Burning Behavior of Aluminized ADN/PSAN Propellants

V. Gettwert, C. Tagliabue, V. Weiser*

Fraunhofer Institute für Chemische Technologie, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany
*Contact: volker.gettwert@ict.fraunhofer.de

Abstract

Solid rocket propulsion is used in the first stage or boosters of space launchers. Three oxidizers are available on the market, which can be used for the preparation of composite propellants: Ammonium Nitrate (AN, NH_4NO_3) or its phase-stabilized (PSAN) version, the widely used Ammonium Perchlorate (AP, NH_4ClO_4), and the relatively new Ammonium Dinitramide (ADN, $NH_4N(NO_2)_2$). To our knowledge, ADN-based solid rocket propellants are used by the Russian for the intercontinental ballistic missiles only [1]. The first application of ADN in Europe is in a liquid monopropellant (LMP-103S) [2]. The current state-of-the-art composite propellant used for about 50 years is based on the oxidizer AP. The aims of new developments are the improvement of the delivered performance and the reduction of environmental impact. Therefor AP must be replaced by a chlorine-free oxidizer. ADN/GAP-based solid rocket propellants were systematically studied in the HISP project (High performance solid propellants for In-Space Propulsion), a three-year collaborative project financed by the Seventh European Framework Project. It turned out that this kind of propellant burns too fast for space exploration. Thermodynamic calculation shows that a blend of ADN and AN is able to replace the AP. This dual-oxidizer system bonded by an either inert or active binder and loaded with metal fuel, is a potential candidate for space solid rocket propellant. In the framework of the GRAIL (GReen Advanced hIgh energy propellants for Launchers) project, supported by Horizon 2020 program, propellants with ADN/AN oxidizer are evaluated.
The paper focuses on the properties of ADN/AN/GAP/Al propellants and their burning behavior.

Keywords: solid rocket propellant, composite propellant, ADN, AN, PSAN, metal fuel, specific impulse, binder

1. Introduction

Propellants based on the dual oxidizers system ADN/AN suffer of many issues, but considering that an alternative to AP has to be found, these difficulties have to be overcame. For example, HTPB, despite its stability, revealed a reaction with ADN which make the long term mechanical properties questionable. To find an alternative non energetic binder is a serious challenge. Most of the polyethers and polyesters dissolve ADN [3] with the exception of Poly (tetrahydrofuran), which, unfortunately, showed a recrystallization in the application temperature range. Furthermore a mixture of the oxidizer ADN and AN forms an eutectic which affects the stability of ADN and the propellant properties. The eutectic can be avoided by coating both oxidizers. The barrier provided by a polymeric layer must cover the entire particle surface otherwise it will be not sufficient [3].

Unfortunately all investigated propellants with non-energetic binder possess inappropriate burning behaviors. PTHF based formulations, like the others with inert binders, exhibit high pressure dependence (n > 1) in the presence of ADN [4], and high PDL (≥7 MPa). Considered that poly(tetrahydrofuran) was the best option so far, an extensive test campaign was carried out, in collaboration with CNRS-IC2MP, in order to find a proper ballistic modifier to adapt the burning characteristic of these propellants. Some enhancements were obtained with benzoylferrocene. The pressure exponent was lowered till 0.84 at the expense of slow burning rate and insufficient I_{sp} [5]. Because of insoluble problems by the use of inert binder, energetic polymers were considered for ADN/AN propellants. Glycidyl azido polymer (GAP) is known for its compatibility and stability with ADN ([6] is just one of many studies). Al/ADN/GAP propellants were already studied within the HISP project. These propellants exhibit high burning rate and I_{sp} with a reasonable ballistic exponent. First results in the GRAIL project shown that the combustion rate is tunable through a partial replacement of ADN with ammonium nitrate (or its phased stabilized version) keeping the pressure dependence almost unaltered. This paper describe the results of this concept with the goal to obtain a propellant formulation with a burning rate in the range from $7 \leq r_b \leq 15$ mm/s at 7 MPa and a pressure exponent lower than 0.6.

2. Experimental procedure

2.1. Materials

All chemicals used in the work are listed in Table 1.

Table 1. Chemical used in the experimental work

Material	Class	Supplier
ADN prills	OX	Synthetized at EUB, prilled at FOI or ICT
Al	MF	Toyal America Inc./ AMG AlPoco UK
Isocyanates	CA	Bayer MaterialScience, Germany
Bis(2-ethylhexyl) sebacate	Pl	Sigma Aldrich
Dibutylsebacate	Pl	Sigma Aldrich
Dibutyltin dilaurate (DBTDL)	Cat.	Merck, Germany
Diisodecyl adipate	Pl	Sigma Aldrich
Dimethyl sebacate	Pl	Sigma Aldrich
DOA	Pl	BASF
GAP-diol	PB	Eurenco
KNO_3-PSAN	OX	Produced and prilled at ICT

2.2. Preparation of propellants

The ingredients were mixed with a planetary centrifugal mixer (ARV-310 Thinky Mixer), in low pressure environment (~10 mbar), in order to minimize air inclusions. The slurries were cured at 40°C for 7 days.

2.3. Investigated propellants

GAP-diol was cured with isocyanates. The reaction was catalyzed with dibutyltin dilaurate (DBTDL). Ammonium nitrate was phased stabilized with KNO_3 (PSAN). With the exception of ADAN270, both ammonium dinitrammide and PSAN were embedded in the polymer with a 70:30 bimodal distribution (coarse:fine). As metal fuel, micrometric aluminum was employed with a mean diameter between 16 and 18µm.

The investigated propellants are listed in Table 2.

Table 2. Propellant compositions [% -wt.]

Label	**ADAN172**	**ADAN173**	**ADAN222**	**ADAN265**	**ADAN270***
ADN/AN ratio	50/50	100/0	100/0	70/30	70/30
GAP binder	20.40	27.20	27.20	21.25	21.25
Plasticizer	3.6	4.8	4.8	3.75	3.75
ADN	29	50	50	39.9	39.9
KNO_3- PSAN	29	-	-	17.1	17.1
Al	18	18	18	18	18

*****bimodal distribution for ADN only

2.4. Thermodynamic Calculations

Thermochemical calculations were carried out with ICT code [7] under shifting equilibrium hypothesis with a pressure expansion ratio equal to 70:1. The necessary data needed to evaluate the theoretical specific impulse were taken from the ICT´s database [8]. The reference specific impulse was determined by an AP/HTPB/Al (68/14/18) formulation. For the calculation the data of ammonium nitrate were used instead of the phase stabilized version. The losses due to the stabilizing agent (potassium nitrate) were considered negligible at the current stage of development.

2.5. DSC analysis

The thermal analysis were performed with an heating rate (HR) of 10°C/min from -90°C to 25°C

2.6. Strand burn test and burning rate evaluation

Propellants were tested as strands (5x5x30 mm^3) in the ICT window bomb at 4, 7, 10 and 13 MPa under nitrogen atmosphere. The burning test was recorded by a color high-speed video camera using and the combustion rate was extracted with computer technique analyzing the videos (for more details [9]). The samples were fired with a booster charge ignited by a hot wire placed at the top end. Every sample was measured at least twice. The Vielle´s law parameters were computed on the average values.

3. Results and discussion

The starting point was a propellant, already discussed in [4], based on GAP-diol, plasticized with an energetic compound, and a filler mixture of ADN, PSAN and aluminum. These propellants showed a very high burning rate, especially when ADN is used as oxidizer only. The burning rate was almost double of the value reported in the HISP project [10] [11], but the pressure exponents were close to acceptable maximum value. The energetic plasticizer was ascribed for the extremely fast burning, so it was replaced by an inert one. Another point of concern is the sensitivity of the propellant when ADN is used as filler. The aim is to avoid a 1.1 hazard classification. Two different strategies were evaluated:

1) Increase of AN oxidizer content in the ADN/AN mixture as high as possible to get the 1.3 classification at the risk of an higher pressure exponent
2) No AN and minimum amount of ADN. This could lead to acceptable pressure exponent at the risk to miss the aim of the 1.3 classification.

DOA, bis(2-ethylhexyl) sebacate, diisodecyl adipate, dimethyl sebacate and dibutyl sebacate were selected as inert plasticizer. Only the latter revealed a good miscibility with GAP-diol. Therefore two formulations were prepared according to the previous points, making some thermochemical calculation in order to have a propellant with the same (theoretical) I_{sp} of Al/HTPB/AP.

The amount of aluminum was set at 18%Al while the content of plasticizer was fixed at 15% of binder (Figure 1). In the case that ADN is used as oxidizer only (ADN/AN ratio 100/0; ADAN173), an oxidizer content of 50% is sufficient to meet the target specific impulse of the reference propellant (AP/HTPB/Al 68/14/18). In case of double oxidizer, with an ADN/AN ratio of 50:50 (ADAN172), a total oxidizer content of 58% is necessary. This adds up to a total solid load of 76%, which seemed a reasonable value for a good castability of the slurry and was selected for determination of the burning behavior.

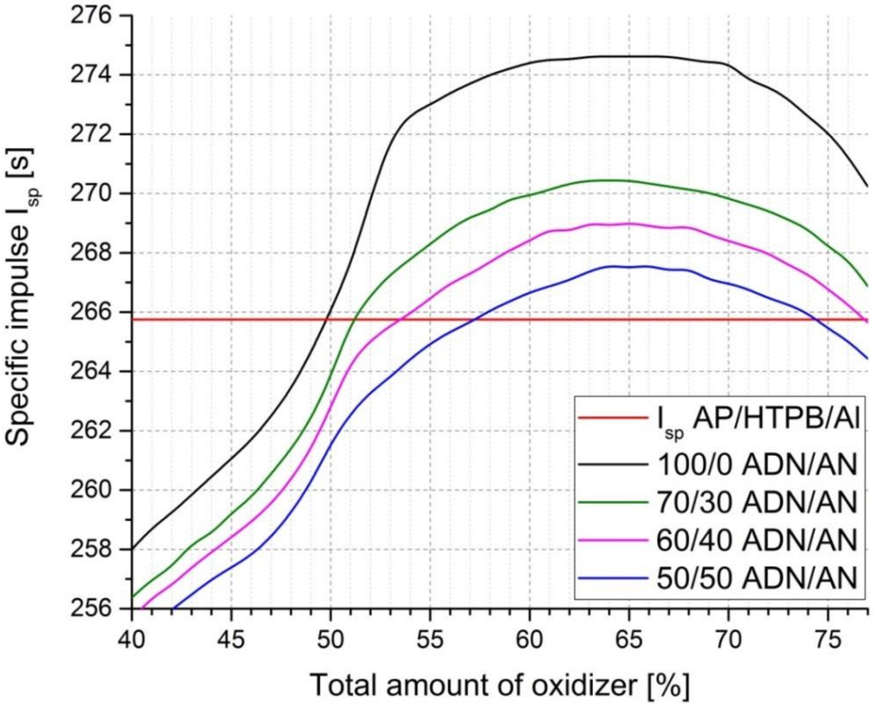

Figure 1. Dependence of specific impulse of Al/ADN/PSAN/GAP/dibutyl sebacate propellants with different ADN/AN ratio and fixed Al content (18%)

In the following Figure 2, the results of the strand burner test are reported. ADAN172 (ADN/AN ratio 50/50) has a combustion rate of ~10.5 mm/s at 7 MPa, which is in the desired range. The pressure exponent was calculated as 0.83 and far over the safe value. On the other hand the propellant with ADN only (ADAN 173) showed an acceptable pressure dependence (0.57) but a fast burning. The upper limit for the desired burning rate is less than 15 mm/s and ADAN173 revealed a burning rate of 16.8 mm/s at 7 MPa.

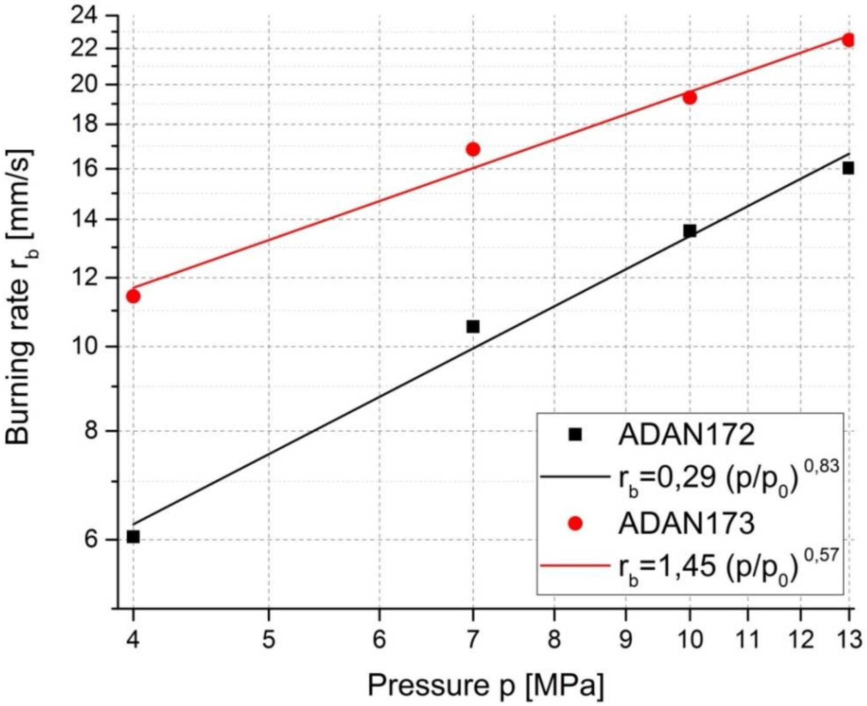

Figure 2. Comparison of burning behavior between a propellant formulation of Al/ADN/GAP/dibutyl sebacate (ADAN173) and Al/ADN/PSAN/GAP/dibutyl sebacate (ADAN172)

The propellants underwent a DSC measurement in order to determine the glass transition temperature. Both formulations revealed endothermic peaks. (Figure 3)

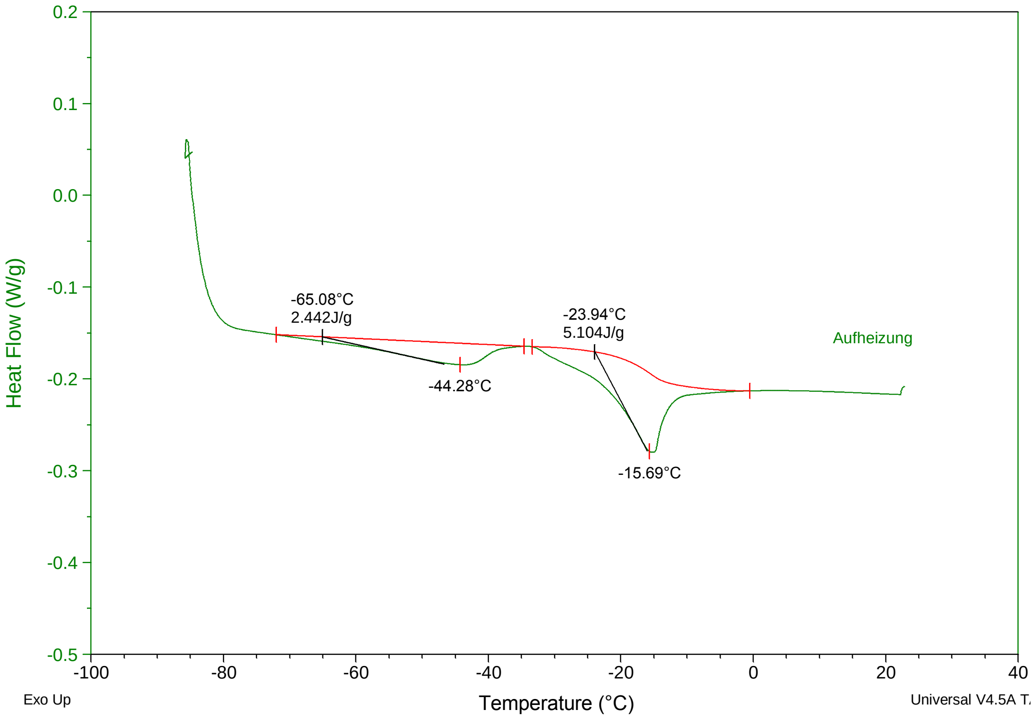

Figure 3. DSC measurement of Al/ADN/PSAN/GAP/dibutyl sebacate (ADAN 172)

This property showed solubility problems of the plasticizer in the binder matrix. Despite the poor thermal behavior, the ballistic properties looked promising. Therefore a plasticizer which is used in military propellants was chosen. This plasticizer, which cannot be named in this paper, is more compatible to ADN and GAP.

The same procedure was followed as previously described. Thermodynamic calculations were done to determine a formulation with a similar I_{sp} (Figure 4). For this calculation the thermodynamic data of KNO_3-PSAN were used in order to get more refined results. In any case the differences between AN and PSAN were estimated as a performance loss of c.a. 0.5%. The aluminum and the plasticizer content were fixed at 18% and 15% of the binder, respectively.

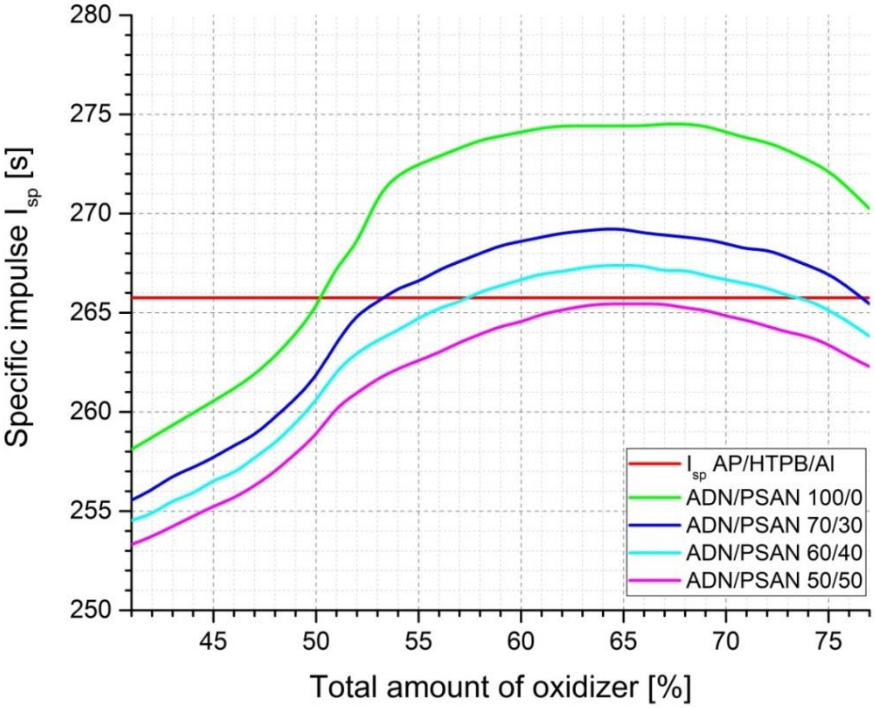

Figure 4. Dependence of specific impulse of Al/ADN/PSAN/GAP/plasticizer propellants with different ADN/AN ratio and fixed Al content (18%)

In case of ADN only (ADN/ADN Ratio 100/0, ADAN222), it was possible to keep the same formulation as ADAN173, with an ADN content of 50%. On the contrary, in formulations with a higher amount of ammonium nitrate the specific impulse is strongly affected by the new plasticizer and the KNO_3 phase stabilizer. An ADN/PSAN ratio of 50/50 almost meets the I_{sp} of the reference propellant (red line in Figure 4) at high solid load that will not be producible. A higher ADN/PSAN ratio of 70/30 was selected to get a feasible formulation with a total oxidizer content of 57% (ADAN265). In Figure 5, the burning behaviors of both propellants are shown.

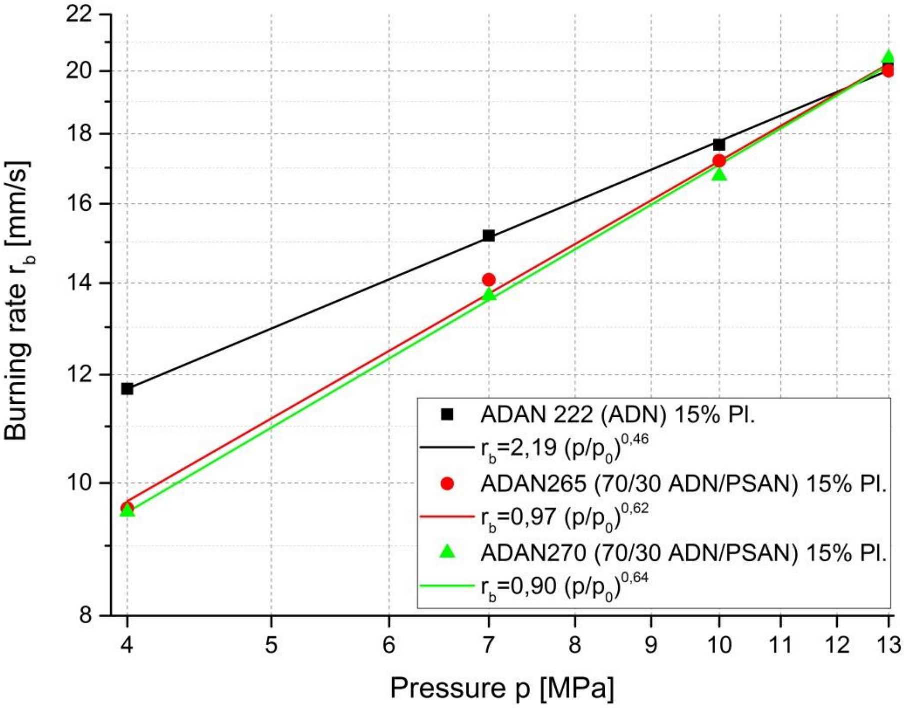

Figure 5. Comparison of burning behavior between a propellant formulation of Al/ADN/GAP/plasticizer (ADAN222) and Al/ADN/PSAN/GAP/plasticizer (ADAN265)

ADAN222 revealed to be slightly too fast (15.2 mm/s) but the pressure exponent of 0.46 is good. For ADAN265 the results are reversed. The burning rate at 7 MPa was 14.01 mm/s within the desired range, while the exponential factor of the Vieille's law was 0.62, just above the limit.

The most promising formulation is ADAN265. It was used to optimize the particle size distribution of the oxidizers in order to furtherly tune the ballistic characteristic. The fine PSAN was completely removed and replaced by coarse material. The ratio between coarse and fine ADN particles was swapped from 70:30 to 30:70 in order to balance the lack of fine PSAN. These changes should decrease the burning rate furtherly. It is known that the combustion rate of ammonium nitrate is inversely proportional to its particle size like AP which means that larger particles burn slowly in comparison with finer while ADN behaves exactly in the opposite way [12]. The propellant with the varied particle sizes of ADN and PSAN (ADAN270) burns with a rate of 13.71 mm/s at 7 MPa while the parameter *n* was evaluated as 0.64 in the range 4-13 MPa. The particle size distribution has a minimal impact on the ballistic properties, but it has to consider the limited changes carried out. The burning rate results slower while the pressure exponent is slightly higher but not too far away from an acceptable value.

4. Conclusion and future work

The current state of the work showed that with a propellant containing an oxidizer mixture of ADN/PSAN propellant in combination with a modified energetic GAP-binder is a change to reach the desired targets of the project. The propellant are able to compete with the actual state of the art solid rocket propellant regarding performance, which can be exceed, and ballistic properties which are close to the desired values and should be adjustable.

For a successfully develop, further enhancements and optimization of the particle sizes of the filler and the composition are necessary but the described guide formulation provides a solid basis. GAP-diol plasticized with an inert compound seems to be able to handle the ADN/PSAN filler. It has been proven that with a proper choice of particle size distribution and a proper oxidizer mixture, the combustion rate can be adapted. The pressure sensitivity could be lowered by the right ratio between the oxidizing agents and by the amount of inert plasticizer. Another option is the use of Alane as metallic fuel alone or in combination with Al. With proper adjustments of these parameters it should be possible to achieve the desired burning behavior.

GAP-diol was not eligible in the GRAIL project because of its energetic nature but with the knowledge gained from the project it seems that the use of an active binder like glycidyl azide polymer is the price to pay to develop an aluminized ADN/AN propellant which could be an alternative to the flight proven industrial AP/HTPB/Al propellant.

There are concerns about the shock sensitivity due to the use of an energetic polymer and ADN. Aluminum and PSAN embedded in the propellant should help to get a 1.3 hazard classification for the final formulation. A card gap test will be performed when satisfactory ballistic properties will be achieved.

But this is not the end of development. The next challenge will be the optimization of the mechanical properties, which, till now, were neglected.

The cost assessment for an application is another questions since GAP-diol and ADN are research chemicals and therefore currently more expensive than HTPB and AP. But this issue has to be answered in the future.

The current state of development has brought it closer to an AP free composite propellant.

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Abbreviations and symbols

ADN	Ammonium dinitrammide
Al	Aluminum
AN	Ammonium nitrate
AP	Ammonium perchlorate
BM	Ballistic modifier
CA	Curing agent
Cat.	Catalyst
CNRS-IC2MP	Centre National de la Recherche Scientifique – Institute of Chemistry of Mediums and Materials of Poitier
DSC	Differential scanning calorimetry
GAP	Glycidyl azide polymer
GRAIL	Green advanced high energy propellants for launchers
HTPB	Hydroxyl-terminated polybutadiene
ICT	Institute für Chemische Technologie
ICT Code	Thermodynamic code from Fraunhofer ICT
I_{sp}	Specific impulse
MF	Metal fuel
n	Pressure exponent
OX	Oxidizer
P	Pressure (Vieille´s law)
P_0	Ambient pressure (Vieille´s law)
PB	Polymeric binder
PDL	Pressure deflagration limit
Pl	Plasticizer
PSAN	Phase stabilized ammonium nitrate
PTHF	Poly(tetrahydrofuran)
r_b	Burning rate