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Energetic Insensitive Propellants for Solid and Ducted Rockets

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After stating that propellants used on operational missiles do not yet meet all insensitive munition (IM) recommendations of the official French document, Instruction Nr 2060 DGA, IPE, characteristics of new formulations of composites and low-signature propellants are discussed. Butacene®, a prepolymer with grafted combustion catalyst species, reduces the sensitivity and reactivity of high-burning rate composite propellants when submitted to thermal hazards (or threats) without any loss of energetic performance in the operational temperature range. For minimum-smoke propellants, the use of energetic binders places limitations on both the amount of explosive fillers (nitramine) and the sensitivity of the energetic plasticizers to avoid the bore effect (with delayed shock-to-detonation transition phenomena) and losses in performance may have to be allowed. Other results obtained on extruded double-base propellants (SD 1175 and SD 1178), and gas-generator propellants show that it may be possible to design a motor that meets all the MIL-STD 2105 IM requirements. It is concluded that some progress is expected to be made in the near future using new energetic molecules such as hexanitrohexaazaisowurtzitane (CL-20), polyazidoglycidyle and hydrazinium nitroformate (mainly in minimum smoke propellant) to produce both high performance and high immunity levels.

Nomenclature

D = diameter
em = strain at maximum tensile stress
h = height
n = pressure exponent
R_b = burn rate
S_m = maximum tensile stress
T_c = critical temperature
T_g = glass transition temperature
π_K = temperature sensitivity
ϕ = equivalence ratio

I. Introduction

FOR more than 10 years, SNPE, charged by the French government to develop and manufacture propellants for military and space applications, has been examining the insensitive munition (IM) emerging requirements and contributing significantly to the definition and writing of recommendations contained in the official French document Instruction Nr 2060 DGA, IPE, the French version of the MIL-STD 2105 B. The recommendations in this document are very useful for designers of propellant, propellant grains, solid rocket motors and missiles.

The main features of the requirements of the new IM are presented in Table 1. The asterisks in the French document identify three levels of immunity. MURAT (French designation for IM), with one, two, and three asterisks denotes increasing degrees of immunity. The requirements for the various threats are "no reaction more violent than," according to NATO definition.

Note that French requirements MURAT* and MURAT** permit detonation reactions for some very energetic threats or stimuli. This is prohibited for a MURAT*** level, the more severe requirement even for MIL-STD 2105 B, which allows a detonation-type reaction in the sympathetic detonation test and the shaped-charge threat. As will be seen later in this discussion, the MURAT*** level can be achieved or approached today, only with a few propellants such as the new insensitive extruded double-base propellant (EDB) propellants and gas-generator propellants. In fact, the conventional operational motors used now (and therefore conceived some years ago) do not have the required design to satisfy the MURAT*** level, and they use propellants that fail in IM tests. Table 2 summarizes the diagnosis of operational propellants and solutions under consideration at SNPE discussed in this article.

To complete this diagnosis we must mention a new type of gas generator propellants developed for ducted rocket applications. Their specific formulations, with low oxidizer content, good immunity characteristics, and the ability to meet MURAT*** requirements, make them very attractive.

II. High-Burning Rate Composite Propellants: Butacene® Propellants

Reduction of the operational time of missiles to reach targets, particularly in surface–air missions, has compelled manufacturers to develop energetic, high-burning rate composite propellants. To meet combustion requirements, ultrafine ammonium perchlorate with catalysts is used. Conventional solid catalysts, such as ferric oxide or copper chromite are not adequate: the performance of such propellants is limited due to the high end-of-mix viscosity obtained during manufacture. In the recent years, liquid ferrocene catalysts (such as Catocene®) have been tested as plasticizers in the binder polymer network. These catalysts allow a high level of fillers, but unfortunately they are not bonded to the polymer, and can vaporize and migrate out of the propellants and come into contact with liners, insulators, other propellants, thermal protections, etc., or come to the "free surfaces" of the grain. These phenomena are regulated by a diffusion process to balance the chemical potential of the ferrocene derivatives in various phases at propellant interfaces. The difficulties described have limited the use of such derivatives in propellants.

In order to solve the previously mentioned problems, SNPE has developed a new prepolymer, Butacene, upon which a ferrocenic catalyst is chemically grafted. The propellants formulated with this new prepolymer demonstrate good processability, high-energetic performance, an extended range of burning rates, good safety properties, and enhanced behavior in thermal vulnerability tests.

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Table 1 Main requirements for new IM in France and the U.S.

Threat	MURAT*	MURAT**	MURAT***	MIL-STD 2105 B, 01/14/94
Electrical	NR	NR	NR	?
Drop	NR	NR	NR	NR
FCO	IV	V	V	V
SCO	III	V	V	V
Sympathetic detonation	III	III	IV	II
Bullet impact	III	III	V	V
Fragment impact	I	III	V	V
Heavy fragment impact	I	III	IV	/
Shaped charge	I	I	III	II

MURAT = Réf. Instruction Nr 2060 DGA, IPE, of 4/08/93.
Reaction (NATO definition):
I = Detonation reaction
II = Partial detonation reaction
III = Explosion reaction
IV = Deflagration reaction
V = Burning reaction

Table 2 Summary of SNPE's improved propellants

Nature of propellant	Main problems to solve	Solutions proposed by SNPE
HTPB composite propellants		
Aluminized or reduced smoke	Violent reaction in thermal aggression (SCO or FCO)	Butacene-based composite propellants
Minimum-smoke propellants		
1. XLDB propellants (French nomenclature: nitramite)	They may detonate as they contain explosive ingredients	XLDB with reductions in energetic performance
2. Extruded double base propellants (French nomenclature: SD)		SD 1175 and SD 1178 without nitroglycerin

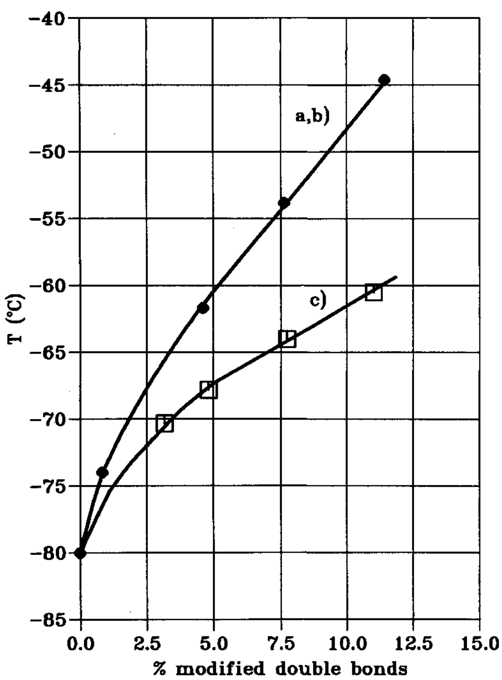


Fig. 1 Glass temperature for HTPB grafted with various hydrosilanes a) (4′ ferrocenyl methyl) phenyl dimethyl silane, b) (3′ ferrocenyl methyl) phenyl dimethyl silane, and c) 4 ferrocenyl butyl dimethyl silane.

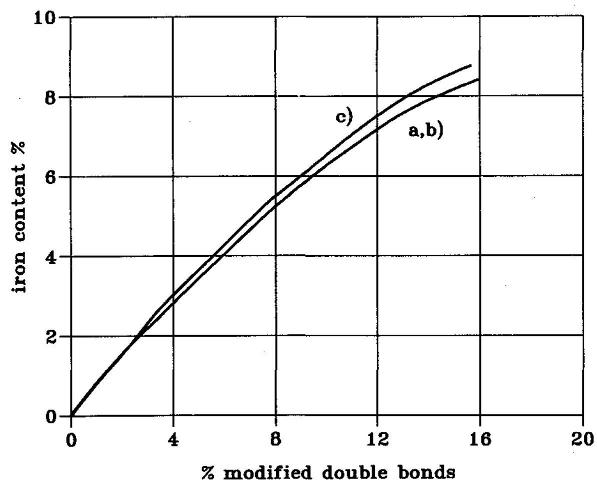


Fig. 2 Iron content vs percentage of modified double bonds of HTPB.

A. Butacene: A New Prepolymer for High-Burning Rate Composite Propellants

The synthesis of Butacene is reported in Ref. 1. It consists of adding a ferrocene hydrosilane to the pendant double bonds of a low molecular weight hydroxy-terminated polybutadiene (HTPB) (R45M or R45HT from ATO, Inc.). The properties of the grafted prepolymer depend strongly on the nature of the hydrosilane derivative. Figures 1 and 2 show the relationships between prepolymer glass temperature, iron content, and percentage of modified double bonds for various ferrocene derivatives: (4′ ferrocenyl methyl) phenyl dimethyl silane, (3′ ferrocenyl methyl) phenyl dimethyl silane, and 4 ferrocenyl butyl dimethyl silane.

As expected, an increasing level of addition of ferrocene hydrosilane leads to a degradation of the very attractive T_g of the HTPB. Derivative *c*, with its alkyl chain, appears to be the best compromise between a low T_g (required for propellants used in an extended range of temperature) and a high level of iron content (required for high burning rate). It has been selected for the manufacture of Butacene, with an iron percentage of 8% (about 75% of pendant vinyl groups are

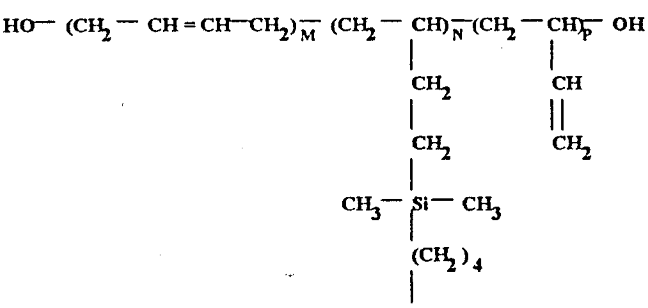
Table 3 Butacene characteristics

Form	Viscosity at 25°C, P	Iron, wt %	OH value, eq/kg	Volatile species, wt %	T_g, °C	Density, g/cm³	Functionality, OH/kg	Antioxidant, %
Viscous liquid	<1000	8 ± 0.5	0.32 ± 0.05	<0.5	> −55	1.00 ± 0.02	2.3	1 ± 0.2

Table 4 Typical characteristics of Butacene-based propellants

Type of propellant	Total solids, %	Mechanical properties: T, °C	S_m, MPa	e_m, %	Burning rate at 1000 psi, in./s	Density, g/cm³	Specific impulse, s 7/0.1 MPa, theoretical
Aluminized	84	+20	0.9	25	1.6–2.5	1.73	262
		−50	2.5	15	——	——	——
	85	+20	0.7	40	1.0–2.0	1.76	263.5
		−50	2.7	14	——	——	——
	88	+20	0.8	30	0.8–1.5	1.82	265.0
		−50	3.2	12	——	——	——
Reduced smoke	86	+20	1.3	35	0.8–2.2	1.70–1.72	249–252.5
		−50	4.4	32	——	——	——

modified). The chemical formula can be modeled as shown in the following diagram:



Fc = FERROCENE

Table 3 presents the analytic characteristics of the prepolymer. The iron content, OH value and single peak in gel permeation chromatograph (GPC) analysis (Fig. 3) are consistent with a strict polyaddition of the pendant vinyl groups of the polybutadiene backbone and confirm the ability of Butacene to be used in propellant manufacture. It is now produced in large quantities at SNPE (300 kg/batch).

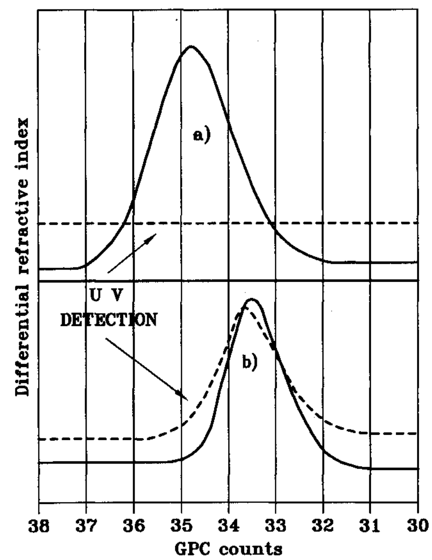


Fig. 3 GPCs of a) HTPB and b) Butacene. Ultraviolet detection of ferrocene groups.

B. Butacene-Based Propellants

A large range of composite propellant formulations has been established.[2] Some typical characteristics are summarized in Table 4 for aluminized and reduced-smoke propellants.

1. Energetic Properties

High density and high specific impulse are obtained in relationship with the high filler contents achievable due to the relatively low viscosity of the polymer. HTPB composite propellants have the same specific impulse for the same content of filler.

2. Propellant Manufacture

A high total of solid contents is achieved by conventional composite propellants manufacturing. The end of mix viscosity complies with the manufacture of case-bonded grains. Some advantages of Butacene during mix must be mentioned[3,4]: 1) fairly uniform dispersion of the ferrocene species which makes it possible to avoid having AP/binder mixtures that are very rich (and consequently friction-sensitive) in ferrocene, and 2) ferrocene derivatives cannot be vaporized during low-pressure mixing phases, and sensitive dry AP/ferrocene mixtures are avoided in the upper part of the mixer.

3. Mechanical Properties

Due to the low T_g of Butacene, the mechanical properties are good over an extended range of temperature, consistent with use in tactical-missile applications.

4. Aging Properties

Oxidization (by ambient oxygen) of double bonds of HTPB polymers, the main process in aging of composite propellants, is accelerated by: the presence of metallic ions created by the oxidization of ferrocene groups and the increased concentration of ferrocene that occurs in liquid catalyst-based propellants (such as Catocene). Catocene migrates towards free surfaces such as the bore of the grain (Fig. 4). A consequence of this is the dramatic increase of surface ignitability demonstrated by the decrease of the self-ignition temperature (Fig. 5).

This mechanism is significantly reduced with Butacene since the concentration of iron is constant during aging (i.e., it is equal to the bulk concentration).

5. Burning Rate

The burning rates achievable with Butacene-based propellants are quite similar to those achievable with Catocene-

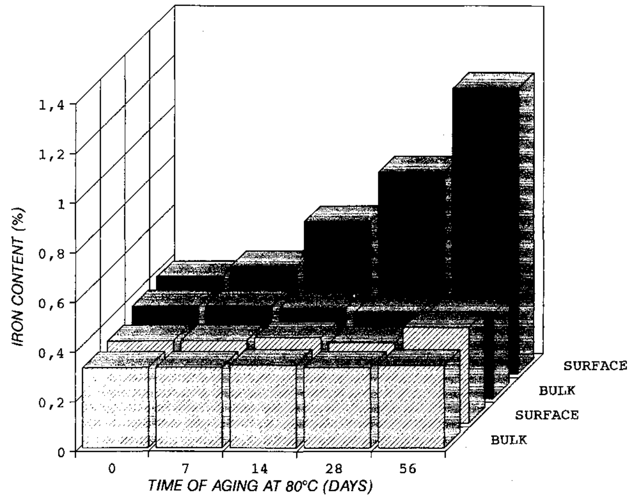


Fig. 4 Iron percentage after aging in bulk and surface of Butacene. Solid black graphs = Catocene-based propellant and shaded graphs = Butacene-based propellant.

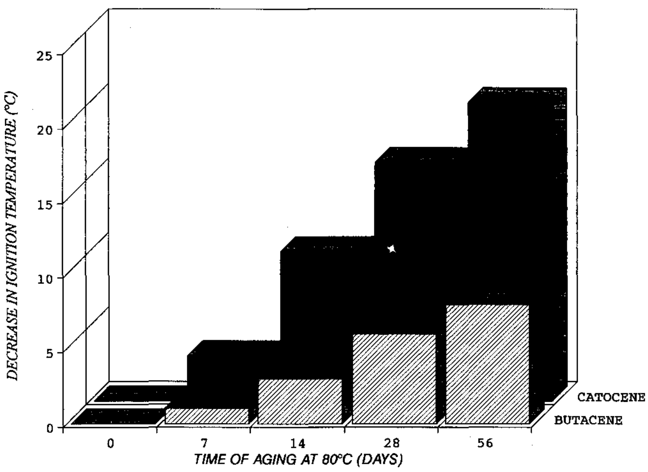


Fig. 5 Surface self-ignition temperature decrease after aging for solid block graphs = Catocene-based propellant and shaded graphs = Butacene-based propellant.

based propellants. At constant iron content, there is a slight increase in efficiency due to the presence of Si atoms in Butacene. Burning rate can be adjusted with conventional parameters: iron content regulated by the ratio Butacene/HTPB in the binder, ammonium perchlorate (AP) particle size, or pressure. Some examples of the influence of pressure and Butacene content on burning rate for reduced smoke propellants (86% of solid fillers) using fine AP (3 μm) are given in Figs. 6 and 7. A noticeable property of these propellants (shared with ferrocene catalyst propellants) is the relatively low pressure exponent (0.4–0.5) even at high pressures.

6. Safety

The safety characteristics of Butacene-based propellants are satisfactory (Table 5). Nevertheless, the friction sensitivity increases with the increasing burning rate. This is not a property peculiar to Butacene-based propellant alone. It is characteristic of all catalysts.

C. Vulnerability

1. General Considerations

We will discuss here only those results obtained with thermal aggression, which is the main problem of composite propellants. Butacene-based propellants may be the mean by which improved results in fast cook off (FCO) and slow cook off (SCO) tests can be achieved.

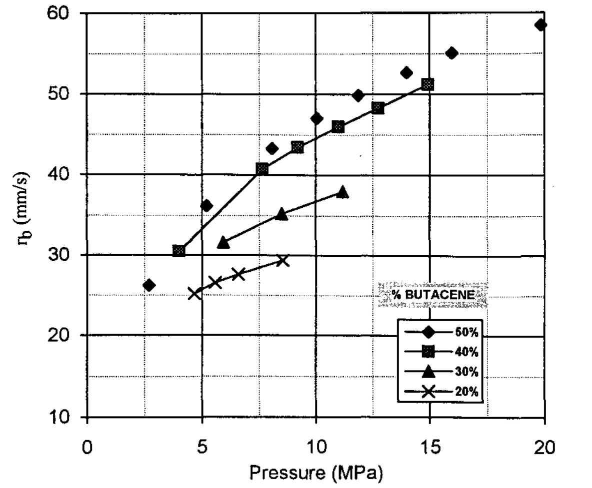


Fig. 6 Burning rate of propellants with a mixture of prepolymers HTPB (R45HT) and Butacene measured on star-shaped grain. (propellant: binder 14%, AP 82%, Al 4%).

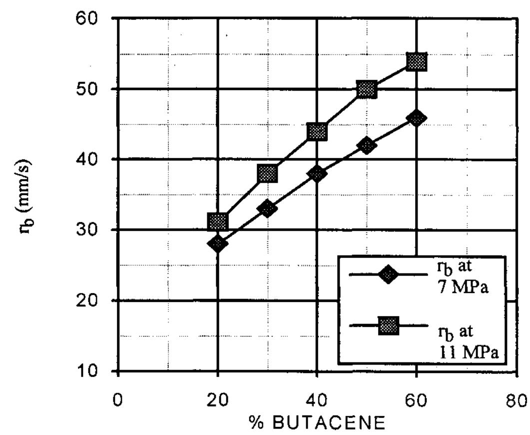


Fig. 7 Effect of percentage of Butacene on the burning rate of propellants measured on star-shaped grain.

Some problems may occur in bullet-impact tests. These propellants have high burning rates and the pressure in the cased motors may increase rapidly after ignition, causing a violent effect when they burst. Although Butacene propellants do not provide improvements in this area at the present time, the possibility remains of investigation for future formulations.

2. Behavior of Thermal Threat

To assess and select propellants able to meet the IM requirements, SNPE has developed three types of steps[6,7]: 1) SNPE test 41: thermoignition temperature, 2) SNPE test 85: unconfined SCO test, and 3) test on models; and very recently some new experiments were developed to understand the mechanism of degradation.

SNPE test 41: thermoignition temperature. Cylindrical propellant samples $D = 50$ mm, $h = 50$ mm are held at various isothermal temperatures. The time to reaction and the nature of reactions are recorded. Two chemical processes may occur: "thermal explosion," always observed with composite propellants, or "chemical stability," very often observed with double-based propellants.

Chemical stability: this case is not discussed in this article, but an example of typical results obtained on crosslinked double-base propellant (XLDB) propellants is given in Table 6. Whatever the temperature of the test, it is possible to find a time of ignition. This time increases as the temperature decreases, and the reaction is always combustion. This behavior is very desirable in meeting IM requirements.

Table 5 Safety and hazards characteristics of Butacene-based propellants

Propellant: total of solid, %	85	86	88
Burning rate at ambient pressure, mm/s	4.2	3.5	2.2
Self-ignition temperature, °C	213	215	247
Friction sensitivity, N	90	60	110
Cook off (SNPE test 41)			
Critical temperature, °C	160	170	172
Reaction type	Combustion	Combustion	Combustion
SCO (SNPE test 85)			
Temperature of reaction, °C	181	178	185
Reaction type	Combustion	Combustion	Combustion
Bullet impact on model	Combustion	Combustion	Not tested
Reaction type	No projection of fragments	No projection of fragments	

Table 6 SNPE test 41: chemical stability reaction type, results on an XLDB propellant

T, °C	Time of reaction, min	Reaction type
80	117,900	Combustion
89.5	20,400	Combustion
95.5	6,000	Combustion
100.5	3,540	Combustion
102.5	2,140	Combustion
105.5	1,660	Combustion
110	740	Combustion

Table 7 Critical temperature of cook off (SNPE test 41) for reduced smoke composite propellants (86% of solids) with various combustion catalysts

Catalyst	Critical temperature, °C
Copper chromite	162
Ferric oxide	180
Butacene	170

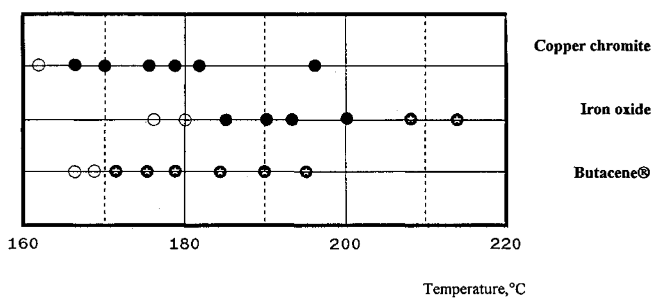


Fig. 8 Reactions in cook off (SNPE test 41). Composite propellants: 86% of solids; burn rate 20 mm/s at 7 MPa. Influence of burning rate modifier.

Thermal explosion: below a critical temperature T_c, no reaction occurs whatever the heating time at constant temperature. Above T_c, there are three cases that depend on the type of reaction: 1) always explosion: motor will react violently in FCO and SCO tests; 2) always combustion: the best case, but the motor response in FCO and SCO will depend on the nature of the case; and 3) explosion up to a given temperature, and combustion above. It can be expected that there is a range of thermal threats that lead to unsuitable responses in FCO and SCO tests.

This test was performed on three types of reduced-smoke propellants with the same level of burning rate (20 mm/s at 7 MPa). The results are given in Table 7. All types show a critical temperature, depending on the nature of the catalyst.

And above this critical temperature (see Fig. 8): propellants with copper chromite always exhibit a violent reaction, propellants with Butacene always involve combustion, and propellants with ferric oxide show a violent reaction between 180–185°C; above 185°C only combustion is observed.

SNPE test 85: unconfined slow cook-off test. This test, which attempts to model the real threats that a motor may be exposed to, uses the same samples as those in test 41. Here, however, the external temperature increases from the ambient to the reaction at a constant rate of 1°C/h or 10°C/min. For SCO problems, the test is generally performed at 3.3°C/h. At this slow heating rate, the reaction levels of the Butacene-based propellants are better than those of propellants with other conventional catalysts (Table 8).[8,9]

Table 8 Reaction in SCO test (SNPE test 85), reduced-smoke composite propellant (86% solids), and influence of burning rate modifier

Catalyst	Test 41	Test 85
Heating rate	Isothermal	3.3°C/h
Copper chromite	Explosion	Explosion
Ferric oxide	Explosion	Not tested
Catocene	Explosion	Combustion
Butacene	Combustion	Combustion

Table 9 Results in thermal aggression on models loaded with 86% solid reduced-smoke propellants catalyzed with copper chromite or Butacene

Tests	Copper chromite	Butacene
SCO		
NATO type of reaction[a]	I	II
Temperature (°C)	225	175
FCO		
NATO type of reaction[a] (two trials per composition)	III or IV	IV or V

[a]See Table 1 for definitions of reaction levels.

Tests on models. To assess the influence of confinement, rocket-motor analogues with a high confinement have been tested: weight of propellant = ~5 kg; grain = central-perforated cylinder, internal diameter 63 mm, external diameter 123 mm; case = steel, thickness ~3 mm; propellant = reduced-smoke propellants with Butacene or copper chromite as burning rate catalyst. Results in FCO and SCO (3.3°C/h) are given in Table 9.

The reactions are violent for the two propellants, and much more so than in SNPE unconfined tests. However, Butacene-

Table 10 Weight losses of cylindrical propellant samples (D = 50 mm, h = 50 mm) at temperatures just below the reaction temperature

Propellant type	Catalyst type	Weight loss, %	Heating conditions T, °C	Heating conditions Time, h	Temperature of reaction, °C
Reduced smoke	Butacene	2	166	88	
		0	168	208	170
		0	160	17	
	Copper chromite	26	172	304	
		26	174	306	180
		24	176	305	
Aluminized	Butacene	2	160	90	160
		0	150	63	

a)
b)

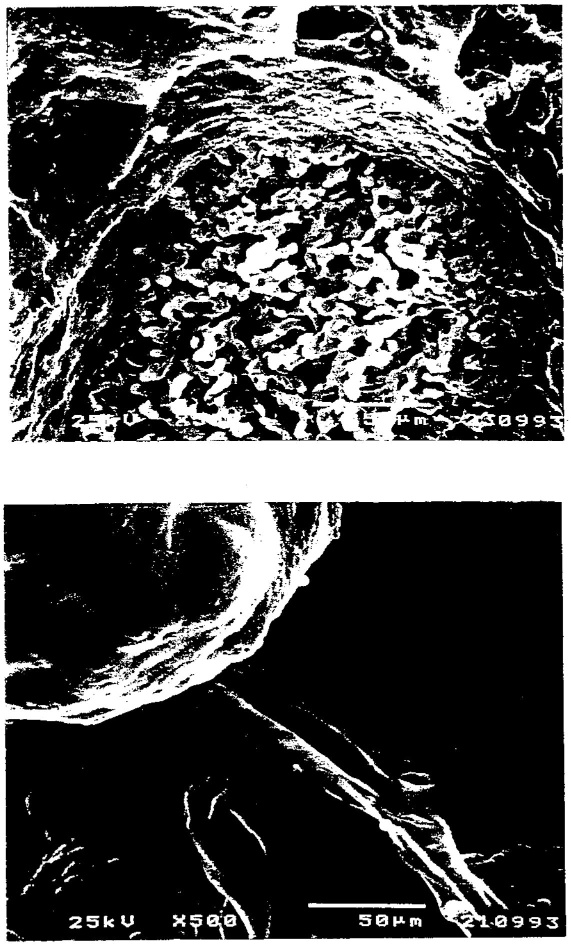


Fig. 9 Scanning micrography of propellants submitted to 160°C for three days: a) copper chromite catalyzed propellant and b) Butacene-based propellant.

based propellants show a reduction of violence compared to copper chromite propellants. These results illustrate the important effect of strength and confinement on reaction severity.

Mechanism of degradation. Some experiments were performed[10] in order to understand the nature of the reaction above the critical temperature in test 41. Table 10 gives the results of weight losses of propellant samples (identical to those used in test 41) for various propellants at temperatures very near just below the critical temperature.

Butacene-based propellants show a reduced weight loss and low porosity just before the reaction. This has been confirmed by the observations in scanning microscopy, which show very spongy AP particles in copper chromite-catalyzed propellants (Fig. 9a). In Butacene-based propellants, AP is not degraded (Fig. 9b).

Table 11 Results of firing tests of 12-in. motors with Butacene-based propellants before and after aging

Parameters	Baseline	After aging six months, 50°C
Combustion time, s	2.88	2.84
R_b at nominal pressure, mm/s	36.4	36.9
Nominal pressure, MPa	9.52	9.61
Maximum pressure, MPa	12.9	12.8
Thrust, N	136,280	134,700
Specific impulse, s	239.8	240.8
Weight of propellant, kg	114.5	114.2

D. Conclusions

Butacene-based propellants now seem to be the best compromise between energetic performance and reduced sensitivity. They exhibit the high specific impulse of conventional composite propellants and allow very high burning rates to be obtained. They burn at high pressure (up to 50 MPa and in some cases above) with a reduced pressure exponent (0.5), and exhibit a mild reaction in SCO and FCO tests when lightly confined. In the high confinement of a steel case, the reactions in SCO tests remain violent even if a reduction in their severity is reported. They have been successfully tested in actual motors. Table 11 shows the results obtained after accelerated aging on a motor for ground-to-air missiles: performance is maintained near initial values.

III. Minimum-Smoke Propellants

To meet the need for energetic low-signature propellants, SNPE has developed XLDB propellants called "nitramites." The formulation of these propellants is based on an energetic binder filled with a nitramine such as hexahydrotrinitrotriazine-cyclotrimethylenetrinitramine (RDX) or octahydrotetranitrotetrazocine (HMX). The binder consists of an hydroxylterminated polyester or polyether prepolymer crosslinked by a polyisocyanate and plasticized by a nitrate ester plasticizer such as nitroglycerin and butanetriol trinitrate. In some cases, where secondary smoke is tolerated in the exhaust combustion products, AP is used as a secondary oxidizer. This makes it possible to achieve higher burning rates, as required by future applications. The use of highly energetic ingredients in these formulations to achieve high specific impulse renders these propellants sensitive to shock threats. For example, the critical diameter for sustained detonation is low (<10 mm), and IM requirements such as bullet impact or sympathetic detonation may be difficult to meet. The need for various compromises between performance and reduced sensitivity, has led SNPE to broaden the range of performance covered by these propellants.

Table 12 Properties of nitramites propellants: basic compositions

Propellant composition	1752	1758	1766
Binder, %	30	35	31
Fillers			
AP	12	30	—
HMX	55	33	63
Additives	3	2	6
Ballistic properties			
Burn rate at 13 MPa, mm/s	20	25	15.5
Exponent n	0.52	0.44	0.35
Temperature sensitivity π_K, % °C^{-1}	4.3	3.5	1.5
Theoretical impulse 70/1, s	257	253	247
Density, g/cm^3	1.755	1.746	1.787
Mechanical properties	Compatible with case-bonded grains		
Velocity limit of detonation			
HVSGT,[a] m/s	340	Not tested	400
Critical diameter for sustained detonation (mm)	<5	<5	<5
Bullet impact test	Bore effect[b]	Bore effect[b]	Bore effect[b]

[a]High velocity shot gun test.
[b]See Sec. III.C.

Table 13 Tensile mechanical properties, composition 1766

Temperature, °C	−54	−30	+20	+60
Maximum stress, MPa	11	1.6	0.85	0.67
Modulus, MPa	316	14	4.7	4.6
Elongation at maximum stress, %	9	47	87	66

A. Properties of the Basic Compositions

The main properties of the basic compositions are reported in Table 12.

1. Energetic and Ballistic Characteristics

1752 and 1758 are representatives of reduced-smoke propellants because they contain AP as a co-oxidizer. They exhibit a higher specific impulse and burning rate than the minimum-smoke propellant 1766. The relatively good pressure exponents are due to the use of ballistic modifiers. Without these additives, the pressure exponents of the propellants with nitramine fillers and energetic binders are too high (≥0.8) for reasonable use in a motor.

2. Mechanical Properties

Mechanical properties are adapted to the requirements of tactical motors over an extended range of temperature (Table 13).

3. Safety, Vulnerability

As already discussed, the main problem of these energetic compositions is due to the high level of shock-sensitive ingredients. In the case of a violent shock, they may experience a delayed transition-to-detonation by a mechanism called the "bore effect" if used in perforated grains of appropriate geometry. The main parameter of the bore effect is the distance across the grain central perforation. New compositions have been developed that meet the IM requirements in bullet-impact tests, regardless of the geometry of the motor. These solutions assume that the other propellant characteristics are maintained.

Thermal threats: when exposed to thermal threats these compositions performed very well. For example, composition 1752 is "chemically stable" (see Table 6) in SNPE test 41: no critical temperature is observed and the reaction is always a combustion. The time of initiation depends only on the temperature. In SNPE test 85 (SCO test) performed at 3.3°C/h the ignition occurs after 24 h of heating at 130°C. This behavior is typical of nitramites, which never leads to a violent reaction in an SCO test. It is also consistent with the results observed in motors. FCO tests performed on a motor for an air–air missile application with a high modulus steel case (external diameter 162 mm, perforated grain, propellant weight 33 kg) have displayed only combustion reactions.

Sympathetic detonation: the behavior of rocket-motors in the sympathetic detonation test is strongly dependent on the test configuration. But, as these compositions have a large content of sensitive ingredients, and consequently, a small critical diameter for sustained detonation, they are a priori able to detonate, and cannot meet the requirements of MURAT***. Some specific formulations with a lower content of sensitive ingredients and with reduced performance are in progress in order to meet this level of insensitivity.

B. New Insensitive Nitramites

These new formulations use 1) a reduced content of nitramine fillers; 2) low-sensitivity, less energetics nitrate-ester plasticizers such as TMETN and BTTN; and 3) ammonium nitrate as an oxidizer to replace some of the nitramine fillers.

The selection of formulations is made through trials in high-velocity shot gun test (HVSGT): a formulation is declared to be satisfactory if the conditions of the test (velocity of the sample <1000 m/s) do not reveal delayed shock-to-detonation transition (XDT)[11,12] phenomena. XDT is not a prompt shock-to-detonation transition, but a delayed reaction that requires a shock, just strong enough to generate a transient more sensitive damaged zone in the grain, which can react on detonation on the stimuli of reflected shock waves. Therefore, the level of shock required to initiate in detonation is lower in XDT phenomena than in SDT.

The main properties of the formulation are reported in Table 14.

Minimum-smoke compositions A and B are derived from composition 1766, and reduced-smoke compositions are derived from compositions 1752 and 1758. XDT phenomena have not been observed with compositions B, C, D, either in HVSGT or in the bullet impact test. In fact, only one model in composition A tested in bullet impact detonated in a bore effect mechanism. By comparison with Table 12, it can be deduced that in order to meet the IM requirements and avoid the bore effect mechanism, it is necessary to permit significant losses in specific impulse and density. The best way to achieve this immunity level is to use a reduced content of nitramine fillers and low-sensitivity nitrate-ester plasticizers in preference to nitroglycerine-plasticized compositions (composition A).

The other characteristics of these compositions are similar to those of the basic compositions. Table 15 shows the main properties of composition A.

Table 14 New insensitive nitramite formulations, energetic performances, and sensitivity

Composition	A	B	C	D
Binder, %	39	31	30	33
Nitroglycerine/BTTN	X	—	X	—
TMETN/BTTN	—	X	—	X
AP, %	—	—	15	32
AN, %	—	—	30	—
HMX, %	—	—	22	33
RDX, %	55	63	—	—
Additives, %	6	6	3	2
Specific impulse (theoretical: 70/1), s	242	240	253	251
Density, g/cm^3	1.74	1.71	1.71	1.73
Velocity limit of detonation HVSGT, m/s	<450	>750	>860	>1000
Bullet-impact test[a] (0.5-in. AP bullet, 1050 m/s)	Detonation[b] Bore effect	ND[c] NB[d]	ND NB	ND NB

[a]Grain: external diameter: 152 mm, length 100 mm, internal diameter is variable.
[b]Detonation for an internal diameter of the grain of 45 mm.
[c]No detonation. [d]No bore effect.

Table 15 Insensitive nitramite, combustion properties of composition A

Burning rate, mm/s				Tensile mechanical properties					
7 MPa	13 MPa	Pressure exponent, n	Temperature sensitivity, π_K, % °C^{-1}	Temperature, °C	Maximum stress, MPa	Modulus, MPa	Strain at maximum stress, %	Critical diameter of detonation, mm	FCO–SCO reaction type
14.2	16	0.23	1.5×10^{-3}	−54	12	236	17	<5	Combustion
				−30	2	7.6	121		
				+20	1.15	3.2	106		
				+60	1.06	3.1	109		

Table 16 New insensitive nitramite with a large critical diameter for sustained detonation

Binder	
GAP, %	35
Fillers	
Ammonium nitrate, %	60
RDX, %	5
Specific impulse, I_{sp}, s	237
Density, ρ, g/cm^3	1.6
Mechanical properties	
Maximum stress, +20°C, MPa	0.7
Strain at break, +20°C, %	29
Strain at break, −54°C, %	23
Burn rate at 5 MPa, R_b, mm/s	8
Pressure exponent, n	0.62
Critical diameter of detonation, mm	35
HVSGT (velocity limit of detonation), m/s	>1000
FCO–SCO reaction type	Combustion

As these compositions still contain some significant amounts of explosive ingredients, they remain able to detonate when submitted to sympathetic detonation testing. To minimize this type of reaction some compositions without (or with a low content of) nitramine have been developed in our laboratories.

The major oxidizer is ammonium nitrate (AN), which is low in energy. To compensate for unacceptable energy losses it is necessary to use a new energetic binder, the glycidylazide prepolymer (GAP prepolymer produced at SNPE under Rocketdyne license). Typical properties of a basic formulation are given in Table 16.

The additional performance losses when compared to composition A of Table 14 are distinct, despite the use of GAP and a limited quantity of RDX (critical diameter decreases very rapidly with increasing content of RDX): −5 s in specific impulse, −0.14 g/cm^3 in density. AN when used as the main oxidizer is also responsible for some limitations of other properties (such as mechanical properties), which nevertheless remain consistent when used in case-bonded grains. In addition, burning rate is strongly reduced and the pressure exponent is increased. However, these types of compositions have entire range of immunity characteristics to meet the MURAT*** requirements: no XDT in HVSGT and, therefore, no bore effect, and a reduced propensity to detonate by an SDT mechanism because of their large critical diameter.

C. Bore Effect

The bore effect was first observed[13] at SNPE in a motor loaded with a star-shaped perforated grain. The mass of propellant was 35 kg, the external diameter of propellant grain was 152 mm, and the bullet velocity was 1200 m/s. At lower bullet velocity (850 m/s), the only reaction was combustion.

1. *Experimental Setup*

To understand the phenomena, the geometry of a propellant grain has been modeled by a perforated cylinder of bare propellant with an external diameter of 152 mm, a variable internal diameter, and a length of 100 mm. The bullet enters the grain at the middle plane perpendicular to a generatrice of the cylinder. The test is performed for various webs in order to determine the probability of detonation as a function of the web. Typical results are reported in Fig. 10. Propellants 1752-1758-1766 give curves of type a. Compositions A, B, C, and D give a flat curve, without detonation.

The results of the test depend on the test configuration: the presence (or not) of a confinement by a case which is generally not favorable; the temperature: probability of bore effect increases when temperature increases, the range of web in which detonation is possible increases; and the bullet velocity: XDT phenomena may occur at high bullet velocity.

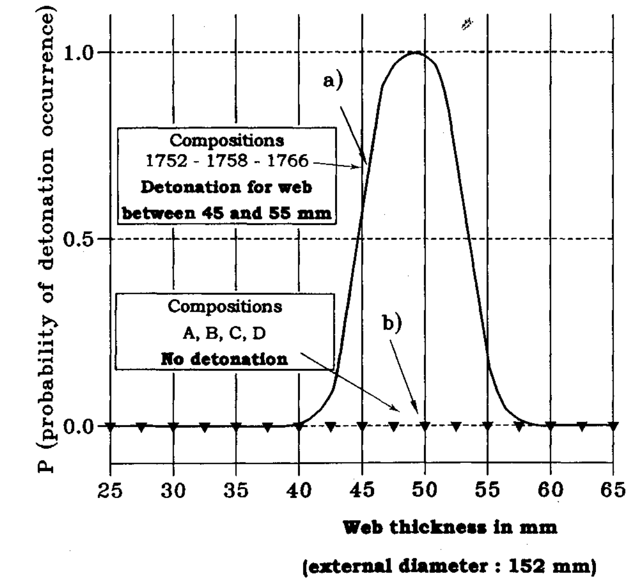


Fig. 10 Bullet impact test: detonation probability as a function of web: a) bore effect: XDT between web = 45 and 55 mm and b) no detonation–no bore effect.

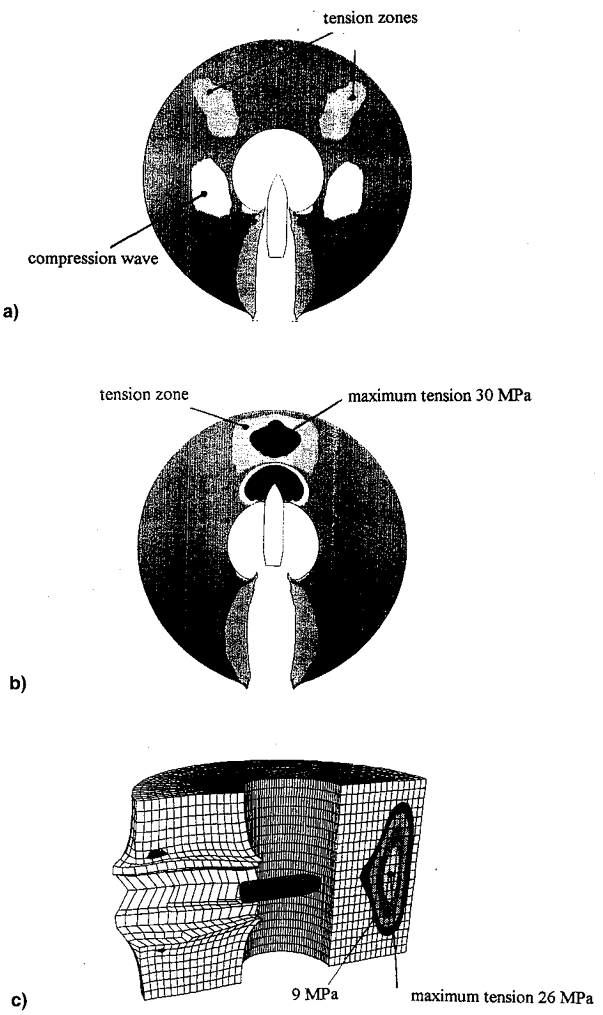


Fig. 11 Bore effect; pressure values in tension zones. Computations with LS Dyna Code; cylindrical sample, D = 152 mm, h = 100 mm, web = 50 mm—bullet: 0.5 AP—velocity: 1050 m/s. Two-dimensional computations at two bullet penetration times t = a) 75 and b) 108 μs; also c) three-dimensional computation at 108 μs time.

2. Numerical Simulation

The numerical simulation uses LS DYNA 2D code,[14] in axisymmetrically modeled (cylinders are modeled by spheres), and validated by three-dimensional computations. The computation consists of the propagation of shock waves induced by bullet impact and pressures generated in the propellant cylinder. Figure 11 shows an example of these computations. The first impact is not energetic enough (pressure, duration) to directly initiate the nitramite propellants in a shock-to-detonation transition (SDT) detonation mechanism, but a succession of compression and tension waves propagate, are refracted (Figs. 11a and 11b) on the inner surfaces of the grain, and focus in the rear part of the cylinder. The computed negative pressures are important (−25 MPa in this case), and function to damage the material. The properties of the damaged material are significantly different than those of the original material and may be represented better by a finely divided propellant than by a compact grain. In this divided state material becomes very sensitive to shock stimuli, and the second impact of the bullet on the opposite side of the center annulus may be energetic enough to initiate a detonation (Fig. 11b).[15,16] Figure 11c shows a three-dimensional computation that simulates the exact geometry of the test item. As in two-dimensional computation the waves focus at the rear part, with levels of damage similar to these computed in two-dimensional simulation. Other computations made with a compact grain without a bore have shown that focusing of the waves is impossible, and that the levels of stress are very low and unable to damage the propellant.

IV. Extruded Double-Base (EDB) Propellants

These old, inexpensive propellants, continue to be useful in certain applications such as surface-to-air-missiles, antitank missiles, rockets, and runway penetration bombs. Because they use nitroglycerine as the energetic plasticizer, it is assumed they cannot meet all future requirements of IM. Thus, SNPE has developed SD 1175 propellant with a low-sensitivity nitrate ester plasticizer. But because future regulations will prohibit the use of lead ingredients as combustion modifiers in SD 1175, new derived compositions that combine insensitivity and low toxicity have been evaluated. The properties of these new compositions are compared with the NOSIH AA2, taken as a reference and manufactured at SNPE.[17]

A. SD 1175 Characteristics

1. Formulation

Formulations of propellants manufactured by conventional processes are reported in Table 17 along with their energetic

Table 17 Insensitive extruded double-base propellants, compositions and energetic properties (AA2 is taken as a reference)

Ingredient, %	NOSIH AA2	SD 1175	SD 1178
NC[a] + NG[b]	89.6	——	——
NC + TMETN	——	92.7	——
NC + TMETN + TEGDN	——	——	94.4
Stabilizer	2	1.8	——
Plasticizers	4.3	1.8	1.5
LC 12-15	4	——	——
Salt n° 1[c]	——	1.8	——
Lead-free modifier	——	——	3
Additive	——	1.8	1
Wax	0.1	0.1	0.1
Properties			
Flame temperature, K	2590	2576	2450
Heat of explosion, cal/g	1000	960	920
Density, g/cm^3	1.60	1.56	1.57

[a]Nitrocellulose. [b]Nitroglycerine. [c]Specific SNPE burn rate modifier.

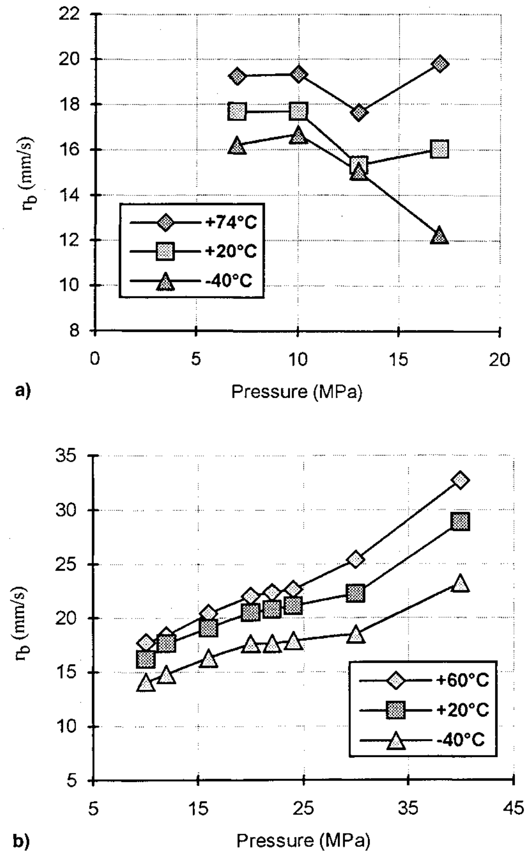


Fig. 12 Burning rate of AA2 and SD 1175 vs pressure (standard motor): a) NOSIH AA2 and b) SD 1175.

characteristics. They could also be manufactured by a continuous twin-extrusion process.

The compositions differ mainly in the plasticizer: nitroglycerine for AA2 vs the lower sensitivity TMETN and TEGDN for SD 1175 and SD 1178; ballistic modifiers: double salt of lead copper for AA2 vs n° 1 in SD 1175. This modifier is specially produced at SNPE to achieve a mesa (plateau) effect over a wide pressure range and to reduce the temperature sensitivity (Fig. 12).

2. Hazard Classification and Vulnerability

After the U.S. TB 700-2 tests were performed on SD 1175, it was classified as DOD Division 1.3 (Table 18).

3. IM Tests Results

The tests of MIL-STD 2105 A (except for the shaped charge jet and the spall tests) were performed on 2.75 rocket motors, using lightly confining aluminium alloy cases. All results are satisfactory (Table 19).

B. SD 1178: A New Insensitive and Nontoxic Propellant

Lead-based compounds have been utilized in SD 1175 propellant to obtain desirable ballistic behavior. The conventional effect in double-base propellants is commonly referred to as mesa or plateau burning. The use of lead salts in any amount is objectionable due to health hazards caused by lead oxides in the exhaust gas and the risk of contaminating workers during manufacture. Because environmental regulations are being strengthened, SNPE is developing new lead-free extruded double-base propellants.

1. Propellant Formulation

Starting with SD 1175, a new propellant that uses lead-free ballistic modifiers, has been developed. The propellant (Table 17) uses a mixture of trimethylolethane trinitrate (TMETN) and triethyleneglycoldinitrate (TEGDN), relatively insensitive energetic plasticizers compared to nitroglycerin and also of lower performance. The propellant takes into account various requirements: 1) compliance with U.S. IM requirements (TB 700 2 and MIL-STD 2105), 2) compliance with environmental regulations, and 3) reproduction of performance of conventional U.S. propellants (NOSIH AA2 as a reference).

Table 18 U.S. TB 700-2 tests: hazard classification of SD 1175 and SD 1178, DOD division 1.3

Tests	SD 1175	SD 1178
Thermal stability	Stable	Stable
Ignition and unconfined burning test	Combustion	Combustion
Impact sensitivity	No reaction	No reaction
Detonation tests	No detc nation	No detonation
Card gap test	50 cards	53 cards

Table 19 SD 1175, results in immunity tests

Hazard tests	Requirements reaction	SD 1175 reaction
SCO	Burning	Burning
FCO	Burning	Burning
Fragment impact	Burning	Burning
Three bullet impacts	Burning	Fragmentation
Sympathetic detonation	No propagation	No propagation

Table 20 Mechanical properties of new insensitive EDB propellants

Propellant	T, °C	S_m, MPa	e_m, %
SD 1175	−40	24	2
	+20	4	26
	−60	1.2	22
NOSIH AA2	−40	44	4.4
	+20	11	31
	−60	1.7	28
SD 1178	−40	38	2.6
	+20	5	38
	−60	0.9	28

Table 21 EDB propellants, thermochemical properties

EDB	Heat of explosion ΔH, cal/g	Stabilizer consumption time at 80°C 50%	100%
SD 1175	960	31 days	85 days
NOSIH AA2	1000	13 days	34 days
SD 1178	920	18 days	50 days

2. Propellant Characteristics

Characteristics are reported in Tables 20 and 21 and Fig. 13.

Note the following:

1) Mechanical properties are similar to those of conventional propellants.

2) The use of lead-free catalysts makes it possible to achieve an extended mesa effect.

3) Aging estimated by the consumption of the stabilizer in accelerated tests is very promising and is significantly improved with SD 1175 and SD 1178.

3. Hazard Classification

As with the SD 1175 composition, the hazard classification of SD 1178 is DOD division 1.3 (Table 18).

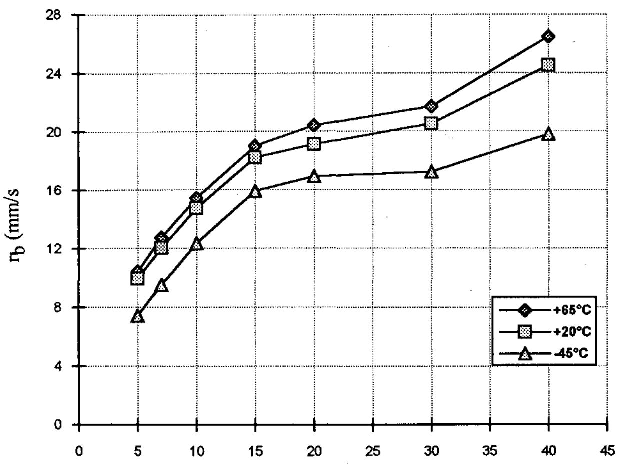


Fig. 13 Burning rate of SD 1178 vs pressure (standard motor).

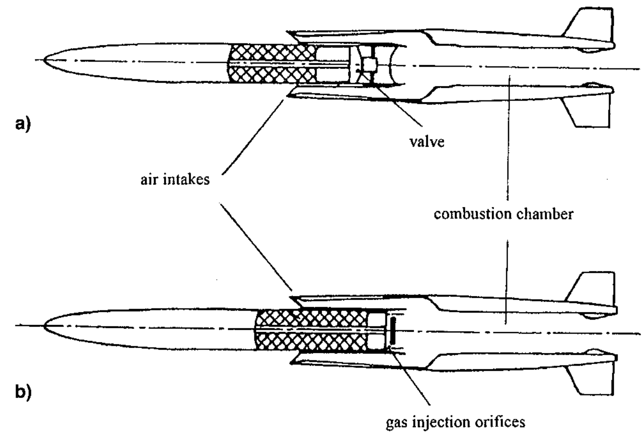


Fig. 14 Two concepts of ducted rockets: a) with a separated gas generator (choked) and b) with an integrated gas generator (unchoked).

No determination has yet been made on this composition in IM tests. However, because it is derived directly from SD 1175 by means of low sensitive plasticizer, a desirable behavior may be assumed, e.g., results of card gap test are very promising.

V. Fuel-Rich Propellants for Gas Generators

For more than 20 years, SNPE has been developing specific propellant compositions to meet the requirements of gas generators for ducted rocket applications.

Two configurations (Fig. 14) are generally used for ducted rockets, one with a choked gas generator, the other with an unchoked gas generator.[18] In the choked gas-generator configuration, the fuel-rich grain is located upstream from the ram burner and the grain operating pressure is controlled by one or more nozzles. In the unchoked gas-generator concept, the grain is situated in the fore-end of the combustion chamber of the ramjet, before the junction of the air inlets in the ram burner. There is no choked orifice between the two chambers; the operating pressure of the gas generator is near that of the ram burner, which depends on the velocity and altitude of the missile.

All the formulations have a main common feature: their combustion must deliver gaseous or solid particles species that are injected into a combustion chamber to ignite and burn with incoming air. For this purpose, the gas-generator products must be as reducing as possible. Therefore, the propellant composition contains a low amount of oxidizer, just enough to sustain pyrolysis or combustion and ensure suitable combustion characteristics: burning rate, pressure exponent, temperature sensitivity, high combustion efficiency, and low combustion residue. For these reasons, basic components of the compositions contain a limited amount of AP (<50%) and polybutadiene binder, and consequently are expected to have attractive safety and immunity properties.[19]

A. Propellant Characteristics: Energetic Properties

Since the energetic properties of the motor are driven by the reducing characteristics of the exhaust gas of the generator and their high heating value, high contents of species such as boron, magnesium, and carbon are suitable.

Figure 15 shows the computed volumetric specific impulse of compositions manufactured at SNPE as a function of equivalence ratio ϕ, which is the quotient of the ratio of the mass flow rate of fuel and air vs the same ratio in stoichiometric conditions. This diagram illustrates the high volumetric specific impulse achievable with ducted rocket motors, mainly in low ϕ (≤ 1) operational range. As can be seen, boron propellants appear to be the most attractive,[20,21] but their use is

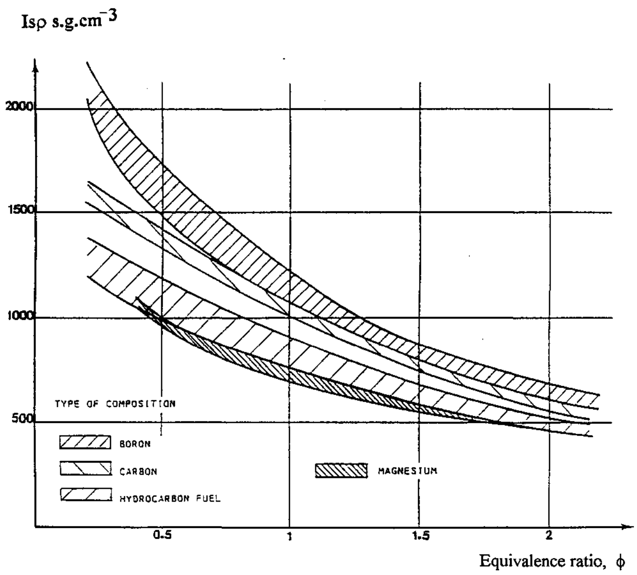


Fig. 15 Energetic performance of gas-generator compositions for ducted rocket: theoretical computations in standard conditions.

limited to applications where low-signature is not required due to the presence of solid B_2O_3 in the exhaust products. When low-signature requirements are specified, the best choice in terms of energetic properties is carbon-filled propellants. Their use is yet limited: high combustion efficiency in the combustion chamber needs a high pressure and a low Mach number, which are incompatible in some applications. Progress in this area is underway. Today, the best choice for low-signature-requirement applications is hydrocarbon fuel compositions, even if they are less energetic. Note that their performance satisfies current potential applications such as air–air or air–surface missiles. These compositions exhibit attractive combustion properties: high combustion efficiency due to absence of solid particles and wide range of adjustable combustion characteristics. They have been used in flight demonstration in MPSR (Missile Probatoire à Statofusée Rustique). The less attractive formulations, magnesium-filled compositions, are not discussed here.

B. Propellant Compositions

Three types of propellants are presented: 1) AEROLITE = hydrocarbon fuel rich propellants, 2) AEROLEBE = boron-rich propellants, and 3) AEROLEGUE = carbon-filled propellants. Representative formulations of the three types are reported in Table 22. Note the low content of oxidizer and the presence of additives required for high combustion efficiency.

C. Mechanical Properties

Because they use a high content of polybutadiene binder, all of these compositions display very good mechanical properties in an extended range of temperature and can be used in case-bonded grains.

D. Ballistic Properties (Table 23)

The extended range of the burning rate covered by these compositions is related to the motor configurations. The combustion at low pressure in the combustion chamber for an integrated gas generator ($p < 1$ MPa) and the grain designs (perforated grain or end-burning grain) require adapted burning rates. For example, boron Aerolebe "a" is adapted to a separated gas generator with an end-burning grain design, and Aerolite is perfectly adapted to a perforated case-bonded grain in an integrated gas generator. It must be noticed that the absence of residue in boron and carbon compositions requires high burning rates.

E. Safety and Immunity Characteristics

These propellants are very safe because of the low content of oxidizer, the high level of polybutadiene binder, and the choice of AP. As composite propellants they generally cannot detonate (no explosive, low content of AP). The response to thermal stimuli is such that a slow cook off has been demonstrated to be mild (Table 24). In the SNPE test 41, these propellants are similar to composite propellants with a critical temperature that is relatively low for boron and carbon-filled propellants. However, the reaction is always a mild reaction of combustion. It may be assumed that similar behavior will occur even in steel-cased motors, particularly with Aerolite propellant, which has a very low burning rate.

Finally, the behavior in IM tests of a ducted rocket motor depends mainly on the high burning rate propellant used as a booster. Today the best choice appears to be the Butacene-based propellants presented previously.

Table 22 Formulation and energetic characteristics of gas-generator propellants

Composition	Aerolite	Aerolebe	Aerolegue
Binder, %	52	30	43
AP, %	38	30	30
Boron, %	—	35	—
Carbon, %	—	—	29
Additives, %	10	5	8
Density, $g \cdot cm^{-3}$	1.267	1.62	1.44
$Is \times \rho$,[a] $s \cdot g \cdot cm^{-3}$	1190	1860	1430

[a]Calculated for a standard generic motor.

Table 23 Combustion characteristics of gas-generator compositions obtained in a generic motor

Propellant	Aerolite	Aerolebe a	Aerolebe b	Aerolegue
Burning rate, mm/s	2.16	14	12	17
Pressure, MPa	0.86	5	0.6	5
Pressure exponent	0.6	0.1	0.3	0.2
Temperature sensitivity, % °C^{-1}	0.15	—	—	—
Residue in gas generator, %	0	0	0	0

Table 24 Results of immunity tests on gas-generator propellants

Propellant	Aerolite	Aerolebe	Aerolegue
Bullet impact test	No reaction	No data	No data
SNPE test 41: reaction	Combustion	Combustion	Combustion
Cook off critical temperature, °C	116	176	143

VI. Conclusions

The results obtained with the new propellants presented in this article show that significant progress has been made in reducing the sensitivities of current types of solid propellants. If lightly confining cases are used, it can be assumed that MURAT** and MURAT*** motors could be designed with SD 1175, SD 1178, gas-generator compositions, and high burning rate Butacene-based propellants without significant loss of other characteristics of current basic propellants. Nevertheless, some problems may be encountered with motors using highly confining cases (e.g., high modulus steel cases) when exposed to FCO or bullet impact threats. The high-burst pressure of these motors may have violent effects such as projections of fragments incompatible with high MURAT levels.

Nitramite, with a formulation based on nitramine fillers and nitrate ester plasticizers are not able to meet the requirements of MURAT*** motors without drastic losses in energetic performance. However, MURAT** motors are possible with a slight reduction in volumetric impulse for the new formulations using reduced amounts of sensitive ingredients. To achieve the MURAT*** level in the future and reduce the ability of these compositions to detonate (useful for low signature motors), new ingredients with greater energy and less sensitivity are required. Chemists around the world have already synthesized new and attractive molecules. We have already seen a new polymer (GAP), and can mention the following:

Fillers: HNIW or CL-20, hexanitrohexaazaisowurtzitane; HNF, hydrazinium nitroformate; and ADN, ammonium dinitramide.

Binders: PolyNIMMO, polynitrato methyl methyloxetane and Polyglyn, polyglycidyl nitrate.

The theoretical energetic performance achievable with formulations of solid propellants using these new ingredients is very high with gains of 5–10% possible. What is difficult to predict is the safety and hazard properties of future formulations. A predictive theory does not exist, and the only way to assess these properties is by experimentation.

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