

Innovative Solid Formulations for Rocket Propulsion

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Abstract

Solid rocket propulsion enjoys several unique properties favoring its use in space exploration and military missions still for decades to come, in spite of being by far the most mature propulsion technology among those currently employed. Yet, solid rocket propellants also suffer a limited performance in terms of gravimetric specific impulse. Although many high-energy density materials have been identified, most of them are far from being practically usable in the short range due to a variety of severe difficulties, including cost considerations. Presently, no integrated vehicle designs make use of these potential propellant ingredients and formulations. Work is continuing worldwide and a broad overview will be discussed in this paper based on a joint international editorial effort just completed. After a quick historical survey, the current situation in terms of advanced solid oxidizers, metal fuels, and binder systems is scrutinized. Particular attention is paid to Ammonium Dinitramide (ADN)-based formulations to overcome the limitations of the currently used ones based on Ammonium Perchlorate (AP). The latter imply not only a limited gravimetric specific impulse but also a negative impact on the environment because of copious emissions of hydrochloric acid (HCl) as well as personal health because of perchlorate competition with iodide in entering the thyroid gland. Based on recent experimental investigations, due to its intrinsic ballistic properties, it turns out that ADN-based dual-oxidizer systems with Al-based dual-metal fuels and inert or energetic binders are promising solutions for a variety of solid rocket propulsion aiming respectively at minimizing environmental impact (ADN + Ammonium Nitrate AN) or maximizing performance (ADN + AP). Yet, a lot of work remains to be done in order to upgrade these formulations to industrial applications. In particular, adequate analyses of manufacture, mechanical, and hazard properties are required.

1. Introduction

Solid rocket propulsion enjoys the unique property of providing a very large thrust with relatively small volume and contained costs. Solid propellants additionally offer the advantages of large density, well extended storage time, and immediate readiness. However, solid propellants overall suffer a limited performance in terms of gravimetric specific impulse I_s . In addition, the composite solid propellant formulations based on AP, currently the most used ones in conjunction with Hydroxyl-Terminated PolyButadiene (HTPB) especially for space exploration missions, also suffer a negative impact on the environment and personal health be-

cause of copious HCl emissions from the exhausts combustion products. Further difficulties stem from the disposal of AP-based energetic materials for all sorts of military applications. More in general, the endless quest for better and better propulsive systems prompts for higher performance levels (in terms of I_s and density ρ) while maintaining acceptable mechanical properties, aging characteristics, cost, processability, hazards, storage, and environmental respect. In particular, new solid rocket formulations should have properties similar or superior to those of the current AP/Al/HTPB-based systems. In addition, for military applications, new formulations are sought which are smokeless, low-signature, and environmentally friendly.

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In this respect, a variety of new ingredients is under examination as possible candidates for industrial applications at several advanced laboratories. Although many high-energy density materials have been identified to overcome the above shortcomings, most of them are far from being practically usable in the short range due to a variety of severe difficulties in large scale manufacture, ground processing, personnel safety at different stages, handling and transportation safety, shock sensitivity, prolonged storage, and cost considerations. Work is continuing every day at worldwide level, but presently no integrated vehicle designs make use of these potential radically new propellant ingredients and formulations.

A broad overview of today's situation will be presented in this paper based on a joint international editorial effort just completed [1]. After a quick historical survey, several promising modern ingredients in terms of solid oxidizers, metal fuels, and binder systems are scrutinized. Among the oxidizers, particular attention is paid to ADN-based systems to advance the current state-of-the-art in solid propellant formulations. However, the intrinsic properties of ADN (physical, chemical, mechanical, ballistic, and so on) are far from the ideal values desired for applications of solid rocket propulsion especially in space exploration. It turns out that a dual-oxidizer system, such as ADN+AN or ADN+AP, with dual-metal fuels and inert or energetic binders are preferable solutions for a variety of solid rocket propulsion. The first type of formulation being more prone to minimum environmental impact (green oxidizer with no HCl production, at the cost of somewhat reduced I_s value), the second one to maximum mission performance (enhanced I_s at the cost of some HCl production).

Thus, new compositions should basically include ADN with the possible support of two more well-known ammonium salts: AP and AN. By properly combining these three inorganic oxidizers, a wide range of interesting applications beyond the current limitations appear feasible. Performance of the investigated composite solid rocket propellants under test will be discussed. Outcomes so far obtained in terms of compound density, ideal thermochemistry, and steady combustion rates will be illustrated. Recommendations about future work needed to overcome some ballistic difficulties faced for space exploration missions will complete the paper. For most configurations, only laboratory level testing is discussed. For motor applications, full-scale ballistic testing is needed to assure a complete mastering of the process. Moreover, adequate analyses of manufacture, mechanical, ageing, and hazard properties are required.

2. A Timeline of Solid Rocket Propellants Development

For centuries, rudimental forms of solid rocket propulsion were based on the use of black powder, following the fortuitous alchemist activities in China dating as early as ca 220 BC. Actually, there is no conclusive evidence of "black powder" in China and probably this historical invention was rather a mixture based on nitrates, which Chinese used in pyrotechnic devices, arrow throwers, and rockets. The real invention of black powder is shrouded in mystery, according to PengFei Li [1, Ch. 42]. Important advances were made in Europe, introducing nitrocellulose (NC)-based smokeless propellants, only in the years 1863-1888. Further decisive advances were made in the USA, introducing castable composite propellants in the framework of the Guggenheim Aeronautical Laboratory at California Institute of Technology (GALCIT) project dedicated to Jet Assisted Take Off (JATO) rockets. This program was directed by Theodore Von Karman and included other prominent figures such as Martin Summerfield, Frank Malina, and Jack (John) Parsons. In June 1942 Parsons, a self-educated and very eccentric but also imaginative chemist, combining an organic matrix (asphalt) with a crystalline inorganic oxidizer (Potassium Perchlorate KP) succeeded in making the first castable composite solid propellant. Just at the end of the GALCIT project, Parsons also occasionally employed AP as crystalline inorganic oxidizer, instead of KP, in order to reduce smoke emission. Systematic testing of AP was later conducted by Aerojet Engineering Corporation (now Aerojet Rocketdyne) starting in 1948 [2].

In addition to composite solid propellants, the GALCIT project also covered liquid propellants and the first studies of Solid Rocket Motor (SRM) interior ballistics, combustion, ignition, and related structural-materials issues. Composite propellants eventually replaced Double-Base (DB) propellants, based on mixtures of NC and Nitroglycerine NG, in most rocket applications. The GALCIT project was the start of modern solid propellant formulations, while a theoretical paper on homogeneous propellant ignition by Zel'dovich in 1942 was the start of nonsteady burning analyses. Thus, for quite different reasons, the birth of modern solid rocket propulsion was almost contemporary in USA and Russia [1, Ch. 42].

Following the breakthrough by Parsons in 1942, composite solid propellants were actively developed in the USA but along a range of different and, sometimes, overlapping directions. Asphalt as fuel binder was replaced by synthetic polymers

by 1950, KP as crystalline inorganic oxidizer was replaced by first AN and then AP by 1960, Al as high-energy fuel was added starting at Atlantic Research Corporation (ARC) around 1955 [1, Ch. 8]. The USA, Russia and all other important worldwide players in rocket propulsion for years followed the liquid propulsion philosophy, impressed by the German V2 success. A strong impulse in favor of composite solid propellants came only in 1956, when the US Navy decided to design a vehicle (Polaris) based on a SRM, instead of another Liquid Rocket Engine (LRE), to replace the Jupiter Intermediate-Range Ballistic Missile (IRBM). This new project focused major efforts in one specific direction and finally the basic formulation AP/inert binder/Al was mastered. This workhorse formulation became operational first with Polaris A1 (1960), Sergeant (1962), and Minuteman (first stages, 1962) and still today is used by most solid propellant space launchers.

As shown in Fig. 1, taken from [1, Ch. 42], the gravimetric specific impulse I_s increased from about 80 to 180 s moving from black powder to the KP + organic binder composite formulations invented by Parson, further raising to 215 s for composite formulations based on AP + synthetic binders. The introduction of micron-sized Al (μ Al) allowed another increase of 15% I_s and 3% density, brought about a sensible mitigation of high-frequency combustion instabilities but also caused the emission of copious white alumina smoke. Studies of the most suitable inert fuel binder continued for many years and is not yet concluded. Gradually replacing the carboxylated PolyButadiene Acrylic Acid (PBAA), PolyButadiene AcryloNitrile (PBAN), and Carboxyl-Terminated PolyButadiene (CTPB), currently the most successful product is the hydroxylated HTPB. This binder was first tested in flight in 1970.

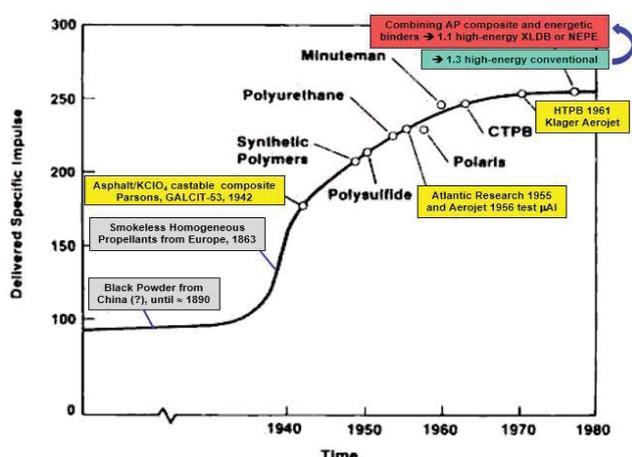


Fig. 1. Delivered gravimetric specific impulse vs. time according to Umholtz [2].

The next step was the introduction of energetic ingredients, such as NC/NG binder for Polaris A2 (1962), Cyclotetramethylenetetranitramine (High Melting eXplosive, HMX) as an oxidizer additive (in partial replacement of AP) for Polaris A3 (1964), and both NC/NG and HMX for Minuteman (3rd stage, 1962). This allowed a further increase of I_s to 2707–275 s and also of density, but still with primary and secondary smoke (Al_2O_3 , HCl). By employing high energy additives and reducing Al and AP, minimum smoke composite propellants for tactical missiles can achieve $I_s = 245–250$ s.

Other important improvements were carried out by the introduction of burning rate catalysts; bonding agents improving the propellant's mechanical properties as well as its resistance to ageing, humidity, and temperature cycling; metal deactivators for improved pot life; acoustic stabilizers for improved oscillatory ballistic behavior; antioxidants; dispersants; opacifiers and so on; for details, see contribution by Manzara in [1, Ch. 1].

The need for more volume-efficient propellant for the launch of ICBM's from submarines (US Navy) or silos (US Air Force) was the strongest driver for advancing solid propellant formulations. But this push toward more and more performance seems now at its end, as shown by the flattening curve of delivered I_s during the last decades; see Fig. 1.

Overall, the development of solid propellants can be portrayed as in Fig. 2, taken from [1, Ch. 42]. Two main families can be distinguished essentially based on the kind of the organic binder system and this implies an important consequence in terms of classification hazards, in turn a discriminating factor for applications. Cross-linked double-base (XLDB) propellants using energetic binders or at least plasticizers generally belong to class 1.1 hazards, while conventional composite propellants using inert binders belong to class 1.3 hazards. High-energy conventional composite solid rocket formulations typically resort to highly metalized AP/HTPB/Al propellants, but performance can further be augmented by adding nitramines. High-energy XLDB solid rocket formulations achieve the max I_s by using energetic instead of inert ingredients for the binder and/or plasticizer and partially replacing AP with HMX. High-energy XLDB formulations in a way represent a combination [3] of the historical class of homogeneous formulations used as gun propellants and the castable heterogeneous formulations first devised by Parsons. Yet, definitions are somewhat loosely applied and the nomenclature is confusing. Despite some intrinsic differences, the various expressions Composite Modified Double-Base

(CMDB), XLDB, elastomer-modified cast double-base propellants (EMCDB), and Nitrate Ester Plasticized polyEther or Nitrate Ester PolyEther (NEPE) can be considered loosely equivalent.

For decades the development of solid rocket propulsion was mainly an American history. The Russians arrived late to the solid propellant arena, due to a more persistent preference for LRE, but they quickly recovered and their advances appear to have surpassed other technologies in this area. The combined use of ADN and AlH_3 in Russia, with inert or energetic binders, dates back many years, but it still is unparalleled in the Western world [1, see Ch.s 42, 43, 44, 45].

At least in the Western world, the state-of-the-art in solid propulsion for space exploration is represented by AP/HTPB/Al formulations. Advanced ingredients currently under study are discussed in [1]. Sinditskii [1, Ch. 3] focused his attention on high-nitrogen energetic materials. Among polynitrogen energetic materials, 1,2,4,5-tetrazine derivatives are of particular interest owing to their high density, thermostability, and remarkable insensitivity to electrostatic discharge, friction, and impact. High enthalpy of formation and good thermal stability of tetrazine cycle allow producing tetrazine-based energetic materials, which can be used as insensitive, thermostable, environmen-

tally friendly ingredient in a number of energetic material applications. Studies of combustion behavior show that most tetrazines are low-volatile substances with high surface temperatures, which determines a dominant role of the condensed phase in combustion of many tetrazine derivatives. The tetrazine cycle shows low reactivity in redox reactions, leading to rather moderate burning rates of its salts with oxidizing acids and coordination compounds despite high energetic characteristics.

According to Singh [1, Ch. 4], use of new powerful and green oxidizers like ADN and ammonium ozonide along with energetic binders like Glycidyl Azide Polymer (GAP), 3,3'-Bis(AzidoMethyl) Oxetane (BAMO) and BAMO-TetraHydroFuran (THF) copolymer can boost I_s above 320 s. Inclusion of energetic plasticizers like tetra azido malonate and tetra azido glutarate can further enhance I_s . Likewise, inclusion of nitrogen-rich compounds like nitro guanidinium azides, N8, N10, etc., can boost energy content further on the higher side. Addition of nano-sized metal powders and nano-sized metal hydrides is likely to enhance burning rates significantly. Thus, there is need to generate reliable exhaustive technical data on the utility of new eco-friendly materials reported recently to obtain unthinkable boost in energy and burning rates.

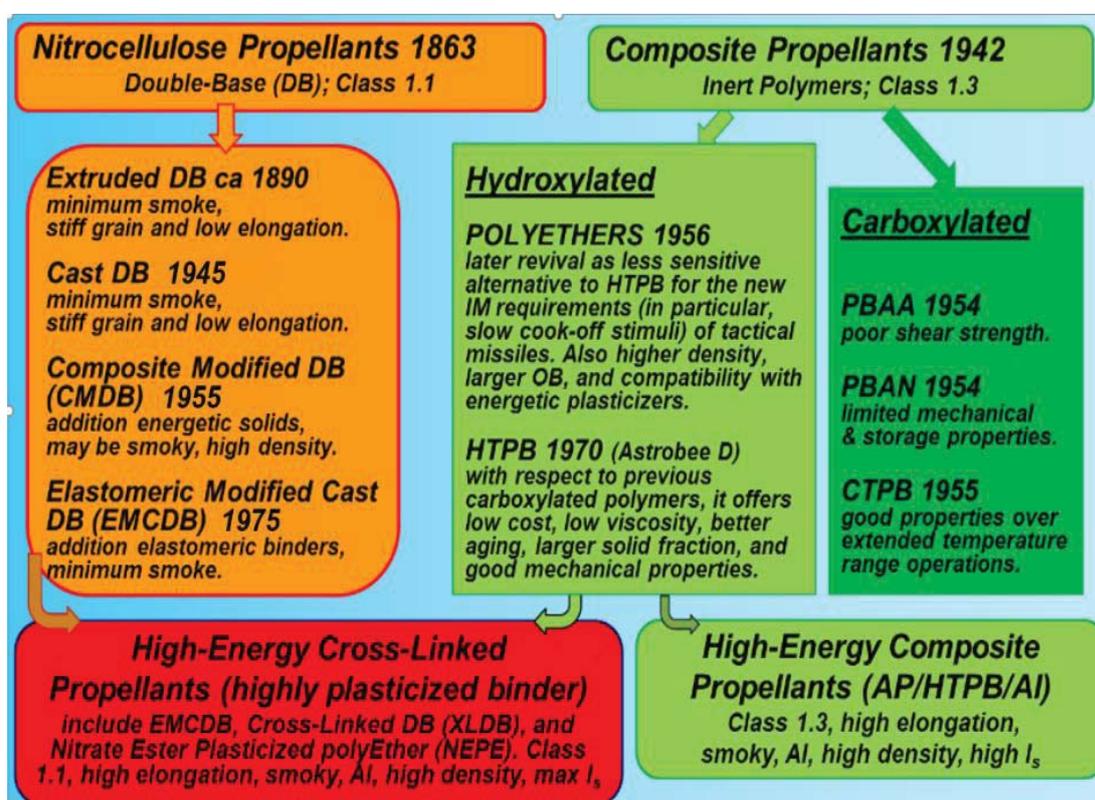


Fig. 2. Combining ingredients from composite and double-base propellants gives rise to high-energy cross-linked propellants with slightly superior performance but of class 1.1 with respect to the conventional high-energy composite propellants [3].

However, these new solid propellant ingredients and formulations have to upgrade from laboratory to industrial level. For example, the well-known technology of nano metal powders successful in many fields is not yet ready for rocket propulsion for a series of drawbacks including clustering of particles [1, Ch. 27 by Zare et al.], decreased active metal content, dependence on passivation technique, and increased viscosity of the propellant.

3. Advanced Solid Oxidizers for Rocket Propellants

The main target for advanced formulations is to identify a green and highly performing replacement for AP. The demands for this ideal solid oxidizer are chlorine-free, as low toxic as possible, thermally stable, compatible with the commonly used propellant ingredients, and a good aging behavior during in-service time [1, see Ch.s 1 by DeLuca et al., 30 by Cumming, 31 by Tunnell, 32 by Bohn and Cerri]. In this respect, new oxidizers were specifically studied in [1, Ch. 2 by Kettner and Klapötke] [1, Ch. 6 by Fan et al.].

Kettner and Klapötke [1, Ch. 2] recall that the quest for novel oxygen sources for chemical propulsion is the main focus for research groups active all around the world. In their systematic and long range investigation, the authors present four different molecule classes as backbones for diverse poly-nitro moieties. The resulting neutral compounds are discussed in detail concerning their properties as oxygen carriers in solid rocket propellants. They all show up advantages as well as disadvantages for the suitability in such applications. The fluorine-containing materials were proven to be inferior compared to their analogue trinitromethyl derivatives in terms of I_s , but they meet the requirements of high thermal stabilities and low sensitivities better than the trinitromethyl compounds.

Fan et al. [1, Ch. 6] characterized two new tetrazole salts, HydroxylAmmonium 2-DiNitroMethyl-5-NitroTetrazolate (HADNMNT) and diHydroxylAmmonium 5,5'-bisTetrazole-1,1'-diOlate (HATO). Theoretically, HADNMNT is a potential oxidizer to replace AP, Cyclotrimethylenetrinitramine (Research Department eXplosive, RDX), HMX, and CL-20 in composite propellants. Safety tests showed that HATO exhibits excellent thermal stability and low mechanical sensitivities. The compatibilities of HATO with HTPB, AP, RDX, and Al powder in vacuum stability tests were good. Results from comparative study of HATO and RDX as ingredient for composite propellants showed that HATO formulations offer the advantages of high burning rate and low mechanical sensitivities.

However, these and other promising suggestions are still far from flight applications. Today, possible candidates as primary oxidizers for solid rocket propulsion are mainly AN (Germany, 1659), AP (France, 1831), HNF (Hydrazinium Nitroformate, USA, 1968), ADN (Zelinsky Institute of Organic Chemistry, Moscow, Russia, 1971), and HNIW (2,4,6,8,10,12 – HexaNitro-2,4, 6,8,10,12 – HexaazalsoWurtzitane, commonly known as CL-20, China Lake, CA, USA, 1987). Moreover, RDX (Germany, 1899) and HMX (USA, first synthesized in 1930 and manufacture sensibly improved in 1943) are often used as secondary oxidizers in high-performance military propulsion missions. While AN and AP are well-known solid inorganic oxidizers and have been used at all levels for several decades, RDX and HMX are well-known solid organic explosives. On the opposite, HNF, ADN, and CL-20 are relatively new solid energetic materials characterized by high-energy content, chlorine-free formulation, and smokeless exhausts. All of them are in principle potential candidates to replace AP. At any rate, castable propellants demand reasonable viscosity and high solid fraction loading. In this respect, particles with minimum spatial extension are sought for, favoring a low aspect ratio and preferably a spherical shape.

Main features of the above solid oxidizers as monopropellants are listed in Table 1 [4]; T_f is the self-deflagration adiabatic temperature at 6.8 MPa. A note of caution: some data are affected by appreciable uncertainty and may be reported with disparate values in the literature. In order to assure consistency, when possible, one common reference was selected for the same property (for example, O_2 balance and T_f). A detailed and comparative experimental analysis of ballistic properties of all (except AN) mentioned oxidizers – as monopropellants – was performed, under strand burner conditions, by Atwood et al. [5]. For ADN the self-deflagration rate is the highest, as shown in Fig. 3 (AN, not reported, would be the slowest), while its initial temperature sensitivity is higher than that of AP for most of the commonly used pressure range (say, 0.1–7.0 MPa for space launchers). In addition, “burning rates of ADN-based propellants are characterized by an inverse relationship with oxidizer dispersity, as compared to the AP-based ones”. This remark was first stated by Pak [6], and later generically confirmed by several authors.

HNF is ruled out as AP replacement because of compatibility problems with ingredients and a decomposition behavior difficult to stabilize [7]. Ballistic tests of HNF-based solid propellants have often revealed an exceedingly large pressure dependence (with the pressure exponents near one),

Table 1
Properties of current solid propellant oxidizers from various sources [4]

Denomination	Chemical Formula	Oxygen % content/balance	Molar mass M , g/mole	Density ρ , g/cm ³	ΔH_f kJ/mole	T_f K	Cost	Environment Impact
Ammonium Dinitramide (ADN)	$\text{NH}_4\text{N}(\text{NO}_2)_2$	51.6 / +25.8	124.1	1.81	-134.6	2051	–	+ (HNO)
Ammonium Nitrate (AN)	NH_4NO_3	60.0 / +20.0	80.0	1.73	-365.7	1247	+	+ (HNO)
Ammonium Perchlorate (AP)	NH_4ClO_4	54.5 / +34.0	117.5	1.95	-295.8	1406	=	– (ClHNO)
CL-20 or HNIW ^a	$(\text{NNO}_2)_6(\text{CH})_6$	43.8 / -10.9	438.2	2.04	+454.0	3591	– –	= (CHNO)
Tetranitramine ^b (HMX)	$\text{C}_4\text{H}_8\text{N}_4(\text{NO}_2)_4$	43.2 / -21.6	296.2	1.90	+75.0	3278	≈	= (CHNO)
Hydrazinium Nitroformate (HNF)	$\text{N}_2\text{H}_4\text{HC}(\text{NO}_2)_3$	52.4 / +25.0	183.0	1.86	-72.0	3082	Nap	= (CHNO)
Trinitramine ^c (RDX)	$\text{C}_3\text{H}_6\text{N}_3(\text{NO}_2)_3$	43.2 / -21.6	222.1	1.82	+61.5	3286	≈	= (CHNO)

= is the reference value; ≈ about equal to reference; – less good than reference; + better than reference (qualitative scale).
^a full name is 2,4,6,8,10,12-Hexanitro-2,4, 6,8,10,12-Hexaazaisowurtzitane; ^b full name is cyclotrimethylenetrinitramine, also called Hexogen; ^c full name is cyclotetramethylenetrinitramine, also called Octogen.

or severe incompatibilities when the pressure exponent could be reduced to a more desirable values, say below 0.6, by burning rate modifiers [8]. Comparative sandwich burning tests [9] revealed, in the case of HTPB inert binder, lack of combustion and thus protruding of the binder above the burning surface, resulting in low burning rates and pressure exponents > 1 . In the case of GAP active binder, a smooth combustion process was evidenced resulting in large burning rates with a reasonable pressure exponent (0.59), with no sensible effect of the particle size. In Europe, HNF was actively produced in the Netherlands; today, mainly India and China continue efforts.

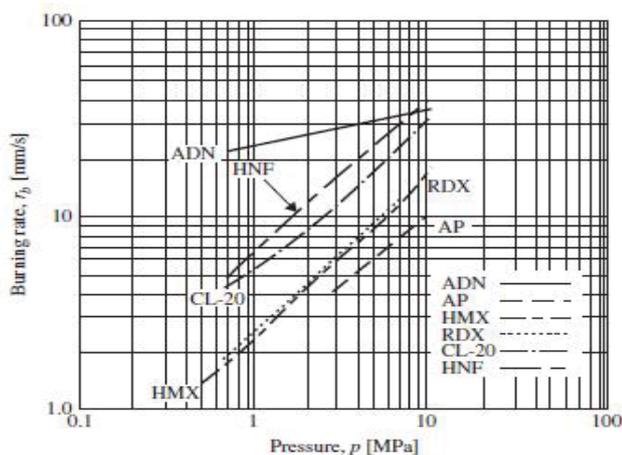


Fig. 3. Steady burning rates of different oxidizers burning as monopropellants at standard initial temperature, showing large burning rates and low pressure sensitivity of ADN [5].

CL-20 is the highest energy as well as the highest density compound known among organic chemicals, albeit some concerns exist about its susceptibility to impact and friction [1, Ch. 29 by Simakova and Parmon]. The concept of a caged nitramine based on amine/glyoxal chemistry was proposed in 1970s resulting later in the development of a number of alternative routes to synthesize CL-20. All known methods are based on the same starting material, HexaBenzylhexaazaIsoWurtzitane (HBIW). But conversion of HBIW directly to CL-20 is a major challenge. A rather low yield of HNIW and high costs of the implemented NO_2BF_4 and NOBF_4 catalysts require improvements of the HNIW synthesis method. Based on the current extensive research, a two-step HBIW debenylation with a separately repeated use of the catalyst in each catalytic stage is considered as a promising way to increase catalyst productivity and to reduce CL-20 production costs. CL-20 is manufactured in the ϵ crystal phase (highest density) by Thiokol in USA and SNPE, now Eurenco, in France; manufacturing is also available in Russia, India, and China.

RDX and HMX are not employed as monopropellants in rocket propulsion because of their explosive nature. But their use as co-oxidizers in high-performance systems is widespread. Several examples of synergistic effect in solid rocket propulsion are discussed in [1, Ch. 13 by Babuk] [1, Ch. 15 by Pivkina et al.] [1, Ch. 16 by Rashkovskiy et al.] [1, Ch. 17 by Pang et al.].

In principle, the main shortcomings of the currently used AP-based composite propellant formulations can be overcome by replacing AP with more energetic and chlorine-free solid oxidizers. In this respect, among the substituted solid oxidizers proposed and tested worldwide at least at laboratory level, based on a large body of experimental testing, use of RDX, HMX, HNF, and CL-20 as main oxidizers for space exploration missions is not recommended for safety and also performance reasons. In particular, it is recommended to put aside HNF because too hazardous, while HNIW or CL-20 still appears way too expensive and maybe hazardous as well for large-scale industrial applications with respect to other candidates. The remaining candidate oxidizers are the ever green AN, the ubiquitous AP, and the promising ADN. AP is in many other ways an excellent solid oxidizer (considered a “miracle of nature” by propellant chemists) and still today is by far the most commonly used one for space exploration missions.

AN is a low-cost green oxidizer much used in a wide range of applications, but one should always bear in mind that mainly its Phase-Stabilized version (PSAN) is viable for practical applications, due to a series of crystalline transitions near ambient temperatures. Due to its overall unfavorable ballistic properties (hygroscopic, high Pressure Deflagration Limit (PDL), low burning rate which is little affected by particle size but strongly sensitive to pressure and initial temperature), AN is mainly used in gas generators (low flame temperature). Being totally gasifiable and nonpolluting, AN is also valued as a (co-)oxidizer but requires phase stabilization.

Comparing the main features of the mentioned monopropellants shows that ADN ideal gravimetric specific impulse neatly overcomes that of AN and AP, while being roughly similar to that of HNF and CL-20, see Fig. 4 taken from [10]. The density of ADN (1.81 g/cm^3) is less than that of all other common oxidizers except AN (1.73 g/cm^3). Systematic analyses were performed by several researchers to understand the complex ADN combustion process. Detailed investigations of pure ADN flame structure, in particular by Sinditskii et al. [11, 12], show that three extended and essentially gaseous zones (like for DB) follow the melt layer floating over the burning surface (like for AN). Thus, ADN flame is not tightly anchored to the burning surface as for AP. This implies a complex multistep heat release mechanism whose role and interplay mainly depend on pressure.

Systematic studies about the aging of ADN containing formulations were conducted by Bohn and Cerri [1, Ch. 32]. Several ADN-based solid

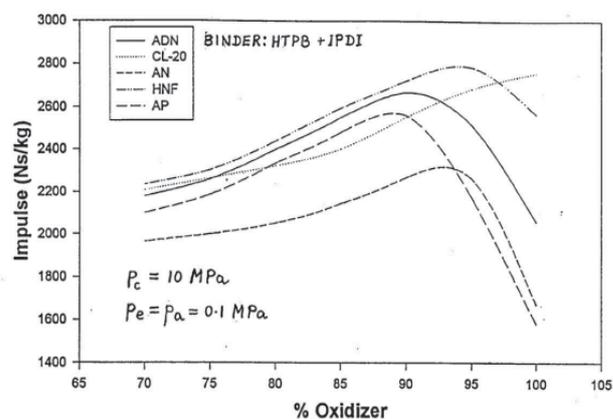


Fig. 4. Variations of ideal gravimetric impulse of HTPB+IPDI binder with various oxidizers and their mass percentages [10].

rocket propellants were tested including different prepolymers (GAP, Desmophen® D2200), curing agents (Bis-Propargyl Succinate BPS, Desmodur® N3400), and filler types (Al, HMX). AP-based formulations were also manufactured for comparisons. The glass-rubber transition temperature was found systematically lower with the AP formulations compared to the ADN formulations. The Desmophen®-based propellant formulations were subjected to an extensive aging program. The aging temperature range was between 60 and 85 °C with aging times adjusted to a thermal equivalent load of 15 years at 25 °C. Whereas the AP-based materials did not change by aging, the ADN-based ones showed significant degradation effects.

ADN, as a monopropellant, features high burning rates and fair pressure sensitivities, low signature, and full environmental respect. ADN also possesses a number of unique physical and chemical properties as compared to other solid oxidizers, such as high condensed phase heat capacity of 0.59 cal/g/K , low surface temperatures, and PDL around 0.2 MPa . But the observed high burning rate may be a drawback for space exploration applications. Moreover, the needle shaped ADN crystals hinder manufacture of propellant samples combining suitable ballistic performance and good mechanical properties. In Europe, manufacture of ADN was licensed by FOI to Eurenco Bofors in Sweden in 1996. Production of ADN prills from needle shaped crystals was developed at FOI (by spraying molten ADN through a nozzle) and ICT in Germany (by an emulsion method) [4].

4. Formulation and Testing of ADN-based Solid Rocket Propellants

In conjunction with oxidizers, metals are the favorite ingredient to impart energy to solid rocket propellants. Important properties of relevant

metals (Al, B, Mg, Zr) and of their most common oxides are summarized in Table 2, taken from [1, Ch. 8]. The volumetric heat release is maximum for B, followed by Al and Zr; while the gravimetric heat release is maximum for B, followed by Al and Mg. The metal melting temperature is much less than that of the corresponding oxide for Al and Mg, while the opposite is true for B. The peculiar properties of B hamper its efficient combustion and nozzle expansion. The interest for Zr in propulsion applications is explained by its large value of density (6.52 g/cm^3), making possible remarkable ΔV increments of the vehicle velocity. The density of all other commonly employed metalized fuels is much less, including AlH_3 (1.477 g/cm^3) not reported in the table. The α crystal phase of AlH_3 can be very stable in time, compatible with most ingredients of common use, conducive to superior ballistic properties, and prone to excellent performance of solid rocket motor upper stages. However, stabilization of α - AlH_3 is an essential pre-requisite to practical applications. As of today, the proper stabilization technique is known only to Russia and not shared.

Updated discussions about metallic ingredients, including nano-sized metals and agglomeration effects, are discussed in [1]. In particular, DeLuca et al. [1, Ch. 8] tested a range of modified Al powders, going from uncoated to coated nano-sized Al (nAl) particles and from chemically to mechanically activated μAl . These variants were duly characterized and comparatively tested under laboratory burning conditions. Mainly the class of aluminized composite propellants (AP/inert binder) and operating conditions typically used in space applications were investigated. Each of the tested Al variants has its own properties, and implementation in full-scale propulsive systems needs to be carefully evaluated for an overall assessment. Based on a wealth of past experimental investigations, the recommended strategy for best results is a dual-mode Al mixture, ($\mu\text{Al}+\text{nAl}$) or ($\mu\text{Al}+\text{AlH}_3$), synergistically exploiting each component. Vorozhtsov et al. [1, Ch. 9] describe a technique for production of metal borides which is known as self-propagating high-temperature synthesis (SHS) and the subsequent mechanical treatment. Micron-sized borides are produced which have an average size of around $5 \mu\text{m}$ with a sharp curve of size distribution. The purity is enough for use as fuel of high-energy materials. Weiser et al. [1, Ch. 10] investigated the combustion behavior of Al particles in an ADN/GAP matrix in comparison to an AP/HTPB matrix at various pressures up to 15 MPa. The agglomeration of Al particles at the surface and burning behavior of aluminized AP/HTPB propellants had already been investigated and their study was ex-

tended to the ADN/GAP propellants. The temperature measurements close to the propellant surface indicate higher values near the Al boiling point that accelerate the melting of Al particles and influence the agglomeration process. At higher pressure the temperatures are in the magnitude of Al_2O_3 evaporation and decomposition close to 3000 K. Zhao et al. [1, Ch. 11] tested nAl coated with Oleic Acid (nAl@OA), Perfluorotetradecanoic Acid (nAl@PA) and Nickel Acetylacetonate (nAl@NA). Their ignition and combustion characteristics were studied using a laser ignition system. The results show that there is a critical value of laser heat flux in the ignition process of the coated nAl powders. The ignition delay time of nAl@NA is shorter than those of nAl@PA and nAl@OA, because of the combustion catalysis of nickel acetylacetonate. The burning rate of the propellant sample containing nAl@NA is the highest among all of the tested formulations and the maximum burning rate reaches 26.13 mm/s at 15 MPa. Babuk [1, Ch. 13] reviewed the state-of-the-art of the experimental results concerning the influence of various formulation factors on the properties of the Condensed Combustion Products (CCP), i.e., agglomerates and smoke oxide particles, formed at the burning propellant surface. The influence of the properties of binder, oxidizer, and metal fuel was investigated with reference to active and inactive binders, AP, AN (pure and phase-stabilized), ADN, HMX, μAl and nAl powder, Al powder with a polymeric and refractory covering. The proposed analysis is based on a general physical picture of the formation of the condensed products. It is shown that the properties of the condensed products (in terms of size, chemical composition, and internal structure) depend on properties of the burning propellant surface layer, which in turn depend on the properties of the propellant ingredients. The importance of the Skeleton Layer (SL) formation and properties were underlined. The results achieved open the possibility to take reasonable formulation decisions when creating new solid propellants.

Binders are an essential ingredient for castable composite propellants. They are needed to bound the propellant solid particles (oxidizers and metal, if present) and attain the wanted mechanical properties. Starting in the late 1970's, HTPB became the material of choice for a variety of commercial applications; a "propulsion grade" HTPB is being tested in the USA as of this writing. Hydroxyl-Terminated PolyEther (HTPE) is another hydroxylated binder primarily used today for rocket propellants that contain energetic plasticizer, usually n-Butyl-NitratoEthylNitrAmine (Bu-NENA), providing formulations with relatively high elongations.

Table 2
Properties of currently used metallic fuels and their most common oxides [1, Ch. 8]

Metals and most common oxides	Density, ρ , g/cm ³	M g/mole	Δh_f^0 kJ/mole	T_{melt} K	Δh_{melt} kJ/mole	T_{vap} K	Δh_{vap}^1 kJ/mole	Δh_r^3 kJ/g	Δh_r^3 kJ/cm ³
Al	2.70	27.0	0	933	10.7	2792	294	31.07	83.89
Al ₂ O ₃	3.99	102/0	-2550	2327	111.1	3253	109	NAp.	NAp.
B	2.34	10.8	0	2348	50.2	4273	480	58.86	137.73
B ₂ O ₃	2.55	69.6	-1272	723	24.6	2133	360	NAp.	NAp.
Mg	1.74	24.3	0	923	8.5	1380	136	24.70	43.00
MgO	3.60	40.3	-601	3098	77	3430 ²	670	NAp.	NAp.
Zr	6.52	91.2	0	2125	21.0	3850	573	12.03	78.43
ZrO ₂	5.68	123.2	-1097	2951	87.0	4573	624	NAp.	NAp.

¹at boiling point ; ²decomposition ; ³O₂ reaction

Table 3
Properties of some prepolymers used for common binder systems

Denomination	Chemical Formula	Oxygen balance, %	Molar mass M, g/mole	Density ρ , g/cm ³	ΔH_f kJ/mole	T_f K
Desmophen® D2200	C ₁₀ H _{16.678} O _{5.267}	-166.9	22.12	1.18	-976.1	-
GAP DIOL	C ₃ H ₅ N ₃ O	-121.1	99.1	1.28	+117.2	1570
HTPB-R45T	C ₁₀ H _{15.4} O _{0.07}	-323.8	136.8	0.92	-62.0	-
HTPE	C ₆ H ₁₂ O ₂	-220.5	116.1	1.04	-485.3	-
PGN	C ₃ H ₅ NO ₄	-60.5	119.1	1.39-1.45	-322.8	1465

Propellants based on HTPE binders essentially feature mechanical properties similar to those that use HTPB, but show a less severe response to slow cook-off, ElectroStatic Discharge (ESD), and bullet impact tests for Insensitive Munitions (IM) compliance. The HTPE density is larger than that of HTPB (1.04 vs. 0.92 g/cm³). In addition, the oxygen balance (OB) for HTPE is larger than for HTPB (-220.5% vs. -323.8%), thus allowing more Al to be loaded and further increasing density. Full details about the polyester diol Desmophen® D2200, recently tested as inert prepolymer for elastomeric binder at ICT, are reported in [13, 14]. A summary of relevant binder properties is shown in Table 3.

Updated discussions about binders, including both inert and energetic binders, are dealt with in [1]. In particular, Babuk [1, Ch. 13] clarifies how using active binders has profound consequences for the CCP properties. The laws of formation of SL and, hence, of CCP for propellants containing an active binder depend on the combustion pressure. In the low pressure domain, a SL is formed but this practically disappears when moving to high pressures, which leads to a sharp falling of the agglomerate mass fraction in the CCP composition. The specified laws depend on the combustion features of the active binder. Although a complete understanding

is still missing, one can state that the domain of high pressures is found above 5.0 MPa for all propellants of this type. Pei et al. [1, Ch. 14] examined the combustion characteristics of propellants based on (BA-MO-GAP) copolymer. The results show that while for the propellant ideal energetic properties there is an optimum ratio between AP and RDX or HMX or CL-20, performance improves linearly when AP is replaced by ADN. When AlH₃ replaces Al in the propellant formulations, the energetic properties are much improved. The propellants based on (BA-MO-GAP) copolymer have excellent properties, such as low flame temperature, high gravimetric specific impulse, good mechanical properties, and stable combustion. It is one of the most promising energetic binders for solid propulsion applications. Pivkina et al. [1, Ch. 15] studied the synergistic effect of AP on HMX and showed that formulations with active binder and coated HMX provide higher burning rate than those ones with mechanical mixtures of HMX with fine AP. This implies the possibility to use considerably less amount of AP to achieve the same level of burning rate. Rashkovskiy et al. [1, Ch. 16] proposed a theoretical combustion model, for mixtures of energetic binders with inert and active fillers, which takes into account the curvature of the binder layer burning surface and ignition delay of the filler. A parametric study of the

proposed model was performed over a wide range of particle sizes of the filler, its concentration in the mixture, and burning rates of the binder. The results of the model were successfully compared with experimental data for mixtures of energetic binders with a number of oxidizers.

Based on the work under progress, the basic propellant ingredients taken into consideration in this paper are the following:

- ADN, AP, AN, and PSAN as solid crystalline inorganic oxidizers.

- Al (of different size and variants by proprietary chemical/physical treatments) and AlH_3 as solid metallic fuels. This list includes on one side propulsion grade micron-sized Al (μAl), activated Al (actAl), amorphous Al (amAl), aluminum hydride (AlH_3) and on the other side nano-sized Al (nAl).

- HTPB, $\text{HO}-[(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2)]_n-\text{OH}$, and a polyester diol-based, Desmophen® D2200, were employed as prepolymers for the inert propellant binders. The energetic polyether polyol-based GAP, $\text{HO}-(\text{CH}_2-\text{CH}(\text{CH}_2\text{N}_3)\text{O})_n-\text{H}$, was employed as prepolymer for the active propellant binder [1, Ch. 32 by Bohn and Cerri].

Detailed properties of most of the ingredients under consideration (oxidizers, metallic fuels, and binder prepolymers) were presented elsewhere [4] [15, 16]. Comparing the ideal gravimetric specific impulse shows that ADN again neatly overcomes that of AN and AP with the indicated either inert (HTPB) or energetic (GAP) binder system; see Fig. 5 from [17].

Specific attention will now be addressed to two European projects coordinated by FOI and including a number of European partners. The current GRAIL (GReen Advanced high energy propellant for Launchers, www.grail-h2020.eu) three-year project, started in February 2015, can be seen as a continuation of a previous three-year project, ca 2011–2013, called HISP (High specific impulse Propellant for In-Space Propulsion, www.hisp-fp7.eu). Two metallized solid rocket propellant formulations, based on either the standard AP/HTPB matrix or the new oxidizer ADN with inert or active binder, were analyzed in the HISP project. Comparing the two basic formulations, as well as a number of variants, in terms of ideal thermochemistry and experimental combustion properties, revealed advantages and disadvantages of each class.

Overall, under the explored operating conditions, the approaches attempted in the framework of the HISP project promoted some progress, but for a variety of reasons no one of the tested ADN-based formulations looked ready to immediately replace

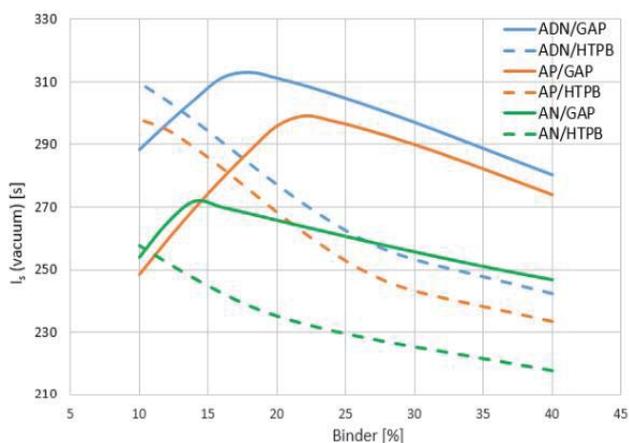


Fig. 5. Ideal gravimetric specific impulse in vacuum for HTPB- and GAP-based formulations [17].

AP for space exploration propulsive missions. This is clearly shown in Fig. 6, evidencing the strong effects of the implemented binder (inert HTPB or energetic GAP) on the steady burning rates of ADN-based composite propellants, with respect to a flight proven industrial AP/HTPB/Al propellant taken as the reference formulation. Under the explored operating conditions, GAP yields a reasonable pressure dependence but with an excessively large burning rates [18]; HTPB yields reasonable burning rates (at relatively low pressures) but with an excessively large pressure dependence [19]. The three aluminized propellant batches (05, 06, 10) tested for ADN/HTPB/Al by FOI differ for the loaded μAl size ($13.2 \mu\text{m}$ for batches 05 and 10 vs. $30 \mu\text{m}$ for 06), and solid mass fraction (75% for batches 05 and 06 vs. 80% for 10).

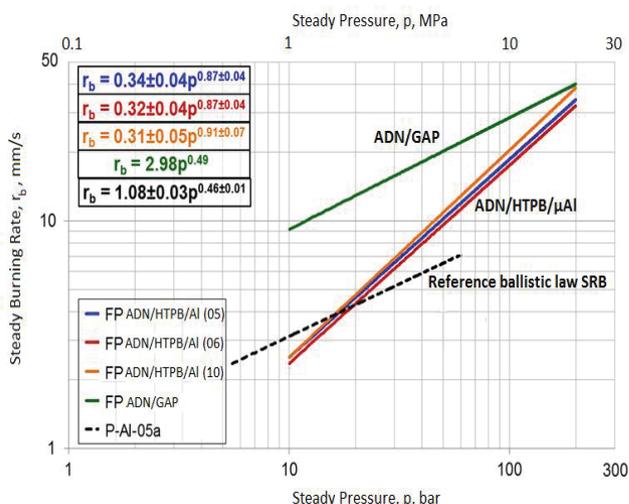


Fig. 6. Experimental testing conducted at FOI [18, 19] underlines the strong effects of the binder (inert HTPB or energetic GAP) and negligible effects of μAl on the steady burning rates of ADN-based propellants with respect to a flight-proven reference.

Within the explored operating conditions, the presence of μAl did not imply, as usual, any relevant effects on the ballistic properties of ADN/GAP, in terms of both burning rate values and pressure dependence [20]. Experimental results obtained at ICT, with 16% of 18 μm Al and over a 2–23 MPa pressure range indicate a slight decrease of burning rate and a slight increase of pressure sensitivity. Similar results were obtained at FOI with 18% of 14 μm Al and over a 3–24 MPa pressure range, under more accurate operating conditions.

5. ADN-based Dual-Oxidizers Solid Rocket Propellants

As reported in a recent paper by Wingborg and Calabro [21], in 2014 the European Commission, ESA (European Space Agency) and EDA (European Defence Agency) launched a new round of the European Non-Dependence Process. This includes the “development of low-cost, solid green propellants which will reduce application costs and are environmental friendly while providing the same or similar efficiency as current propellant in use at the same time”. Sustainable Development for the space industry in Europe is reflected by ESA’s Clean Space Initiative and the Green Propulsion Harmonization Process [22, 23].

Following the experimental findings of the HISP project discussed in Sec. 4, another joint effort is currently under way with the objective of directly affecting the oxidizer behavior. The GRAIL project, funded by the European Union’s Horizon 2020 research and innovation program, has been granted to determine if it is possible to develop a green AP-free solid propellant. ADN and AN are the only oxidizers allowing the manufacture of green propellants. ADN has a dual advantage over the workhorse oxidizer AP in terms of clean combustion and superior heat of combustion. But due to lower oxygen content it is not possible to replace AP by ADN one-to-one and for high performance ADN has to be combined with an energy-rich binder. On the other hand, AN is in general not used in high-performance propellants, see Sec. 3. Neither ADN nor AN are able to replace AP on its own [24, 25].

By implementing compositions based on dual-oxidizers, such as (ADN+AP) or (ADN+AN), a partial replacement of ADN can be put into effect thus mitigating its intrinsically large self-deflagration rates. Slowdown effects on burning rate were experimentally reported, for either AN or AP replacing ADN, in several sources from the open literature [15, 16]. But the overall ballistic properties of the resulting dual-oxidizer systems are also

sensibly influenced, depending in particular on the ADN replacement fraction (AP/ADN or AN/ADN relative mass ratio). Moreover, it should be borne in mind that in both cases the ideal specific impulse is penalized, although only slightly as discussed next. In addition, the possible presence of AP again implies the presence of some chlorine in the exhausts, while AN being not suitable for high performance propulsive missions requires a phase stabilizer. Comparing ADN-based dual-oxidizer solid rocket propellants in terms of ideal thermochemistry and experimental combustion properties reveals advantages and disadvantages of each formulation.

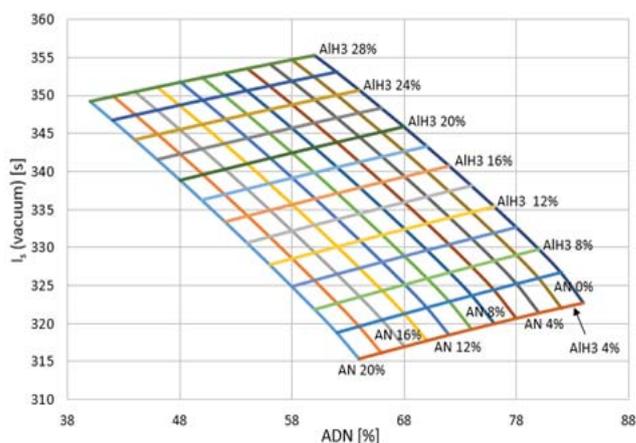


Fig. 7. Ideal thermochemistry for (ADN+AN) dual-oxidizer formulations with 12% GAP binder and AlH_3 fuel [17].

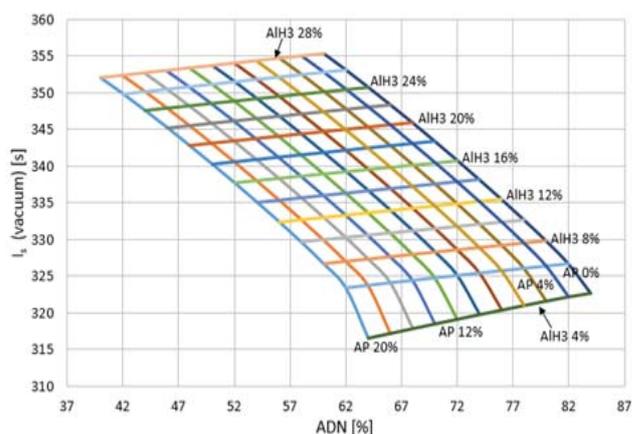


Fig. 8. Ideal thermochemistry for (ADN+AP) dual-oxidizer formulations with 12% GAP binder and AlH_3 fuel [17].

Ideal gravimetric specific impulse values were systematically computed by Palmucci [17] for a series of dual-oxidizer formulations, (ADN+AN) or (ADN+AP), using different inert or energetic binders and a variety of metallic fuels. As an example, results obtained for the formulations (ADN+AN)/GAP/ AlH_3 and (ADN+AP)/GAP/ AlH_3

are respectively reported in Figs. 7 and 8. In the case of the ADN/GAP/AlH₃ 60/12/28 formulation, a 20% replacement of ADN (1/3 of the oxidizer) implies a decrease of I_s from 355.3 s to 349.2 s for AN (-1.72%) and to 352.0 for AP (-0.93%). Similar trends are observed for Al as fuel as well as other propellant formulations, thus making in reality metal agglomeration the crucial parameter for the precise choice of the best composition from the performance viewpoint. Moreover, keep in mind that for (ADN+AN) also the presence of phase stabilizers will play a role.

5.1 (ADN+AN)-based Dual-Oxidizers for European Space Launchers

The standard AP/Al/HTPB composite propellants, burning several hundreds of tons of AP in about 2 min at each space launch, release large quantities of hydrogen chloride (HCl), which can be more than 20% of the combustion products at the nozzle. This compound has a negative impact on the environment due to ozone depletion and acid rain formation. Moreover, the perchlorate anion is hazardous to human thyroid gland, amphibian pigmentation and growth, and maritime life forms. AP is now known to be toxic for human beings and animals; contamination due to its production has been detected for groundwater, fruits, and vegetables [26, 27, 28]. Environmental damage and corrosion caused by HCl are observed all around the launch base, while ozone depletion takes place all around the vehicle trajectory. Also aluminum chloride and other intermediate reaction products, which actually are less than 2%, cause additional serious problems once the huge quantities of expelled mass are considered [24, 25]. The European GRAIL project precisely seeks for a replacement of AP by using a green mixture of the high-performance ADN and the low-cost AN.

In a preliminary series of tests conducted at ICT, a total of 24 different formulations were investigated, changing the AN/ADN ratio. GAP, HTPB, Desmophen® D2200, and a mixture GAP/Desmophen® D2200 (80/20) were tested as binder systems. This led to different amount of oxidizer for each binder system due to processibility issue, but the ratio of coarse/fine particle distribution was kept constant (70/30). ADN was used in a bimodal distribution of prills with 48 μm and 212–218 μm nominal particle size. Spherical particles of PSAN were produced at ICT stabilized with either KNO₃ (KNO₃-PSAN, 30 μm) or NiO (NiO-PSAN, 120 μm). Al powder was used in two particle sizes: Alcan400 (nominal diameter 4 μm) and X81 (nominal diameter 20 μm). For all formulations, Al was 18% of the total mass.

Ignition revealed difficult for both inert binders at the low range of the tested pressures. For HTPB-based samples, PDL would increase with a larger content of ADN: from 1 MPa with AN to 3 MPa with ADN. For Desmophen®-based samples, PDL would increase with a larger content of AN: from 2 MPa with pure ADN to 10 MPa for AN/ADN ratio 70/30. Desmophen®-based samples with pure AN oxidizer could be ignited only occasionally.

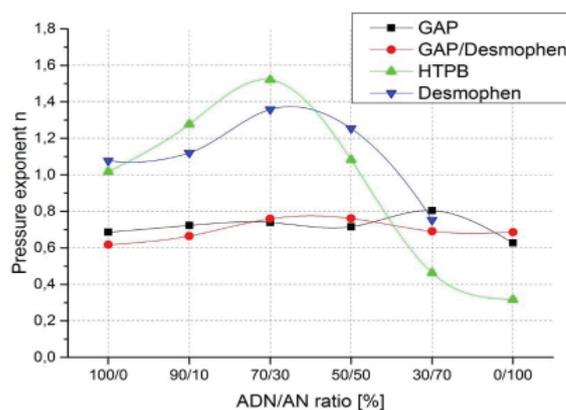


Fig. 9. Pressure exponents of the tested (ADN+AN)/Al/binder dual-oxidizer solid propellants [24, 25].

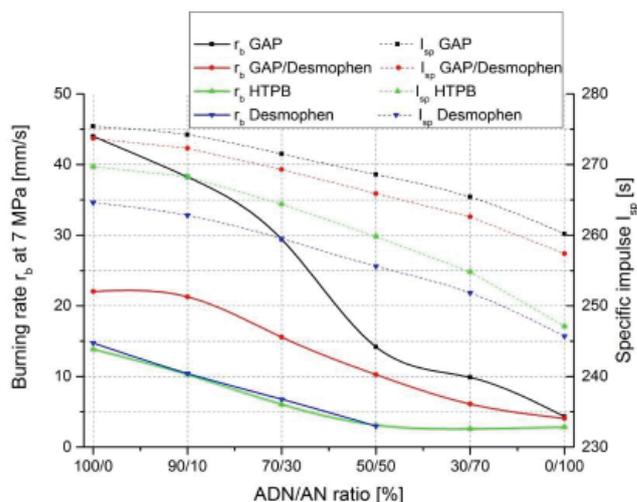


Fig. 10. Burning rates and specific impulses of the tested (ADN+AN)/Al/binder dual-oxidizer solid propellants at 7.0 MPa combustion pressure and 0.1 MPa exit pressure [24, 25].

An overview of the obtained results is presented in Figs. 9 and 10. Partially replacing ADN with AN led to a monotonically gradual and fair reduction of the ideal I_s going from pure ADN to pure AN. Within the explored operating conditions, steady burning rate was also reduced but in a less regular way: the wanted decrease became considerable only above, say 30% ADN replacement. In particular, the partial replacement of GAP by Desmophen® was able

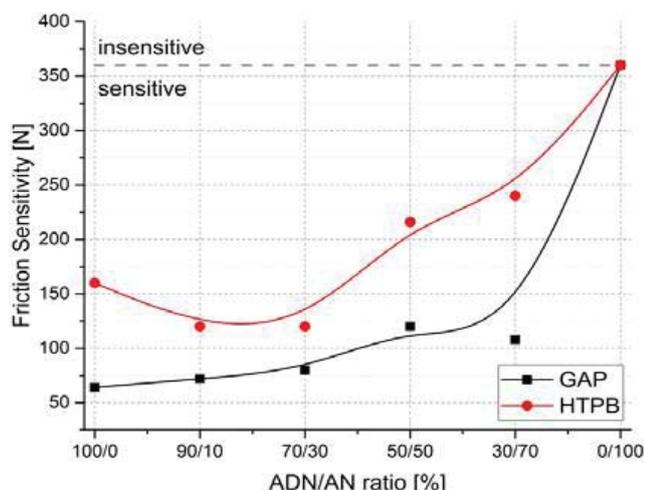


Fig. 11. Friction sensitivity of the tested of the tested (ADN+AN)/Al/binder dual-oxidizer solid propellants vs. ADN/AN ratio showing somewhat increased sensitivity for active binder [29].

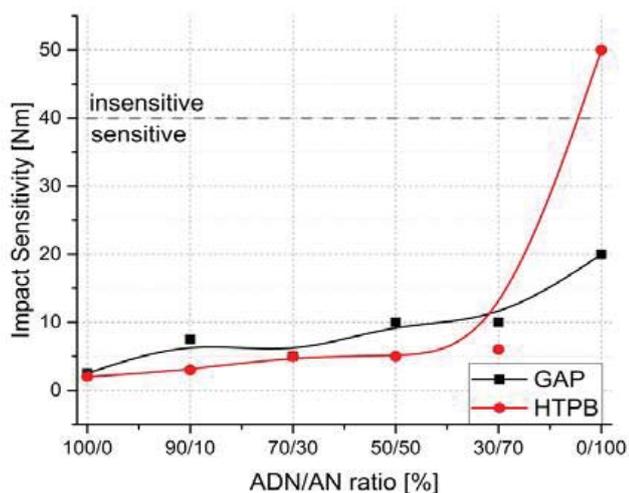


Fig. 12. Impact sensitivity of the tested (ADN+AN)/Al/binder dual-oxidizer solid propellants vs. ADN/AN ratio showing minor differences between active and inert binders [29].

to halve burning rates over most of the AN/ADN range. Unfortunately, the pressure sensitivity was also dramatically affected. The pressure exponent was already too large for pure ADN: above 1 (!) for inert binders and around 0.7 for active binders. With increasing ADN replacement, the pressure exponents further increased (!! for inert binders (by about 50% for HTPB and 26% for Desmophen®), while remained very roughly constant for active binders. Thus, within the explored operating conditions, at least 70% AN of the total oxidizer content is required to achieve a reasonable value of pressure exponent with inert binder. This mixture ratio corresponds to considerable reduction of steady burning rates but also heavy losses of I_s .

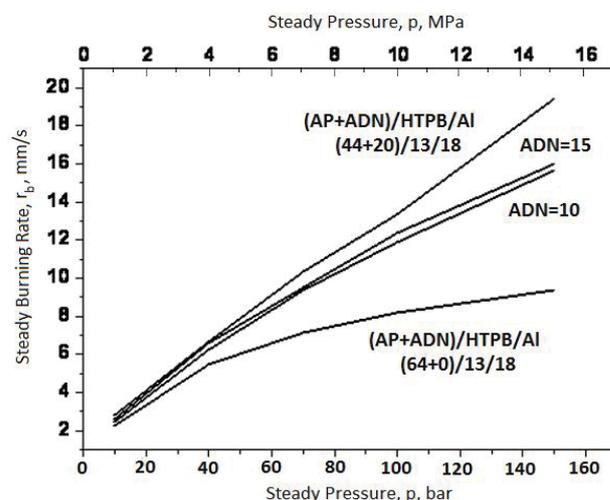


Fig. 13. Steady burning rate vs. pressure of (ADN+AP)/Al/HTPB dual-oxidizer propellants, showing increase of rate and slope (from 0.41 to 0.71) for increasing ADN mass fractions with respect to AP [30].

GAP- and HTPB-based propellants underwent further investigation on friction (see Fig. 11) and impact (see Fig. 12) sensitivity, in order to have a better comparison between active and inert binders. Experimental testing pointed out that altogether insensitive, or reduced sensitivity, propellants can be obtained only with pure AN as oxidizer and the effect of ADN/AN ratio is quite low. In particular, friction sensitivity in Fig. 11 is somewhat worsened by GAP binder, while impact sensitivity in Fig. 12 appears about the same for both active and inert binders.

Another issue regarding the stability of the propellants is the formation of eutectic mixture between ADN and AN, despite the oxidizer were embedded in the polymer matrix. This problem is noticeable in DSC analysis which showed an anomalous increasing endothermic peak at around 60 °C. An attempt was made to avoid the eutectic formation by using coated ADN prills in order to avoid any direct contact between ADN and AN particles. This approach needs further investigation to prove its effectiveness.

Overall, replacing AP by the green mixture (ADN+AN) with the tested inert binders can in fact reduce burning rates but still faces severe challenges for other ballistic aspects, in particular the pressure exponent. The chemical stability and mechanical properties of (ADN+AN)-based propellants with inert binders need further investigations.

5.2 (ADN+AP)-based Dual-Oxidizers

Experimental investigations were carried out for the dual-oxidizer system (AP+ADN)/HTPB/Al at Xi'an Modern Chemistry Research Institute [30]

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5.2 (ADN+AP)-based Dual-Oxidizers

Experimental investigations were carried out for the dual-oxidizer system (AP+ADN)/HTPB/Al at Xi'an Modern Chemistry Research Institute [30] by testing formulations including in mass 64% oxidizer (AP+ADN), 18 μ Al, 13% HTPB binder, and 5% additives. Four (AP+ADN) mixtures were implemented ranging from 64+0 (pure AP) to 54+10, 49+15, and 44+20 mass fractions. AP was used in a bimodal grain distribution size: the average size was 105–147 μ m for the coarse particles and 1–5 μ m for the fine particles. ADN prills were obtained by spraying molten ADN through a nozzle and the average diameter was in the range 147 to 205 μ m. The solidified ADN drops were then coated by a polymer binder.

Little difference could be observed for the tested four formulations of (AP+ADN)/Al/HTPB composite propellants in terms of computed ideal thermochemical properties, under the standard operating conditions of 7.0 MPa combustion pressure and 0.1 MPa exit pressure: specific impulse I_s (from 256.8 s to 260.1 s) and characteristic velocity c^* (from 1518.5 m/s to 1540.3 m/s) slightly

increase with increasing AP replacement by ADN. On the contrary, the adiabatic flame temperature T_c (from 2895 K to 2851 K) and density (from 1.718 to 1.674 g·cm³) slightly decrease by increasing the AP ($\rho = 1.95$ g·cm³) replacement by ADN ($\rho = 1.81$ g·cm³).

Experimental ballistic results point out a sensible increase of burning rate and pressure exponent (from 0.41 to 0.71) for increasing AP replacement by ADN; see Fig. 11. Experimental hazard results reveal that using the tested coated ADN particles involves a considerable increase of the propellant friction and impact sensitivity. This requires attention and warrants further work in possible ADN-based propellant applications. Both the impact and friction sensitivities increase for increasing AP replacement by ADN.

Further analyses were indirectly carried out by Pei et al. [1, Ch. 14] to investigate the effects of the Al mass fraction on the performance of a series of propellants made of (BAMO-GAP) copolymer 15%, GAP 5%, Al 10%, and oxidizer 70%. The oxidizers were gradually replaced by Al up to 20%. Ideal performance was calculated by a Chinese thermochemical code at 7 MPa. The results show that the performance corresponding to each oxidizer can be quite different. For the formulations containing RDX, HMX, or CL-20, the propellant I_s first rises and then reduces when the Al mass fraction replacing the oxidizer goes beyond a certain value. Thus, an optimum value exists for the Al amount, say 8% for CL-20 and 10% for RDX or HMX. The value of T_c vs. the Al mass fraction shows the same trend as that of I_s . However, for the propellants containing ADN or AP, the value of I_s monotonically increase with the oxidizer mass fraction increase up to 20%. This may be attributed to the large oxygen content of ADN and AP. For the propellants containing different oxidizers, the maximum increasing values of I_s are in the order of [ADN]>[CL-20]>[AP]>[RDX]>[HMX].

Overall, replacing AP by the more energetic mixture (ADN+AP) with HTPB inert binder can in fact reduce burning rates while simultaneously increasing the pressure exponent within acceptable limits. The mechanical properties and hazard features of (ADN+AP)-based propellants need further investigations.

6. Conclusions and Future Work Recommendations

For the near future, formulations including dual-oxidizers based on ADN, such as (ADN+AN) or (ADN+AP), in conjunction with a dual-metallic fuel based on μ Al, such as (μ Al+nAl) or

($\mu\text{Al}+\text{AlH}_3$), bound by a suitable active or inert binder, are expected to advance the state-of-the-art of solid rocket propellants. However, the quite peculiar properties of ADN require a careful design and implementation of the propellant formulation. Most investigations so far accomplished did not fully exploit the unusual dependence of ADN ballistic properties on particle size. Appropriate burning rate modifiers may be needed to fully control the propellant ballistic properties. At this time, in view of the experimental results described in Sec. 5, the mixture (ADN+AP) seems easier to be mastered than (ADN+AN). Overall, when dealing with ADN, it is the binder system still demanding a decisive effort to manufacture well-behaved formulations; other critical areas are the implementation of a suitable phase-stabilizer for AN and bonding agent for the propellant. At any rate, the mechanical and hazard properties of the resulting formulations have to be closely monitored and possibly improved.

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