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History of the Development of Solid Rocket Propellant in France

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The real development of solid rocket propellants in France started in 1946 for tactical missiles applications mostly based on cast or extruded double-base propellants. The decision by General de Gaulle at the beginning of the 1960s to develop an independent Strategic Force based on ballistic missiles had a tremendous effect on the research, development, and production level of activity in the field with a strong effort on composite and high-energy propellants. The results of these efforts were applied to three generations of strategic systems, many tactical missiles, and to space boosters like DIAMANT, the first French satellite launcher (1965), or European launchers like Ariane V, which will fly in 1995. This article describes the evolution of the main propellant families and their applications during this period of 50 years.

Introduction

FOR centuries a government agency in France had the monopoly of the production of "explosive substances" (today we would say, "energetic materials").

The origin of this organization may be considered to be 1336, through a law passed by King Philippe 6 de Valois, its modern shape coming from the revolution: 1791 creation of the "Agence des Poudres et Salpêtres," the 1797 creation of the State Monopoly on the production of gun powders, and the 1816 law on the organization of the "Service des Poudres." Famous chemists have worked at or have been in charge of Service des Poudres, like Berthelot and Lavoisier (his lab was still visible at Le Bouchet some years ago), Paul Vieille, one of the inventors of single-base powder. The young Eleuthère-Irénée Du Pont learned modern processes there. With some skilled employees he later created a powder mill on the Brandywine near Wilmington, Delaware. Nobel worked at Sevran for a few years and it is still possible to visit his lab. During the 19th century and the first part of the 20th century, it was one of the great French chemical groups where fundamental research in the field of physical chemistry was most advanced.

In 1971 the French government created a company—SNPE—to replace the Service des Poudres, mostly for reasons related to the Rome Treaty creating the European Common Market that forbade monopolies. The tasks of the Service des Poudres were then split in two parts: 1) the research and industrial part went to SNPE 2) while the regulations and control of this industry stayed with the Ministry of Defense.

Protohistory of Solid Rocket Propellants: 1945–1960

After the interruption of World War II, because of the occupation of France, there was practically no technology available in the field of solid rocket propulsion: the only rocket systems studied previously were based on black powder! However, some industrial capacity did exist at Direction des Poudres in the field of extruded double-base propellants for guns. The U.S., Great Britain, Russia, and Germany had already developed and used some rocket systems based on extruded double base (EDB) propellants, and composite propellants for JATO rockets had been developed in the U.S.

In 1945, a special section of the government agency in charge of aeronautics was created under the direction of Emile Stauff for the study of tactical rocket and missile systems.[1] At Nord Aviation and Aerospatiale Emile Stauff was to later become the "father" of numerous missiles like MILAN, HOT, ROLAND, EXOCET, etc. After analyzing some German systems like Air to Air X4 and Antitank X7, he became quickly convinced of the superiority of solid propulsion for small tactical systems for simplicity, cost, and safety reasons. EDB propellants were then immediately developed and were to be used on the first wire-guided French antitank missiles (SS 10, Entac). The limitation in size due to the EDB production process and also the fact that the combustion properties were quite bad (the platonization effect was at that time still an American-English secret), quickly led to research efforts on other types of propulsion: liquid propulsion or other types of solid propellants.

At that time three Establishments of Direction des Poudres in the Paris area were involved in research on energetic materials: the Central Laboratory, downtown Paris, Sevran, north of Paris, and Le Bouchet, south of Paris. Quite rapidly, Le Bouchet, the farthest from Paris, was chosen for the development of new types of rocket propellants. It is, however, interesting to note that until 1974 when all research activities were united at Le Bouchet, some work on things like nitrate esters or beryllium hydride and others were performed less than a mile from Notre-Dame (it is true to say that only small quantities were involved).

When the new special section at Le Bouchet headed by G. Maire was created in the middle of 1946, work started by evaluating all the known combinations of fuels and oxidizers like asphalt, rubbers, potassium perchlorate, including ammonium perchlorate (AP). The team consisted then of no more than 10 people doing the manufacturing and the ballistic testing, with the help of many university and research people outside and the cooperation of a few foreign specialists. Successful results came quite quickly, particularly the discovery that some formulations tested had low pressure exponents in useful pressure ranges when some combustion experts thought this was not possible. G. Maire visited California (JPL, Caltech, and Aerojet) during the summer of 1947 and discovered that this effect had been observed in the U.S. on composite propellants, but that the main trend there was still on liquid propulsion.[2] He returned convinced that the solid propellant option was the best, and did a lot of lobbying to obtain the funding of real research

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Table 1 Propellants used in systems developed in the 1950s

Systems and organizations	Missile	Type of propellants
Antitank (DTAT, Nord Aviation)	LRAC 73 ENTAC SS 10 SS 11	EDB CDB
Air-to-grounds rockets (Thomson Brandt)	37, 68, 100 mm	EDB
Ground-to-ground rockets (DTAT)	150 mm, 3"5	EDB
Target drones (Nord Aviation)	CT10, CT20	EDB
Air-to-ground missiles (Nord Aviation)	AS 12 AS 20 AS 30	EDB Booster: PVC composite Sustainer: CDB
Surface-to-air (DCN)	Masurca	Booster: PVC composite Sustainer: CDB
Air-to-air (MATRA)	R 511 R 530	EDB PVC composite
Sounding rockets (ONERA, Nord-Aviation Sud-Aviation, TB)	Bélier, Centaure Bélisawa, Tibère Dragon	CDB, PVC and PU composites, EDB (Bélisawa)

and development programs in the field. More importantly, he received the support of E. Stauff.

The development of the first real industrial composite propellants based on polyvinyl chloride (PVC) plastisol and AP started, in fact, in 1952. The discovery of the interest in the PVC binder is quite amusing. G. Reure, a colleague of G. Maire worked at Le Bouchet using PVC binder in order to make smoke obscurants since it looked like a good candidate to have a "bad" combustion and give a lot of smoke. They were quite surprised to observe a very nice combustion with AP and took a patent on it.[3] A visit from officials of the U.S. Navy in 1953 led to the funding by the Mutual Weapons Program (MWP) for the development of this promising original propellant. A production plant was installed in Saint-Médard and 200-k (390-mm-diam) grains were produced by 1954. The U.S. officials then discovered that this propellant had been developed by ARC in the U.S. since 1950.[4] These were two completely independent developments, but clearly, ARC deserved the merit of having introduced aluminum first in order to increase the energetic characteristics; the French on their side developed big grains (the biggest produced, for an experimental missile of Sud Aviation, weighed 1800 k, it was named Mammoth!), while ARC stayed with smaller grains. Their calculations showed that because of exothermicity during the curing phase big grains were impossible to produce; G. Maire thinks that the values for thermal diffusivities in the calculations were wrong.

Cast double base (CDB) propellants development started in 1950. This family received a very special name in French: Epictète. The reason is that Epictète is the most famous of the greek philosophers, the Stoïcians, which were particularly insensitive to external influence, which was the case for these propellants using efficient ballistic modifiers: the rate of combustion was not much influenced, compared to previous propellant families, by pressure and temperature variations! They were studied at Le Bouchet and produced at Angoulême, which was the plant where nitrate esters could be manufactured and handled. In the beginning of the 1950s, the situation was similar to what it is today: research in the Paris area, production for composites and EDB in Saint-Médard, and CDB in Angoulême (the paste base for EDB being also produced in Angoulême). Table 1 gives a list of a few systems developed in that period with the types of propellants used.

French Strategic Force and the Development of Solid Propellants in the Sixties

In the beginning of the 1960s, the main formulations of extruded double base and cast double base were established, and their manufacturing process more or less stabilized. Later progress in the formulations was an increase in the rate of combustion range of both propellants, and some improvement of the density and the level of energy of the CDBs by an increase of the level of nitroglycerine and introduction of RDX in the formulation. The last type of propellant was used in the first versions of the Exocet AM39 and MM40, the Shahine of the Crotale surface-to-air missile family, and is to be used in the short range antitank ERYX missile and the Trigat long range antitank missile. On the processing side the biggest evolution has been since the beginning of the 1980s, the production by the continuous twin screw extrusion of EDB propellant grains used, e.g., in the DURANDAL antirunway bomb booster, which was procured by the U.S. Air Force during the 1980s. A stamping process, made possible by the thermoplastic behavior of EDBs, has also been developed and implemented. It makes tridimensional geometries possible. An example of such a grain is shown in Fig. 1.

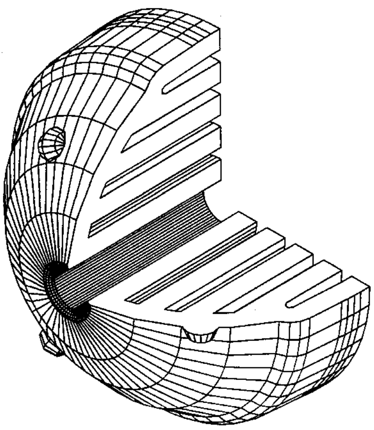


Fig. 1 Tridimensional geometry EDB grain obtained by stamping.

Some research work was recently restarted with success on EDB formulations for air-to-ground rocket systems in two directions: 1) replacement of the lead ballistic modifiers by other ballistic modifiers more innocuous to the environment and 2) modifications to satisfy the insensitive munitions requirements while keeping the level of energy and lowering visible signature. Demonstrations of insensitivity to sympathetic detonation were made in 1991 and 1992 with 2.75-in. rockets using this propellant.[5]

The main problems that had to be solved during the development of these minimum smoke propulsion units during the sixties and the seventies were not related to propellants, but to the smoke emission of current polyester inhibitors. These problems led to the development of new inhibitors either based on silicon polymers and refractory additives,[6] or having completely gaseous decomposition products.[7]

On the composite side the situation was very different at the beginning of the 1960s.[8] Big grains using PVC plastisol propellants had been produced, but they could not be used for case-bonded applications, which means that high performance could not be achieved for tactical applications, and very big grains for long range or space applications could not be produced. Only crosslinked composite propellants in association with good liner systems could achieve this goal. Most of the effort of R&D in this period was to be devoted to these propellants and their applications. During the period of 1960–1975, polyurethane and polybutadiene (CTPB and HTPB) propellants using polyurethane-polybutadiene-based liners were developed. Those propellants were, and will, certainly stay for many years the base of most of the applications.

Fundamental Decision: The French FNS (Nuclear Strategic Force) Development

In 1959, General de Gaulle, back to political authority, decided that the development in France of an independent strategic force would be based on three components: 1) air transported, 2) ground-based ballistic missile (SSBS), and 3) submarine-based ballistic missile (MSBS).

After a short debate on liquid and solid propulsion, technical arguments and U.S. example led to a decision in favor of solid propulsion. Four main areas were in fact considered where major technical progress was necessary to achieve the goal: 1) compact and efficient nuclear warheads, 2) inertial guidance, 3) submarine nuclear propulsion, and 4) rocket propulsion.

In the first area people were on the eve of the first French nuclear test (1960). A nuclear motor for submarines was already being tested. On the propulsion side things were much less advanced. The only technology available for very big propellant grains at that time was the polyurethane binder technology. It satisfied one of the most difficult requirements we have always had to satisfy, that of utilizing a national source of raw materials. AP was also produced by a French manufacturer (Péchiney at that time), aluminum's simplest qualities being also produced in France. But everything else still had to be developed. Only small grains had been produced. No optimization had been made, even for ballistic properties. Computer codes for the prediction of theoretical performances had been developed,[9] but no software for ballistic or structural analysis existed, no liner system was available, the management and quality methods were crude, and all the production facilities had to be created.

Because of the importance of the stake, means and budgets were quite generous, but capable and knowledgeable people were very limited in number. Practically all of the program, the conception and the building of facilities, and the design of propellants, liners and grains have been made and conducted by a very limited number of people, among which Pierre Martinet, Guy Pontvianne, and Robert Soulat had probably the most importance.

The structural design of the grains was done with very simplified methods based on analytical calculations.[10] The propellant behavior and its viscoelasticity were very crudely modeled.[11] In fact, most of the problems encountered on this first generation of ballistic missiles were related to structural analysis. Even with modern computers the appreciation of the stresses at critical bonding triple points is not easy! Stress relief boots had to be adapted. Excellent strides were made in this area[12] after 1968, and the experience acquired with the first generation helped to build a very good reliability on the next generations.

The propulsion system of the missiles and the main dates of their development have been described by Calabro.[13] The decision to start the development was made in February 1962, and the SSBS system was declared operational in mid 1971, whereas the submarine "Le Redoutable" with the MSBS system was operational by the end of 1971.

The first generation of MSBS and SSBS used the same technology: the first stage had a star-shaped, dual polyurethane composition grain in order to suppress propellant slivers,[14] and a dual composition second stage later to be improved with axisymmetric trimmed slotted monocomposition grain designs (called RITA 1 and RITA 2).

It must be said that the practical industrial experience of Direction des Poudres on polyurethane systems also increased during the sixties through the HAWK motor production under license of Aerojet, mostly in the field of raw materials specifications and quality insurance and management.

Polybutadiene Propellants

The highest energy propellant used on the first generations was a polyurethane, AP, Al propellant with 63.5% AP, 20.5% Al. At that time research people were already working on propellants able to deliver higher specific and volumetric specific impulse with better mechanical behavior at low temperatures. The problem here was to develop a new binder, not available through the chemical industry. Carboxy terminated polybutadiene (CTPB) was then developed through cooperation between the French chemical company Plastimer and Service des Poudres (France never went through PBAA and PBAN, but went directly to telechelic prepolymers). The curing system was based on a polyepoxide similar to the commercial Epon 812 of Shell, but developed specifically to get a very good reproducibility of the functionality that was a critical parameter for the reproducibility of the mechanical properties. This compound is produced at the SNPE plant of Sorgues. Since no cocuring agent, like MAPO used in the U.S. formulation, was used, it was necessary to add a specific bonding agent. The bonding agent used is an aminosilane. Its efficiency was discovered in the frame of research projects dealing with wetting agents. The first use of CTPBs was on a tactical missile: the MARTEL antiradar of MATRA in 1968. It was later used on the strategic MSBS M4 that was developed after 1975 and delivered to the submarines in 1984 (first flight test 1980). This system was developed with modern methods, sophisticated computation tools, and the experience of the previous generations. All the objectives were met and the aging of the system is very good (maybe too good)! CTPB propellant is in fact an excellent propellant, the only two drawbacks being its sensitivity to aging through hydrolysis of the ester links of the binder if it is exposed to high levels of humidity and temperature (motors must be sealed in dry conditions), and the viscosity that limits its level of solids to 88–89% for usual AP size distributions and lower levels with fine or ultrafine AP. The basic propellant is a 68% AP, 20% Al that has become the workhorse of French solid propulsion (except that CTPB has since been replaced by HTPB, hydroxy terminated polybutadiene).

Since the second part of the 1970s most new developments began to use HTPB composites either for tactical or strategic systems, and SNPE that had succeeded to Direction des Poudres had the problem of establishing a reliable source of HTPB. In that case, and after some unsuccessful trials at using a hydroxyl polymer derived from CTPB by condensation of two molecules of propylene oxide, no national production was established (by that time the cost problems had become more and more important and the french quantities used are limited, at least compared to the U.S.). SNPE signed in 1975 with the producer of R45M at that time (ARCO chemicals) a license agreement that was in fact never put into practice, the polymer being procured in the U.S. with occasional problems (mostly political and a few technical). With R45M (or HT) it was necessary to develop a new bonding agent. The result of extensive research in the field of nitriles and imines

Table 2 Propellants used in systems developed in the 1970s and 1980s

Systems and organizations	Missile	Type of propellants
Antitank (Aérospatiale)	ERYX	CMDB
Air-to-ground rockets (FZ)	68 mm, 100 mm	HTPB
Ground-to-ground artillery rockets	MLRS	HTPB
(NATO MLRS, SAKR)	S 30	HTPB
Air-to-air	MAGIC	CTPB
(MATRA)	MARTEL (antiradiation)	CTPB
	SUPER 530 D	HTPB
	MICA	HTPB
Air-to-ground (Aérospatiale)	ASMP	HTPB
Surface-to-air	ASTER	HTPB
(Aérospatiale, MATRA)	Mistral	HTPB
Strategic ballistic	M4	CTPB
(Aérospatiale)	HADES	HTPB

was the choice of a compound we called Methyl BAPO (Methylamino-bis methyl aziridinyl phosphine oxide).[15] This compound is produced at the SNPE plant of Toulouse. In order to use its very good rheologic capability, the HTPB binder was used for the development of high burning rate formulations. UFAP production was developed at the beginning of the eighties, and also Butacene,[16] a nonmigrating ferrocene grafted HTPB that improves the safety characteristics of these propellants was developed.

Safety Problems and Technologies

With the industrial development of aluminized HTPB formulations at the middle of the seventies accidental ignitions began to be observed on cured propellant, without any significant shock or friction stimuli. Little by little the origin of these ignitions was traced back to static electricity, when the standard test used on very small quantities of propellant gave a negative result to an electrostatic discharge (ESD). It was SNPE researchers[17] who identified the phenomenon, created a model reproducing the incidents, defined a new test to ESD, and partially clarified the mechanism involved. At that time the international propellant community apparently considered this with limited polite interest as some kind of academic issue; this was to change later. The main reason this phenomenon had not been observed before is because there has been a systematic increase of resistivity of the propellants when going from polyurethanes to CTPB and then to HTPB as binders, when at the same time case and insulation materials were also evolving in the direction of greater resistivities: the sensitivity of the propellant was increasing when the Faraday cage protection effect was disappearing.

Most of the recent work in the field is now related to the characterization of the response to stimuli and the adaptation of propellants to the insensitive munitions requirements.

Production Technology

Two specific and original production technologies were applied since the first generations on the motors of ballistic missiles that stayed has a secret, even if they were patented, for years: the machining of axisymmetric internal bore configuration as shown at Fig. 2 and the curing under pressure of grains case-bonded to composite cases. Finocyl designs were introduced later, mostly in relation with integral molding for high-energy binders. An important experience was also acquired during that period on end-burners either in the ballistic missiles postboost control systems or on tactical systems. The French may be some of the people in the world with the greatest experience on burning rate enhancement at the propellant-insulator interface! At least six different possible mechanisms have been encountered and treated.

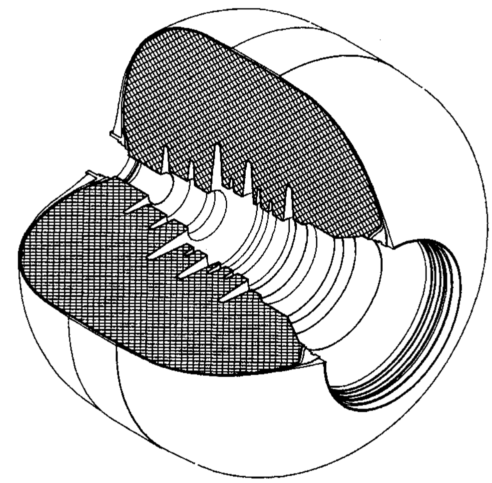


Fig. 2 Typical propellant grain configuration used on second stages of French ballistic missiles.

Table 2 gives a description of the main systems using polybutadiene-based composite propellants developed in the 1970s and 1980s. In that period SNPE also acquired the license from ARC for the production of the MLRS motor. The level of this production (two-thirds of the European production, the other part being produced by BPD in Italy), 20,000 motors/yr, justified the building in Saint-Médard of a completely dedicated and integrated facility, the only one existing at SNPE.

Space Launchers Propulsion: From Diamant to Ariane 5

The first French satellite launcher was partly a byproduct of technology programs involved in the development of the nuclear deterent force. This launcher called DIAMANT A used a liquid first stage and a second and third solid stage based on composite polyurethane propellants. Various experimental vehicles[14] were flight tested between 1960–1965, which can be considered as advanced developments from which the first MSBS and SSBS and the Diamant launcher were derived. The second stage had a metallic case and a case-bonded aluminized polyurethane propellant grain, and the third stage used a glass filament case and a case-bonded 641-k grain. The last one was the last big propellant grain to be produced at Le Bouchet Research Center. Diamant launched the first French satellite on November 26, 1965. Besides the access to the possibility of launching small satellites, this first launch, followed by 11 others with improved versions in the next years, was considered as proof of the capacity of the French to develop their own ballistic force. It was also the

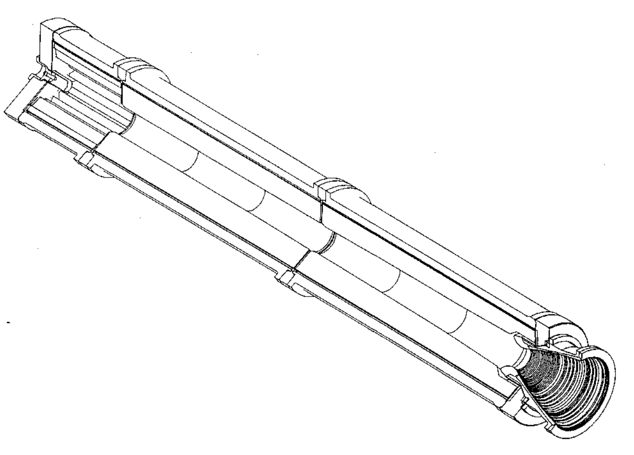


Fig. 3 Subscale model of the Ariane 5 booster grain used for research purposes.

last French space program! The cost of developing a heavy launcher was such that a European cooperation was the only solution and, as a consequence of shares of program between different states, SNPE who had succeeded to Direction des Poudres, nearly disappeared from the area of space launchers main motors for many years, its involvement on the first Ariane launchers being limited to some small auxilliary grains, pyrotechnic devices, and UDMH production.

The last specimens of the Diamant family were fired from Kourou, French Guyana, where the facilities of the Sahara had been transferred. Kourou was to become the space launch facility of the European Space Agency operated by CNES, the French Space Agency. In 1985, the decision was taken to develop a new heavier launcher, Ariane 5, with a different technology: a main cryogenic engine associated with two segmented solid boosters.[18] Since this is the first segmented motor designed in Europe, theoretical and experimental work (Fig. 3) has been conducted on ballistic problems specifically related to segmentation. After a lot of studies, the decision was made by CNES to produce the two heavier segments in Kourou rather than extend the existing European facilities and transport the segments from Europe. A propellant production facility had to be built in Kourou (and a vertical static test stand). The design and construction contracts were attributed to SNPE Ingénierie that built the facility between 1989–1991. A Franco-Italian company, REGULUS, a subsidiary of BPD and SNPE,has operated this facility since 1991, and the first firing-test of the booster was performed on February 16, 1993. The main characteristics of this facility are 1) its specialization, this plant produces only the two big segments of the Ariane 5 booster; 2) the very high level of automatization that is made possible by the singular dedication of the plant; 3) the implementation of a computerized system for real time process control; 4) the use of a low cost HTPB/AP/Al propellant (86% solids) and an HTPB liner; 5) the use of batch mixers of the highest capacity (1800 gal) available industrially today; and 6) the use of dynamic radioscopic, computer aided, nondestructive inspection.

Today, with the help of CNES funding, SNPE is preparing for the next generations with research work on: 1) clean propellants, 50-k scavenged propellant motors have been test fired in 1992 and research work is done on formulations based on glycidyl azide polymer and ammonium nitrate; and 2) the continuous mixing of composite propellants, a pilot plant operates at Le Bouchet.

Hybrids and Ramjets

Hybrids

The hybrid concept for rocket propulsion was extensively studied by ONERA[19] from 1956 to 1974. Various combinations of liquids and solids were tested, some of them quite exotic like LiH or Li AlH_4 with ClF_3. Some tests were conducted using pressed grains of pure ClO_4NO_2 (the reaction was very hypergolic). However, most of the development work was done on a solid fuel made of nylon and metatoluenediamine with nitric acid/N_2O_4 as the oxidizer. Nine flight tests were conducted between 1964–1969 by ONERA on a rocket called LEX02. A target drone was also studied (SPAL 30) with some success, for which grains were produced at Le Bouchet. Funding consideration led to a termination of this work. Some thinking has been going on again during the last years on the hybrid concept for space applications at ONERA, SNPE, and AEROSPATIALE, but the money consideration is still there!

Ramjets, Ducted Rockets, Ramrockets

In France there has always been a lot of interest for the ramjet concept that was invented by René Lorin, who published it in 1913. Many static and flight demonstrations were done between 1930 and the 1950s on aircraft and missile vehicles, particularly by Nord Aviation and ONERA.[20] Demonstrations of great progresses leading to the definition of a modern concept of ramjet adaptable to missile propulsion were obtained at the beginning of the seventies: 1) in 1970, the turbulent combustion with lateral air inlets; 2) in 1972, the solid fuel or ducted rocket technology; and 3) in 1974, the integral booster.

The success of these advanced developments led to the decision by French authorities to base the development of a supersonic standoff nuclear missile called ASMP, designed to replace the free-fall nuclear bomb on Mirage aircrafts, based on this concept. After a 1-yr competition between the ducted rocket and the liquid fuel ramjet solution, the latter was chosen. At that time the level of modulation possible with solid fuels could not satisfy the range requirement.

The development of the propellant grain of ASMP (shown at Fig. 4), from 1975 to the first flight tests in 1983 was full of significant accomplishments:

1) The silicon-based thermal insulation was specifically designed for an aptitude to bond directly to the propellant without any liner system and to have a very low plasticizer absorption capacity. It was later modified to treat also a strong vibration problem due to instabilities of the ramjet combustor.

2) The HTPB propellant uses a ferrocene derivative specifically designed for a low migration tendency.

3) The propellant grain has a very high loading fraction.

Rustique Concept

All the technology investments made on ASMP led to the idea that it was necessary to capitalize on it for the next generations of long-range missiles (e.g., ASLP). For shorter

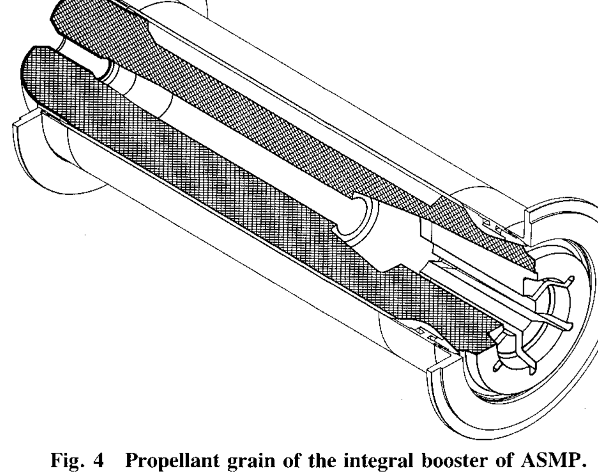


Fig. 4 Propellant grain of the integral booster of ASMP.

ranges, ground-to-air or air-to-ground tactical systems, value analysis conducted by ONERA led to a simplified ducted rocket called the rustique in which the gas generator propellant operates at the aerodynamic conditions of the ramjet. The integral booster is a nozzleless booster. A first advanced development conducted in the mideighties included five very successful flight tests. A second program is conducted today on a bigger caliber. The fuel designed by ONERA and SNPE has sophisticated combustion characteristics and a low-temperature coefficient. Industrial developments using this concept could start in 1995.

High-Energy Propellants

The research work done during the 1960s encountered great difficulties in the synthesis and production of new molecules designed to increase the energy of composite propellants.

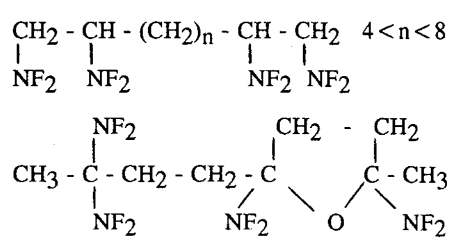
A great number of oxidizers more powerful and denser than ammonium perchlorate were synthesized, tested, and abandoned because of a high chemical reactivity (e.g., ClO_4NO_2), or a lack of stability (e.g., HNF, but we are slightly revisiting this molecule after TNO in The Netherlands recently restarted some work), made them incompatible with the existing binders, or because of high sensitivity to shock or friction for industrial production (e.g., hydrazine mono or diperchlorate).

Techniques were subsequently developed to improve the compatibility of energetic solid oxidizers included in the propellant, surface modifications and, in particular, encapsulation of the particles by organic polymers insoluble in the binder and compatible with the rest of the composition. These techniques resulted in a decrease of the energy gain expected from the formulation, and a significant cost increase for the preparation of the propellant, but they may conceivably be used again in the future.

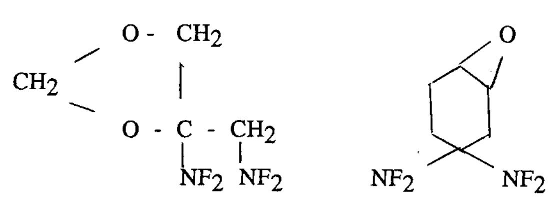
Many failures were also experienced with metallic fuels. Metallic hydrides either exhibited densities that were too low to be interesting when the hydrides were stable (LiH, $LiALH_4$), or they were not stable unless complexed with an organic molecule, thereby losing a good deal of their advantage (AlH_3, BeH_2).

A great effort was devoted to NF_2 chemistry during the 1960s and 1970s. Many molecules were synthesized and evaluated.

For example, plasticizers



Polymers based on monomers like



etc.

None of these molecules has had an application in France. This is a difficult and expensive chemistry, but it is probably needed if very high-performing propellants are required.

Beryllium

Extensive research was conducted at Le Bouchet during the 1960s on beryllium. The addition of this metal significantly increases the specific impulse without creating any problem of compatibility with usual binders, AP or HMX. An important integrated facility was designed, built, and operated between 1968–1973 in which, because of toxicity problems of beryllium and beryllium oxide produced by the combustion, all handling, production, testing, and firing was done. Nuclear industry types of safety devices and measures were used; everything was under reduced pressure and the firing of grains (of a few kilos) was done in two tunnels with an enormous redundancy on the exhaust treatment: two times a set of two systems of filtration, every system being in principle sufficient to take care of the beryllium oxide, plus a very high chimney that was in itself sufficient to dilute the toxic effluents to the legal level in the atmosphere in case of problems on the filters. Later, when the research program was successfully completed, the facility was decontaminated and used for other propellant work on nonberyllium, high-energy propellants without using the firing test part.

High-Energy Binders

On all strategic missile systems only inert binder propellants were used for big motors. Only smaller tactical motors produced in Angoulême used energetic binder propellants. Saint-Médard where big motors are produced, could not accommodate the production and testing of class 1.1 propellants because the extension of the city of Bordeaux had reached the facility in the 1970s. After the development of Trident 1 in the U.S., and when the development of the M4 with polybutadiene composite was sufficient to be assured of success, the problem of production of high-energy propellants for the next generation was considered. The basic idea was to build a plant in the vicinity of Saint-Médard operated by teams of Saint-Médard on government-owned land, under a Goco contract, for activities limited to the active detonable part of the production: nitrate esters production, mixing, casting, curing of propellant, and first testings of motors.

The land, 10 times greater than Saint-Médard, on which the facility was to be built was bought by the Ministry of Defense in 1978, and the decision for building the facilities was taken in 1983. The building work for which the SNPE subsidiary—SNPE Ingénierie—got the contract went on in 1985 and 1986; the first mix happened in the middle of 1986. Two advanced developments were conducted based on typical second and third stages. The first firing (2.5 tons of propellant—NEPE type) took place in July 1987, and the facility was officially opened in September. Since then many other 2.5- or 8-ton motors have been tested with total success. This facility allows France to develop any new desirable kind of high-energy propellant application for the future.

A lot of research work at SNPE was devoted to safety and vulnerability problems related to rocket motors using high-energy binder propellants. Among the threats considered, the reaction to bullet impact of motors using minimum smoke high-energy propellant was studied. During the experimentation on real motors, detonations were observed that could not be explained by the classical scenarios. A new model was established[21] that involves the propellant mechanical and detonics behavior, but also the geometry of the grain. The new scenario was called the "bore effect."

Glycidyl Azide Polymer (GAP) and Azide Derivatives, Other New Compounds

A small, but efficient team of chemists is permanently working at Le Bouchet on government contracts to synthetize and evaluate new energetic molecules. At the beginning of the 1980s they began to work on the organic azide chemistry that had just been discovered in the U.S.[22] By the end of the period, for greater efficiency, an agreement was signed with Rockwell to develop GAP in Europe under license. This cooperation is currently under extension in the field of other energetic molecules. This team is also responsible for the development of some new (or rediscovered) energetic or nonenergetic molecules for energetic materials formulation (NTO, Butacene, etc.), and is currently working on cage nitrocompounds and other candidates for the replacement of the good old AP, HMX and nitrate esters.

Conclusions

Solid propulsion is now a mature technology,[23] which means that if there is still a need and capacity for performance improvements the emphasis for the future will certainly be put on the cost issue: research, development, and production costs, and also, of course, life cycles and reliability. This evolution takes place at a time when defense and space budgets are reduced or strictly controlled and international cooperation is enforced. The consequences are technical and political.

SNPE inherited from Direction des Poudres in 1972 an organization in which it was only responsible for the energetic part of the rocket motor, design, and production. This organization could appear surprising and sometimes puzzling to outsiders, especially foreign observers. Even if it can be shown that it is possible to demonstrate the existence of a subsystem called the propellant grain (as an entity with a perfectly defined status and set of specifications), it is certainly not the best organization to simplify management of developments of motors and optimize cost and performance. This led to evolutions, still underway, of the industrial organization.

In 1972 the French government took a step to rationalize the organization of solid propulsion for strategic ballistic missiles. Three companies were involved: SEP for nozzles, TVC, part of thermal insulations and some cases, Aerospatiale for some composite cases; and SNPE for all the energetic materials. A joint venture was then created between SEP and SNPE called G2P. This organization is the prime contractor for propulsion and coordinates the work between the companies. It is difficult to know today if there will be an evolution of this organization since it depends a lot on the political evolution of the European Union.

In the field of space launchers, we saw previously that the programs became European at the end of the sixties. Special consortia involving companies of different countries are formed to be propulsion contractors in each case.

In the field of tactical systems, the situation was still more complicated. There were (at least) four companies directly involved in solid propulsion in France and, at least one in most of the European countries. A significant step of the evolution was taken recently when Aerospatiale and SNPE formed a new company called CELERG to unite their inert and energetic materials teams and facilities in the field. It is the intention of CELERG and the mother companies to unite most of the European tactical motor development and production in or around this new organization.

References

[1]Pontvianne, G., private communication, SNPE Research Center, Le Bouchet, Vert le Petit, France, June 1992.

[2]Maire, G., private communication, Neuilly sur Seine, France, June 1992.

[3]Maire, G., and Reure, G., French Patent 645814, April 2, 1953.

[4]Martin, J. D., "PVC Plastisol Propellants," AIAA Paper 84-1237, June 1984.

[5]Fonblanc, G., "A New Insensitive Non Toxic Double Base Propellant for Rocket Motors," AIAA Paper 94-3193, June 1994.

[6]Gonthier, B., "Minimum Smoke Rocket Motors with Silicon Inhibitors," AIAA Paper 84-1237, June 1984.

[7]Tauzia, J. M., Gonthier, B., and Grignon, J., "Nouveaux Inhibiteurs de Combustion à Base d'Élastomères Polyuréthannes Oxygénés," French Patent 2538578, May 1982.

[8]Boisson, J., and Tavernier, P., "Préparation et Propriétés des Propergols Solides Composites," *Mémorial des Poudres*, Vol. 42, 1960, pp. 305–320.

[9]Boisson, J., "Programme Général pour l'Évaluation des Performances Théoriques des Propergols," *Mémorial des Poudres*, Vol. 44, 1962, pp. 59–74.

[10]Soulat, R., "Méthode Approchée d'Étude de la Tenue Mécanique des Blocs Moulés-collés," *Mémorial des Poudres*, Vol. 45, 1964, pp. 169–194.

[11]Boisson, J., and Napoly, C., "Propriétés Mécaniques des Propergols Solides," *Mémorial des Poudres*, Vol. 43, 1961, pp. 195–219.

[12]Lhuillier, J. N., Gonard, R., Gossant, B., Hinnen, A., Langlois, G., Lebois, J., and Schaeffer, B., "Tenue Mécanique des Chargements à Propergols Solides," *Sciences et Techniques de l'Armement*, Vol. 52, No. 1, 1978, pp. 11–144.

[13]Calabro, M., and Perret, J., "History of Solid Propellant Rocket Motors at Aérospatiale," AIAA Paper 92-3615, July 1992.

[14]Pontvianne, G., Ternier, L., and Vacelet, L., "Etude de Blocs à Deux Compositions sans Résiduels Théoriques," *Mémorial des Poudres*, Vol. 43, 1961, pp. 166–194.

[15]Finck, B., and Doriath, G., "Agents d'Adhésion Liant-Charge et Composition Propulsive Contenant cet Agent d'Adhésion," French Patent 8513871, Sept. 1985.

[16]Raynal, S., and Doriath, G., "New Functional Prepolymers for High Burning Rate Solid Propellant," AIAA Paper 86-1594, June 1986.

[17]Kent, R., and Rat, R., "Static Electricity Phenomena in the Manufacturing of Solid Propellants," 20th DOD Explosives Safety Board Seminar, Norfolk, VA, 1982.

[18]Gil, P., "Ariane 5, Solid Boosters for Future European Launchers," International Astronautical Federation Paper 92-0628, Aug. 1992.

[19]Barrère, M., "La Propulsion par Fusées Hybrides," Rapport 122, *14éme Congrès International d'Astronautique*, Paris, France, Sept. 1953, pp. 137–145.

[20]Berton, P., Marguet, R., and Petit, B., "Le Statoréacteur à l'ONERA: Histoire et Perspective," *l'Aéronautique et l'Astronautique*, No. 153, 1992, pp. 32–40.

[21]Hamaïde, S., Quidot, M., and Brunet, J., "Tactical Solid Rocket Motors Response to Bullet Impact," *Propellants, Explosives and Pyrotechnics*, Vol. 17, No. 3, 1992, pp. 120–125.

[22]Frankel, M., Grant, L., and Flanagan, J., "Historical Development of GAP," AIAA Paper 89-2307, July 1989.

[23]Davenas, A., "Future of Solid Rocket Propulsion," *Solid Rocket Propulsion Technology*, 1st ed., Pergamon, Oxford, England, UK, 1993.