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# THE WAYS FOR DEVELOPMENT OF ENVIRONMENTALLY SAFE SOLID COMPOSITE PROPELLANTS

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The paper considers a wide set of issues concerning the creation of high energetic solid composite propellants causing the minimal polluting effect on the environment. Thereby, the level of toxicity of products of different compositions is discussed and propellants with perchlorates oxidizers are compared with propellants with halogen free oxidizers (mainly, ammonium dinitramide, HMX, CL-20). The main methods for creating compositions having a required performance and the highest energetic characteristics are also under discussion. The dependences of the specific impulse on the mode of formulation arrangement and on the compounds' properties (i.e., formation enthalpy, density, element content) are demonstrated. The main principles for the maximal use of energetic potential of chemical substances are under consideration. These are the proper selection of the binder type which would be optimal for the given mixture of oxidizer with fuel (or energetic) component and the opportunity of using metals and their hydrides (mainly, aluminum hydride (AH)). Main obstacles in using different kinds of compositions, as well as advantages of specific propellants are under consideration as well. A special attention is paid to the interrelationship between the energetic parameter and other performances (thermal stability, combustion law, sensitivity, and compatibility).

## 1 INTRODUCTION

Low environmental impact of combustion products often becomes a prime condition for rocket propellants. What products constitute the environmental problem? Naturally, both the amount of a certain component released and its relative toxicity should be taken into account. At high toxicity, even trace concentrations of supertoxicants (e.g., dioxins) in the combustion products may become a major problem, whereas less toxic HF, HCl, and even CO become dangerous only in large amounts. Since a rocket launch is occasional, its environmental impact should be assessed differently from that produced by the exhaust of the same products in continuous industrial processes. The conditions in which a

solid propellant is used are also important. For example, the use of beryllium is absolutely unacceptable in the first stages of rocket launchers, while it can be used in the outer space.

## 2 MAJOR TOXIC COMBUSTION PRODUCTS OF SOLID COMPOSITE PROPELLANTS RELEASED INTO ENVIRONMENT

Toxic substances cannot be avoided completely. Even CO and NO are toxic and always form (especially, CO) at equilibrium concentrations at high-temperature combustion of CHNO systems. For example, combustion of a simple formulation of 13% hydrocarbon binder (HB) + 20% Al + ADN results in the CO concentration at the nozzle exit (at 2200 K) of  $9.6 \text{ mol/kg} = 270 \text{ g/kg}$ . Since the limiting allowable concentration (LAC) for CO is  $3 \text{ mg/m}^3$  (Russian standard),  $2.7 \cdot 10^9 \text{ mg}$  CO released in the course of combustion of a 10-ton propellant charge must be diluted in  $1 \text{ km}^3$  to bring it to the LAC.

Similar pattern is observed for 14% HB + 20% Al + ammonium nitrate (AN) (the formulation temperature at the nozzle exit  $T_a$  is 1800 K). It is virtually impossible to fight CO, as the shift in oxygen balance and elimination of Al (this will reduce CO concentration as well) result in the dramatic drop of pocket performance. In addition, one should take into account that after leaving the nozzle, the hot ( $\sim 2000 \text{ K}$ ) gaseous products containing CO mix with air and a substantial part of CO is oxidized to  $\text{CO}_2$ . For this reasoning, this paper does not deal with CO as an environmentally harmful substance.

Similar consideration applies to nitrogen oxides. Those are always present in the rocket motor exhaust in the concentrations not lower than the equilibrium one. In fact, NO concentrations are even higher, since NO, the second (after molecular nitrogen) major nitrogen-containing product of combustion, is quenched due to gas cooling during expansion. The calculated equilibrium NO concentration at the nozzle exit at  $\sim 2100 \text{ K}$  comprises  $10^{-8}$ – $10^{-7} \text{ mol/kg}$ . Thus, the concentration of NO is 8–9 decimal orders lower than that of CO, so even with the account of LAC, two orders of magnitude lower than that of CO, atmospheric pollution with NO can be considered as minor.

During '50s–'70s of the XX century, an interest arose to the formulations containing beryllium and its hydride. As a matter of fact, substitution of aluminum by beryllium brings a substantial increase in the specific impulse. Table 1 presents the calculation data on energy properties of the formulations based on HB, oxidizer, and metal. One can see that substitution of aluminum by beryllium increases the specific impulse by approximately 20 units. Naturally, the largest gain is achieved for the formulations with AN which need the additional energy to the utmost. It will be seen below that a ratio of components in each

**Table 1** Comparison of beryllium- and aluminum-containing formulations:  $I_{sp}$  is the specific impulse at  $P_c : P_a = 40 : 1$ ;  $P_c$  and  $P_a$  are the pressures (in atm) in combustion chamber and at the nozzle exit, respectively;  $\rho$  is the density; and  $E_3$  — see subsection 4.1

Formulation	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$E_3$ , g, cm <sup>3</sup> , s
12% HB + 20% Al + AN	244.4	1.67	270.8
14% HB + 12% Be + AN	268.7	1.52	292.2
12% HB + 20% Al + ADN	261.7	1.73	292.0
14% HB + 12% Be + ADN	281.8	1.60	309.6
10% HB + 22% Al + AP	251	1.85	283.9
12% HB + 12% Be + AP	265.5	1.705	295.4

composition described in this paper has been chosen based on the following principles:

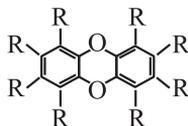
- (a) binder content is not lower than 18–20%(vol.), otherwise, it would be too hard or even impossible to create the composition; and
- (b) maximal metal content is not higher than the value when at which the mass percentage of its oxide in the combustion products is higher than 36%–38%, otherwise, a slagging occurs in the course of combustion process.

Finally, the composition meeting conditions (a) and (b) with the highest  $I_{sp}$  value or highest ballistic efficiency has been selected.

Nevertheless, the excessively high toxicity of beryllium and its derivatives (LAC in air is 0.001 mg/m<sup>3</sup>, i.e., combustion products of each ton of Be-containing propellant contaminate 100 km<sup>3</sup> of air) prohibits the use of such fuels in the first stages of rocket launchers. Of course, their use in the upper atmosphere and especially in the outer space is well justified, especially, as they are more efficient for the higher stages. However, even test ground firings of such formulations can result in dramatic beryllium pollution.

For combustion of perchlorate-based formulations, hydrogen chloride is a massive product (up to 20–25%(wt.)). It is an ozone depleting gas. In addition, upon launch or disposal of rockets on the Earth surface, vegetation suffers on a vast territory (HCl LAC is 5 mg/m<sup>3</sup>). Hydrogen chloride precipitates mainly as hydrochloric acid directly over the launch site covering the area of 1–2 ha. However, its fallout was detected at a distance up to 7–8 km, and its concentration in nearby localities sometimes exceeds the LAC by a factor of 20.

The other dangerous combustion products of chlorine-containing formulations are excessively toxic dioxins, the compounds of general formula:



where  $R = H$  or  $Cl$ , with 1 to 8 chlorine atoms. As their LAC in air is  $5 \cdot 10^{-11} \text{ mg/m}^3$ , a very small amount of dioxins may create a serious problem. Particularly, strong release of dioxins occurs at thrust cutoff, i.e., when the motor completes its operation. When the concentration of hydrogen becomes lower than that of chlorine, the equilibrium concentrations of dioxins increase by many decimal orders and constitute major chlorine-containing products.

Thus, the major objective of this paper is to describe a possibility to substantially reduce the environmental danger of solid propellants through the use of formulations based on ammonium perchlorate (AP) and to propose the most promising formulations containing neither beryllium, nor fluorine or chlorine.

### 3 POSSIBILITIES OF DEVELOPING PROPELLANTS BASED ON AMMONIUM PERCHLORATE WITH SUBSTANTIALLY IMPROVED ENVIRONMENTAL PERFORMANCE

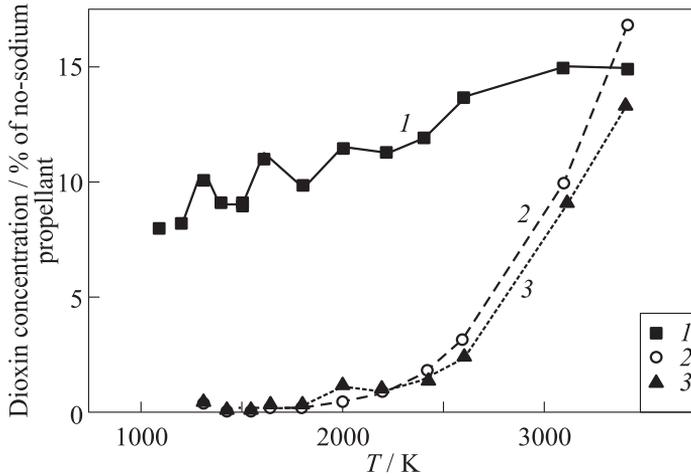
At present, AP is the cheapest and most available oxidizer among highly potential ones (those based on cheap AN have low density and specific impulse, those based on ammonium dinitramide (ADN) provide high  $I_{sp}$  but possess lower density and are substantially more expensive), but whenever a formulation incorporates only C, H, O, N, Al, and Cl, the chlorine in the combustion products appears in the form of gaseous HCl. Chlorine can be neutralized to safe solid products only with alkaline metals in quantities no less than equivalent to chlorine. This is possible with substitution of AP by lithium, sodium, or potassium perchlorates [1], but lithium perchlorate is excessively hygroscopic and the formulations based on potassium perchlorate have lower energy due to high atomic mass of potassium. There is a possibility to prepare a formulation with equimolar mixed oxidizer AP :  $\text{NaNO}_3$  (SN).

The data of Table 2 show that at the nozzle exit at about 3000 K, the formulations based on the mixed AP : SN oxidizer yield HCl concentration 5 times lower than the formulations based on AP; with further cooling, this concentration drops due to the reaction of HCl with sodium species (primarily, sodium vapors) and at 1200–1300 K, the concentration of HCl becomes negligible.

How does introduction of sodium affect equilibrium concentrations of dioxins? The calculations were performed for equilibrium concentrations of dioxins

**Table 2** Some formulations based on AP : SN oxidizer.  $T_c$  and  $T_a$  are the temperatures in combustion chamber and nozzle exit, respectively

System	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$T_a$ , K	HCl + Cl <sub>2</sub> , mol/kg	CO, mol/kg	H <sub>2</sub> , mol/kg
AP + HB + Al	251	1.84	3610	2520	6	7	10
AP + HB	240	1.76	3000	1900	7.8	0.8	0.5
NaClO <sub>4</sub> + HB	211	2.0	3080	2030	0.25	2	0.5
NaClO <sub>4</sub> + HB + Al	225	2.05	3650	2610	1.1	10	7
AP : NaNO <sub>3</sub> + HB + Al	230	1.96	3665	2990	1.5	4.7	4.4
AP : NaNO <sub>3</sub> + 20% HMX + HB + Al	234	1.936	3630	2610	0.9	7.1	10.3

**Figure 1** The equilibrium concentration of dioxins in combustion products for the formulations based on AP + SN vs. temperature: 1 — AP : SN = 1 : 0.9; 2 — 1 : 1; and 3 — AP : SN = 1 : 1.1

in the combustion products of a standard formulation Al + AP + HB. The thermodynamic calculations showed that with the introduction of SN, the content of dioxins drops dramatically and depending on temperature it comprises from 0.5% to 15% of that attained without sodium.

Figure 1 shows the examples of the formulations based on AP : SN, with the molar ratio AP/SN = 0.9, 1.0, and 1.1. In the temperature range below 2500 K, the yield of dioxins drops as the sodium to chlorine molar ratio increases to 1. Further increase of SN molar fraction in the oxidizer does not lead to reduction in dioxin concentration compared to equimolar AP : SN.

Thus, the formulations based on AP : SN mixture provide a possibility of reducing substantially the release of both hydrogen chloride and dioxins to the environment.

## 4 FORMULATIONS BASED ON HALIDE-FREE OXIDIZERS

In the course of development of propellant formulations, not only energy parameters and environmental performance discussed afore must be taken into account. The issues to be addressed also include thermal stability, compatibility of constituents, sensitivity to impact and friction, required combustion law, and others including the cost. Each of the halides-free oxidizers discussed below has its own merits and drawbacks, which must be taken into account when developing a composition for a particular task (conditions of storage, safety margin, strength of combustion chamber casing, etc.).

The list of chlorine-free oxidizers presented in Table 3 is exhaustive for practical applications. Possible extensions of this list will be discussed further.

Ammonium-nitrate-based formulations are considered in a complementary paper. Here, it is worth mentioning that AN is the oxidizer with the lowest energy potential due to its low  $\Delta H_f^0$  value and low density; nevertheless, a proper choice of binder in the presence of metals can narrow the loss for AP-based formulations.

Starting to discuss the solid propellants based on other oxidizers listed in Table 3, note that it is mainly the oxidizer (depending on its chemical formulation and  $\Delta H_f^0$ ) that predetermines the energy potential of solid propellant. However, in order to make a formulation where the energy potential of an oxidizer is materialized to its best, one must carefully select other components, namely, energetic component (metal, hydride) and binder according to the rule of thumb: the binder should compensate in its chemical composition the disadvantages of other components.

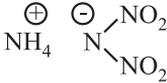
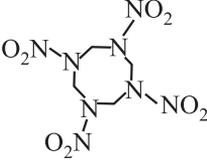
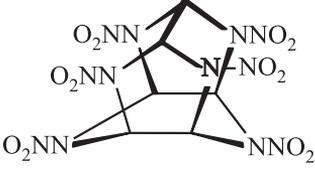
For example, if oxidizer is rich in oxygen and the formulation contains little or no metal, the binder should be rich in hydrogen; if the formulation contains hydride or an oxygen-deficient oxidizer (e.g., HMX), the binder must take some oxidizer functions (say, contain functional groups like  $\text{NO}_2$ ,  $\text{NO}_3$ ), etc.

In this paper, the formulations with different types of binder are considered, namely:

HB,  $\Delta H_f = -390$  kJ/kg,  $\rho = 0.91$  g/cm<sup>3</sup>, hydrogen content  $\sim 12\%$ ;

poly(methylvinyltetrazol) (PMVT)-(C<sub>4</sub>N<sub>4</sub>H<sub>6</sub>)<sub>n</sub>, a high-enthalpy polymer with high nitrogen content ( $\sim 46\%$ ),  $\Delta H_f = +1255$  kJ/kg,  $\rho = 1.28$  g/cm<sup>3</sup>;

**Table 3** Major halide-free oxidizers

Oxidizer	Merits	Drawbacks
Ammonium nitrate, $\text{NH}_4\text{NO}_3$ AN	Availability, low cost, high oxygen content, bility, good compatibility with other components, low sensitivity	Low energy potential because of the low enthalpy of formation ( $\Delta H_f^0 = -4514$ kJ/kg), low density ( $1.725$ g/cm <sup>3</sup> ), low combustion rate, phase transitions in the operational temperature range
 ADN	High energetic potential, satisfactory combustion law, satisfactory thermal stability, compatibility, and sensitivity	Limited supply, high cost
 HMX	Availability, moderate cost, high thermal stability, satisfactory compatibility	Poor combustion law (large exponent $\nu$ in the pressure dependence of combustion rate $W = AP^\nu$ ), relatively high sensitivity, susceptibility to deflagration-to-detonation transition
 CL-20	High density, satisfactory thermal stability and compatibility	Same as HMX + high cost
Hydrazonium nitroformate, $\text{N}_2\text{H}_5^+ \text{C}(\text{NO}_2)_3^-$ HNF	High energy potential	High sensitivity, poor compatibility, lack of mass production

active binder (AB), a model binder analogous to practical ones, 20% PMVT, extended with a mixture of trinitroglycerol with 2,4-dinitro-2,4-diazopentane; its gross formula is close to  $\text{C}_{19}\text{H}_{34.5}\text{N}_{19}\text{O}_{29.5}$ ;  $\Delta H_f = -757$  kJ/kg,  $\rho = 1.49$  g/cm<sup>3</sup>, oxygen content  $\sim 47\%$ ; and

poly(vinylmethoxydiazen-N-oxide) (PVMDO)  $(\text{C}_3\text{H}_6\text{N}_2\text{O}_2)_n$ ,  $\Delta H_f = 0$  kJ/kg,  $\rho = 1.31$  g/cm<sup>3</sup>, a model binder rich in hydrogen ( $\sim 6\%$ ) and oxygen ( $\sim 31\%$ ).

### 4.1 Formulations Based on Dinitramide Salts

Ammonium dinitramide is a relatively new oxidizer first synthesized in Russia in 1972. During 10–15 years, methods of synthesis, purification, and stabilization were developed, industrial production was implemented, and even practical motors based on ADN-propellants were manufactured [2]. Ammonium dinitramide has a favorable chemical composition and sufficiently high  $\Delta H_f^0$  value; hence, the ADN-based formulations have the highest  $I_{sp}$  among those based on other oxidizers (except HNF) listed in Table 3. However, a low density of ADN makes it better suited for the formulations used in the higher stages. On the lower stages, it loses a bit to AP.

Table 4 presents the calculated properties of the formulations based on ammonium, hydrazoneum, and guanidinium salts of dinitramide. Since different oxidizers possess different density and the density of propellant ( $\rho$ ) substantially affects the ballistics, the formulations were compared not only by  $I_{sp}$  but also by the so-called ballistic efficiency ( $E_i$ ) of the  $i$ th stage of a rocket launcher. The ballistic efficiency [3] of the  $i$ th stage ( $E_i$ ) is defined as  $E_1 = I_{sp}\rho^{0.6}$ ,  $E_2 = I_{sp}\rho^{0.4}$ , and  $E_3 = I_{sp}\rho^{0.2}$ . These exponent values (0.2, 0.4, and 0.6) correspond to three-stage rocket launchers with optimized stage masses and tank volumes of every stage. Using these equations, one can affirm that, e.g., if there are two different propellants (the first one possessing  $I_{sp1}$  and  $\rho_1$  while the second one possessing  $I_{sp2}$  and  $\rho_2$ ) the usage of the first propellant in the first stage would provide higher speed growth than the usage of the second propellant (the propellants

**Table 4** Energy potential of formulations based on dinitramide salts

Oxidizer	Binder type	Binder, %(wt.)	Energetic compound, %	HMX, %	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$E_1$ , g	$E_2$ , cm <sup>3</sup>	$E_3$ , s
NH <sub>4</sub> N(NO <sub>2</sub> ) <sub>2</sub>	HB	12	0	0	246.9	1.625	330.4	299.8	272.1
	PMVT	18	14 Al	0	258.0	1.767	363.0	324.0	289.1
		18	20 Al	0	259.5	1.802	369.5	328.4	291.9
	HB	12	16 Al	0	260.7	1.704	358.9	322.6	290.0
		12	20 Al	0	261.7	1.725	363.0	325.5	291.9
		18	16 Al	20	258.3	1.833	371.6	329.1	291.6
		18	22 Al	20	259.6	1.870	377.9	333.5	294.2
	AB	18	11 B	0	256.4	1.781	362.5	323.0	287.8
		18	—	0	251.2	1.625	336.1	305.0	276.8
	N <sub>2</sub> H <sub>5</sub> N(NO <sub>2</sub> ) <sub>2</sub>	HB	12	—	0	251.2	1.625	336.1	305.0
20		—	0	251.6	1.742	351.0	314.1	281.1	
AB	20	10 B	0	262.3	1.774	370.0	329.9	294.2	
	20	10 B	0	262.3	1.774	370.0	329.9	294.2	
C(NH <sub>2</sub> ) <sub>3</sub> N(NO <sub>2</sub> ) <sub>2</sub>	AB	18	20 Al	0	254.2	1.824	364.6	323.3	286.7

used in the 2nd and 3rd stages being equal) if  $I_{sp1}\rho_1^{0.6} > I_{sp2}\rho_2^{0.6}$ . Naturally, the exponents for density depend on the volume-to-mass ratio for each stage and can differ substantially.

To date, ADN is the most efficient oxidizer for solid propellants (especially, for upper stages) among the industrially produced ones. The formulations with AB and boron can provide the highest ballistic efficiency, as boron-based propellants have no condensed combustion products and hence, experience no two-phase losses of specific impulse (this losses are typical of Al-based formulations).

## 4.2 Formulations Based on Organic Oxidizers

The available choice of candidate inorganic oxidizers suitable for propellants is limited indeed. Those include onium nitrates, perchlorate, and dinitramide salts. Salts of other acids are either less energetic or unstable (when the acid is weak). The chemistry of organic oxidizers provides a wider choice.

## 4.3 Formulations Based on HMX

RDX and HMX are the well developed commercially produced explosives. HMX takes over RDX in energy, as with the same element content and approximately equal  $\Delta H_f^0$  (314–334 kJ/kg) HMX has a substantially higher density (1.91 vs. 1.80 g/cm<sup>3</sup>). Therefore, this subsection deals only with HMX. HMX is not used as an individual oxidizer in solid propellants. Its advantage of high  $\Delta H_f^0$  is combined with a disadvantage — it is not sufficiently rich in oxygen. For this reason, it should be used only with a highly active binder (Table 5).

Another drawback of HMX (typical also of other CHNO oxidizers) is that the formulations based on it have a high value of exponent  $\nu$  in the combustion law  $W = AP^\nu$ . Therefore, systems with high HMX content are dangerous for

**Table 5** Energy potential of formulations based on HMX and AB

Binder, %(wt.)	Al, %	Additional compound	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$T_a$ , K	$E_1$	$E_2$	$E_3$
							g, cm <sup>3</sup> , s		
10	0	0	252.4	1.85	3210	1690	365.1	322.8	285.4
16	0	0	251.3	1.82	3180	1660	359.9	319.3	283.3
16	16	0	262.0	1.91	3670	2360	386.3	339.4	298.2
16	16	6% AP	261.2	1.91	3713	2425	385.0	338.3	297.3
16	12	0	261.0	1.88	3590	2300	381.2	336.0	296.1
16	0	6% B	250.7	1.84	3120	1820	361.4	319.9	283.2

possibility of deflagration-to-detonation transition or failure of motor casing due to uncontrolled pressure rise in the combustion chamber. At the same time, use of up to 25% HMX in combination with another oxidizer is relatively safe and for certain systems, this secures improved energetic parameters (e.g., when AP is the major oxidizer). But this is not a common rule; ADN does not require HMX. In order to secure a favorable combustion law for the formulations based on HMX and an AB, one usually introduces a small amount of AP (5%–10%) even at the expense of a small drop of energetic parameters.

#### 4.4 Formulations Based on High-Enthalpy Organic Oxidizers

Recently, a number of publications has been devoted to synthesis and investigations of properties of other organic compounds with high oxygen content and relatively high  $\Delta H_f^0$ . Those are mainly the compounds based on high-enthalpy structures: strained carbon cycles (cubane), acetylene derivatives, nitrogen-containing heterocycles (aziridines, furazanes, furoxanes, triazoles, tetrazoles, etc.).

Recently, CL-20 has been studied extensively [4]; this is a high-density high-enthalpy compound ( $\Delta H_f^0 \sim 840$  kJ/kg,  $\rho = 2.04$  g/cm<sup>3</sup>, see Table 3). However, authors' analysis has shown that despite these advantages over HMX, CL-20 is more efficient than HMX only in first stages of multistage rocket launchers (exclusively due to higher density). Because of a lower hydrogen fraction (almost twofold as compared with HMX), CL-20 is virtually equivalent to HMX in the second stage and less effective in the third stage.

In early 1980s, octanitrocubane ( $\Delta H_f^0 = +250$  kcal/kg,  $\rho \approx 1.98$  g/cm<sup>3</sup>) arose much hope. Much effort was devoted to synthesis of this oxidizer. However, the attainable energy performance of octanitrocubane (Table 6) may not payoff the bitter problems encountered in the synthesis. Not so high ballistic efficiency of octanitrocubane stems from the absence of hydrogen.

There is a variety of onium salts of organic acids-oxidizers. Among those, there are many onium salts of primary nitramines. These compounds are readily available; as a rule, their synthesis is not complicated.

**Table 6** Energy potential of formulations with octanitrocubane

Binder	Binder, % (wt.)	Boron, %	Al, %	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$T_a$ , K	$E_1$	$E_2$	$E_3$
								g, cm <sup>3</sup> , s		
HB	8	0	0	262.5	1.87	3730	2360	382.2	337.2	297.5
HB	10	0	0	260.8	1.83	3650	2090	374.8	332.1	294.3
HB	10	0	6	263.4	1.88	3770	2330	384.7	339.1	298.8
PMVT	12	10	0	262.9	1.96	4100	2800	393.7	344.1	300.8

**Table 7** Energy potential of formulations based on salts of methylenedinitramine

Oxidizer	Binder	Binder, % (wt.)	Al, %	B, %	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$E_1$	$E_2$	$E_3$
								g, cm <sup>3</sup> , s		
$(\text{NH}_4)_2\text{CH}_2(\text{NNO}_2)_2$	PMVT	10	0	0	206.2	1.50	1710	263.0	242.5	223.6
	AB	18	0	0	221.9	1.52	2130	285.3	262.4	241.3
	PMVT	12	18	0	246.2	1.62	2590	328.8	298.6	271.1
	AB	16	20	0	258.0	1.67	3150	351.0	316.7	285.9
$(\text{N}_2\text{H}_5)_2\text{CH}_2(\text{NNO}_2)_2$	AB	16	0	10	245.2	1.58	2330	322.6	294.4	268.7
	PMVT	10	0	0	219.5	1.64	1910	295.4	267.5	242.3
	AB	10	0	0	233.9	1.67	2270	318.2	287.2	259.2
	PMVT	12	16	0	251.7	1.73	2640	349.7	313.4	280.9
	AB	16	20	0	265.2	1.78	3180	374.8	334.0	297.6
	AB	16	0	10	252.2	1.70	2350	346.7	311.8	280.4

The energy potential of the formulations based on ammonium and hydrazonium salts of methylenedinitramine are presented in Table 7. One can see that high properties can be attained using hydrazonium salt; however, stability of this salt is insufficient for its use as a component in solid composite propellants.

Additionally to that, almost all hydrazonium salts manifest remarkably strong impact and friction sensitivity, whereas hydroxylammonium salts are too hygroscopic, have poor compatibility with other components of solid propellants, and often insufficiently stable. The stability of hydrazonium and hydroxylammonium salts depends on the strength of the acid and its activity as an oxidizer. Thermal stability of the salts grows with increasing the acid strength and reducing its activity as an oxidizer, as thermal decomposition of the onium salts proceeds via proton transfer and the formation of the free base in equilibrium concentration. The base either reacts with free acid or decomposes itself. Hydroxylammonium perchlorate (HAP), the salt of a very strong perchloric acid, manifests insufficient stability to be promptly used as a component for solid composite propellant.

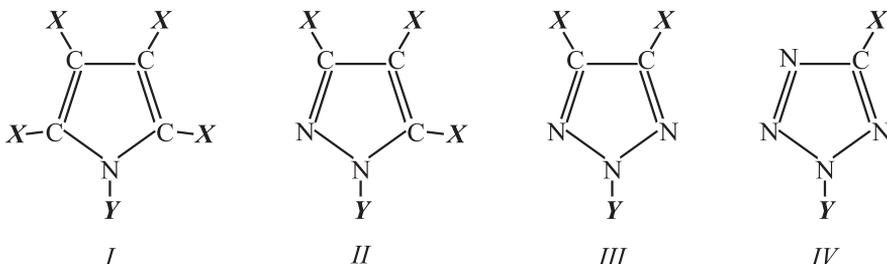
Using special methods, by achieving a shift in the equilibrium to formation of a little excess of free acid, one can substantially increase its thermal stability [5]. In the series  $\text{NH}_4^+\text{X}^-$ ,  $\text{N}_2\text{H}_5^+\text{X}^-$ , and  $\text{NH}_3\text{OH}^+\text{X}^-$ , ammonium salts are the most stable, hydrazonium are less stable, and hydroxylammonium salts are the least stable. The first reason is that alkalinity of onium base decreases substantially from ammonium to hydroxylammonium. The second, the reducing activity of the base increases in the same series while thermal stability of the base as a compound drops.

Table 8 shows the formulations with ammonium and hydrazonium salts of nitroform. The higher energy parameters of hydrazonium salts are obvious.

**Table 8** Energy potential of formulations with nitroform salts

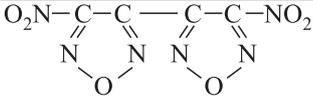
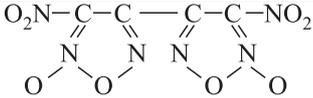
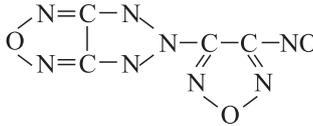
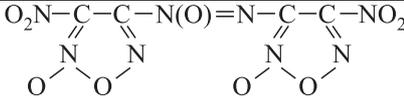
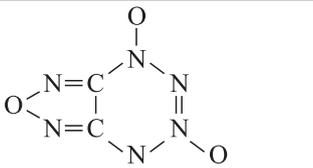
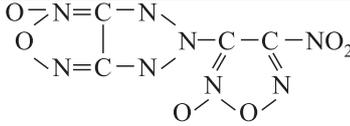
Oxidizer	Binder	Binder, %	Al, %	B, %	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$T_a$ , K	$E_1$ , g, cm <sup>3</sup> , s	$E_2$	$E_3$
NH <sub>4</sub> C(NO <sub>2</sub> ) <sub>3</sub>	HB	8	0	0	252.8	1.75	3190	1980	353.7	316.2	282.7
	PMVT	13	0	0	250.9	1.80	3180	2140	357.0	317.4	282.2
	HB	10	20	0	260.1	1.81	3660	2430	371.3	329.8	292.9
		10	0	2	250.4	1.72	3150	1750	346.7	311.1	279.1
	PMVT	12	20	0	257.5	1.90	3880	2740	378.5	332.9	292.8
		12	12	0	255.5	1.85	3570	2450	369.6	326.8	289.0
		12	0	6	252.1	1.81	3350	2000	359.9	319.6	283.9
AB	16	0	11	254.9	1.85	3540	2310	368.7	326.0	288.3	
N <sub>2</sub> H <sub>5</sub> C(NO <sub>2</sub> ) <sub>3</sub>	HB	8	0	0	258.9	1.75	3230	1870	362.2	323.9	289.6
	PMVT	9	0	0	257.8	1.82	3250	2200	369.3	327.6	290.6
	HB	10	18	0	265.1	1.80	3590	2330	377.2	335.4	298.2
		10	10	0	263.0	1.76	3420	2100	369.2	329.7	294.5
	PMVT	12	18	0	263.5	1.89	3810	2610	386.1	339.9	299.3
		12	6	0	260.9	1.83	3460	2280	374.9	332.2	294.4
		12	0	4	258.0	1.81	3340	1940	368.3	327.1	290.5
	AB	16	0	8	261.1	1.84	3520	2280	376.4	333.2	295.0

Recently, a number of papers have been devoted to studies of possible application of high-enthalpy CHNO oxidizers, e.g., from the series of substituted five-member N-heterocycles (pyrrole (*I*) → pyrazole (*II*) → 1,2,3-triazole (*III*) → tetrazole (*IV*) [6, 7].



where  $X$ ,  $Y$  are NO<sub>2</sub>, C(NO<sub>2</sub>)<sub>3</sub>, or other oxidizing groups. These compounds may be interesting as components of solid composite propellants only with a large number of constituents incorporating oxidizing groups. In the series from pyrrole to tetrazole, the  $\Delta H_f^0$  value of such oxidizers increases and so does oxygen balance. The derivatives of furozanes, furoxanes, and other five-, six-member N-heterocycles can also make potential oxidizers (Table 9).

**Table 9** Energy potential of formulations based on high-enthalpy organic oxidizers

Oxidizer	$\Delta H_f$ , kJ/kg	$\rho$ , g/cm <sup>3</sup>	Binary formulation with	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$E_1$	$E_2$ g, cm <sup>3</sup> , s	$E_3$
	1852	1.85	16% AB	257.3	1.781	363.8	324.1	288.8
	1505	1.90	15% PVMDO	261.4	1.780	369.5	329.2	293.4
	3511	1.91	16% AB	260.3	1.827	373.7	331.3	293.6
	1296	1.88	18% PVMDO	257.6	1.743	359.5	321.7	287.9
	3051	1.85	16% AB	261.3	1.781	369.4	329.2	293.3
	3177	1.96	15% PVMDO 16% AB	269.9 268.7	1.824 1.865	387.1 390.5	343.3 344.8	304.4 304.4

## 5 A POSSIBILITY TO SUBSTANTIALLY ENHANCE ENERGY POTENTIAL OF SOLID COMPOSITE PROPELLANTS THROUGH INTRODUCTION OF ALUMINUM HYDRIDE

A possibility to use AH ( $\text{AlH}_3$ ,  $-12$  kJ/mol,  $\rho = 1.48$  g/cm<sup>3</sup>) as an energetic component instead of aluminum was studied from early 1960s. Indeed, AH plays not only the role of energetic component, but also gas-generating one; this provides a possibility to increase  $I_{\text{sp}}$  dramatically. The efficiency of AH, however, is materialized only when an AB is used. Therefore, the extensive search aimed at synthesis and manufacturing of binders incorporating large fraction of nitroether-, nitro-, or nitramine groups was performed in parallel with the search of optimal ways for AH synthesis and improvement of its operational properties. The initial AH-containing compositions were really created and manufactured in small amounts of AP as oxidizer; further, several years later, the ones with ADN were created as well. Table 10 shows the efficiency of AH on the example of formulations with ADN. Note that the binder volume fraction is also presented in the table. Since AH particles constitute a very fine fraction, there must be at least 25% by volume of binder for 25%(wt.) of AH in the formulation (while for aluminum-containing formulations, the minimum volume fraction of binder is 18%–19%). For a lower content of binder, it is virtually impossible to prepare a propellant with satisfactory mechanical and rheological properties.

Table 11 presents the data for AH-containing formulations with different oxidizers and AB. It shows that the use of AH allows one to overcome to a certain extent the disadvantages of an oxidizer; the formulations based on AN do not lose much to those with ADN, HAP, or HNF. Presently, the major factor limiting wide use of AH is its high cost.

**Table 10** Energy parameters of formulations 25% AH + binder + ADN depending on binder type and content

Binder	Binder content		$I_{\text{sp}}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$E_2$ g, cm <sup>3</sup> , s	$E_3$
	%(wt.)	%(vol.)					
HB	13	21.9	270.2	1.532	2788	320.5	294.3
	16	26.3	263.7	1.494	2631	309.6	285.7
	18	28.6	260.0	1.470	2527	303.3	280.8
PVMDO	20	25.5	279.2	1.603	3379	337.2	306.8
	25	30.1	278.8	1.576	3258	334.4	305.4
	29	34.4	276.0	1.560	3100	329.7	301.7
AB	25	27.2	277.5	1.621	3542	336.6	305.6
	30	32.6	277.2	1.618	3525	336.0	305.2

**Table 11** Energy parameters of formulations with AH, AB, and different oxidizers

Oxidizer	AH, %	Binder AB, %(wt.)	$I_{sp}$ , s	$\rho$ , g/cm <sup>3</sup>	$T_c$ , K	$E_2$ g, cm <sup>3</sup> , s	$E_3$
AP	25	25	270.1	1.685	3587	332.8	299.8
		30	270.8	1.663	3546	331.9	299.8
HAP	25	25	277.5	1.634	3564	337.7	306.1
		30	274.1	1.700	3674	338.9	304.8
ADN	25	25	277.5	1.621	3542	336.6	305.6
		30	277.2	1.618	3525	336.0	305.2
AN	25	25	267.4	1.595	3208	322.3	293.6
		30	268.0	1.583	3202	322.1	293.8
HNF	25	25	279.8	1.666	3584	343.2	309.9
		30	279.2	1.646	3537	340.8	308.5
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>2</sub> (NNO <sub>2</sub> ) <sub>2</sub>	21	25	271.9	1.588	2873	327.2	298.2
		30	271.3	1.574	2776	325.3	297.1

## 6 THE WAYS TO SECURE NECESSARY COMBUSTION PROPERTIES OF SOLID COMPOSITE PROPELLANTS

A solid propellant can be used in practice only when a proper combustion law is secured, i.e., the combustion rate must equal a required value for a prescribed pressure within a chamber, the exponent  $\nu$  in the formula relating the combustion rate to pressure ( $W = AP^\nu$ ) must belong to a certain range (in the majority of cases,  $0.3 < \nu < 0.4$  is optimal).

The combustion mechanism of solid composite propellants cannot be satisfactorily formulated and described without a preliminary description of the combustion mechanism of oxidizers. The latter mechanism is primarily governed by exothermic decomposition and sublimation (evaporation) of the substance. This provides a controlling and stabilizing action on the formulation combustion as it enters the overall heat balance at the combustion surface. The combustion rate can be varied not only via oxidizer decomposition accelerated with a catalyst but also by reducing oxidizer volatility (e.g., due to introduction of alkaline metal salts).

The kinetics plays an important role in the combustion mechanism of solid composite propellant; important is the ratio of oxidizer decomposition rate to the rate of fuel oxidation at the initial stages of combustion. For a sufficiently stable oxidizer (e.g., AP), a nonvolatile fuel can get partially oxidized in condensed phase and thus contribute to the heat balance; this has a stabilizing effect on combustion and enhances the combustion rate, compared to pure oxidizer.

In the case of readily decomposing oxidizer (e.g., ADN) and a relatively thermally stable fuel, the conversion rates for both components can have such a ratio that, owing to heat consumption for heating and gasification, the fuel oxidation does not occur in the condensed phase and, as heat flux from the gaseous phase is insufficient, the combustion rate of the formulation becomes lower than that for a neat oxidizer.

The same mechanism accounts for the anomalous dependence of the combustion rate on the particles size for this type of oxidizer, the combustion rate grows with increasing oxidizer particles. Therefore, the use of sufficiently thermally stable components bearing highly reactive functional groups, the latter oxidizing fast and with high heat effect, provides efficient way to enhance the combustion rate.

At all stages of propellant combustion, the heat and mass transfer between the components affect both the combustion rate and its dependence on external conditions and intrinsic features of the formulation (particles size, reactivity). The interplay of these factors and reaction kinetics determines combustion proceeding in kinetic, diffusion-kinetic, heat exchange, or autonomous regime. The ways to control these regimes include variation of components dispersion and also higher homogeneity of propellant by combining in one phase or one component the features of both oxidizer and fuel (e.g., guanidinium nitrate or guanidinium nitramide) or oxidizer, fuel, and catalyst (e.g., ferricinium salts).

These ways also include surface covering of oxidizer particles with the films, which have a catalytic, inhibiting, or highly energetic effect. The combustion rate depends on chemical reactions of oxidation and decomposition proceeding in both condensed and gaseous phases. The nature of intermediate products of combustion (decomposition) is also important. For example, some chlorine oxides, which are the intermediates in combustion of AP, are active oxidizers, whereas the decomposition products of AN and certain organic oxidizers are much less chemically reactive.

The rate of condensed-phase reactions governs the combustion rate for formulations based on low-volatile compounds (primarily, inorganic ion salts: AP, ADN). This rate, in its turn, depends on the temperature of the surface, which is controlled by the ratio of evaporation and decomposition rates [8]. For the above mentioned compounds, this ratio is of such a value that  $\nu$  in  $W = AP^\nu$  is within 0.3 to 0.5.

For volatile organic compounds, the condensed phase evaporates completely at relatively low temperature, where thermal decomposition has not occurred yet and gas phase reaction at the maximum combustion temperature controls the process (combustion mechanism described by Belyaev-Zel'dovich theory). In this case, the combustion rate strongly depends on pressure ( $\nu \approx 1$ ). The case of not very stable and relatively volatile organic compounds like HMX, RDX, etc. is an intermediate one. Here, heat transfer from gaseous phase becomes noticeable. For such systems,  $\nu \approx 0.5-0.7$ . Therefore, for the formulations with high HMX

content, one must introduce some small concentrations of AP (5%–10%) in order to bring  $\nu$  down.

## 7 CONCLUDING REMARKS

The combustion products of the formulations containing beryllium and/or AP are most harmful for the environment.

The environmental impact of propellants based on AP can be substantially reduced through the use of the mixed oxidizer, equimolar mixture of AP with sodium nitrate. This, however, brings down the energy potential of the propellant.

The major pollutant in the combustion products of chlorine-free formulations is carbon monoxide and its formation is unavoidable. Nevertheless, fast dilution of gaseous products in atmosphere and partial oxidation with air rapidly bring CO concentration to admissible values.

The energy potential of propellant components can be materialized in optimal formulations, e.g., with a choice of a proper binder for a particular oxidizer, presence or absence of metal or hydride.

When developing new propellant formulations, from the very start, one should consider for what class of rockets this propellant is made for; the formulation should be optimized for particular case with the ballistic efficiency depending on both specific impulse and density.

Use of aluminum hydride provides the way to substantially enhance energy potential of propellants; it should be employed with ABs enriched in oxygen.

The development of new propellant formulations requires consideration, in addition to high energy potential of a formulation, of a number of other properties (appropriate combustion law, sufficient thermal stability, compatibility, low sensitivity to friction and shock, etc.).

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