sustained fashion. Considerable progress has in fact been achieved. Hart and Mc Clure[79] proposed in 1959 a theory of the response of a burning solid propellant to a sound wave. Culick papers[80–83] on combustion instabilities published in the 1960s and the early 1970s are the foundation for stability prediction methods now in use.

Works on combustion instabilities have focused during 50 years on the understanding of propellant response and the chamber acoustic field, but aerodynamic instabilities like vortex shedding play an important role in the motor behavior. Works done in France during the 1990s on Ariane V SRM instabilities led to the discovery of a new phenomenon, called parietal vortex shedding. This phenomenon was first highlighted from computations by Lupoglazoff and Vuillot,[84] then a stability theory was established by Casalis et al.[85] and verified experimentally by Avalon. Flandro[86] successfully integrated the latest results on propellant surface rotational effects in the original Culick's theory.

The 1990s have seen an acceleration of computer science and performance, leading to new classes of analysis. Computations can be used as virtual experiments to study propellant combustion. Cai and Yang[87] developed a detailed description of flow/combustion interactions, giving steady-state burning rate and erosive burning. Jackson and Buckmaster[88] made the direct numerical simulation of three-dimensional heterogeneous combustion of a solid propellant, taking into account the random packing of the oxidizer charges, with nonsteady coupling between solid-phase and gas-phase physics. These detailed models will allow the development of new physics and understanding of combustion and combustion interactions.

An influence of the mode of elaboration of the propellant grain on various characteristics and particularly on local mechanical properties and burning rates has been often observed. In the case of composites, after mixing, during the casting operations, when the suspension moves, the concentration of particles varies under the influence of a nonhomogeneous shear field.[89] With a monomodal suspension particles concentrate in the less sheared zones. For a bimodal suspension the effect will be more important for the bigger particles. For instance, the propellant composition in zones of high shear, like zones where two flows of high viscosity merge, will be significantly modified, leading to a modified burning rate (this is called the "knit-line" effect). Modeling of these phenomena is underway, based on a model coupling the flow pattern and particle segregation proposed by Phillips.[90] In that direction an important development in the rocket motor operation analysis, the code MOPTI, has been recently presented by Le Breton.[91] This code was developed with the ultimate objective of predicting a SRM ballistic characteristics, without the use of semi-empirical parameters related to scaling factors or Hump effects, which are in fact "coefficients of ignorance." This means computing the real local composition at any point after casting and taking in account the local burning rates in the final thrust and pressure vs time predictions.

Mechanical Behavior of Solid Propellants

The most classical mechanical failures, cracks and debondings, can create in propellant grains an accidental increase of the burning surface, which leads at least to a modification of the motor response, at worst to the destruction of the SRM. The main loading cases that are to be analyzed are storage (thermal shrinkage and slump), thermal cycles, acceleration phase, and ignition. Grain design for a solid-propellant rocket motor frequently necessitates compromises among the conflicting requirements of ballistic performance, structural integrity, mission reliability, and geometric constraints. The methodology to predict a margin of safety involves a lot of technical disciplines: the study of mechanical properties of propellant and bondings, stress analysis, failure criteria, aging, and so on. The present knowledge on these different topics is the result of a very large body of work. A synthetic presentation of structural analysis at the end of the 1980s has been done by Gondouin,[92] and more recently an AGARD working group[93] has published an excellent advisory report, which recapitulates the methods used worldwide.

Propellant Behavior Laws

The very first contributions to the theoretical description of solid-propellant mechanical behavior can be regarded as a legacy from 19th century scientists concerned with the physics of rubber elasticity: Joule, Faraday, Boltzman, among the most famous ones. Though solid propellant contains only a scarce proportion of synthetic rubber, its mechanical behavior is controlled by this weakest constituent, and the theoretical description is invariably built upon the basis of the statistical theory of elasticity. This physically coherent thermodynamic description of long chain molecules network deformations cannot be mentioned without recalling the fundamental contributions of Treolar[94] and Mullins,[95] who first described the softening effect of a cyclic stretching in filled elastomers and of Mooney, together with Rivlin and Saunders,[96] who have given their name to the widely used hyperelastic contitutive laws for elastomers.

These theoretical approaches provide a strong link between the material physics and its macroscopic behavior but are still inadequate to describe all of the specific features of the propellant mechanical response. As could be expected from such a complex microscopic structure, the response is not elastic, and considerable time-dependence is observed. This important nature of the behavior places the solid propellant in a blurred border between fluids and solids for which the theoretical description is addressed as nonlinear viscoelasticy.

Decisive contributions are from scientists of the rocket propulsion community. Tribute should be made to JPL from which arose the time-temperature superposition principle introduced by Williams et al.[97] still of daily use in the construction of master curves of the mechanical properties of propellants. Together with the development of numerical simulation, the requirement of constitutive modeling of the propellant behavior became a crucial goal. The complex structure of the propellant needs rather sophisticated models to include particular mechanical behavior features such as the particles detachment from the binder leading to a noticeable volume dilatation. Important results on the process of debonding of a rigid particle from an elastic matrix are described in the works of Gent[98] and of Oberth and Bruenner.[99]

The work of Farris[100] in collaboration with Shapery[101] addressed the global problem of volume dilatation under strain in a comprehensive description, which is still a basis to more recent descriptions (the latter being from Becker and Özupek[102]). It was also the scientific base for the improvement of mechanical properties of composite propellant formulations with bonding agents as already mentioned. More phenomenological concepts of damage mechanics were also introduced by Bills[103] and Francis[104] to model the dewetting process.

Failure Assessment

The developments of mechanical response modeling for these strongly nonlinear viscoelastic damaging materials has led to considerable achievements in the field of elastomer fracture. Taking as a starting point the fundamental theories of network fracture from Flory,[105] Taylor and Darin,[106] Bueche and Halpin,[107] Thor Smith published a considerable amount of work from which arises the concept of intrinsic failure envelopes.[108,109] This concept, a general approach to fracture of both filled and unfilled elastomers constructed on the physical basis of single chain statistical failure, has received particular attention and is still of common use in structural design around the world.

A theoretical tool to evaluate stresses from the numerical structural analysis of the propellant grain during its service life loading history and a physical description of material fracture provide the first tools in assessing structural integrity and avoid failure of the grain, but it is also important to measure the distance towards failure at any instant of the SRM service life. Despite the wide spread of topics to be addressed, significant progress was achieved by R. A. Shapery[110–112] and C. T. Liu[113] in terms of modeling the viscoelastic damage growth at the tip of a propagating crack. The field of fracture mechanics applied to solid propellants recalls energy momentum concepts as introduced by former researchers in the field. The work of Rivlin and Thomas[114] is a significant example as long as crack initiation is concerned and so is the work of Mueller and Knauss[115] for crack propagation in viscoelastic media.

Modes of Decomposition, Sensitivity, and Hazards

As with any kind of energetic material, propellants are characterized first in tests that measure their sensitivity to various stresses to which they will be submitted during their nominal life cycle or during possible accidental situations. Classically, tests like impact, friction, projection of fragments, and elevation of temperature are applied to measure a threshold value over which the material will react. The response to these stimuli is very dependent on the mode of decomposition of the energetic material. The major modes, by order of importance of their effects, are combustion (conductive or convective), thermal explosion, and detonation. Another, more complex mechanism was discovered during the 1970s, which involves a transition from accidentally created convective combustion into a detonation.

For safety analysis ordinary (conductive) combustion behavior must be known, not only in operational pressure ranges but also at ambient pressure (low pressure index—observed for instance with AP propellants with ferrocene derivatives—will give high flux of high-temperature gases in case of accidental ignition) or at the very high pressures that can develop when the propellant is highly confined.

Another mode with more violent reaction is the thermal explosion caused by internal decomposition and self-heating inside a massive piece of propellant that has a very low thermal conductivity. This effect was discovered in cook-off tests applied to massive specimens and really evaluated during the 1980s. The requirement of mild response to cook-off is one of the most difficult in insensitive munitions (IM) requirements. The resulting explosion can be as powerful as a weak explosive.

Detonation, a shock-wave process, is the most violent mode of decomposition of energetic materials. When a rocket motor explodes, the case ruptures, and the propellant merely burns. No rocket motor detonation had been observed until the 1970s, when detonations of SRMs occured during static testings, which were part of the development of the Trident I C4 missile. A new scenario, leading to a new mechanism called deflagration to detonation transition (DDT), was necessary to explain this detonation. The scenario includes mechanical damage of the propellant material leading to the development of conductive combustion followed by a process of transition from combustion to detonation in this porous medium and final detonation. The initial failure was a mechanical failure caused by insufficient design safety margin. The second failure was related to the propensity of this propellant to fine fragment fragmentation. An empirical "shotgun" test in which a piece of the propellant was impacted against a wall was designed. The fragments were tested in the combustion mode in a closed vessel or in a confining tube. For a critical impact velocity DDT was observed on the "damaged" sample. These tests helped establish empirical conditions for nondetonation and helped compare propellants according to their toughness. These phenomena have been studied and described by Kincaid,[116] Brunet and Paulin,[117] Weiss,[118] etc.

As soon as the important role of propellant damage had been established, its participation in other mechanisms that could lead to explosion or detonation was discovered to be of fundamental importance. It has also a role in models of thermal explosion,[119] and it was part of the explanation of another detonation phenomenon that was observed during testing the effect of bullet impact on a high-energy minimum smoke tactical motor.[120] It could be proven in that case that the detonation was caused when the bullet that had first travelled through the propellant impacted on the propellant of the other side of the bore that had been damaged by the compression wave that had travelled inside the propellant. Finally, damage has an essential participation in the response to the stimuli induced by accidental or operational threats associated to IM developments. It is then possible to conclude that the unpredicted events of the 1970s (during which nobody was even injured) had extremely positive consequences: it helped design propellant formulations and motors not to detonate, and it gave keys to the design of insensitive munitions.

Another type of hazard was however identified after accidental ignitions attributed to static electricity discharge. A severe accident happened in 1985, in Heilbronn, Germany, on a U.S. Army Base during the assembly of a Pershing II missile. A SRM was being separated from its container when, without any apparent reason, an autoignition happened inside the propellant grain. The accidental ignition could be related to an internal electric field buildup inside the propellant grain incorporated in an electrically insulating Kevlar® case. The discovery of the sensitivity of aluminized HTPB propellants by SNPE and its explanation by a percolation model greatly helped the understanding and solution of the problem.[121]

Solid Propellants in the World

Most developments in solid propellants after World War II were initiated in the United States. Other countries contributed to their further technical development. Today nearly every country with some defense industry develops ordnance rockets. Because of volume limitation, a general panorama is here totally impossible. We will then just give refererences of some existing historical papers in most cases. In one case, Russia, we will try a slightly more detailed description for two reasons: Russia brought innovations, and Russia had its own path in rocketry and was followed in that path by a part of the world.

The Russian Way

Work on smokeless powder rockets started in 1921 in Russia. In 1928, a gas dynamics laboratory (GDL) was created in Leningrad for the study of the combustion of propellant charges and combustion chambers. The 68-, 82-, and 132-mm caliber rocket chambers, which became standards in Russia, were defined at this time. Various types of solid rocket projectiles and JATO rockets were studied and developed. In 1933, the very succesful GDL was consolidated with a Moscow laboratory into a large institute, the RNII3, Research Institute for Reaction Propulsion. After 1937, the RNII3 developed the multiround stand, BM13 for the launch of the 132-mm rockets, which became famous under the name Katyusha. After World War II, the Institute became a research institution, which was given a specific mission in rocket engines and space energetics after 1965. It is now the Keldysh Research Center.

The history of the GDL and RNII3 is quite well known. On the other hand, the evolution of the organizations involved in managing, designing, and producing solid propellants, solid rocket motors, or solid stages from 1930 to the end of the Soviet Union is complex, to say the least. The biggest part of the propellant industrial organization started with NII6 located in Moscow. In 1938, it became OTB 6, divided into three divisions for pyroxiline (nitrocellulose), ballistite (relatively new in Russia at this time), and pyrotechnics, with factories in various locations, among which Schlissenbourg near Leningrad and Pavlograd in Ukraine. During WW II, the OTB was evacuated to factory 98 in Perm (Ural), which later became part of the NPO Kirova. It produces today solid rocket motors mainly for tactical propulsion. OTB returned to Moscow in 1943 and was later incorporated into the NII 125, which had produced artillery rockets. It became later Nihkti and still later LNPO Soyuz, headed by the academician B. P. Joukov for many years and by Z. Pak from 1988 to 1995. Soyuz produced the solid propellant for the rockets of Korolev (RT1, RT2), Yangel, Tiourine, Nadiradze (Pioneer, Topol), and others. It also produced double-base propellants and various tactical motors and gas generators. In 1959 a subsidiary of Nihkti had been created in Siberia at Bijsk. This Institute and its chemical combinat became the NPO Altai headed during many years by Academician G. B. Sakovitch. It produces solid propellants, solid motors, and energetic compounds. These three organizations NPO Kirova, Soyuz, and Altai are probably the main actors in solid propellants in Russia today, but Ukraine should be added to the picture with the NPO Yuzhnoye from Dniepropetrovsk, which has for instance developed the RS 22 (SS24) ICBM. Most of the time, but not always, the propellant for Yuzhnoye systems seems to be produced by the chemical combinat of Pavlograd. The genealogy of the Russian organizations in solid rockets has been quite recently described by C. Lardier.[122] Important institutes and laboratories depending of the Academy of Sciences conduct also research activities in energetic materials, which support the solid propellant development, for example, the Zelinsky Institute of Organic Chemistry in Moscow and the Institute of Chemical Physics of Chernogolovska, laboratories at the Mendeleev University in Moscow, and the Institute of Chemical Kinetics and Combustion in Novosibirsk, etc.

Russians were late in using solid propulsion in their strategic forces. The first Russian ICBM (SS 13) with solid propulsion was deployed in 1968. This was followed by the RS22 or SS 24 using polybutadiene-based composite propellants and, maybe, a high-energy propellant on the first stage and the RS 12M or SS 25 Topol (mobile) and 27 (fixed) with solid propellant from Soyuz. The first solid-propelled SLBM, the SSN 20, was developed from 1971 to 1980.

It is very diffficult to present a synthetic view of the state of the art of the technology of solid propellants in Russia. There are very few publications mentioning solid propellant compositions and no patents describing the technologies. As easily accessible papers, we can only mention a glimpse of the "state and prospect of solid propellant rocket development" by Kukushkin[123] in 1992, a paper by Pak in 1993 on propellants based on dinitramide salts[124] containing limited experimental data, and a paper by Sakovich[125] in 1995 disclosing very few informations on compositions. The laboratories of the academic world, which are more used to international exchange of information, are very specialized, and the research people are generally ignorant of the utilization and applications of their discoveries. Under these conditions a general view can only be based on fragmentary information, feelings, and inferences. In general, it seems that most Russian SRMs are based on EDBs or composite propellants. CDBs do not seem to have been much developed, if at all developed. This might explain the use of EDBs in applications for which CDBs would have been used in the West (especially very big grains).

The older systems use propellants that have sometimes particular characteristics that might be related to their origin and to local competences or local resources. As typical examples, it is possible to mention the following:

1) The EDB compositions often use the historical Russian plasticizers TNT/DNT instead of nitroglycerine.

2) In the field of composite propellants, butyl rubber binders that have not been developed in other countries are often mentioned, for instance, in the propellant of the RT2 or SS13 Savage ICBM deployed in 1968. (One could link this to polyisobutylenes that have been used as binders in the United Kingdom in the 1950s and 1960s, but they were thermoplastics.)

3) Also in the field of composites, a specific propellant formulation has been used in past versions of the SAM 7, in which a binder based on a derivative of a terpenic resin found only in the Ural forests is used.

A quite original propellant example is the magnesium-rich composition used in the generator of the SAM 6 ducted rocket. It is a pressed mixture of Mg and $NaNO_3$ with a very low binder content.

More recent formulations seem to use raw materials with less specific characteristics: polybutadiene binders, ferrocene burning catalysts, etc. are used. On the other hand, Russians are great chemists, and mention has been made in reports or papers of the use of ingredients that have not been mastered in the West like aluminum hydride or ammonium dinitramide (ADN), but it is difficult to appreciate the extent of their use. The history of the discovery of the existence of ADN in Russia is an example of strange situations that could result (in the past?) of the secrecy policy. ADN was synthetized by Robb Schmitt and Jeff Bottaro at SRI International in 1989 during research on new energetic compounds sponsored by the U.S. Department of Defense and managed by Richard (Dick) Miller of the Offfice of Naval Research. A U.S. patent was granted to the inventors and SRI. In 1993, Z. Pak presented his paper[124] on ADN at the AIAA Jet Propulsion Conference, and the community quickly learned that it had been produced in Russia for over 20 years (some even visited the plant), but the SRI patent still holds!

An area in which Russian engineers have demonstrated great imagination and cleverness is architecture of solid-propellant grains, with often ingenuous and simple solutions in tactical systems. Combination on the same grain of inhibited parts, temporary inhibited parts, and uninhibited parts and sections with a cental bore followed by end-burning sections (sometimes with metal-wire burning-rate enhancement!) are used to realize dual- or multiple-thrust laws. Tube and slots burning surfaces architectures are sometimes used with slots opened on the external surface of the grain.[126] This configuration is probably favorable to reduce erosive burning and differences of pressure between the forward and aft ends while keeping a high loading ratio. On the other hand erosive burning is quite often used as a means to attain high thrust. In most cases in which some information is available, it seems that the propellants of this systems do not have high solids loadings, and this is probably part of a philosophy that involves simple and robust definitions.

Europe

The position of France is particularly unique because it is the only country in Europe besides Russia to have developed independently its own nuclear deterrent force, and it was the third nation to launch an artificial satellite (in 1965). All of the propellants (and in fact all of the energetic materials) in France have been developed by SNPE, a company that originated in 1971 from a government organization, Service des Poudres, which had a legal monopoly since 1336 for the production of explosive substances. Famous chemists have worked at, or have been in charge of, Service des Poudres: Lavoisier, Berthelot, Vieille. The history of solid rocket propellant in France has been presented by Davenas.[60] All families of propellants have been developed and applied to tactical propulsion through its subsidiary CELERG, to strategic propulsion through the JV G2P with

SNECMA, to space launcher propulsion through the JV Regulus with Fiat Avio, and to airbag inflators in partnership with AUTOLIV. Among other research institutions ONERA played an important role in research on combustion and advanced propulsion concepts.

The history of solid propellants development in the United Kingdom after World War II has been described by Harlow.[127] Two sites were mainly involved in the development and production: Westcott and Summerfield. The latter under the management of ICI Metals Division (IMI), developed very succesfully motors based on CDBs and EMCDBs and strip laminated cases. Basic research was done by the government at Waltham Abbey and later Fort Halstead. The organizational event at the turn of the century is the creation of the company ROXEL, which merges CELERG and the United Kingdom activity in tactical propulsion. The activity of the new company should be equivalent to that of ARC in the field.

The developments of solid rocket propulsion in Germany before and during World War II were more limited than in liquid propulsion. Most of the developments in the field were made at the company Bayern Chemie founded in 1969, now Bayern Chemie Protac. High burning-rate propellants, glycidyl azide polymer (GAP) propellants for gas generators, and fuel-rich boron-based and magnesium-based propellants have been developed. On the research side the Institute of Chemical Technology of the Fraunhofer Gesellshaft plays an important role in basic and applied research.

Italy based most of its development in the field on a policy of intelligent acquisition of technology. SNIA BPD produced the motors of the Hawk Missile and a part of the NATO European Nations MLRS motors. Today FIAT AVIO (which took over BPD) develops the small launcher Vega and produces motors of some tactical systems, besides its participation in the Ariane program. Raufoss in Norway produces the motors of some tactical systems, among which the Penguin sea-to-sea missile and in cooperation with ATK developed the motor of the Sea Sparrow. Netherlands has no national propulsion industry but a center of research and expertise in the field, the Prins Maurits Laboratory (PML), belonging to TNO, the national research organization. FOI in Sweden is very active in research on new energetic compounds for use in propellants and other energetic materials.

Asian Nations

The three most important nations in Asia—Japan, India, and China—have all launched artificial satellites as a demonstration of their technological (and in some cases strategic) capacity. Both countries have a propellant industry and national sources of the basic raw materials.

A detailed history of solid propellants in Japan with a comprehensive bibliography has been presented by Aoki and Kubota.[128] Japan limits its national forces to a defensive role, which probably forbids long-range missiles, but has nevertheless developed every kind of propellants for tactical systems. Nippon Oil and Fats has developed and produced all solid propellants of the space motors, especially the 65 tons of HTPB propellant for the SRBA of the HIIA space launcher and the solid propellant for all of the stages of the heavy small launcher M5 of ISAS.

Two organizations have been important in the development of solid propellants in India: the Defense Research and Development Organization (DRDO) and the Indian Space Research Organization (ISRO). India has a policy of self-reliance in technologies and had a systematic practice of "indigenization" during the last 20 years. Detailed information on the developments and applications of solid propulsion today in India is scarce, except for space systems.[129,130] The biggest SRM developed by the Indian Space Agency, ISRO is the first stage of the PSLV Space launcher with 128 tons of HTPB propellant.

Chinese papers published in the field are generally devoted to energetic ingredients[131] or to space launchers applications. The development of solid rocket technology was similar to other countries, according to Zhang and Ye.[132] The evolution of composite propellants has then undergone the course polyurethane-PBAA-CTPB-HTPB until compositions with HMX. All types of propellant have been developed in China. Reduced smoke propellants with 89% solids and high-energy XLDBs with a delivered *Isp* of 256 s are mentioned.

Other Countries

The activity in many countries should be cited. We will content ourselves by underlining the important development in Israel of SRMs for tactical systems by RAFAEL, and of long-range ballistic systems of the Jericho family (while applied research work is conducted, for instance, at the Technion), and the important development of composite propellants for space launchers by the Centro Técnico Aeroespacial in Brazil. Also, Somchem of the Denel Group in South Africa has a significant activity in composite and EDB propellants and is reknowned for having developed the first fielded base-bleed motor.

The 1990s: New Needs, New Developments

At the end of the 1980s, tremendous changes appeared in the world landscape. The disappearance of the Soviet Union and its consequences all over the world are of course the most important. It led to profound changes in the world relations, the associated strategies, and the nature of defense systems appropriate to the new era. Another important factor of change was the development of national and international conscience on issues like the environment, the use of technology for the welfare of humanity, and the nature of the industry in general.

Subjects like environmental impact of the propulsion industry, hazards, costs, life cycle, dual uses, etc. became very important in the orientation of the development of technologies in the last decade of the century. On the other hand, research in energetic compounds has led to exciting discoveries of new chemical families and fascinating long-term perspectives in which many answers to the new needs will be found.

Life Cycle, Clean Disposal, Recycling, Green Propellants

The evolution of environmental consciense and the strengthening of environmental laws obliged the industry to adapt. This is a critical problem considering the increasingly stringent regulations, the necessity of clean disposal of propellant wastes and obsolete motors, and the remediation of some sites closed in the restructuring and downsizing of the industry. Also controversies developed at the end of the 1980s on the impact of solid propulsion on the atmosphere needed scientific answers.

The answer of the industry was at three levels: replacement of substances having toxic properties (chlorinated solvents, lead salts, asbestos) by environmentally begnign substitutes, better management of wastes and development of clean disposal technologies, and orientation towards a life-cycle management of energetic materials "from cradle to grave."

Various technologies have been developed to replace open-air burning of propellants. Propellant removal by high-pressure water jets followed by the treatment of the residues and purification of the water is one of the most commonly used. For the treatment of the residues, clean thermal or incineration processes were developed. In the case of AP propellants, a biological treatment,[133] which converts AP into NaCl, is now implemented for the Ariane V propellant. Oxidation by supercritical water is being scaled up for the destruction of energetic propellants containig nitramines, nitrate esters, etc.[134,135] This should be combined with a minimization of wastes. The advent of continuous processing should be very favorable. Finally, the ideal material should be based on safe ingredients, processed without solvent, and able to be recycled, after the end of its service life. The development of thermoplastic elastomers (TPEs) with elastic blocks and plastic blocks is an important direction because it would allow a recovery of the material and its ingredients by melting. Energetic TPEs are now being developed and tested for instance at the NSWC Indian Head.

Insensitive-Munitions Requirements

IM are munitions that reliably fulfill their performance, readiness, and operational requirements on demand, but will minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned stimuli. The concept of IM appeared in the middle of the 1980s, after many catastrophic incidents and disasters resulting from accidents or from battle action. Typical responses to consider are those related to agressions by fuel fire (also called fast cook-off), slow cook-off, bullet impact, fragment impact, and sympathetic detonation. The phenomena have been analyzed,[136] specifications have been defined, and standards and policies elaborated. The violence of the reaction has been classified according to a scale recommended by the NATO Insensitive Munition Information Center (NIMIC).*

Despite the fact that the rocket propellant is only one aspect of a system, there are specific characteristics that have been identified as contributing factors. They lead to the following general approaches to reducing sensitivity: 1) modify the reaction of propellants to slow cook-off, 2) increase the "toughness" of the propellant, 3) develop less sensitive ingredients, and 4) better manage the partitioning of energy between binder and fillers.

This area of research has triggered the research of new energetic ingredients to lower the sensitivity of the final formulation.

Environmental Effects of Rocket Effluents

The last results on this question were summarized at a symposium in May 2002, especially by Bennett[137] and Ross and Friedl.[138] There are two main areas of environmental concern: stratospheric ozone effects and local launch-site effects. Most stratospheric ozone models have predicted a very small impact on the global stratospheric ozone from launching rockets. Estimates have varied from 0.01 to 0.03% change in global stratospheric ozone. Changes this small will never be detected and can only be calculated using computer models. The question of the local stratospheric effects of a single launch remained open until recently, when heavily instrumented aircrafts were flown through rocket plumes. These studies have revealed that even if the ozone is destroyed in the plume the cloud disperses in such a way that there is no ground effect and the concentration of ozone restores to the normal level. It was also found that species from LOX/kerosene engines can have an effect at least as great as the effect of the chlorine of solid propellants.

New Energetic Compounds for Solid Propellants

The last dozen years has seen a remarkable increase in the families of compounds being synthetized and evaluated in propellant systems as the interaction between Western scientists and those in Russia and China pollinated the field. This section focus upon the "major players," nitramines, organic azides, and at the same time look at those materials that are now advancing into actual operational systems. Excellent complimentary reviews of energetic materials has been published by workers at Lawrence Livermore National Laboratory (LLNL)[139] and SNPE.[140] A comprehesive review[141] of the present knowledge of their mechanisms of decomposition during the combustion process has been recently presented.

Nitramines, Cages, Azides, and Nitrato Compounds

The nitramines RDX and HMX (densities 1.82 and 1.91 gm/cc) are still the most studied of all energetic compounds with the exception of AP. However, hexanitrohexazaisowurtzitane (HNIW or CL-20), which was first made by Nielsen et al.[142] at China Lake, has now become commercially available, and it is moving into several operational applications. The epsilon form of HNIW has a density of 2.02 gm/cc and provides approximately 5 s more *Isp* than HMX (as a monopropellant). HNIW burns at approximately twice the rate of RDX and HMX.[143] Numerous other nitramines have been synthesized, but very few have shown the ability to improve on HMX in *Isp* calculations. Two families of caged compounds have been the focal points over the last two decades, cubanes and adamantanes. The "holy grail" was octanitrocubane, which was successfully made[144] at the University of Chicago. Unfortunately, it did not possess the predicted density (>2 gm/cc) and hence is not as attractive as HNIW. Nitramine polymers have been synthesized for over 40 years, but the resultant poor physical properties or the dilution of enthalpy, which results from incorporating functional groups such as ester linkages, have rendered virtually all nitramines polymers as unimportant.

Organic azides had a "bad" reputation for a long time, but that began to change in the late 1970s with the development of GAP.[145] GAP, $[CH(CH_2N_3)\text{-}CH_2O\text{-}]_x$, has become the workhorse energetic polymer, but two other azidooxetanes are also important materials. The diazide BAMO, $\text{-}[O\text{-}CH_2\text{-}C(CH_2N_3)_2\text{-}CH_2\text{-}]_x$, and the monoazide AMMO, where one $\text{-}CH_2N_3$ is replaced by a CH_3- group, are now finding utilization in many propellant systems. Because GAP is hydroxy terminated, a variety of plasticizers can be made using the backbone. Replacement of the -OH groups with either $\text{-}N_3$ or $\text{-}ONO_2$ groups or esters such as the acetate have been extensively investigated. Many other azidoplasticizers have been made especially by the simple and straightforward displacement of the $\text{-}ONO_2$ group. TEGDN, DEGN, NG, NIBTN, and many other nitrate esters have had their analogs produced in this manner. Perhaps the most studied material has been 1,5-diazido-3-nitrazapentane (DANPE), which is produced in one step from the oldtime material DINA. Recently, a series of azide materials containing the $\text{-}CH_2C(NO_2)_2CH_2N_3$ terminal group have been produced by the synthesis group at the Beijing Institute of Technology.[146]

The chemistry of standard nitrate esters (NG, TMETN, NC, etc.) is well known. The two areas where some work is being conducted are polymers and NENA plasticizers. The two polymers of interest are PGN or PGLYN and NMMO. PGN has been worked since the 1950s, but the last 15 years has seen a revival of interest. PGN's structure is exactly like that of GAP with $\text{-}N_3$ instead of $\text{-}ONO_2$. NMMO's structure is the same as AMMO again with the $\text{-}N_3$ replaced by the $\text{-}ONO_2$ group. Both polymers are currently in the preoperational phase of development. NENA plasticizers have the structure, $X\text{-}N(NO_2)\text{-}C_2H_4\text{-}ONO_2$ where X can be a methyl->pentyl moiety. The butyl (BuNENA) has seen the largest amount of research both in solid rocket and gun propellant research.

Dinitramides, Heterocycles, Hydrazinium Salts, Triaminoguanidinium Salts

As mentioned in an earlier section, the material known as ADN was first discussed "openly" by Russian scientists in 1993. ADN was first made either in St. Petersburg or Moscow (an ongoing debate). From a performance standpoint ADN is superior to AP in terms of *Isp*, but it suffers from a lower density (1.81 vs 1.95) and a melting point below 100°C. A review of dinitramide chemistry has been presented by Zelinsky scientists.[147] The combustion characteristics of ADN are given by Atwood et al.,[148] but a temperature-sensitivity issue renders it undesireable for many potential applications. Two other dinitramides are of increasing interest, that is, the potassium salt[149] and the guanylurea material researched in Sweden.[150] Heterocycles constitute an enormously expanding area. The sheer volume of publications on furazanes has expanded in bursts during the last decade. The first paper dealing with a pernitrofurazane was the work of Colburn at Los Alamos[151] as well as other furazane materials. Recently, the Russian literature as well as Latvian literature has covered hundreds of potential candidates.[152,153] Furazanes are 1,2,4-oxadiazoles, and their structure is the most energetic of the four possible configurations. For instance, 3,4-dinitrofurazane is more than six times more energetic (from a heat of formation standpoint) than the corresponding 4,5-dinitrooxadiazole (Ref. 154). Furoxanes tend to yield slightly higher performance as a result of the additional resonant oxygen, but this same oxygen yields other unwanted problems in terms of compatibility and stability. BTF (benzotrifuroxane) is the most studied of these materials. Triazole (C_2N_3), tetrazole (CN_4), and tetrazine (C_2N_4) compounds as well as fused combinations of furazanes with these compounds are now under very active research.[155–157] The combustion characteristics of some of these newer materials can be found in the work from the Mendeleev Institute.[158]

There are many salts of hydrazine that have all looked good theoretically, but always suffered some terminal problem such as incompatibility, gassing at elevated temperature, high burn-rate exponents,

*Data available online at http://www.hq.nato.int/related/nimic.

and impact sensitivity. In the 1960s and 1970s the mono- and dihydrazinium perchlorate salts were pursued but to an unhappy conclusion.[159] During the same timeframe, the nitroform salt (HNF) was also studied in depth and now again during the last decade. Dutch scientists have revived the quest.[160] Although some strides have been made in an improved production process, all of the other problems remain, especially the high burn-rate exponent. HNF has a high exponent itself, which was first measured by McHale and von Elbe[149] and detailed by Atwood.[148] The probability of an HNF propellant ever being anything but a class 1.1 explosive is very low. Work on the nitrate salt was never successful.

Although many triaminoguanidinium salts have been researched, only the nitrate (TAGN) has been successfully utilized in both solid propellants and gun propellants.[161]

Other Compounds

The utilization of difluoroamino (NF_2) compounds has not been realized as yet. The utilization of nitroform (trinitromethane) to form compounds with the $-C(NO_2)_3$ group as well as the fluorodinitro $-CF(NO_2)_2$ group has given birth to hundreds of compounds. FEFO, CH_2-[O-$CH_2CF(NO_2)_2$]$_2$, is the most employed material, and it has been produced in thousands of kilos.

Aluminum hydride (AlH_3) was one of the exotic compounds studied in the 1960s. The U.S. work from that timeframe is based upon the data developed at Dow Chemical.[162] Recent Russian work on both AlH_3 and BeH_2 has been published,[163] as well as the recent work in the United States on AlH_3.[164]

New Rocket Propellants Developments

It might look surprising, but there were still some developments in EDBs, CDBs, and CMDBs during the period, mainly as a consequence of IM and nontoxicity requirements. As an example, the replacement of NG by TMETN and TEGDN in a typical EDB formulation was studied in France.[165] This leads to a 1.3 hazard classification of the propellant, which also passes the MIL 2105 A when IM tests are applied to 2.75 rocket motors. Insensitive lead-free EDBs were also developed. The ballistic properties of these propellants with comparison to a NOSIH AA2 propellant have been described by Doriath.[166]

Composites

Two significant evolutions of composite propellants are related to sensitivity and IM requirements. ATK has developed a new binder called hydroxy terminated polyether (HTPE), which combines a polyether that is a copolymer of ethylene oxide and tetrahydrofurane with a NENA plasicizer. This propellant has a milder response to slow cook-off and bullet impact than HTPB/AP propellants.[167] With an objective of better aging and reduced sensitivity, SNPE developed a new nonmigrating ferrocene compound called Butacene.[168,169] It is an HTPB polymer with ferrocene functions grafted on the polymer chain and as such part of the final binder network. A propellant using butacene is used in the integral booster of the newly developed ASMP A.

Another trend in SRMs today is related to the use of lighter and stronger motor operating at higher pressures, then delivering higher *Isp* without a weight penalty. Pressures of 20 MPa and much higher can be considered in tactical motors. This is a pressure range in which AP composite propellants can exhibit a very high pressure index. Some empirical solutions can be found, but more fundamental work is needed and has been started by Atwood et al.[170]

At the end of the 1980s, before a sufficient knowledge on the environmental impact of rockets was accumulated some research programs were conducted to develop alternate propellants,[171] especially to neutralize or eliminate hydrochloric acid in the exhausts. Today, the evolution of solid propellants for space applications is approached with the objectives of improvements in performance and in cost efficiency and in relation with a predicted relatively small increase of the number of launches during the next 20 years. A road map coherent with this goal has been recenty elaborated under the auspices of the International Academy of Astronautics by a group of experts.[172]

Minimum Signature Propellants

Various formulations have been tested in order to take advantage of the newly synthetized energetic compounds. The general idea is to improve on the high-energy propellants based on PEG/nitrate ester binders and RDX, in increasing the energy and/or improving the IM characteristics. GAP/HMX formulations have been successfuly tested, and a GAP/HNIW propellant has been demonstrated in motors with excellent results[173]: an increase of 10 s in *Isp* is obtained with a density of 1.82 instead of 1.70 gm/cc. The main issue now for a future industrial development is the cost of compounds, which have had today a significant but still limited industrial development.

A systematic evaluation of some of the new energetic fillers and polymers is actually being conducted in the frame of a European Cooperation for Long Term in Defense (EUCLID) cooperative program on Clean Rocket Propellants.[174] New energetic compounds are also involved in the U.S. Integrated High Payoff Rocket Propulsion Technology (IHPRPT) Department of Defense/NASA/industry program, which started at the middle of the 1990s with the objective to double the capability of rocket propulsion by 2010 (Ref. 175).

One of the main final goals of all of these efforts is the class 1.3, IM compliant, minimum signature propellant with the highest possible *Isp* and density. In that direction the use of mixed oxidizer systems might be of interest. Results of investigations of combinations ranging from AN/TAGN to ADN/HNIW have been reported by Chan and Turner.[176]

Nonpropulsion Applications of Solid Propellants, Propellants for Airbag Inflators

Solid propellants have found significant applications outside of propulsion, especially in commercial systems in which gas generation is used. This is certainly an area where solids are far superior to liquids because of simplicity, compacity, and cost efficiency. The most spectacular use of solid propellants in nonpropulsion applications during the last decade has certainly been in airbags: 130 to 140 millions inflators were produced in 2002; 250 millions are expected in 2010. More tons of airbag propellants are produced today in France than tons of propellant for missiles. Technical requirements for this application are a high gas yield, a low combustion temperature, nontoxic gases, absence of condensed particles in the bag, high rate of combustion, easy ignition, and good aging.

Propellants based on sodium azide (NaN_3) were used first. TRW and Morton were the main producers. Oxidizers like metallic oxides or chlorates and perchlorates and a reducing metal (Zr, Mg, Al) are part of the formulations. A very small quantity of binder is added, and the mixture is pelletized following a dry or, better, a wet process. They can generate 99% nitrogen in their combustion while the solid residues produced are trapped as a slag. The main drawback of azide propellants is the high toxicity of sodium azide, which is a big problem in handling, storing, recycling, or disposal. There are also some risks of generating metallic azides that are very sensitive through hydrolysis of NaN_3 to HN_3.

In parallel to the azides, two other concepts were developed. ARC developed a hybrid gas generator in which an inert gas was stored under pressure and expanded and heated by a small grain of an ARCITE propellant based on potassium perchlorate. The main drawback was the emission of a high level of hot solid particles. The second concept was developed in Europe by the company LIVBAG (a subsidiary of AUTOLIV) using a double-base propellant produced by SNPE and a system for CO to CO_2 conversion. There was a high gas yield allowing an important reduction of propellant mass and of the size of the generator. Filters could be suppressed, and continuous production lines could be used. The main drawbacks were a high gas temperature and a limited resistance of the propellant to thermal cycles that were imposed for the U.S. market. Those who know what is the "Arizona cycle" will understand.

The second generation appeared in 1994 (Fig. 7). SNPE and LIVBAG developed a propellant based on a silicon binder, which brings high thermal stability and high burning rate, AP as oxidizer, and a chlorine scavenger.[50] The level of condensed particles is lower than with ARCITE, which is favorable but still high and requires filtration. It was possible to develop continuous mixing and extrusion

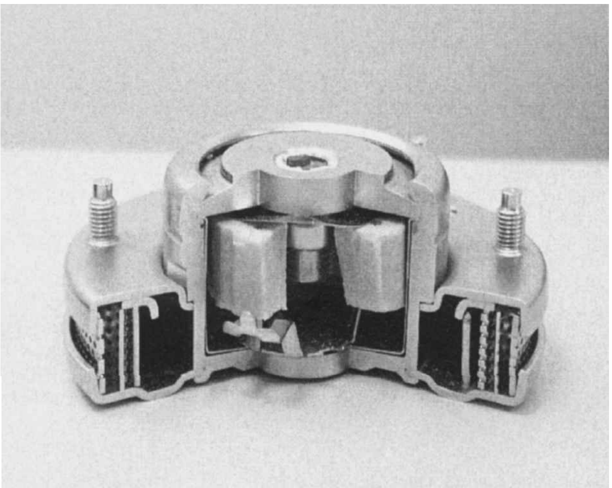

Fig. 7 Crashbag gas generator of Livbag and its propellant grain from SNPE.

lines based on twin-screw machines, even if this is a thermosetting formulation. TAKATA, a U.S. company, developed propellants based on aminotetrazole, a nitrogen-rich compound (85%) following the philosophy of the azide generator. However there is still some carbon to produce CO and NO_x, which must be eliminated. ASP, which took over Morton, has industrialized in 1998 a propellant based on HACN, hexamine cobalt nitrate, which is stoichiometic in the composition. It is also thermostable because of the complexation by cobalt.

A third generation of propellants for airbags is currently being developed.[177] New propellants will appear in 2003. These developments have been some of the most exciting in the field of solid propellants during the 1990s. Besides the airbags, new products like (inflatable) curtains have just appeared, others like inflatable belts, knee airbags, or antisliding bags are being designed. The next decade should also be very hot!

Long-Term Research in Energetics

Theoretical calculations show that several polynitrogen species, species composed solely of nitrogen atoms, should have high heats of formation making them attractive energetic candidates that might be stable enough for practical use. These compounds could perform as highly energetic monopropellants and would emit environmentally benign nitrogen gas as the exhaust product. Quantum chemical calculations were performed as early as 1981[178] to assess the potential stability of nitrogen analogs of isoelectronic phosphorous compounds. Many theoretical studies of polynitrogen systems have followed and give hope that stable compounds can be prepared in the future.

Polynitrogen species can be classified into three categories: covalent molecules, ionic species, and network solids. All of these species derive their large energy content by having nitrogen atoms bound to one another with relatively weak single bonds. There is a large thermodynamic driving force to form stable N_2 molecules in which the atoms are bound by very strong triple bonds. The most energetic covalent species that have been predicted to be stable have regular polyhedral geometries that require very strained bonds. These species include the tetrahedral form of N_4 and the cubic form of N_8, with heats of formation of 175 and 455 kcal/mol, respectively. They have, however, not been conclusively observed to date because of the extreme difficulty in having the nitrogen atoms form molecules in such restrictive geometries and perhaps the questionable long-term stability of these compounds. The large energy content of these systems, however, makes them intriguing systems for further study.

The synthesis of compounds containing the N_5^+ cation by Christe and coworkers[179] has led to a great interest in ionic polynitrogen compounds. Several compounds containing N_5^+ with various anions have been synthesized, but preparation of an all-nitrogen ionic compound would require the synthesis of an all-nitrogen anion that could form a stable lattice with N_5^+ or another all-nitrogen cation. Christe and coworkers demonstrated that the N_3^- anion will not form a stable solid with N_5^+. They have, however, recently announced the observation of the stable pentazolate anion, cyclo-N_5.[180] This anion and its derivatives is also the goal of a work conducted in Sweden.[181] Fau et al.[182] have performed calculations that predict that an $N_5^+N_5^-$ lattice would be a stable compound.

Progress has been made in the development of new polynitrogen compounds over the past few years, however, continued breakthroughs will be required in the years to come to see if polynitrogen compounds can make the leap from chemical curiosities to practical propellants.

Conclusions

It took a thousand years to develop powder rockets, 70 to develop extruded double-base propellants in tactical systems, 20 to develop solid rocket propellants used on the first artificial satellite launcher, and 10 more to obtain 80 to 90% of the technologies, which are today available for solid rockets. The community, especially the U.S. community, can be proud of what has been accomplished. And the international solid-propellant community is no more a community of inventors and entrepreneurs only but also of solid-propellant scientists, as demonstrated by some of the developments that were underlined. On the other hand, we are probably still not great communicators. Solid propellants and the solid propulsion industry have never been given the credit they deserve for their contribution to national defense of the Western nations during the second part of the 20th century. They have been overly criticized for the Space Shuttle *Challenger* accident in 1986, a failure which was more an improper management decision rather than a solid rocket motor hardware failure. Recent articles have been published against the continued use of solid-propellant rockets for man-rated launchers because of the *Challenger* accident and erroneously conclude that liquid-propellant rockets are safer. Historical launch reliability data do not support this conclusion, especially if we include the huge numbers of casualties on the ground in the launch vicinity in Russia and China as a result of liquid rocket failures over the past 40 years, including a recent ground fatality associated with the failure of the highly reliable *Soyuz* Rocket in Russia.

What are the prospects for the future of the solid-propellant activity? Solid propellants will continue to be the propellants of choice for all military systems throughout the world for decades to come. Production of solid propellants for tactical missiles will continue at near current levels, and more advanced tactical missiles will dictate needs for further tailoring of propellants for unique ballistic, hazards, and plume signature requirements. Space launch systems will continue to use large solid strap-on boosters and upper stages with solid-propellant motors for orbit transfer; however, there does not appear to be any real need to change current propellant formulations from today's composite solid propellants. After initial concerns with potential damage to the Earth's stratospheric ozone, the environmental impact from solid rockets has been shown to be negligible and probably less than liquid LOX/kerosene propellants.

The solid-propellant industry has transitioned from a defense industry to a defense and space launch industry. As a result, any major downturn in space launch needs for solid rockets could have a major impact on the availability and cost of critical ingredients for solid propellants that are used in all systems. Because of obsolescence and the relatively low demand of this industry, many critical ingredients are becoming in short supply or are in need of substitutes.

The solid-propellant industry, whose growth was spawned more than four decades ago by the development of strategic missiles, is currently losing the pioneers and needs new blood. Solid-propellant chemistry is the backbone of many systems including solid rockets, flares, smokes, gas generators for automobile airbags, decoys, warheads, explosives, and new energetic materials. Long-term research in new energetic compounds has brought promising concepts. Future requirements will present new challenges and will provide opportunities for good scientists, chemists, and engineers for generations to come.

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