



Towards New Directions in Oxidizers/Energetic Fillers for Composite Propellants: an Overview

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Abstract: There is continued interest in the development of safe and reliable composite propellant formulations using modern energetic ingredients such as energetic oxidizers/energetic ingredients, energetic binders, and energetic ballistic modifiers. There are continued efforts by energetic materials researchers, scientists, technologists and engineers to design composite propellant formulations with better ballistic properties than conventional formulations. The efforts in many research and development (R & D) laboratories all over the world are aimed at utilizing modern oxidizers/energetic fillers for the development of composite propellant formulations for both space and defence applications. Composite propellants are considered to be the major source of chemical energy for rockets and missiles. Energetic oxidizers/fillers play vital roles in the preparation or manufacture of composite propellant formulations. Various energetic oxidizers/fillers have been developed during the last five decades to address environmental safety, high energy and processing conditions. In this article, the authors have reviewed the characteristic properties of the energetic oxidizers/fillers used in the preparation of composite propellants. The characteristic properties of the energetic ingredients play an important role in the preparation of composite propellant formulations with the desired mechanical properties. The advantages and disadvantages of various energetic oxidizers/ingredients for specific and potential propellant applications are also highlighted throughout the course of this review article. The future direction in composite propellant formulations calls for the development of green propellant formulations. Efforts will continue to seek alternative and more energetic oxidizers/fillers in comparison to conventional oxidizers. There is an urgent

need to replace conventional oxidizers such as ammonium perchlorate with eco-friendly ingredients.

Keywords: binder, oxidizer, composite propellant, burn rate modifier, plasticizer, high energy materials

1 Introduction

A rocket or missile is developed to deliver a payload, which may be in the form of a warhead or a satellite at a specific point in space. The propulsion system forms one of its major sub-systems. Chemical propulsion systems are widely used to achieve this and find application in defence as well as space exploration. Propellants are the substances, or a mixture of substances, which produce gases at the high temperature and pressure of combustion. In a chemical propulsion system, the propellants can be either in liquid or solid form. However, solid propellants find wide application in both missiles and the booster phases of satellite launch vehicles [1].

Various types of solid propellants are used in propulsion systems. Solid rocket propellants are the most widely used systems for tactical missile propulsion owing to their various advantages over liquid propellants, which otherwise offer superior performance and variable thrust as per the specific requirements. The quest for superior performance, longer missile range and higher payload capability has resulted in the synthesis of various high energy materials (HEMs). Subsequently, their thorough characterization and precise theoretical evaluation have become part and parcel of the development of new generation materials.

Solid propellants are categorized into two broad classes viz., double base (homogenous) and composite (heterogeneous) propellants. In this review, the major emphasis is on the use of various types of energetic oxidizer/filler and their effect on the performance of composite propellant formulations.

To meet the growing requirements for increasingly high energetics in terms of the specific impulse, R & D work on the improvement in performance of composite propellants (CPs) was initiated in the late 1960s. CPs are heterogeneous in nature and consist of particulate fillers uniformly dispersed in a polymeric binder matrix, in addition to minor ingredients like plasticizers, bonding agents, processing aids, curing agents, *etc.* These propellants have higher energy in terms of their specific impulse, I_{sp} (240-250 s), and are of higher density (1.76 g/cm^3) in comparison to double base propellant formulations. Composite propellants are generally inferior in regard to mechanical properties.

In view of their capability of being ‘cast-in-situ’, they are most widely used for defence rockets and missiles. A representative sketch of the different parts of a case bonded rocket motor is shown in Figure 1.

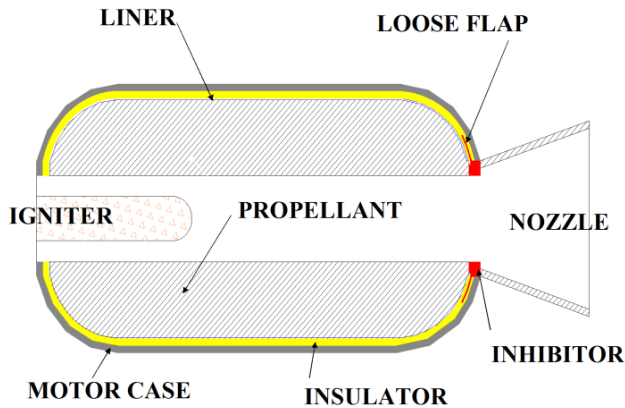


Figure 1. Case Bonded Rocket Motor.

Future defence and space missions will require high performance propellant formulations (with a high Isp) for achieving their goals in terms of increased range, increased payload, reduced lift-off weight, *etc.* High acceleration missiles, particularly for anti-missile role systems, will require high burn-rate propellants. In addition, solid propellant motors with variable thrust will be required for undertaking ambitious future missions. Current R & D in allied areas is much focused on these aspects. Efforts are already in process in these directions to achieve the mission requirements. A major emphasis is to increase personal safety during processing and reduce human exposure during handling. Other goals for future development will be propellants with eco-friendly exhaust emissions and minimum signature, and laser ignition systems for safe, reliable and reproducible performance.

As far as future systems are concerned, they will require an increased range, with reduced time to reach the target, reduced cost and reduced vulnerability. Key topics of interest include soft vertical launch, controllable thrust, high performance propellants, high performance, inert materials, and accurate modelling of rocket systems. The key parameters in the design of composite propellant formulations are also considered here. Specific impulse is one of the key parameters, computed theoretically prior to the design of the composite propellant formulation. The specific impulse (Isp) is a theoretical maximum of the mechanical work derived from the decomposition of a unit mass of propellant,

followed by expansion of the decomposition products in an environment of specified pressure, which is usually the near total vacuum of outer space. In other words, the Isp is 'the thrust delivered per unit weight flow rate' of the propellant.

The heat of formation depends on the bond energies between the atoms of the various ingredients used in the propellant formulations. To achieve as high a combustion temperature as possible, one must select reactants with large positive heats of formation and products with large negative heats of formation. The maximum energy output from a material is possible when it contains bonds with as low bond energies as possible, and combustion products with as high bond energies as possible.

The density of the solid propellant should be as high as possible to provide higher energy per unit volume. The combustion and expansion of a dense solid into a lot of gaseous material (much expanded by the heat released) produces the desired effect. For propellants though, the critical performance parameter is Isp; the density impulse (the product of Isp and density) becomes more important for applications where there is comparatively a low propellant mass in comparison with the total mass of the missile/launch vehicle, *e.g.* boosters or first stage of launchers. Maximizing the density is important because it permits the volume fraction of the particulate (solid loading) within the composition to be minimized. It also improves the flow properties of the mixture. However, in addition to the above, the cured propellant must possess improved energy absorbing capacity or toughness, because of the low solid loading in the system.

Significant progress has been made in the synthesis and development of new energetic compounds for their use in propellant formulations. These materials offer attractive propellant systems with improved performance in terms of density and energy (Isp), and as well as generating clean and environmentally acceptable combustion products. Propellant formulations based on a combination of energetic binders and oxidizers can help to achieve Isp levels exceeding 300 seconds.

2 Composite Propellant Formulations

The primary ingredients of composite propellants include an energetic filler (65-70%), metallic fuel (10-20%) and polymeric binder (8-15%). The secondary ingredients for composite propellants also includes 2-5% of the composition. These are burning rate catalysts, process aids, cross linking agents, bonding agents, curing catalysts and antioxidants.

3 High Energy Materials

3.1 Oxidizers

The primary function of the oxidizer in the propellant is to provide the necessary oxygen for the complete combustion of the fuel. Therefore, oxidizers must release as much oxygen as possible for the combustion. Apart from this, the stability and melting point of the oxidizer are also important for its practical use in a solid propellant, during manufacture and also during its lifetime (shelf life). It is always better to have an oxidizer with a reasonably high melting point as the curing of the propellant takes place at elevated temperatures. The density of the oxidizer should be high enough to accommodate a high solid loading. In addition, it should have a low heat of formation and a high oxidation potential.

In the present scenario, ammonium perchlorate (AP) [2] is the most widely used oxidizer as it satisfies most of the requirements of a propellant. It is characterized by high heat output and a high yield of gaseous products (not a smoke producer). The most perceptible disadvantage of AP is its chlorinated exhaust products, which are detrimental to the environment and produce a distinct signature behind missiles that can be easily tracked. During the burning of propellants containing AP, enormous quantities of HCl are produced which could cause 'ozone depletion' and 'acid rain'.

For different strategic requirements, propellants with different burn rates are required. The particle size of the AP is one of the key factors for determining the burning rate. As the particle size of AP decreases, the burn rate increases and *vice versa*. In this connection, different forms of AP have been developed and used in propellant formulations.

Thus, hexahedral crystal-habit-modified AP [3] was synthesized from an ethylene glycol medium. Modified AP contains a remarkably dense lattice plane (210), and exhibits better thermal decomposition and ignition behaviour compared to standard AP. The enhancement of the burning rate is dependent upon the extent of the modification. Hence, modified AP is an effective oxidizer for enhancing the burning rate of a composite propellant.

Kohga *et al.* [4] have synthesized fine porous or hollow ammonium perchlorate by the spray-drying method. Propellants which were prepared with porous or hollow AP, were often contaminated with bubbles. However, the void structure inside the porous or hollow AP particles has positive effects on the burning rate.

In this connection, another attempt has been made to modify the crystalline structure of ammonium perchlorate by using hexane [5]. The particle characteristics of these modified crystals of AP and their influence on the burning

rates of composite propellants have been investigated. The shape of this modified AP is dendritic. It has been found that AP modified by hexane is an effective oxidizer in the preparation of propellants with the highest burning rate.

Theoretical calculation have shown that partial replacement of AP with a nitramine (HMX) [6] increases the specific impulse appreciably (e.g., the increment of the specific impulse is 25.46 N·s/kg when 20% of AP is replaced by HMX). It also results in a decreased flame temperature and a decreased HCl content in the exhaust gas.

Potassium perchlorate (KP) [7] is used as an oxidizer in propellants of higher burning rate. KP gives rise to a higher heat output, along with a lower gaseous throughput when decomposed, as compared to AP. Thus, it is characterized by high heat output, and as a low gas producer. It has also been found [8] that KP is particularly suitable for forming solid solutions with AP. The resulting solid solution is thermally more stable than AP alone and can be satisfactorily used in explosive and propellant mixtures. In particular this solid solution offers less risk of decomposition during storage.

Ammonium nitrate (AN) [9] is used as the oxidizer where slower burning rates are required. It is characterized by low heat output, and as a high gas producer, and is good for gas generator propellants. It requires a greater amount of binder (fuel) to make a castable formulation. But the higher amount of binder produces excessive smoke. AN exists in five crystalline phases. A phase transition at 32.5 °C is accompanied by a volume change. Attempt have been made to overcome this drawback by phase stabilization. The stabilizer contains no toxic elements and no solid elements, and most importantly it produces no solids by decomposition, and therefore, is a high energy, non-polluting fuel, and could provide a more “environmentally friendly” solid propellant for future applications.

Kohga *et al.* [10] have used a HTPB/PTHF (PTHF-polytetrahydrofuran) blend as a binder in AN based composite propellants. This blend shows superior curing behaviour and tensile properties. The thermal decomposition behaviour of AN/HTPB-PTHF based propellants has been studied. The decomposition temperature range shifted to lower values when the PTHF concentration in the binder was increased. It exhibited a two stage decomposition. The thermal decomposition of AN/HTPB-PTHF occurs at a lower temperature than the normal AN/HTPB composition.

These authors have also studied PTHF/glycerin [11] as a binder for AN based propellants. PTHF could not be cured with the curing agent alone. Hence glycerin has been used as a crosslinking modifier. The PTHF/glycerin mixture was found to be an effective binder for improving the burning and physicochemical

behaviour. It also increased the performance of the AN based propellant. One drawback was an ignition problem with the AN/PTHF/glycerin propellant.

Kohga *et al.* [12] have also investigated the effect of ammonium dichromate on ammonium nitrate (AN) based composite propellants. Ammonium dichromate (ADC) worked as a burning catalyst for AN-based propellants; however, the effect of ADC on the burning characteristics has yet to be explored. The Kohga *et al.* have prepared AN/ADC propellants with various AN and ADC contents and studied their burn rate characteristics. An enhancement in performance of ammonium nitrate was observed theoretically on addition of ADC. The optimization of ADC in the propellant formulation was also carried out.

Nitronium perchlorate (NP, NO_2ClO_4) [13] was also used as an oxidizer. It was used as a potential oxidizer in high-energy propellants. It decomposes above 80°C or in contact with water and with many organic compounds. The decomposition of NP releases oxides of nitrogen (NO , NO_2) and chlorine (Cl_2). The maximum allowable concentration of gases is 5 ppm. Mixtures of NP with nearly all organic compounds are dangerous and explosive. Mixtures with other oxidizers also create similar risks. Hence, their limited use in high energy propellants is observed.

Lithium perchlorate [14], a proposed oxidizer, is very hygroscopic and may be used as an oxidizer in high-temperature propellants. It is not toxic, unless a large amount is consumed orally. It is similar to potassium perchlorate. Mixtures with reducing agents are explosive in nature.

Hydrazinium perchlorate (HP, $\text{N}_2\text{H}_5\text{ClO}_4$) is an energetic oxidizer and is used in high energy propellants. It decomposes to evolve chlorine gas (Cl_2). It is a very hazardous material to handle. It is extremely sensitive to impact and friction, with a low auto-ignition temperature. It is used in high-energy propellant systems.

Hydrazonium diperchlorate (HP_2) [15] is an exceedingly energetic oxidizer. In addition to its exceptional potency, it has certain other advantages which would make it a desirable oxidizing component in solid propellant compositions. These advantages include high density, high burning rate and relatively low sensitivity towards initiation by shock. It is also available commercially and is cheaper. All of these attributes are important considerations in military and aerospace operations. Besides the advantages, it also has a few disadvantages, such as poor compatibility with binders, a short processing life and most importantly poor curing properties when compounded with most of the desirable hydrocarbon fuel binders.

Dinitrodiazenefuroxan (DNAF) has received much attention in view of its energy potential, being superior to HMX. However, detailed characterization of

the sensitivity of this compounds is not well reported in contemporary literature.

Ammonium dinitramide (ADN, $\text{NH}_4^+[\text{N}(\text{NO}_2)_2]^-$) [16-21] is currently one of the most promising candidates as an oxidizer. It is an ionic substance containing ammonium cations and dinitramide anions, in which the negative charge is delocalized over the whole anion. It is as dense as RDX with a positive oxygen balance and enthalpy of formation, and superior to AP and AN. It is also less sensitive to impact and friction. Below 130 °C ADN is converted to AN by elimination of N_2O . At higher temperatures, N–N bond cleavage occurs and NO_2 is evolved. Being halogen free, propellants containing ADN instead of AP are expected to show a significantly reduced plume signature and atmospheric ozone depletion. Compared to AN, ADN has a higher energy content, exothermic decomposition takes place at lower temperatures and there are no phase transitions affecting changes in volume and density during combustion. ADN is thus a possible replacement for AP, to give an environmentally clean system by eliminating the emission of chlorine from rocket motors. However, ADN is thermally less stable and slightly more shock sensitive than AP.

Korobeinichev *et al.* [22] have investigated the characteristics and mechanisms of combustion of a composite solid rocket pseudo-propellant of stoichiometric composition based on ammonium dinitramide and polycaprolactone (PCL). They have also investigated the dependence of burning rate on pressure in the pressure range 4-8 MPa for ADN/PCL propellants, and the effect of the molecular weight of PCL on this dependence. In addition, the effect of a CuO catalyst on the pressure dependence of the burning rate and temperature profile has been investigated.

Hydrazinium nitroformate (HNF) [23] is another potential oxidizer. Its production was initiated in the late 1980s in the Netherlands. It can be produced by an acid-base reaction between nitroform and hydrazine.

HNF has a superior heat of formation to that of ADN (ΔH_f° : -18 kcal/mol). It is one of the most powerful solid oxidizers available, but it has poor compatibility with HTPB binders, which is attributed to oxidation of the double bond ($\text{C}=\text{C}$) in HTPB by the HNF. In order to characterize HNF [24], many thermo analytical techniques, such as DSC and TG/DTA, have been used to obtain more information about its stability and its compatibility or incompatibility with other materials. When the oxidation of HTPB occurs, it results in deterioration of the binder, which leads to unacceptably low mechanical properties. Isocyanates also show poor compatibility with HNF. Glycidyl azide polymer (GAP) does not contain carbon-carbon double bonds and may be safely used with HNF, and could offer higher performance than the existing AP-Al-HTPB propellant formulations. The exhaust gases from an HNF-GAP propellant system are halogen free. The purity

of HNF is important as unreacted nitroform or hydrazine gets absorbed in the HNF crystals, posing serious safety problems during handling and storage. HNF based propellants show high burn rates (30 mm/s at 5.5 MPa) and a high pressure exponent 'n' (0.81-0.83). The 'n' value can be reduced to 0.59 with suitable burn-rate modifiers (as described in the following section). It is estimated that by using HNF based propellants an increase in I_{sp} of more than 7% and a payload gain of 10% can be achieved. The European Space Agency (ESA) has identified the HNF-Al-GAP combination as a very promising high performance propellant.

HNF has many advantages, such as higher specific impulse, lower signature and with negligible pollution, compared with ammonium perchlorate (AP). Test results have shown that, thus far, the synthetic process, product purity and stability of HNF [25-28] have been important developments. However the mechanical properties and long term stability of propellants containing HNF must be improved for its application.

Van der Heijden [29] has reported the effect of the particle size of HNF on the ballistic properties of composite propellants. The ballistic properties of three HNF/HTPB-based propellants (two monomodal and one bimodal) revealed that fine HNF (mean size 5-10 μm) leads to a lowering of the pressure exponent of the propellant. The burning rate of the propellant can be tuned by varying the mean size of the HNF present in the propellant.

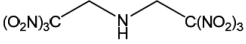
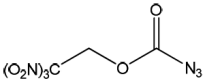

HNF has certain disadvantages, such as sensitivity towards friction and impact. These restricts the use of HNF in propellant systems. Javaid *et al.* [30] have reduced the friction sensitivity (from 2 to 9.6 kg) and impact sensitivity (upto 55 cm), without loss of energy, by using sono-mechanical crystallization with carboxy methyl cellulose (CMC) as a crystal shape modifier, followed by double coating of the nanocomposite.

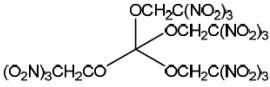
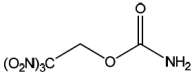
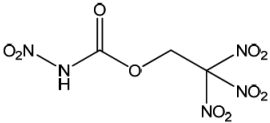
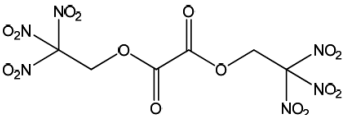
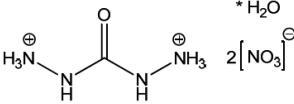
Several energetic perchlorates have been synthesized and characterized for future applications. In this connection, Bachurina *et al.* have synthesized copper tetrakis[cyclopentamethylenetetrazol] perchlorate [31, 32] by reacting copper(II) perchlorate hexahydrate with cyclopentamethylenetetrazol. It has favorable explosive characteristics and can be used as an energetic ingredient in composite solid propellants.

Currently, researchers are trying to synthesize perchlorate and halogen free High Energy Dense Oxidizers (HEDOS). Klapötke *et al.* have synthesised several compounds such as bis(2,2,2-trinitroethyl)amine (BTNA) [33, 34], tris(2-nitroethyl)borate [35] and tris(2,2,2-trinitroethyl)borate [36], 2,2,2-trinitromethylazidoformate (TAF) [37], 2,2,2-trinitroethyl azidoformate [37], 1,1,1,6,6,6-hexanitrohex-3-yne [38], tetrakis(2,2,2-trinitroethyl) orthocarbonate (TNEOC) [39], 2,2,2-trinitroethyl carbamate (TNC) [36],

2,2,2-trinitroethyl nitrocarbamate (TNC-NO₂) [36], bis(2,2,2-trinitroethyl) oxalate (BTNEO) [40, 41], and diaminourea dinitrate [36]. The detailed structures and properties of these are highlighted in Table 1.

Table 1. Structures and properties of future oxidizers

No.	Oxidizers	Properties
1	Bis(2,2,2-trinitroethyl)amine (BTNA) [Refs. 33, 34] 	<ul style="list-style-type: none"> ❖ BTNA is a high oxygen explosive (oxygen balance $\Omega = +7.0$) ❖ Valuable intermediate for energetic materials preparation. ❖ Moderately sensitive towards impact (15 J) and insensitive towards friction (> 360 N). ❖ Density $1.881 \text{ g}\cdot\text{cm}^{-3}$ and calculated heat of formation ❖ $-138 \text{ kJ}\cdot\text{kg}^{-1}$. ❖ Velocity of detonation: $8815 \text{ m}\cdot\text{s}^{-1}$
2	Tris(2-nitroethyl)borate B[OCH ₂ CH ₂ NO ₂] [Ref. 35]	<ul style="list-style-type: none"> ❖ High energy density oxidizer. ❖ Used for smoke-free, green coloring agents in pyrotechnic compositions. ❖ Oxygen balance: -59.7%, Density: $1.524 \text{ g}\cdot\text{cm}^{-3}$
3	Tris(2,2,2-trinitroethyl)borate B[OCH ₂ C(NO ₂) ₃] [Ref.36]	<ul style="list-style-type: none"> ❖ High energy density oxidizer ❖ Used for smoke-free, green coloring agents in pyrotechnic compositions. ❖ Oxygen balance: $+13.07\%$. Density: $1.982 \text{ g}\cdot\text{cm}^{-3}$
4	2,2,2-Trinitroethylazidoformate (TAF) [Ref. 37] 	<ul style="list-style-type: none"> ❖ Isp (with 20% Al, 70 bar): 250 s, higher than AP:243 s ❖ Velocity of detonation: 8254 m/s, ❖ Density: $1.85 \text{ g}/\text{cm}^3$, higher than RDX (density: $1.80 \text{ g}/\text{cm}^3$)
6	1,1,1,6,6,6-Hexanitrohex-3-yne [Ref. 38] 	<ul style="list-style-type: none"> ❖ Enthalpy of formation $\Delta fH^\circ = 367.0 \text{ kJ}/\text{kg}$ (at 298.15 K). ❖ Oxygen balance: -9.1%. ❖ Impact sensitivity: 3 J, Friction sensitivity: 72 N, Electrostatic discharge 0.8 J. ❖ Velocity of detonation: 8821 m/s, higher than RDX (8748 m/s). ❖ Isp (with 20% Al, 70 bar): 263 s, higher than AP: 243 s

No.	Oxidizers	Properties
7	Tetrakis(2,2,2-trinitroethyl) orthocarbonate (TNEOC) [Ref. 39] 	<ul style="list-style-type: none"> ❖ Highly sensitive towards impact and sensitive towards friction and electrostatic discharge. ❖ Velocity of detonation: 8419 m/s, is slightly greater than the value for PETN (8400 m/s). ❖ Isp (with 20% Al, 70 bar): 249 s, higher than AP: 243 s
8	2,2,2-Trinitroethyl carbamate (TNC) [Ref. 36] 	<ul style="list-style-type: none"> ❖ Oxygen balance: 0. ❖ Density :1.839 g·cm⁻³. ❖ Insensitive towards impact (BAM fall hammer: > 40 J) ❖ Friction : 64 N. ❖ ESD: 0.15 J. ❖ It is stable up to 165 °C. <p>These facts would make it a great potential precursor for unknown HEDOs. The compound is soluble in polar organic solvents, but poorly soluble in water.</p>
9	2,2,2-Trinitroethyl nitrocarbamate (TNC-NO ₂) [Ref. 36] 	<ul style="list-style-type: none"> ❖ New and quite stable, potential highenergetic oxidizer. ❖ Density 1.725 g/cm³. ❖ Isp (with 20% Al, 70 bar): 245 s, higher than AP: 243 s. ❖ Velocity of detonation: 7571 m/s.
10	Bis(2,2,2-trinitroethyl) oxalate (BTNEO) [Refs. 40, 41] 	<ul style="list-style-type: none"> ❖ Detonation velocity is comparable with nitroguanidine $DNQ = 8200$ m/s. ❖ Isp (with 20% Al, 70 bar): 245 s, higher than AP: 243 s. ❖ Density 1.884 g/cm³.
11	Diaminouronium dinitrate [Ref. 36] 	<ul style="list-style-type: none"> ❖ A new secondary explosive. ❖ DAU·2NO₃ is completely insensitive towards impact and friction, but, unfortunately, already decomposes at 115 °C.

Ref: ICT Data Base of Thermochemical Values : Fraunhofer-Institut für Chemische Technologie ICT, Joseph-von-Fraunhofer-Strasse, 776327 Pfinztal.

3.2 Energetic fillers

High explosive nitramines (RDX, HMX) also find application in solid rocket propellants as they offer good performance and easy processibility. HMX and RDX are excellent ingredients in propellants. The energetics of HMX and RDX are comparable, although RDX is relatively more sensitive to shock and impact.

They are normally prepared by nitration of hexamethylenetetramine under different nitration conditions. The decomposition and kinetics of pure HMX [42, 43] have been reported extensively in the literature. An initial investigation into the decomposition of composite propellants composed of HMX in a HTPB based binder was reported. It has been found that the addition of a binder to HMX has little effect on the decomposition of HMX itself. The HMX retains its previously established activation energies and decomposition characteristics in the presence of the HTPB binder, at similar temperatures. The binder, however, seems to cause small amounts of the HMX to degrade at temperatures below its normal decomposition range.

Dey *et al.* [44] have formulated a novel RDX based composite propellant formulation, where RDX is used as the energetic filler. RDX enhances the mechanical and ballistic properties of the composite propellant. It has not only positive effect on the mechanical properties, but it is found to be beneficial for reducing the burn rate. It also decreases the initial viscosity (*i.e.* improved processibility) and increases the specific impulse. In the same work, RDX has been used in composite propellants in varying amounts. Besides the variation in the RDX concentration, the NCO/OH ratio was also changed to obtain the desired physicochemical properties. As the NCO/OH ratio decreases, the tensile strength decreases but the elongation increases. The mechanical properties have been studied at ambient as well as under extreme conditions. As the RDX concentration increases, the burning rate gradually decreases. But in terms of specific impulse, this increases to a certain level of RDX loading, but subsequently decreases.

In 1987, polycyclic compounds became significantly important. Nelson and co-workers at China Lake synthesized the energetic solid hexanitrohexaazaisowurtzitane (HNIW, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo(5.5.0.0^{5,9}.0^{3,11})dodecane), commonly known as CL-20. It has been a highly popular product for many years at the US Naval Air Warfare Centre (NAWC), amongst the synthesis of novel nitramines and related energetic materials [45]. These compounds have already been prepared in the authors' laboratory, in adequate yield and purity, by the reported schemes [46]. These routes have been modified by the Thiokol Corporation, USA, and scaled up to pilot plant scale. Presently, Industrial Pilot Scale (50-100 kg) has been established by SNPE, France [47].

CL-20 is one of the densest organic compounds known (other than fullerenes and diamonds) [48]. The cage like structure in CL-20 [49] imparts distinct characteristics on the material, viz. greater density, greater stability, increased heat of formation and the ability to alter the oxygen to fuel ratio.

CL-20 has many favorable properties, such as density 2.04 g/cm³,

VOD: 9380 m/s, ΔH°_f : +97.61 kcal/mol and DSC decomposition temperature 228 °C. In addition this polycyclic nitramine is compatible with nitrate esters, nitramines, azidopolymers, hydroxy terminated polybutadiene (HTPB), polyethylene glycol (PEG), ammonium nitrate (AN), ammonium perchlorate (AP) *etc.* CL-20 has high inherent chemical energy, due to the presence of the six N-NO₂ groups and its strained structure. It delivers superior performance (14% higher than HMX) compared to existing high energy propellants and explosives [50, 51].

CL-20 based compositions have the potential for remarkable stability, and resistance to external stimuli. It is one of the important energetic ingredients for boosting propulsion for strategic missile and space launches, and in special warheads for “Smart” or light weapons. It burns cleanly, making it a green ingredient by reducing a missile’s plume signature without encountering combustion stability problems [51-53]. Hence, CL-20 has become the world’s most powerful non-nuclear explosive and gives the greatest promise for major technological advances in future weapon systems.

It is produced by the nitration of hexabenzylhexaazaisowurtzitane (HBIW). It exists in different polymorphic forms with slightly different densities. The epsilon (ϵ) polymorph has the highest density of 2.036 g/cm³ with a melting point of 243 °C. Its energetic features emanate from its superior heat of formation (+108 kcal/mol) and oxygen balance (-10.95%), in comparison to currently used explosives such as RDX and HMX. CL-20 is an ideal candidate for achieving increased performance in I_{sp} , ballistics and density in several broad classes of propellants. However, the crystal quality of the material determines the safe use and processibility of the material.

Similarities and differences between the decomposition products of HNIW, RDX, and HMX have been observed by Pesce-Rodriguez [54]. At 500 °C and 1000 °C, their thermolysis produces nearly the same amounts of CO and NO. However, the amounts of the other gaseous products viz. CO₂ and N₂O, produced by HNIW are twice and half the amounts from RDX and HMX, respectively.

Cubane, used as a binder for propellants, is not only a thermodynamic power house (ΔH°_f : 147.6 kcal/mol), but corresponds to a total strain energy of 165.4 kcal/mol [55], and is also kinetically stable (decomposition only above 200 °C). When used as a binder for propellants it delivers a high specific impulse (Cubane/AP/Al and Cubane/HAP/Al) [56]. The hydrocarbon is also used as a high density metal fuel [57]. It is predicted that highly nitrated cubane derivatives would have high energy output, high density, shock insensitivity, with great potential for propellants and explosives [58]. These molecules cannot be synthesized directly because the cage-like structure does not survive under the

reaction conditions. Elaborate multi step reaction sequences are often necessary [59]. One of the challenging target molecules is octanitrocubane(ONC).

Recently, Zhang *et al.* [60] reported the synthesis of heptanitrocubane (HpNC) and the long sought ONC, in 45-50% isolated yield. HpNC and ONC exhibit high decomposition temperatures (>200 °C). These compounds are not initiated by mechanical stimuli. Synthetically, HpNC is easier to make than ONC. It has a high density (2.028 g/cm³), and has proved itself to be a more powerful explosive/propellant due to its high heat of formation (only about 6% less than ONC), and density. During combustion, it will also produce light weight gaseous products [61, 62]. In the literature, the calculated heat of formation of solid ONC [(CNO₂)₈] is 141.4 kcal/mol, corresponding to 17.6 kcal/mol per (CNO₂) unit [63]. However in the case of hexanitrobenzene [(CNO₂)₆], the heat of formation is 47.6 kcal/mol corresponding to 7.85 kcal/mol per (CNO₂) unit, less than half that for ONC [64]. These decreases can be attributed to the presence of the resonance energy of the aromatic compound. The increased energy in ONC is caused by the strain energy of its exceptional carbon skeleton. The density of the most stable polymorphs of ONC [65] is predicted to be 2.10 g/cm³ from the X-ray crystal structure. With the higher predicted density and detonation pressure, a $>20\%$ increase in performance over HMX [66] could be achieved. The detonation velocity was found to be 9900 m/s [67] by theoretical estimation. For hexanitrobenzene, HMX, and CL-20, the detonation velocities were found to be 9500 [63], 9100 and 9200 m/s, respectively [69]. Less nitro substituted cubanes, such as tetranitrocubane, *i.e.* TNC [69] has been found to be an extraordinary material for high energy applications. This is a crystalline solid with high density (1.814 g/cm³) and is kinetically quite stable (does not melt until 270 °C). The evaluation of the detonation pressure has been carried out under controlled condition by the US Army Armament Research & Development Command (now ARDEC). The explosive energy output was found to be superior, but the quantitative details are not publicly available. By calculation, TNC was found to be a better monopropellant than ONC [70].

Octanitrocubane (ONC, density: 2.1 g/cm³) [71] is one of the recently synthesized explosives in which all of the hydrogens in cubane have been replaced by nitro groups bound to carbon. This compound has no hydrogen and hence no water molecules are formed during its combustion. In propellants, such zero hydrogen compounds leave little or no visible smoke (steam) in the plume behind the rocket. Such low signature rockets are difficult to track. It is estimated that ONC is less competitive and perhaps less shock sensitive than the newest experimental explosive CL-20. It is also a kinetically stable compound (decomposition only above 200 °C), but a thermodynamic power house

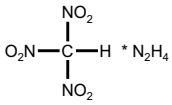
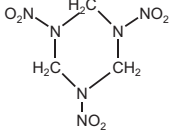
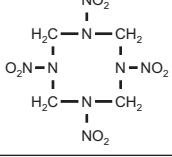
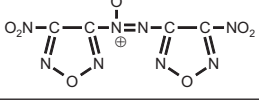
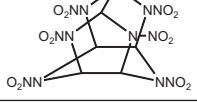
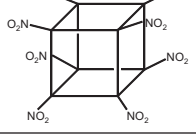
($\Delta H_f^\circ \sim 150$ kcal/mol) corresponding to a total strain energy of 165.4 kcal/mol. Both hepta- and octa-nitrocubane (HpNC and ONC) exhibit decomposition well above 200 °C. The current winner in the most powerful explosive debate is HpNC, which is currently easier to make than ONC. It has outperformed the theoretically more powerful ONC in actual tests recently performed. Octanitrocubane is anticipated to enhance the energy output by 14% compared to HMX.

Highly nitrated small ring heterocycles are also interesting as energetic materials because of the increased performance expected from the additional energy release upon opening the strained ring system during decomposition. The most widely studied energetic small ring compound to date is 1,3,3-trinitroazetidine (TNAZ), a potentially melt castable explosive that has been investigated as a possible replacement for TNT. TNAZ is attractive as an explosive or as a near term candidate component for explosives/propellants with low sensitivity, good stability and enhanced performance (high energy and density) over existing military formulations. The characteristic properties of various oxidizers and high energy materials are presented in the Table 2.

4 Theoretical Prediction of Advanced Propellant Compositions

The theoretical prediction of ballistic performances for different advanced propellant compositions based on metallized solid composite propellants (binder, Al and AP, ADN, HMX, CL-20, NTO, TNAZ, FOX-7) have already been carried out through thermodynamic calculations (ICT Thermodynamic code) (see Figure 2, Ref. 72). The corresponding results are given in Figure 2. The calculations were carried out for rocket equilibrium at 7 MPa, considering an adiabatic through a nozzle in a one dimensional flow at chemical equilibrium, with an expansion ratio of 70:1.

Table 2. Characteristics of some oxidizers/high energy materials

Serial No.	Oxidizer	Molecular Formula	Molecular weight	State	Density [kg/m ³] D×10 ³ at 25 °C	Oxygen balance [wt.%]	ΔH _f ^o [kcal/mol]
1	AP	NH ₄ ClO ₄	117.5	Solid	1.950	34.0	-70.7
2	KP	KClO ₄	138.5	Solid	2.519	46.2	-103.4
3	LP	LiClO ₄	106.4	Solid	2.428	60.1	-91.1
4	HP	N ₂ H ₅ ClO ₄	116.5	Solid	1.939	13.7	-----
5	HP ₂	N ₂ H ₆ (ClO ₄) ₂	232.9	Solid	2.200	41.2	-70.1
6	HAP	HONH ₃ ClO ₄	133.5	Solid	2.126	41.9	-66.3
7	NP	NO ₂ ClO ₄	145.4	Solid	2.220	71.5	8.7
8	HNF		183.1	Solid	1.860	13.1	-18.4
9	RDX		222.1	Solid	1.816	-21.6	16.0
10	HMX		296.2	Solid	1.910	-21.6	17.9
11	DNAF		272.1	Solid	1.82	-5.9	154.7
12	CL-20		438.2	Solid	1.97	-10.9	81.0
13	ONC		464.1	Solid	2.1	0.0	98.9

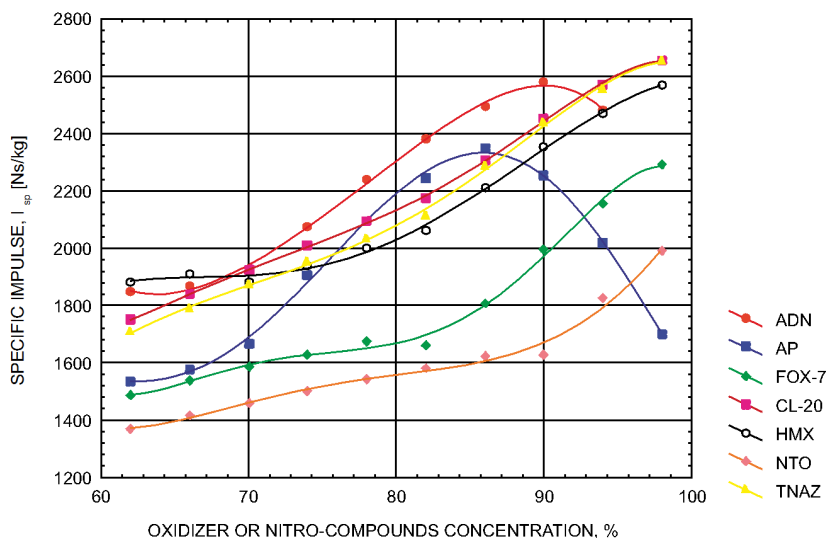


Figure 2. Specific impulse of binder-oxidizer or nitro compound (solid loading in the range 62-98%) [72].

5 Conclusions

Propellant engineers and chemists have attempted to increase the specific impulse of propellants. Increasing the solid loading has been one major route. However, this has levelled off and further achievable improvements had been marginal. Another route has been in creating energetic components as propellant ingredients to improve the energy output. The thrust of recent research has been in this area, aiming to create novel and newer energetic oxidizers, plasticizers and binders. Improved mixers to achieve increased safety in processing and homogeneity of the mix in a shorter time, have been developed. Lower temperature curing has been attempted by process modifications, and formulation improvements to make processes more energy efficient where large scale processing is concerned. Modifications to casting and curing have been attempted to improve the physical and mechanical properties of the propellant. There will be continued use of ammonium perchlorate as an oxidizer due to its availability on a large scale at a cheap price. The efforts of the high energy materials scientific community will continue to replace conventional oxidisers with more environmentally compatible energetic oxidizers, such as ammonium dinitramide, hydrazinium nitroformate *etc.* The efforts will also continue to further the use of CL-20 as an energetic oxidizer

for composite propellant formulations. Energetic materials researchers continue to seek an energetic alternative binder to HTPB. The overall trend is to make the composite propellant more energetic by choosing energetic ingredients, such as energetic binders, energetic ballistic modifiers and by using more energetic and denser oxidiser ingredients in the formulations. The use of energetic ingredients will help to achieve higher Isp (specific impulse) for the formulations. At the cost of increasing the Isp, the sensitivity and mechanical properties of the composite propellant formulations may be compromised. An extensive amount of R & D work is needed in order to achieve an efficient composite formulation with a specific impulse greater than the conventionally obtained Isp. This is still a Herculean task and a challenge for the propellant chemists and propellant engineers to design safer and user friendly propellant formulations using modern energetic ingredients with the appropriate mechanical properties.

Nomenclature

AP	Ammonium perchlorate
AN	Ammonium nitrate
ADC	Ammonium dichromate
ADN	Ammonium dinitramide
CP	Composite propellant
CMDB	Composite modified double base
CDB	Cast double base
DNAF	Dinitro diazene furoxan
GAP	Glycidyl Azide polymer
HNIW	Hexanitrohexaazaisowurtzitane
HpNC	Heptanitrocubane
HTPB	Hydroxy terminated polybutadiene
HP	Hydrazinium perchlorate
HNF	Hydrazinium nitroformate
HMX	Cyclotetramethylene tetranitramine
Isp	Specific impulse
KP	Potassium perchlorate
LP	Lithium perchlorate
NP	Nitronium perchlorate
N	Pressure exponent
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	Ammonium dichromate
NiGU	Nitroguanidine
ONC	Octanitrocubane
PCL	Polycaprolactone

PEG	Polyethylene glycol
PTHF	Polytetrahydrofuran
PSAN	Phase stabilized ammonium nitrate
RDX	Cyclotrimethylene trinitramine
UFAP	Ultrafine ammonium perchlorate

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