

SOLVENTLESS EXTRUDED DOUBLE-BASE (EDB) PROPELLANT CHARGES—A REVIEW OF THE PROPERTIES, TECHNOLOGY, AND APPLICATIONS

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Extruded double-base (EDB) charges are used mainly due to their efflux having minimum smoke, attractive oxygen balance, and low corrosivity. The propellant class also has desirable burn-rate characteristics since it exhibits plateau burning and has a low temperature sensitivity to burning rate (π_k). External ballistic modeling results are presented that illustrate the performance advantages that EDB propellants can provide, compared to more energetic propellants that are also not minimum smoke. For rocket motors, the plateau behavior is generally achieved by the inclusion of lead salts as ballistic modifiers, although these have had increasingly restricted availability, and lead-free alternatives are not yet generally in use. The manufacturing processes, both traditional batch and continuous, are described, including that used for medium- and large-caliber solventless gun propellants. The inhibition methods for rocket propellant charges are discussed. Strengths and weaknesses are considered together with potential developments in processing and materials (e.g., synthetic/nano cellulose). Various current and recent applications for such charges are reviewed, as well as insensitive munitions (IM) aspects. Consideration is also given to the maturity and potential further implementation of other minimum-smoke propellants to predict the future opportunities for solventless EDB propellants in the next five years. This includes an assessment of some historical issues that have arisen when propellant and motor technology advances have been attempted. This paper focuses on topics that are either new or have not been included in previous reviews; it includes more than 65 references.

KEY WORDS: solventless double base, propellant, charge, grain, pyrogen, inhibition, manufacture, continuous, nitrocellulose, missile, insensitive munitions, solid rocket motor, gun, ballistic modeling, shear roll milling, twin-screw extrusion, REACH, minimum smoke

1. INTRODUCTION

Solventless extruded double-base (EDB) propellant charges (both rocket grains and gun propellant charges) have been extensively deployed in service for more than 90 years. Nitrocellulose (NC)-based gun propellants are conventionally produced using solvents and comprise NC as the main energetic constituent. Classically, NC-based gun propellants are subdivided into single-base propellants, comprised mainly of NC as the energy carrier; double-base propellants, also containing energetic plasticizers like nitroglycerine (NG) and diethylene glycol dinitrate (DEGDN); and triple-base propellants, which contain both NG and the solid nitroguanidine (NQ). In more recent times various modifications have been developed, introducing different types of energetic plasticizers such as bis-(2,2-dinitropropyl) acetal mixture with formal (BD-NPA/F), 1,5-diazo-3-nitrazapentane (DANPE), and nitratoethylnitramines (NENAs) as well as particulate energy carriers like nitramines (Rozumov, 2017; Volk and Helmut, 1997).

For rocket motors, the subject is extremely well described in the book edited by Alain Davenas (1992), with this English version based on the French text published in 1989. The chapter by Herve Austruy (1993) contains a wealth of information on EDBs for rocket propellants. Gun propellant developments from 2010 to 2016 are well described in Rozumov (2017), but there is limited detail given on the solventless EDB type; based on the progress described in this review, it appears that alternative types of gun propellant are unlikely to displace solventless EDB in the near future.

In this paper we have attempted to include topics that are either new or have not been included in previous reviews. This includes some older processes that are considered interesting but are not necessarily well known. To the authors' knowledge, there has been no literature review of solventless EDB propellants for more than twenty years. Although many papers from China have been published in the last 20 years, there are few that concern actual applications—most are to novel formulations that are at the early stages of research and development (R&D). This review is generally focused on propellants at later stages of development and production.

The current quantity of solventless EDB manufactured for gun and rocket motor/missile applications is difficult to establish, although US and European manufacturers alone are estimated to produce more than 1000 tonnes of each type per year. The most important applications for EDBs are described in this paper. At the level of the all-up round (AUR), where EDBs are employed, e.g., a tank round or, say, a guided 70-mm rocket, the overall market value is estimated to be more than €1 billion per year, although the value of the finished EDB products typically represents less than 5% of this amount.

This review includes considerable information on AA-2 propellant and its equivalents, plus the resulting charges and motors, as used in 2.75-in. (70 mm) diameter rockets. This is because it is one of the best-documented and most important EDB propellants.

When referring to a complete rocket propellant subsystem (final shape, potentially inhibited), we use in this paper the terms “charge” and “grain”; for gun propellants the term “charge” is also used, meaning a multitude of “grains” with similar relatively small dimensions. In general, “solventless” is used when discussing gun propellants, but the term is redundant for rocket propellants as their web precludes manufacture by a solvent process.

2. PROPERTIES AND COMPARISON WITH OTHER PROPELLANT TYPES

Double-base propellant is often assumed to have inferior characteristics to alternative higher-energy propellants that can be used for both gun and rocket applications; however, this is not necessarily correct.

Considering the application of EDBs for rockets/missiles, in general the perceived lower EDB performance is primarily because freestanding grains are the preferred configuration for this propellant type. The primary disadvantages of such a design are

1. potential propellant volume loss, as there is a void along the casing's inner diameter;
2. mass loss for the spring assembly that ensures the grain is properly sealed at the nozzle grain interface;
3. inability to withstand lateral acceleration as the grain is not fixed, especially once the grain web has decreased; and
4. increased thermal insulation compared to a case-bonded design.

With the advent of the possibility of case bonding an EDB grain, due to advancements to the ever-increasing polymer toolbox, a primary limitation is potentially eliminated. This can increase the volumetric efficiency of a motor in excess of 10% on the standard motor design, as shown by Hong (2019); this point is discussed further in Section 4. Case bonding also reduces the lateral acceleration and ignition limitations that are often assumed.

2.1 Mechanical Properties

One of the primary limitations described by Davenas (1993) is that EDB grains cannot be used for case bonding during ignition at low temperatures. Typical mechanical properties of EDB propellants are shown in Table 1.

Though the work of Hong (2019) holds great promise, no low-temperature firings have been reported in the public domain. However, the stress that is encountered during low-temperature ignition varies greatly depending on the motor design, casing material, and caliber. It should also be noted that various stress relieving techniques can be employed to enable such grains to survive and that the increasing array of ambient cast and cure polymers offers further opportunities.

2.2 Combustion Products

One of the primary advantages of double-base propellants is that their combustion products are predominantly constituents of air. This is of specific interest for ground-based infantry launch systems. Ballistic modifiers having lead content are a concern for personnel that may breathe in such gases. However, with lead compounds typically making up less than 2% of the composition of a typical EDB rocket propellant, the molar fraction of the gas is relatively small compared to the Cl gas production of composite-type propellants, as shown in Tables 2 and 3.

TABLE 1: Mechanical properties of EDB propellant (reprinted from Austruy with permission from Elsevier, copyright 1993)

Property/Temperature	−40°C	20°C	60°C
Stress (MPa)	51	11	2
% Strain	2.8	2.5	8
Modulus (MPa)	1835	439	21
% Strain at ultimate stress	3.4	15.7	31.8

TABLE 2: Combustion products for a typical double-base propellant, mole % calculated by NASA's Chemical Equilibrium with Application software at 10 MPa and 298 K

CO	43.89%	H ₂	14.53%	N ₂	11.56%
CO ₂	9.93%	H ₂ O	19.74%	OH	0.02%
H	0.07%	NH ₃	0.00%	Pb	0.24%
HCN	0.00%	NO	0.00%	PbO	0.01%

TABLE 3: Combustion products, typical 85% ammonium perchlorate composite propellant, mole % calculated by NASA's Chemical Equilibrium with Application software at 10 MPa and 298 K

CO	13.35%	Cl ₂	0.01%	H ₂ O	39.99%
COCl	0.00%	H	0.37%	NO	0.08%
CO ₂	10.49%	HCl	17.94%	N ₂	9.40%
Cl	0.66%	HOCl	0.00%	O	0.02%
ClO	0.00%	H ₂	6.95%	OH	0.69%

The combustion gas products from the EDB propellant lead produced is less than 0.24 mol percent of the combustion gases produced, as shown in Table 2. The largest component of the combustion gases is carbon monoxide; however, as there is a shortage of oxygen, this will react with the air almost immediately to form carbon dioxide. Table 3 shows the combustion products for composite propellants, with nearly 18% of the combustion gases being hydrochloric acid, which in many operational scenarios is unacceptable. Though ammonium dinitramine has been researched and produced for nearly 30 years, and effectively removes this shortcoming of ammonium perchlorate composite propellants, it is not currently used in any operational system.

The combustion gases of most typical double-base propellants fall in the category of no-smoke or minimum smoke, producing only a vapor trail with metal additives and refractory additives as the only smoke components.

Gun and rocket motor propellants have differing requirements. In the case of gun propellants, the formulation is optimized for low-molecular mass combustion products such as CO on H₂ with relatively low temperatures. This allows for the gun barrel to be kept cooler (reducing barrel wear) and also increases driving force by generating more pressure per unit propellant mass, reducing both propellant mass required and the loading chamber volume. Typical force-flame temperature relationships for gun propellants are given in Fig. 1.

More barrel-friendly propellant compositions can be achieved by lowering the nitroglycerine content with a higher nitrocellulose content. This, however, lowers the energy content and density of the propellant. In contrast, rocket motors require higher-energy and higher-density propellants since the impulse delivered is directly related to the mass flow and the specific impulse (related to energy) of the propellant combustion gases. The rocket motor combustion chamber is not as sensitive to high flame temperatures as it is single-use, has a relatively short operational time, and can be thermally insulated, allowing for higher-energy propellants to be considered. To achieve the higher impulse and density, the NG content is increased, resulting in higher oxygen content and higher flame temperatures.

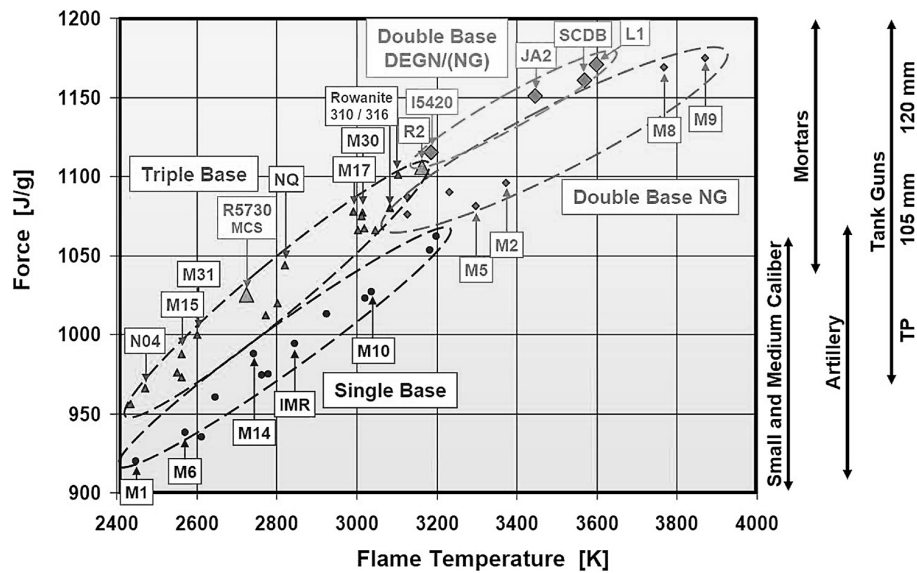


FIG. 1: Overview of gun propellant types and their force values and flame temperatures (reprinted from Vogelsanger et al. with permission from Nitrochemie, copyright 2007)

2.3 Ballistic Properties

The ballistic properties of cast double-base (CDB) and EDB propellants allow internal ballisticians significantly more flexibility in terms of grain design. Platonization of the propellant using lead and copper salts allows for plateaued burn-rate characteristics over a wide range of pressures for various desired burn rates, as shown in Fig. 2.

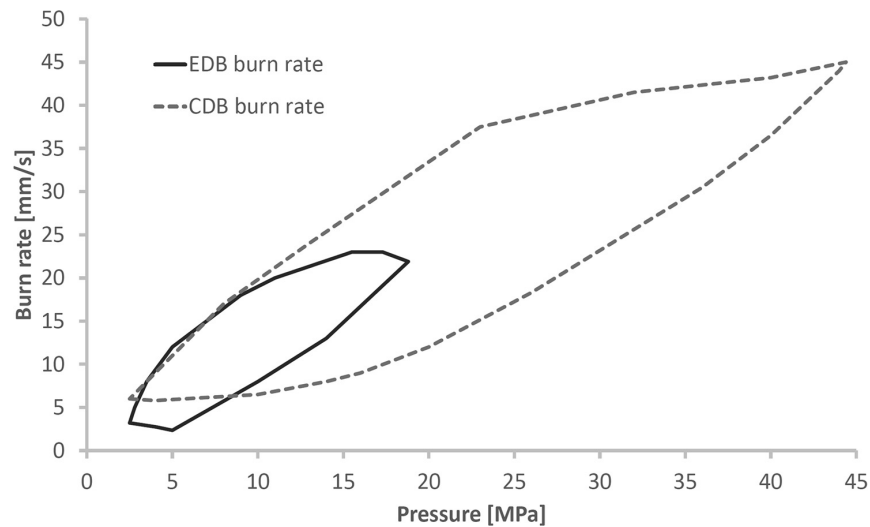


FIG. 2: Burn-rate region for double-base propellants (reprinted from Austruy with permission from Elsevier, copyright 1993)

In military systems that are expected to operate from -40°C (or lower if air carried) to 70°C , it becomes challenging to design a system that conforms to all performance specifications due to the temperature sensitivity of the propellant. Platonization not only reduces the response of the propellant to area fluctuations, resulting in smaller pressure/thrust changes due to changes in surface area, it also reduces the effect of the temperature sensitivity. For composite propellant, Vieille's burning rate law is commonly applied, with the burn rate being a power curve of the form aP^n . To compare the effect of the platonization, the mass flow from a propellant grain as a function of pressure can be generated as shown in Figs. 3 and 4.

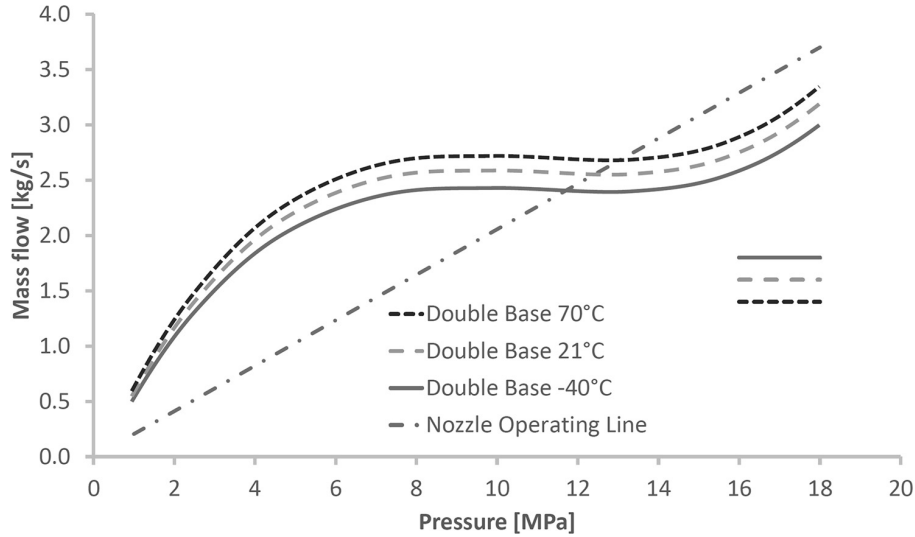


FIG. 3: Operating points for double-base propellant with temperature sensitivity coefficient of 0.0016

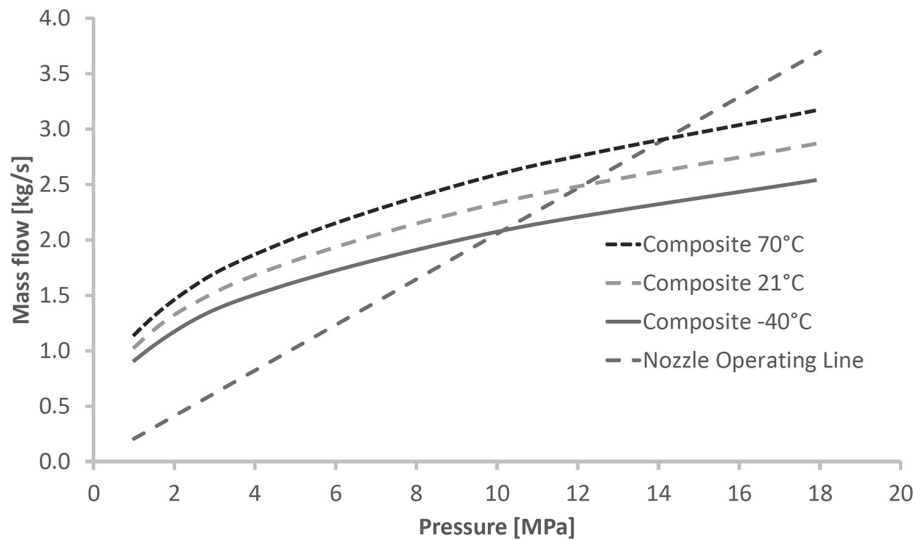


FIG. 4: Operating points for composite propellant with temperature sensitivity coefficient of 0.0016 and $n = 0.35$

The nozzle throat can be sized to obtain the desired mass flow at ambient conditions, for illustration purposes chosen to be 2.5 kg/s. Then, the intercept of the nozzle operating line for the high- and low-temperature curves represents the operational variation. Table 4 shows the variation for these two hypothetical cases, with the composite temperature variation being nearly double that of the double-base propellant. However, it must be noted that in the case of platonization, and especially propellants that exhibit a strong mesa (negative slope), it is often possible to find a point where the variation can be minimized further. Composite propellants often exhibit even greater variation, as the slope n does not remain uniform across all temperatures and exponent breaks; this often occurs in the preferred operating pressures for tactical missiles (12–14 MPa), which can increase temperature variation significantly. For applications that require lower variation in performance, such as ejection seats, double-base propellants allow for a significantly more robust design.

High-energy binders and propellants such as the crosslinked double-base (XLDB) type may not offer the expected performance benefits due to the limited burn-rate range of some of these propellants. As shown by Rousseau et al. (2011), it is possible to achieve significant range extension using double-base propellant properties, especially when the maximum velocity is restricted to subsonic conditions.

It should be further noted that temperature sensitivity is a significant limiting factor of the nominal system range on gun systems. Since the pressure generated at high temperature (70°C) needs to be under the maximum pressure of the gun, this in turn means that the nominal operational pressure is well below the design capability of the gun, greatly limiting the muzzle velocity that can be achieved.

2.4 Specific Impulse

Double-base propellants offer lower impulse when compared to other propellants, as well as a lower propellant density, as shown in Fig. 5. This has resulted in several studies into the addition of nitramines such as RDX and HMX into double-base propellants; see Davenas (1993) for further information. However, in a volume-constrained system, there are several other factors to consider, as the delivered impulse is not only a function of propellant composition but also other factors such as nozzle expansion constraints, nominal operating pressures, and smoke requirements.

However, it should be noted that energy delivered does not equate directly to increased system performance. If one uses the ideal gas law ($PV = nRT$) to evaluate the ability of a gas to deliver impulse or drive gun propulsion, it becomes clear there are two ways to increase the

TABLE 4: Performance variation due to temperature sensitivity

—	Double Base			Composite		
	−40°C	21°C	70°C	−40°C	21°C	70°C
Pressure [MPa]	10.0	11.0	11.8	9.5	11.0	12.4
Mass flow [kg]	2.3	2.5	2.7	2.2	2.5	2.8
% Pressure difference nominal	−9%	0%	8%	−14%	0%	13%
% Mass flow/thrust difference nominal	−8%	0%	8%	−14%	0%	13%

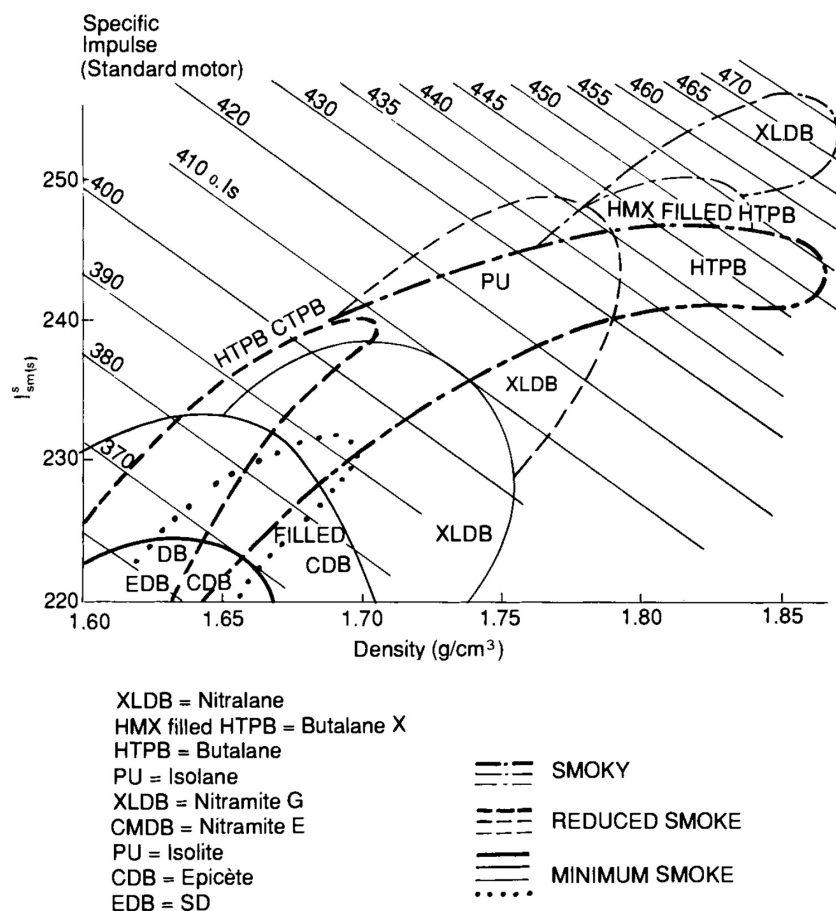


FIG. 5: Specific impulse for propellant families (reprinted from Davenas with permission from Elsevier, copyright 1993)

ability to deliver performance. Either increase the number of moles generated (H_2/O_2 rocket systems deliver the highest performance due to the combustion gases having the lowest molecular mass possible) or increase the temperature. For solid rockets the focus has been primarily on increasing temperature by the addition of metal additives or high-energy molecules, as shown in Table 5. Note that specific impulse I_{sp} calculations for a propellant with a high aluminum content (e.g., 18%) are not included in Table 5, since such formulations are not relevant for comparison purposes when considering applications for EDB propellants.

The increased temperatures, however, have implications for rocket motor casing, insulation, and ablative technologies, particularly for nozzles/blastpipes. This can have a significant impact on the end-product cost as well as adding unnecessary inert weight. In the case of guns, low-temperature, low-molecular weight combustion products are preferred, but increased energy propellant is sometimes also applicable for maximum range, although this generally results in reduced IM performance.

One of the additional advantages of using platonized propellant is increasing the nominal operating pressure. At the risk of having an exponent break that may result in an unacceptable

TABLE 5: Combustion gas properties at 10 MPa and 298 K, calculated by NASA's Chemical Equilibrium with Application software

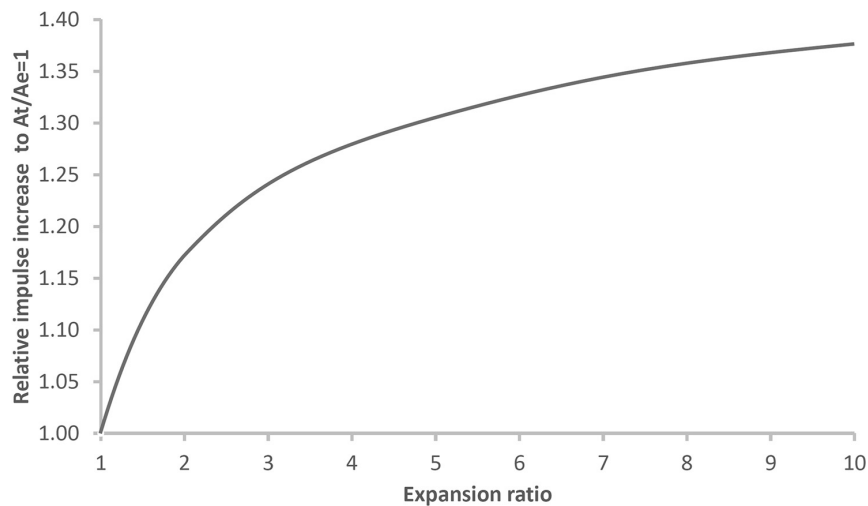
—	Typical double base	RDX/HMX double base	Low-smoke composite (0% aluminum)	4% Aluminum composite
Flame temperature [K]	2432	2820	2938	3088
Combustion gas molecular weight [kmol/kg]	24.28	25.01	25.25	25.9
I_{sp} , vacuum [s], expansion = 6	233	250	260	265

pressure peak or erosive burning peak, double-base propellants can be operated in many cases at a higher pressure if the plateau characteristics allow it. This allows the nozzle throat to be reduced and the nozzle expansion to be increased without significant volume or mass penalties. As shown in Fig. 6, increasing the expansion ratio has significant impact on the delivered impulse.

2.5 Rocket System Study Examples

To illustrate the flexibility of double-base propellant for rocket motor applications, a simplified three degrees of freedom trajectory analysis was undertaken using the methodology presented by Rousseau et al. (2011). Two cases are considered: 70-mm and 122-mm artillery rockets. These are chosen as they are systems currently in the marketplace with both double-base and composite propellant variants.

The first example is that of a 70-mm rocket, which in many ways is a more difficult rocket to optimize than a larger-caliber rocket, where a thicker web is possible. This is due to the

**FIG. 6:** Impulse increase as function of expansion ratio

difficulty of avoiding erosive burning effects with the relatively small port area available, while a star-shaped charge design removes propellant and results in a reduced volumetric loading. For this analysis, an EDB and composite propellant charges are compared with the improved performance offered by a case-bonded EDB, as described by Hong (2019), and the effect of nitramine-additive propellant.

Figure 7 shows the predicted trajectories for the 70-mm (2.75-in.) options considered. As all cases are boost or single-level thrust motors, increasing the impulse is the only feasible method of range extension. Thus the 12% increased propellant mass and related impulse increase result in a 10% range increase (see Table 6). It can be seen from this analysis that the impulse does not scale linearly with range extension, with the additional impulse required to increase range increasing. This is primarily due to the drag being a quadratic function of velocity, resulting in a higher proportion of the impulse being consumed by drag losses for little increase in range. Though the nitramine-filled double base does not quite match the composite propellant's performance, given the smokeless and noncorrosive efflux characteristics of the double-base option, this would still result in it being preferred in the typical helicopter launch environment of these systems. Since these rockets fly for less than 30 seconds, extended burn times to reduce base drag losses are not considered.

The mass-produced 122-mm artillery rocket allows for slightly more novel approaches to be employed, such as boost-sustain profiles. These rockets are fired platforms that can have up to 40 barrels. To keep these systems relevant, composite propellant rocket motors have replaced double rockets. These motors can become quite complex, some having multiple propellant layers, and

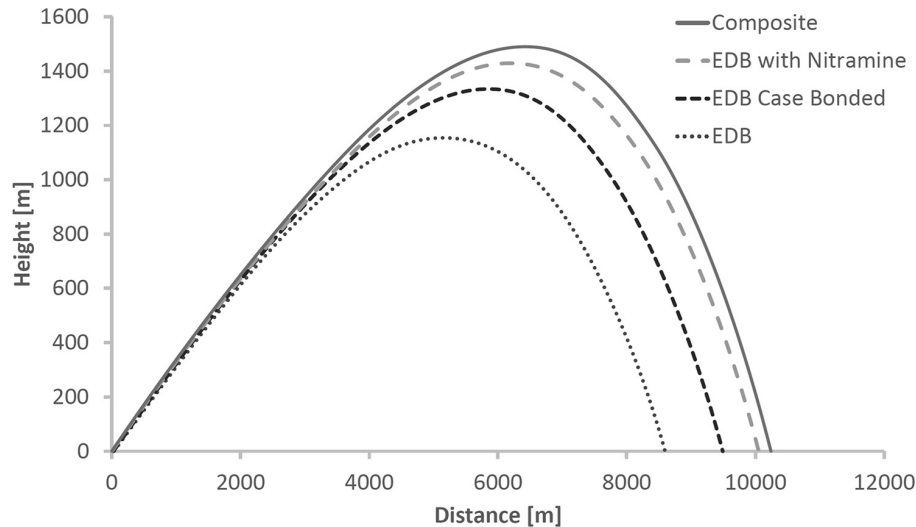


FIG. 7: Predicted 70-mm artillery rocket trajectories with a 20° launch angle at sea level

TABLE 6: Predicted 70-mm artillery rocket data, 20° launch angle performance at sea level

	EDB	Composite	EDB case bonded	EDB with nitramine
Range [km]	8.61	10.25	9.50	10.05
Range increase [%]	0%	19%	10%	17%
Impulse increase [%]	0%	23%	12%	20%

in some cases contain aluminum to increase specific impulse. This results in relatively expensive rockets, as high-cost ablative materials and improved thermal protection for the motor casing are required. The HCl and smoke generated for a salvo launch, especially with a convoy of launch platforms, is less than ideal.

Figure 8 shows the predicted trajectories and Table 7 the key performance characteristics for the varying configurations evaluated. As can be seen, the increased impulse doubles the predicted range of baseline EDB standard. Unlike the 70-mm case, increasing impulse is not curtailed by increasing drag losses to the same extent as these rockets achieve elevations where the air density is greatly reduced. It should be noted that the original EDB motor used in some 122-mm systems is a particularly low-specific impulse motor, and any high-energy double-base propellants would have marked improvement. By using a nitramine-filled double-base propellant, the range is extended to 36 km.

Another more novel approach, without resorting to increasing the energy of the propellant, considers a boost-sustain EDB motor. The aim is to extend the burn time to reduce the base drag losses during the initial flight through a denser atmosphere. By moving a significant portion of the impulse to sustain, the maximum velocity is also greatly reduced, reducing the peak velocity drag losses. Thus it is possible to design a system that can match the range while using standard EDB propellant. The required boost sustain is achieved by bonding two sections of propellant to each other, one with a high-burn rate propellant and the second with a low-burn rate propellant. The fast-burning propellant gives the boost phase high thrust; once this is consumed, the remaining slow-burning propellant keeps a minimum thrust level as long as possible.

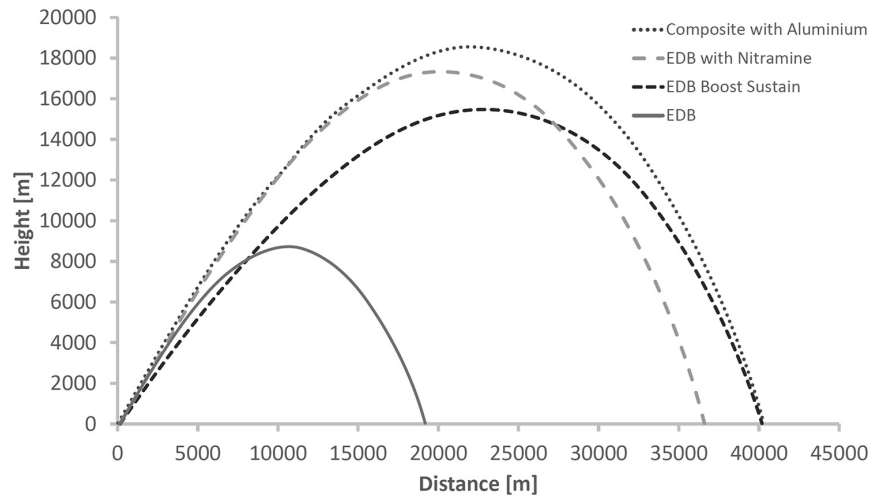


FIG. 8: Predicted 122-mm trajectories with a 56.7° launch angle at sea level

TABLE 7: Predicted 122-mm data with a 56.7° launch angle at sea level

—	EDB	EDB with nitramine	Composite with aluminum	EDB boost sustain
Range [km]	19.08	36.53	40.30	40.10
Range increase [%]	0%	91%	111%	110%
Impulse increase [%]	0%	49%	58%	46%

From these analyses it is clear that considering a rocket propellant group solely in terms of potential maximum delivered impulse may not identify the best propellant solution. It is possible to achieve comparable system performance from many typical rocketry applications by tailoring the ballistic properties of a double-base propellant and using more innovative grain designs. The lower sensitivity of EDB propellants (particularly the unfilled type) gives superior IM performance to the crosslinked double-base type, while the smoke characteristics are superior to composite propellants.

3. PROPELLANT MANUFACTURING (CONVENTIONAL AND CONTINUOUS PROCESSES)

Historically, gun propellants based on NC have been produced by a batchwise ram-extrusion process. For single-base, double-base, and triple-base propellants, solvent is traditionally used during the mixing and shaping steps of the manufacturing process. When introducing an energetic plasticizer to the NC, such as NG, double-base propellant may be produced solventless at elevated temperatures as the flow properties of the NC composition are improved by the incorporation of the energetic plasticizer. Depending on the type of NC and other components, triple-base and multiple-base propellant types can also be produced without using solvent.

The second main solventless process for the manufacturing of double-base gun propellants is repeated rolling, resulting in the formation of sheets that are cut into strips or flakes. Typical applications of this type of propellant are found in mortar and short-action rocket charges. This technique is not considered here as it is beyond the scope of this paper.

Several small- and medium-caliber gun propellant types contain lower amounts of NG (10%–20%) for reasons of performance increase. Although sometimes called double-base propellants because of the presence of NG, these types are produced like single-base propellants, either in ram-extrusion or slurry processes, and then impregnated with NG in a separate step. This type of double-base propellant is to be clearly distinguished from double-base propellants with higher NG contents, for which the production process involves mixing NG into the NC paste before shaping.

Tunestål et al. (2016) have described the propellant production processes at Eurenco Bofors AB. The conventional production process, by means of ram extrusion, is used for single-base propellants and for large-caliber gun and rocket propellants. The latter two propellants are produced solventless, while processing single-base propellants requires solvent. The water-based production process was developed in-house during the 70s at Bofors. First NC, NG, and/or other additives are added and mixed in a water slurry. A solvent is added to the slurry, which partly dissolves the NC. Pellets are then produced after evaporating the solvent. These pellets are water ejected to storage tanks and finally to two single-screw extruders. The first extruder produces granulate, which is then fed into the second extruder, which shapes the final propellant grain or stick. The advantage of this process is that it is a very safe production process since the energetic material is under water during the entire process. The disadvantage, however, is that no water-soluble ingredients can be added to the composition. As a result of this, and because of the need for a high-capacity and cost-effective production line for multibase propellant, a dry, continuous production process was developed.

The target for the new solventless process was to both replicate the closed vessel performance and match the throughput rate in the single-screw extruder compared to the ram extruder. Based on the already-available single-screw extruders, this new line was developed using the familiar batchwise rolling mill process to gelatinize the propellant ingredients. The propellant produced

by the new process showed a similar performance as the propellant produced by the conventional ram-extrusion process. It is claimed that this process is safer (as it is fully remotely controlled) and has better labor effectiveness, as the throughput is higher and fewer operators are required. Additionally, the process is said to be more efficient, as the scrap level is significantly reduced due to the continuous extrusion process. The next step, as described in the paper by Tunestål et al. (2016), was to implement a continuous rolling process utilizing shear roll mills for the gelatinization step, as depicted in Fig. 9.

Thomas et al. (2006), from Indian Head Division Naval Surface Warfare Center, describe R&D associated with improvements in the production of the DB AA-2 propellant; one of the primary objectives was to lower the environmental impact of the conventional process. The batchwise pressing process was replaced by a continuous process using a 40-mm co-rotating twin-screw extruder. For this continuous process, homogeneously mixed DB propellant pellets were required for proper feeding of the pellets into the twin-screw extruder, which extrudes the propellant into its final desired shape. The solventless pellets were produced using a shear roll mill. This facility was used to homogenize the AA-2 DB propellant and to produce granules/pellets in one step. According to Thomas, Nitrochemie Aschau GmbH found that any NC-based propellant composition with a total plasticizer level greater than about 30% (by weight) is a candidate for continuous processing on the shear roll mill. By integrating both a shear roll mill and a twin-screw extruder in the process, two major changes to the baseline process were obtained. The shear roll mill replaced the carpet rolling steps, and the twin-screw extruder replaced the batch extrusion and the machining steps. This is illustrated by Figs. 21 and 22 in the ESTCP report of Thomas et al. (2006).

An example of the application of this more environmentally friendly process is the solventless manufacturing of a new double-base propellant for 25 mm-caliber applications (Manning et al., 2006).

In 2013, Manning et al. reported their effort to produce a JA-2 equivalent propellant for tank munition applications by means of continuous solventless extrusion to eliminate residual solvents in ammunition and to reduce the emissions of volatile organic compounds to the atmosphere. The standard JA-2 propellant formulation was modified slightly for this work, as the viscosity of JA-2 propellant is too high to safely produce this by a solventless twin-screw extrusion process. TNO uses its own stepped approach to safely operate twin-screw extruders for the production of EDB propellants. The rheological properties and die design of the JA-2 equivalent propellant were optimized. Subsequently, ram-extrusion experiments were executed to validate the simulated pressure drop over the die. After optimizing the process parameters such as screw design, mass flow, screw rotations per minute, and processing temperature, the propellant was successfully produced by solventless extrusion using TNO's 45-mm twin-screw extruder, shown

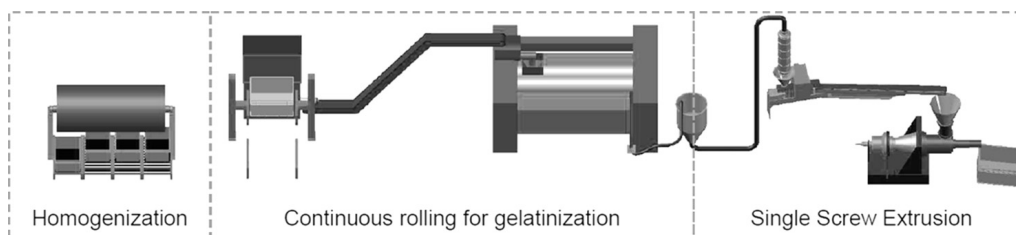


FIG. 9: The production line at Eurenco Bofors AB including a continuous rolling process (reprinted from Tunestål et al. with permission from Eurenco Bofors AB, copyright 2016)

in Fig. 10. Closed-bomb tests showed that the extruded 19-perforation propellant had the desired burn properties, which will result in a comparable gun performance as the baseline 7-perforation JA-2 propellant.

Van Driel et al. (2016) has reported the work done at TNO to convert a solvent twin screw extruder (TSE) process into a solventless one for testing 35 mm-caliber projectiles. In an earlier stage, double-base propellant was produced with a 45-mm co-rotating TSE using a solvent process. The same propellant was required, however a solventless process was desired. In order to tune the viscosity and to decrease the flame temperature of the chosen composition, a nonenergetic and environmentally friendly plasticizer was added. As a result of the addition of the inert plasticizer, the grain dimensions had to be optimized such that appropriate combustion properties were obtained. This led to a die geometry resulting in 19-perforation double-base propellant grains with an outer diameter of 5.1 mm. After optimizing the die design and executing ram-extrusion trials, the propellant was successfully produced solventless using TNO's 30-mm co-rotating TSE. The performance of the new, solventless manufactured propellant appeared to be almost equal to the performance of the reference propellant, measured both during life firings as well as closed-bomb tests.

4. INHIBITION (INSULATION)

Inhibition of rocket propellant grains must be clearly distinguished from burn-rate retardation, which is applied in gun propellant charges. The latter is described in Section 6.3.

Most applications for rocket propulsion require one or more of the grain burning surfaces to be inhibited for a number of reasons, but in particular in order to provide the correct burn-rate profile. Unfortunately, NG, which is typically present at levels above 35% in EDB propellants, is quite a mobile species, so unless the inhibition is carefully designed, migration issues can cause

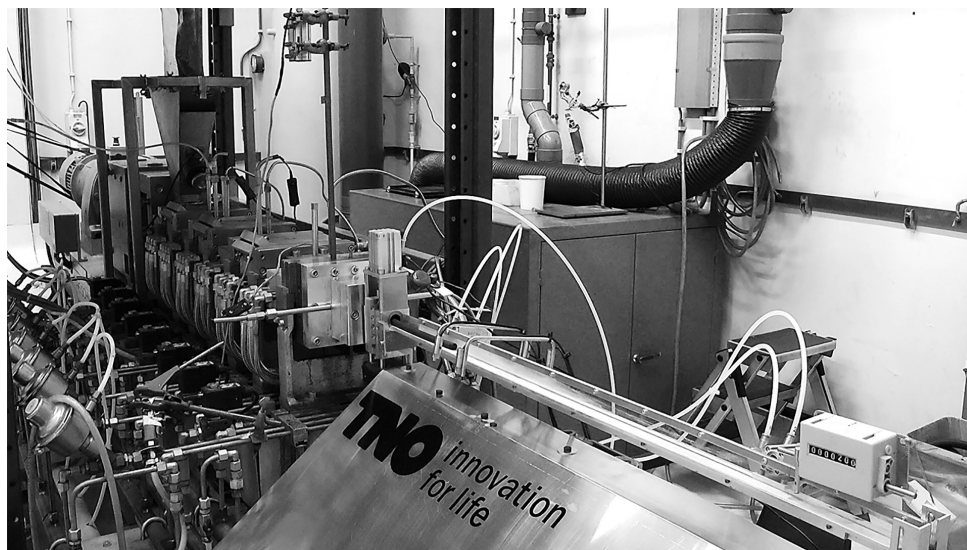


FIG. 10: TNO's 45-mm twin-screw extruder during the solventless extrusion process of a JA-2 equivalent propellant. The propellant strand in the center of the picture is guided over the takeaway system. Photo by TNO.

abnormal ballistics or complete grain failure, as a result of debonding between the propellant and the inhibition. Pröbster and Schmucker (1986) describe the phenomena very well, including factors affecting plasticizer migration, methods to prevent liquid species migration, and methods to obtain plasticizer-resistant insulations. Barrier coatings, such as the one described by Sutton and Biblarz (2001) and Gordon and Evans (1981), are also reported. Silicone inhibitors have been described quite extensively, e.g., the paper by Gonthier and Tauzia (1984), but this system does not appear to have been widely adopted for in-service grains. Other techniques, such as cast polyurethane formulations with oxamide to minimize smoke formation, are described in some detail by Tauzia (1993).

For 2.75-in grains, the circumference is typically spiral wrapped with ethyl cellulose tape, while the end faces use washers of the same type of material. However, some migration of NG is normal with 2.75-in grains using ethyl cellulose, and this can sometimes result in ballistic failures.

Hong (2019) has reported recent efforts by BAE Systems in the US to use a resin/adhesive system for the circumferential inhibition that includes case bonding, so eliminating the tape wrap and allowing a greater propellant mass representing the annular space between the outer diameter of the conventional 2.75-in tape-wrapped grain's outer propellant diameter and the inner diameter of the case. Hong reported a 12% increase in total impulse compared to a standard AA-2 grain. The ability of such a case-bonded charge to survive extended temperature shocks/cycling does not appear to have been established but is a likely risk at fixed wing temperatures, if not rotary wing.

5. NOVEL MANUFACTURING PROCESSES

5.1 Stamping

Austruy (1993) describes stamping as a hot forming process, with the operation carried out in several stages: the propellant piece is placed in the mold, which is then closed, and the temperature is raised to 80°C–90°C; the forming temperature and pressure (3 KPa) are applied with the softened propellant and then compressed to obtain the final shape desired. The process enables closed-end shapes, which aren't possible to be manufactured via extrusion. Other complex shapes can also be achieved without excessive machining.

5.2 Segment-Assembled Grains/Pressed Solvented Sheets

Segment-assembled grains and pressed solvented sheets are two variants of the same process whereby propellant sheets or extruded sections are glued together with the aid of solvent.

In the first case, with sheets of propellant, Groundwater (1965) describes the following process to manufacture 200 mm–diameter grains of mass 47 kg:

“... the rocket propellant was rolled into thin sheets (2.5 mm thick). The sheet was then die cut to the required outside diameter. The punched out die was then perforated in the same manner in the centre with a seven point star internal cavity shape. Enough dies to comprise one motor were then mounted on an eight-point star shaped mandrel, spaced loosely along the mandrel. The mandrel was lowered into a solvent bath. On withdrawal from the solvent, the dies were compressed together with a pneumatic press and the solvent allowed to evaporate. This process took considerably longer than the regular extrusion technique, but produced motors

of equal integrity. On X-ray, no cracks were evident longitudinally or between layers of propellant. This fact was confirmed when several motors were cut open for inspection. While the process was markedly slower (due in part to lack of tooling for the specific process), it had no limitations as to diameter or length of motor possible to produce. Quality of the motor was at least as good as the extruded motors and any possible residual stresses due to extrusion were eliminated.”

Although Groundwater describes successful static testing of such grains when gun fired at 7900 g and 1500 m/s, there were problems with grain failures. Subsequent to Groundwater’s report, Bull and Murphy (1991) have described how the grain collapse was avoided by filling the star cavity (of a 159-mm diameter gun-fired motor) with a zinc–barium solution matching the density of the EDB propellant.

In the other variant of this EDB grain manufacturing process, extruded sections, which might be either in the plane of extrusion as radial “wedges” or perpendicular to the direction of extrusion, are joined to form a larger grain. The former has the advantage of enabling a relatively small extrusion press to produce large grains, while the latter enables dual burn-rate formulations to be joined together or extrudate that has defects to be removed but the required grain to be made up of “off cuts.” Bellotte (2014) has proposed that the extruded radial wedges of propellant grains could be bonded with elastomeric epoxy to generate grains of diameters exceeding 1000 mm for both cartridge-loaded and case-bonded designs. However, it is unknown if such concepts have been demonstrated. At least one example of this process, with the sections to be glued together perpendicular to the direction of extrusion, is known to have been qualified and employed with an in-service missile system.

5.3 Multi-Ply Process; Grains ≥ 1 m in Diameter

Bellotte (2014) has also briefly described historical US work to manufacture EDB grains up to diameter 1300 mm, including demonstrating propellant grains of variable radial formulation. Although neither the segment assembly nor the multi-ply process lend themselves to series manufacture of propellant grains, it could be argued that they are well suited to production of propulsion for missiles in the 21st century, when the volumes required are often only a few hundred, or fewer, charges per year.

5.4 Snail Charge

The Anglo-French MCM ITP has been investigating a novel propellant charge that can provide a boost/sustain thrust profile at high length-to-diameter ratios. This is achieved using a so-called “snail charge,” with the propellant folding inside the rocket motor casing. Although the type of propellant being considered is not disclosed, it appears that an EDB could be used, potentially stamped or adhesively bonded, as described above.

5.5 Additive Manufacturing

Additive manufacturing, or 3-D printing, of energetic materials is a new manufacturing method rapidly emerging in recent years. Although its possibilities regarding new shapes and internal grain structures are almost endless, and even production volumes are likely to become comparable to those of conventional extrusion techniques (Van Lingen et al., 2018), EDB compositions seem to be unlikely candidates as base material in the short term. Extrusion of EDB pastes in

printing techniques comparable to fused deposition modeling (FDM) seems feasible as demonstrated, for instance, for pastes with NC simulants (Chiroli et al., 2019), but this will require the use of solvents to obtain enough stickiness to bond together successive layers without loss of energy content. Evaporation of the solvent results in shrinkage, requiring special attention to the design of the shaping process. The use of composite formulations in combination with FDM and other 3-D printing techniques seems more obvious in the years to come.

6. FORMULATION

6.1 Nitrocellulose

Since NC for propellants is currently manufactured industrially either from cotton or wood cellulose, it has variabilities that are associated with natural products. Sloan and Wall (2007) report that apparently minor changes in cellulose properties can have a major influence on CDB propellant properties and give examples of many changes in linter and NC manufacturing sources experienced by a rocket motor manufacturer. The different linter and NC sources resulted from supply chain obsolescence, and this issue has continued in recent years to such an extent that propellant manufacturers have now become better able to manage such changes. Similarly, Schimansky (2012) has described how

“the situation of being totally in control of what was supplied to you as NC manufacturer (cultivar, cut length and precise growth area) changed to a situation where you can only test the incoming batches” (of cotton) “against the MIL STD and ... with these methods one does not really measure the variation in the linters.”

Although some gun propellants use wood-sourced cellulose EDBs, rocket propellants are currently generally manufactured from cotton sources (although historically this was not the case). Sloan and Wall (2007) report some data on the mechanical properties, etc., of CDB propellant manufactured from cotton and wood cellulose. Since trees grow over many seasons, it might be expected that propellants from such a source would result in propellant with more consistent properties; however, there is no known published data that confirms this.

Torry et al. (2016) have reported on research into the use of bacterial cellulose to produce NC, with the aim of having consistent, long, nanosized fibrils that would avoid reliance on uncertain supply chains and the variance in naturally produced cellulose. NC was produced at a lab (10 g) scale and characterized; it was concluded that the % nitrogen (N) could potentially be exploited in gun propellants.

Improvements to the burn rate and sensitivity of NC, by downscaling it to nanosized powder and the addition of carbon nanotubes (during a supercritical antisolvent process), are discussed by Muravyev in his presentation at 12ISICP.

Szala (2020) has analyzed options of eliminating NC in solid propellants. With regard to double-base propellants, he concludes that the structure-forming role of NC seems irreplaceable in the foreseeable future.

6.2 Ballistic Modifiers for Rocket Motors

Double-base rocket propellants have, for more than 50 years, used such modifiers to both increase the burn rate of propellants and to platonize the propellant, resulting in a pressure range where there is only a small increase in burning rate. Such platonization results in good performance (reduced maximum pressure, relatively constant thrust) over an extended temperature

range. Such behavior must also be exhibited after storage and deployment of propulsion systems, i.e., there must be a low ballistic drift.

As described by Fleming and Jones (2019), due to the EU's Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) and other regulations, the use of lead-based compounds is being restricted, with three of these (that aren't used as ballistic modifiers) already considered substances of very high concern (SVHC). Since most lead-based ballistic modifiers, e.g., lead beta resorcyate, LC 12-15, are not generally used outside the defense industries, they may not attract immediate attention by the European Chemicals Agency (ECHA) or Member States; however, if/when they do, or the precursor chemicals required for the manufacture of ballistic modifiers are themselves banned, major issues are expected. Lead monoxide is an example of a "dual-use" ballistic modifier; it has been listed on ECHA's website as a candidate SVHC since 2012 but has not yet been confirmed, and thus a sunset date has yet to be defined.

Lead-based ballistic modifiers are currently used in many in-service propulsion systems and are also employed in systems that are currently in development. It is not unusual for the manufacture of any particular rocket motor to continue over 30–40 years (from the start of propellant/motor development to the last motor manufacture for a particular missile application), with small batches of charges manufactured at particular times. Thus, the implications for a change in legislation would be significant.

The technical challenges for lead-free alternatives include compatibility (e.g., avoiding gas cracking) and platonization over a full range of burning rates, ideally from 10–45 mm/s, over an extended operational temperature range, including after long-term storage/deployment. Aromatic lead salts act as scavengers, protecting the propellant's stabilizers so a shorter chemical shelf life could result, unless lead-free ballistic modifier propellant formulations can be developed that incorporate this same function.

Headrick (2010) describes US lead-free efforts on EDB charges for 2.75-in motors from 1991 to 2010. Three key performance criteria were identified, compared to the existing LC 12-15 ballistic modifiers used in AA-2 propellant, all after aging: (i) stabilizer retention, (ii) plateau burn-rate behavior, and (iii) temperature sensitivity. The more recent of the work reported by Headrick (i.e., 2003 to 2010) showed that bismuth compounds performed well but copper ones didn't, though none worked well after aging. The most promising of the candidates was based on a bismuth formulation designated RPD-540, although it didn't fully meet the defined criteria.

In 2015, Thompson reported on heavy and flightweight testing of propellants with an RPD-540 bismuth-based modifier. However, the burn-rate behavior was considered too temperature sensitive for qualification as a replacement to the currently fielded AA-2 propellant. Interestingly, the level of modifier in the propellant could be lowered from 4% to 2%, offering the possibility to reduce the loading of the propellant by 2%. Thompson also noted that

"the major roadblock to implementing any future extrudable propellant in the Hydra weapon system maybe the economics. Extruded (double base) propellant has long been recognized as a much less expensive alternative to castable propellant in configurations where the rocket motor diameter is < 100 mm (as in the case of the Hydra). Recently, the cost of producing extruded propellant has risen to the point that the Hydra PMO has determined that a castable propellant may be the next rocket motor concept considered for future implementation."

However, the only minimum-smoke castable propellants in service in the US are the crosslinked double-base type, which have very poor insensitive munitions (IM) performance.

The total expenditure in the US on such replacement activity, since the 1990s, is not reported but is probably many millions of US dollars.

As reported by Fleming et al. (2010), Roxel Group had then studied lead-free compositions for EDB propellants for five years, and they had found it easier to find potential replacements to lead in high-burning rate (i.e., 30 mm/s at plateau) propellants than with lower-burning rate formulations (i.e., 15–20 mm/s).

Warren (2021) very recently published a detailed review of the trends in burn-rate control for energetic materials; they conclude that the most promising routes to replace lead involve the application of carbon materials, falling into two groups: nanopowdered carbon and carbon nano-materials (CNM), with the latter including carbon nanotubes (CNTs) and graphene. Both groups are described as offering the advantages of large surface areas and strong gas adsorption capacities. The latter group is claimed to also enhance mechanical properties, including improved friction insensitivity.

Given that there have been more than 30 years of efforts with bismuth and other lead-free modifiers that initially gave promising results, it seems unlikely that CNM and other recent developments will result in service use before 2030. The bismuth modifiers appear to offer the potential for service use in the next few years, assuming some relatively minor reductions in motor performance could be accepted. Although bismuth has some hazards, the European Union's report (2020) states that "several bismuth-containing substances are registered with REACH. However, none of them are on the list of Substances of Very High Concern. Bismuth (...) is generally acknowledged for its non-toxicity in many of its uses." Thus, modifiers based on bismuth are much less likely than the ones containing lead to experience environmental and health restrictions.

The price of lead-based ballistic modifiers, purchased in production volumes, is typically approximately US \$100/kg. Generally, they comprise 2%–4% of the propellant, so assuming a charge requiring 5 kg of propellant, the purchase price of the lead compounds is, say, approximately US \$20 per charge. For an unguided rocket (e.g., Hydra), this represents less than 2% of the price of the all-up round, or much less than 0.2% of a missile's price. In summary, ballistic modifiers are relatively low-cost ingredients, purchased in small quantities, but are critical ingredients that have proven very difficult to replace.

If the relevant lead ballistic modifiers are banned under REACH, then authorization applications, defense waivers, or the introduction of "next-generation" propellants will be necessary.

6.3 Burn-Rate Adjustment for Gun Propellants

Burn-rate retardation in gun propellant charges can be viewed as a kind of ballistic modification. Working at much lower pressures, however, the modification mechanism in case of rocket propellants differs from the mechanism in gun propellants. In the latter case, the composition of the grain surfaces differs from the propellant core, aiming at an increase of the gas production rate during the ballistic cycle. For this reason, small- and medium-caliber gun propellant grains are often impregnated with a less energetic or nonenergetic plasticizer, reducing the burn rate. In the case of larger-caliber gun propellants, with web sizes of up to several millimeters, this type of burn-rate regulation is not feasible because of the larger diffusion distances making it impossible to effectuate sufficiently deep penetration of the plasticizers. Moreover, double-base propellants contain too much energetic plasticizer to keep burn-rate retarding nonenergetic plasticizers in the outer layers of the grains, although attempts have been made to apply polymerizable substitutes like acrylates to obtain stable impregnation (O'Meara and Murray, 1996).

The application of co-layered propellants comprised of propellant compositions with different burn rates and energy contents makes it possible to obtain high progressivity. This results in both an increased muzzle velocity and decreased erosivity. Computer simulations presented by Zebregs and van Driel (2009) have shown that with co-layered stick propellant configurations, a decrease of the gas temperature during the ballistic cycle of several hundred degrees may be obtained, compared to single-composition propellants with equal or less performance (see Fig. 11).

Ritter et al. (2007) reported on the labor-intensive manufacturing process of co-layered sheet propellants with sandwich structure. This process, involving the rolling of assembled sheets of two propellant layers with different compositions, folding them, and rolling again, requires practically identical rheological properties of both propellant compositions in order to maintain a constant ratio of the thicknesses of both layers.

Durand et al. (2015a,b) have described a co-extrusion process for cylindrical multi-layered propellant for which a complex die was developed. They also patented a manufacturing method in which a conventionally extruded outer propellant layer is filled with a low-viscosity propellant material as an inner layer that is later polymerized.

Zebregs et al. (2007) and Zebregs and van Driel (2009) have reported on the development of experimental setups for the co-extrusion of cylindrical gun propellants. Practical results were obtained for both double base- and composite LOVA-type propellants (Figs. 12, 13, and 14). Manufacturing of such co-layered propellants may be done by a double ram press, having the advantage that the ratio of the mass flows of the core and outer layer materials is always constant, which will result in a constant product. Co-extrusion around a premanufactured core strand is another possibility, requiring fewer adaptations of existing process equipment. Perhaps the most flexible process setup for co-extrusion consists of two simultaneously operating continuous extruders, outlined in Fig. 15. These facilities offer the possibility to adjust both mass flows exactly as required for a specific grain and die design, offering more flexibility than with the double ram press.

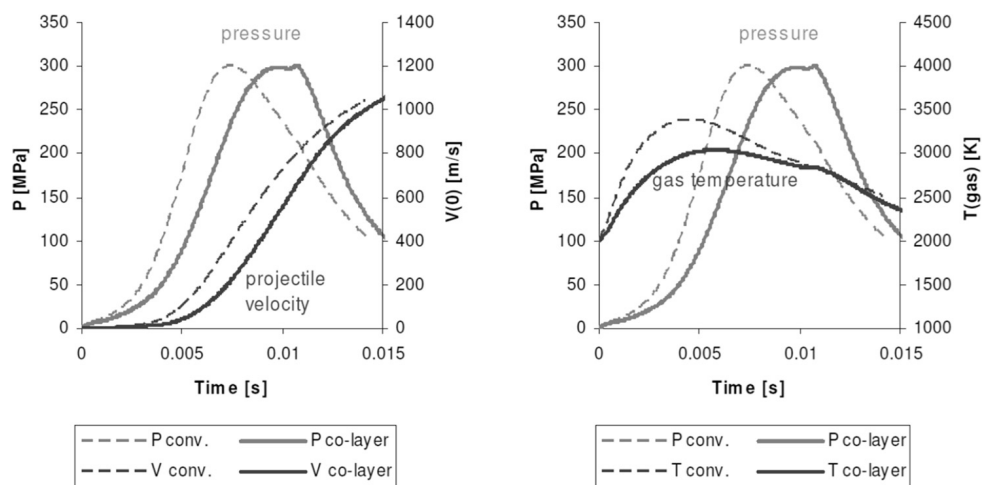


FIG. 11: Computer simulation results for non- and co-layered stick propellant showing a decreased gas temperature profile for co-layered propellant relative to a single-composition propellant with equal performance (reprinted from Zebregs and van Driel with permission from TNO, copyright 2009)

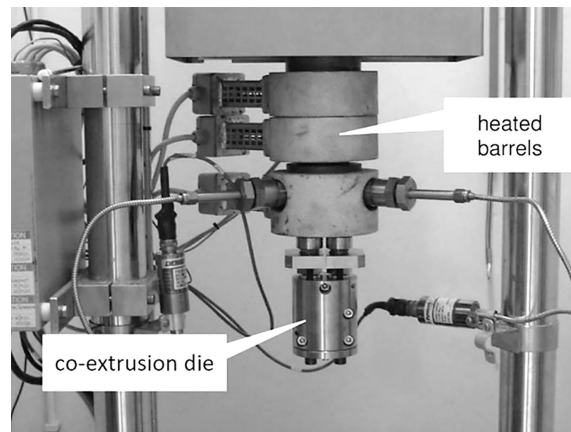


FIG. 12: Double-barrel capillary extrusion rheometer (CER), equipped with co-extrusion die (reprinted from Zebregs and van Driel with permission from TNO, copyright 2009)

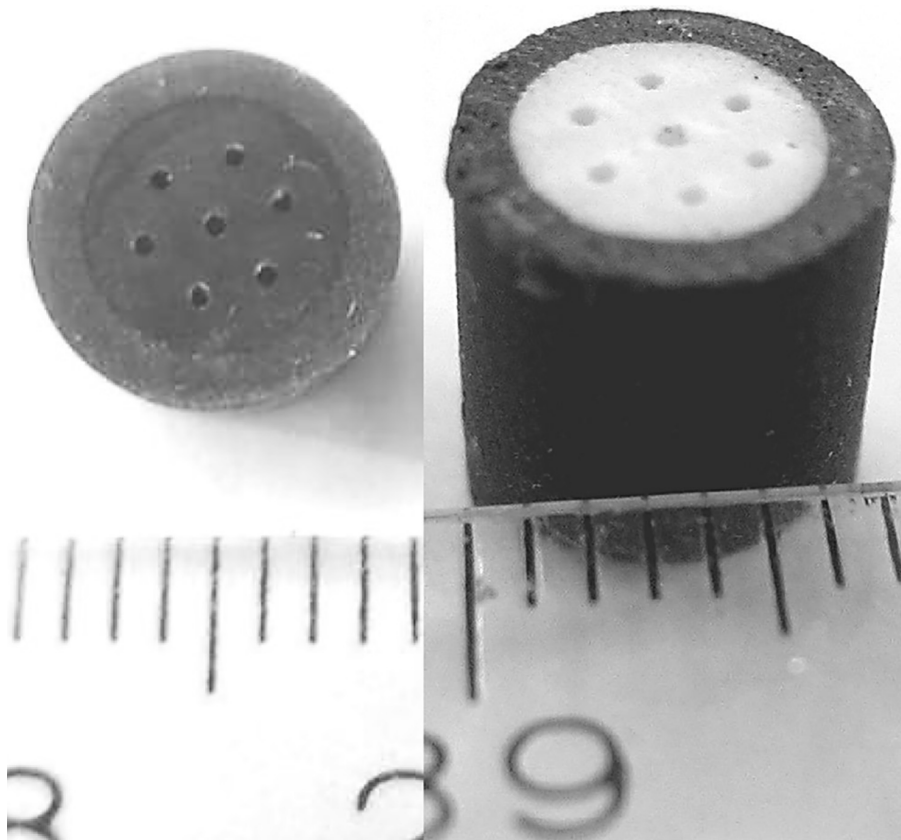


FIG. 13: Co-extruded grains produced for demonstration purposes. On the left picture a double-base grain is shown, which was solventless and produced with TNO's CER. The right picture shows a solventless produced composite propellant using the same test setup as used for the double-base grain (reprinted from Zebregs and van Driel with permission from TNO, copyright 2009).

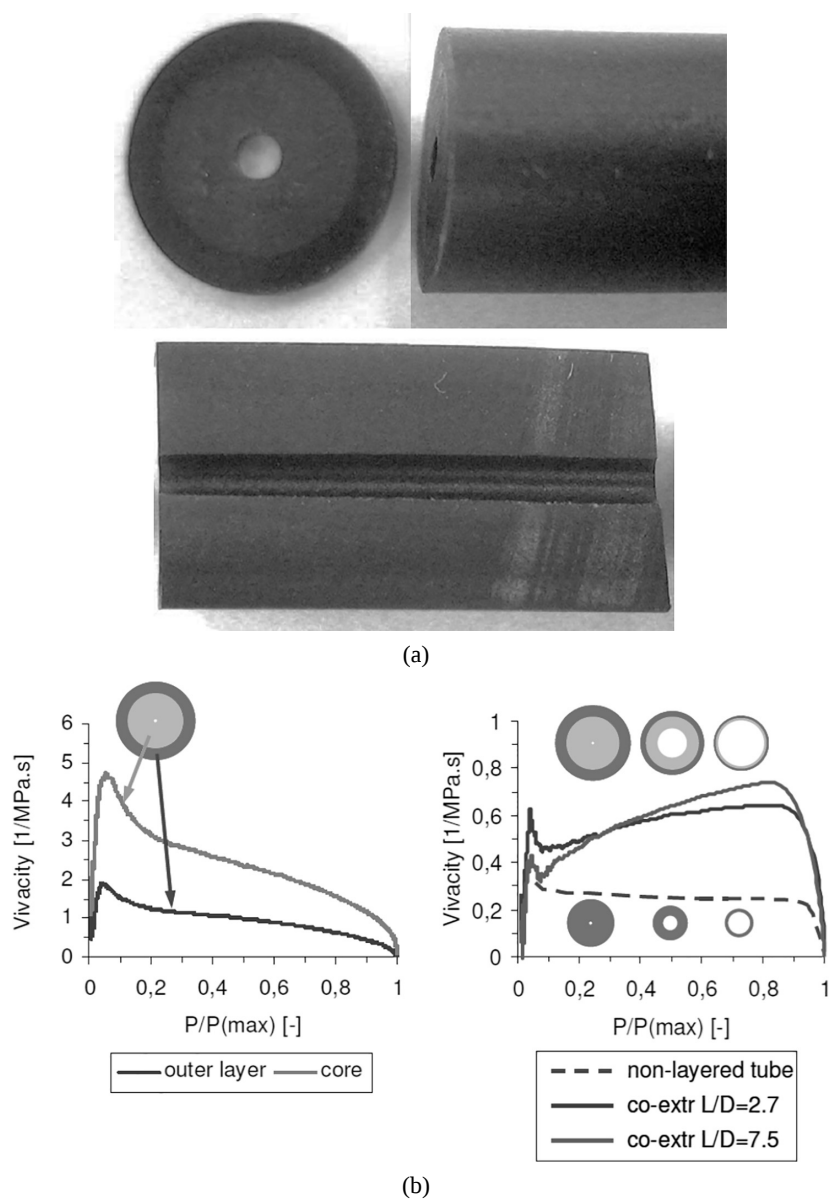


FIG. 14: Left: A 6.8-mm solventless produced co-extruded double-base propellant with both excellent layer distribution and bonding between the layers. Middle: Experimental vivacity curves obtained for non-perforated propellant grains with the compositions of the inner and outer layers of the co-extruded propellant. Right: Closed vessel test results obtained for co-extruded propellant with two different length/diameter ratios (reprinted from Zebregs and van Driel with permission from TNO, copyright 2009).

In the same paper, Zebregs and van Driel also described the ballistic performance of co-layered propellant sticks produced by co-extrusion. Initially producing relatively cool combustion gases and hot gases in a later stage of the ballistic cycle, non-, single-, and multi-perforated

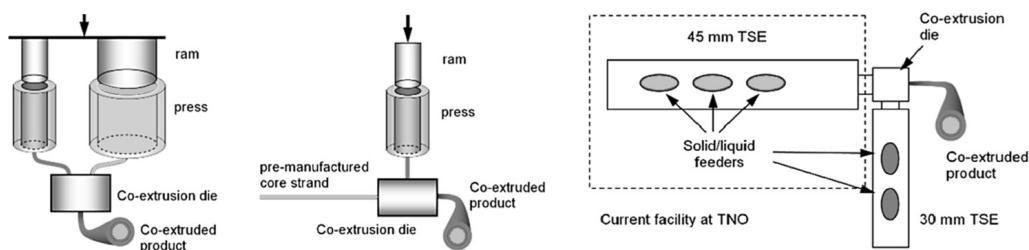


FIG. 15: Extrusion processes for the production of co-extruded energetic materials. Top: double ram press (left) and co-extrusion around premanufactured core strand (right). Bottom: simultaneously operating continuous extruders (reprinted from Zebregs et al. with permission from TNO, copyright 2007).

co-extruded propellants have superior properties with respect to erosivity and performance. They conclude therefore that co-extruded propellants will be well suited for use in direct-fire systems, for the upgrading of munitions of conventional howitzers, and for other systems.

Van Driel et al. (2019) have described configurations for co-layered propellants potentially resulting in progressivities even higher than obtained for conventional multi-perforated propellant grain shapes.

6.4 Other Ingredients

The inclusion of RDX to increase the total impulse of EDBs, for both gun and rocket propellants, has been known since at least the 1980s. Baker (1986) described improvements in the performance (density $\times$ impulse) of EDB propellants by the addition of nitramines, while retaining good plateau ballistics over a wide range of burning rates (3–30 mm/s). Ballistic modifier combinations were used that enabled the propellants to be safely processed using standard UK manufacturing techniques. Increases of 10% in impulse were reported to have been confirmed in large-diameter boost motors, with retention of low temperature coefficients, and with minimum impact on other design aspects. Gautam (1998) reported that if the RDX loading exceeded 15%, then the EDB propellant's mechanical properties were reduced significantly.

More recently the use of RDX to provide plateau burning has been reported by Elghafour et al. (2018). Stabilizers have yet to be mentioned in any detail in this review, but there do not appear to have been any significant developments in this area, for solventless EDB propellants, in recent years. Generally, with a well-formulated propellant and charge design, service life is not a major issue. Such propellants include other minor ingredients, but these are not considered in the current review. Rozumov (2017) describes advances with such ingredients, plus NG, etc., in considerable detail.

7. INSTABILITY

All propellant types used in rocket motor applications, including HTPB composite propellant, can experience combustion instabilities. Combustion instability is essentially the interaction of an acoustic wave with the combustion processes, with associated fluid dynamic gain and loss terms. There are also two further possible initiation mechanisms: motors that are inherently unstable, i.e., they become unstable without any prior event, and pulsed or induced instabilities, which are often caused by the shock wave caused by the nozzle being momentarily blocked due to some internal material being ejected through the nozzle. The final distinction is the modes that

can be encountered: longitudinal, tangential, and radial. Double-base propellants usually exhibit inherent instability with tangential modes, and composite propellants exhibit pulsed instability with longitudinal waves.

The reason double-base propellants exhibit inherent instability with high-frequency tangential modes is due to the fact that double-base and most homogenous propellants maintain a high acoustic response function even at high frequencies, as described by Blomshield (2009). Double-base propellant can supply energy to significantly higher modes, as the pressure-coupled response is still significant at higher frequencies.

Three main tools are available to reduce or suppress combustion instability, as shown in Blomshield (2001):

- Mechanical devices such as resonant rods or Helmholtz resonators.
 - Typically found in older systems and, especially in the case of resonant rods, in artillery rockets.
- Particle suppression has been widely used, with Evans and Smith (1978) presenting a wide array of possible refractories that can be used.
 - If the particle sizes are chosen correctly, then acceptable stability limits can often be achieved with refractory levels of less than 1%.
 - Refractories, being abrasive in nature, are not commonly used in extruded products due to the increased wear on extrusion tooling.
 - However, particle suppression remains the primary means for acoustic instability suppression.
- Grain and nozzle design changes. As noted by Kang (2014), changing the number of star points from even to odd can suppress combustion instability by forcing a nonsymmetric plane. Nozzle damping is also a primary loss mechanism; by designing the nozzle inlet in such a way that most of the acoustic energy exits through the nozzle, the stability limit of the motor can be increased.

Resonance rods are often used to reduce instabilities, especially when the propellant is formulated without refractories, which is generally needed if the IM performance is important.

EDB propellants without refractories have card-gap results (as a result of the NC and NG) that start reasonably high (e.g., 45 to 55) but still comfortably below the 70-cards cutoff point for hazard division (HD) 1.3. Composite propellants have the advantage of starting at zero card gap if no nitramines are included. In practice, once a motor with composite or EDB propellant requires a significant amount of refractories and/or nitramines, it is difficult to meet the ≤ 70 card-gap requirement. This aspect is discussed further in the section on IM performance of EDBs.

Kang et al. (2014) present another method for reducing combustion instabilities, as demonstrated for a 2.75-in Hydra-type motor using AA2-type propellant. The modification was to change the shape of the star to an uneven number of tips; refer to Fig. 16, while Fig. 17 illustrates the reduced burning instability.

8. INSENSITIVE MUNITIONS

This section considers IM aspects for both gun and rocket propellant applications. It should be noted that IM performance depends on the complete subsystem, not just on the propellant type;

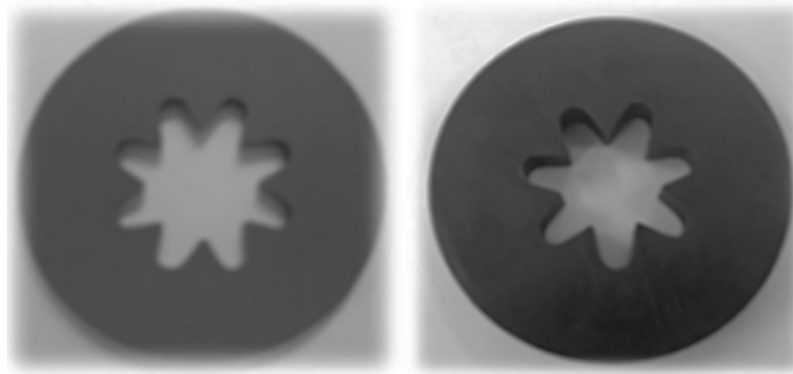
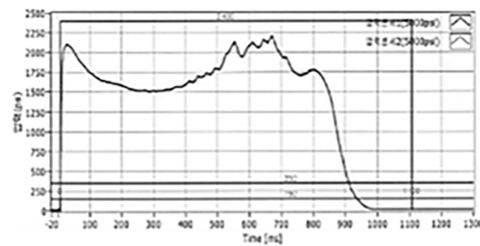
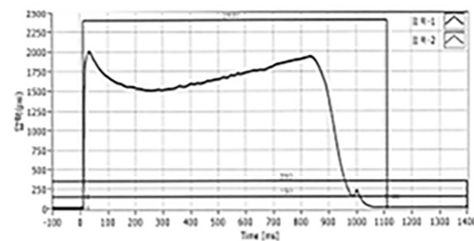


FIG. 16: Propellant charge star shape with eight tips (original design) and seven tips (right image) (reprinted from Kang with permission from Journal of the Korean Society of Propulsion Engineers, copyright 2014)



(a) 8-star shaped propellant.



(b) 7-star shaped propellant.

FIG. 17: Pressure vs. time curves of 2.75-in. rocket motor at 66°C, with standard and modified starshape EDB grains (reprinted from Kang with permission from Journal of the Korean Society of Propulsion Engineers, copyright 2014)

this is particularly important for rocket systems, as there are many system variables (case type, conduit form, igniter, etc.) that can significantly alter the IM response.

8.1 Gun Propellants

Several authors (Andres et al., 2006; MSIAC, 2019; Vogelsanger et al., 2007) have pointed to developments over the last few decades resulting in the introduction of NC-based gun propellants with improved properties, partly because of the application of new ingredients and partly due to

new production techniques like solventless extrusion. One of the most significant improvements concerns IM properties.

As stated by Rozumov (2017), the use of plasticizers in the EDB propellant improves the mechanical properties of propellants, giving the final product more ductile material properties relative to propellants that are manufactured using a solvent process. Andres (2006) shows that many conventional NC-based propellants are sensitive toward impact stimuli, in particular if they contain NG. In newer generations of double-base and triple-base propellants, NG has been wholly or partially replaced by diethylene glycol dinitrate (DEGDN). Together with the more ductile properties of these propellant types, the replacement of NG results in reduced impact sensitivity. In the German LSP test (less sensitive propellant), developed by Rheinmetall and described by Schaffers and Stein (2005), the latter propellants show a less violent response compared to conventional propellants with NG; refer to Fig. 18.

Examples are the RDP-380 multiplex stick charge for the 120 mm APFSDS, the European version of the 120 mm M865 round (M865C1), where the sensitive and toxic M14 propellant is replaced, and Rheinmetall's modular charge system (DM72/92) that uses a solventless triple-base R-type propellant, which has a very good IM signature and is in service with five NATO countries, with more than 1.5 million charges reported to have been delivered (MSIAC, 2019).

According to Andres (2006), the German solventless R-type propellants can be viewed as modifications of the Gudol propellants developed around World War II. Knobloch (2007) has explained that these consist mainly of NC, DEGDN, and NQ and that they are the most barrel-friendly among the well-known classic gun propellants, successfully used in weapon systems with relatively large combustion chambers. The low erosivity of this propellant type can be attributed to the low nitrogen content of the applied NC, the replacement of NG by DEGDN, which has a lower energy content, and the relatively large content of nitrogen in the combustion gases. These Gudol propellants have been modified by the addition of RDX, resulting in R-type propellant compositions that improve performance while still producing relatively cool combustion products.



FIG. 18: Shaped charge jet (left cartridge remains) and hot fragment responses (right cartridge remains) in the German LSP test. Left picture: typical response of conventional propellants with NG. Right picture: response of next-generation SCDB (surface-coated double-base) propellant (reprinted from Andres et al. with permission from Nitrochemie, copyright 2006).

LOVA propellants, based on RDX rather than on NC, have the potential to offer higher performance with equal or better IM characteristics. However, they have generally suffered from low-temperature ignition difficulties (Rozumov, 2017) and lesser IM performance (Vogelsanger et al., 2004) at temperature extremes in particular. There appears to have been very little replacement of EDB gun propellants by LOVA types; only three LOVA gun propellants are known to have entered service (MSIAC, 2019). Further information concerning the limited deployment of LOVA gun propellants is described in the report by Collet (2021), which is available to MSIAC member nations upon request. Publications concerning LOVA R&D continue in some countries, but little has been reported from the US in the last ten years. Similarly, from 2006–2009 an impressive number of LOVA propellant formulations were reported by the High Energy Materials Research Laboratory (HEMRL) in Pune, India, but nothing after 2013.

8.2 Rocket Propellants

Strickland et al. (2009) reviewed Roxel's IM technology; for EDB-type propellants it was concluded that

“generally there is a Type V or IV response for fast heating (FH) and slow heating (SH), with Type V or IV responses with adequate barrier or storage configuration for bullet impact (BI), fragment impact (FI) and sympathetic reaction (SR). However, without this configuration then Type I, II or III for FI, SR, since they are more sensitive to intense shocks due to NG, explosive fillers and combustion instability suppressant content.”

It was reported that 1% of refractories in some EDB and CDB propellants increase the FI shock to detonation transition sensitivity by 500 m/s.

Recent results reported by Turner (2019) show that for a CDB propellant, in a particular 180-mm diameter motor configuration, it is possible to significantly improve the IM response to SR by decreasing the refractory agent to a level that still reduces the combustion instability. The inclusion of refractories was reported to result in a step change to the propellant's shock sensitivity, while some different refractory materials gave better results. The increases in shock sensitivity were not linear, with the point of diminishing returns achieved at relatively low levels of refractory content. The improvements were also demonstrated in full-scale IM motor trials.

Fleming and Jones (2019) assessed the IM signature of 39 missiles that used solid rocket motors using EDB, composite, crosslinked double-base, and EM/CDB propellant types. The IM data for the motors is shown as a function of time in Fig. 19; it can be seen that there has been a generally gradual improvement in the IM signature of motors used in missiles. Based on the methodology of Jones, an EDB motor without refractories or energetic filler (e.g., the AA-2 propellant used in the Hydra rocket) has a predicted IM performance indicator response of $\geq 50\%$ with an aluminum construction. This compares with 15% for the Hellfire missile, which used a crosslinked double-base propellant with more than 50% RDX in an aluminum case.

Fisher and Sharp (2003) reported data showing that an AA2 propellant without refractories passed SR, but a reference propellant with refractories failed this test. The Hydra motor (with AA2 propellant) requires a resonance rod, but an equivalent motor using a similar reference propellant with refractories can avoid the need for a resonance rod. However, in the case of the latter configuration, there is a penalty of a reduced ability to survive fragment impact and SR.

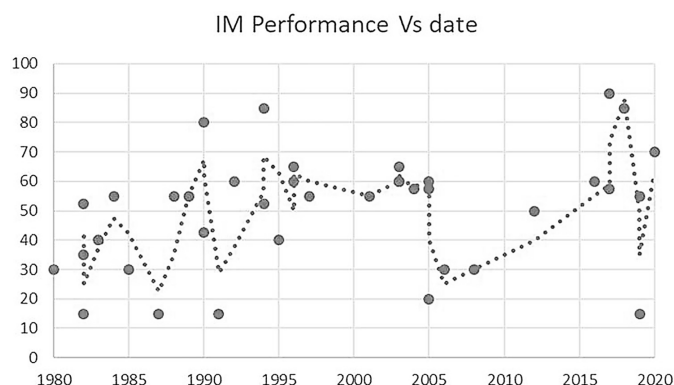


FIG. 19: IM performance for a selection of 39 motors used in missiles over the time period of 1980 to 2020 (Fleming and Jones, 2019)

Strickland and Nugyre (2007) illustrate how the lower cook-off temperatures associated with double-base igniters can be used to preempt a less severe response to fast heating in composite propellant rocket motors. But as described subsequently by Strickland (2015),

“the interaction between the initiator, the gaine charge” (note that gaine charges generally employ pyrotechnic powder to transfer ignition from the initiator to the pyrogen) “and the pyrogen is complex and requires careful design. The aim is to find the balance that ensures fast motor ignition at the cold end and limits the peak pressure hot. A difficulty to overcome is to achieve an effective ignition of the pyrogen without risking it cracking under cold firing conditions due to close proximity to the initiator and its associated shock wave.”

Nammo’s GAP-RDX-BuNENA composite propellant with minimum signature is an alternative to EDBs. As reported by Løkke et al. (2016), it has a medium burn rate of 8.5 mm/s, a pressure exponent of 0.6, burn-rate sensitivity (10 MPa) of 0.18%/K, and a specific impulse of 229 seconds. The propellant’s card-gap result is 131 cards (compared to approximately 50 for a typical unfilled EDB, with a value of less than 70 being one of the considerations for a 1.3 HD). The reported insensitivity of the lightweight modular missile (LMM) motor to fragment impact at 1830 m/s seems in part to be due more to the bore design (stellated conduit) rather than to the propellant itself, as delayed detonation (XDT) results were obtained with a cylindrical conduit (Holden et al., 2016).

In conclusion, EDBs are used in a number of missile systems, some without refractories. When refractories and energetic fillers are avoided or reduced to low levels, a well-designed motor case that also vents can give a relatively good response to FI (at 1830 m/s) and SR stimuli. Although it is possible to have a pass for SR and FI even with a high-card gap propellant, it is more difficult to achieve and can also depend on the conduit shape, barrier layers, diameter of the charge, etc.

8.3 Applications

The US Army’s ManTech website lists the following applications that either employ solventless EDBs, or where consideration is being given to replace an existing solvent propellant (e.g., JA2) by a solventless EDB; most are used in gun systems:

- M865 and M1002 tank training rounds.
- AA2 propellant for MK90 rocket grains.
- N5 propellant for mine-clearing line charge (MICLIC) and anti-personnel obstacle breaching system (APOBS).
- JA2 solvent propellant for M830A1 tank cartridge.
- RPD-380 propellant for M829A3 tank cartridge.
- Surface-coated double-base (SCDB) propellant for 120 mm tactical rounds.
- High-explosive anti-tank multi-purpose training (HEAT-MP-T) rounds.
- 25 mm M793 training rounds.
- M1A2 Abrams main battle tank.

Other applications for solventless EDB gun propellants are for 25-mm ammunition using single- and 7-perforation grains as described by Manning et al. (2006) and 35-mm ammunition as discussed by van Driel et al. (2016). Large-caliber applications are discussed by Andres (2006), Dahlberg (2006), and Dahlberg and Gustafsson (2007), with solventless processes employing low-nitrogen content NC with energetic plasticizers like NG or DEGDN, and solid constituents like NQ, RDX, or guanylurea-dinitramide (GUDN).

DM63 propellant for the 120-mm APFSDS-T is reported by MSIAC (2019) to be a solventless SCDB that has been in service since 2005 with five European countries; it is claimed to result in only one-third of the barrel wear of the earlier DM53 propellant, with this compensating, at least to some extent, for the propellant's higher price.

Air-to-ground rockets (68/70 mm and 127 mm Zuni) are generally produced by the EDB process, with the Hydra 2.75-in system described previously. In the case of the 5-in diameter Zuni motor, for fixed wing applications, the EDB motor operates over a temperature range of -46°C to 71°C .

Ejector seats are sometimes produced using composite propellants, but EDBs are still widely used.

Missile propulsion currently uses relatively small EDB charges, although there are some current or recent applications utilizing relatively large EDB grains, e.g., ALARM, APKWS, and ASTER 15 and 30 [for the divert attitude control system (DACS)]. Although currently EDB propellants are not employed for 180-mm diameter missiles (which are EMCDB or crosslinked double-base) the ALARM missile, which used an EDB propellant (Kentgens et al., 1996), has a diameter of 230 mm and has remained in service until recently. There are a number of open sources that contain information on the types of propellants used in missiles, for example, Roxel Group's listing (Roxel, 2021); based on this source, EDB propellants are employed in approximately 35% of the missiles that are currently manufactured. Blip/eject motors for missiles generally utilize EDB propellants due to minimal smoke being required for launch but also a desire for low cost. Kentgens et al. (1996) provides an excellent overview of the technology and describes it being "ideal for . . . short-action rocket motors with burning times ranging from some milliseconds up to approximately 200 ms." In the example of the Serbian 136 mm Bumar anti-tank missile, Gligorijevic (2018) reports the use of an EDB propellant for the flight motor.

Very large-caliber guns are a particularly interesting example of systems that have used EDB propellants. The HARP gun used 450 kg of seven perforated modified M8 propellant (with an outer diameter of 32 mm) to launch a rocket that, as described earlier in this paper (Section 5.2), also employed an EDB propellant. The US is now in the early stages of revisiting very large-caliber guns, with the strategic long-range cannon (SLRC); although the gun propellant has not been disclosed, it is considered likely to be a solventless EDB (due to the required web size of the propellant grain inherent with a gun of high caliber). Controlling the burn rate of the propellant granules by co-extrusion (as described in Section 6.3) or by the SCDB method (discussed briefly in Section 8.1; see also Vogelsanger et al., 2007) would be expected to be favorable for the new SLRC system since it could give high force without excessive flame temperature. Compared to the M8-type propellant used in the HARP gun, the flame temperature of SCDB propellant is 200°C lower for the same force (see Fig. 1, Section 2.2).

Other applications for solventless EDBs include decoy rockets, gas generators for turbines, automobile air bags, flotation devices for submarines, and flake propellant for mortars. The propellant is still used as a gas generator in some fire extinguishing systems, but EDBs for automobile air bags are thought to have switched to alternative propellant types during the 1980s.

9. STRENGTHS AND WEAKNESSES, INCLUDING NEW DEVELOPMENTS

Major strengths of EDBs, compared to other candidate minimum-smoke propellants, include their maturity, ease of ignition, low cost, and that there are several potential sources of supply. For rocket motors, new minimum-smoke solid propellants (e.g., RDX/GAP type) have been under development for many years, but the first and only application to date (a 76-mm diameter short-range missile known as LMM) recently completed qualification, with the missile due to enter service with an initial operating capability (IOC) in 2021. This motor was also described in Section 8.

A 2008 US study by the Office of the under Secretary of Defense for Acquisition illustrated the delays that have been experienced when new motor technologies have been introduced. The study showed that increasing motor complexities, mainly associated with the adoption of new propellants and charge design/complexities, introduced an additional average delay of almost five years in the time to undertake the development (from Technology Readiness Level 6) and qualification (ending at the Critical Design Review) activities. Thus, considering potential performance issues and program delays, the low risks of EDB propellants makes them attractive to the missile prime and the end customer.

10. CONCLUSIONS

Solventless EDB remains an important technology for both gun and rocket/missile propulsion, with an estimated 35% of current missiles employing EDB propellants (mainly for launch rather than flight). External ballistic modeling results are presented that illustrate that EDB rocket propellants can result in similar firing ranges to more energetic propellants that are also not minimum smoke. EDB propellants also provide low risk and cost combined with minimum smoke and quite-good IM properties.

The EDB gun propellants have been improved in several areas, in particular with respect to IM properties. There appears to have been quite-limited replacement of EDB gun propellants by LOVA types. In new generations of both double-base and triple-base propellants, NG has been wholly or partially replaced by less vulnerable plasticizers. New generations of double-base as

well as triple-base propellants are manufactured without solvent. The introduction of solventless processes leads to a reduction of costs and hazardous waste emissions. These processes are mainly executed by means of ram extrusion or continuous extrusion. One of the main obstacles to continued long-term use of EDBs is the requirement, for rocket propellant applications, for lead-free ballistic modifiers. However, several alternatives are available for the short to long term, although their use may require the acceptance of a small performance reduction.

Trials with double-base propellants have shown that, in at least some rocket motor configurations, it is possible to sufficiently reduce the level of refractory materials to still dampen combustion instabilities and in this way achieve IM compliance. Thus, where IM is critical to future requirements, it may be possible to further improve the performance of EDB propellant motor systems in a similar manner.

Short-term developments are expected to include lead-free modifiers and an increased adoption of continuous processing. Improved NC, possibly including the use of a bacterial cellulose or nanocellulose, is likely to remain at the R&D stage for a significant number of years.

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