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Energetic Characteristics of Solid Composite Propellants and Ways for Energy Increasing*)

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Abstract: Energetic characteristics of solid composite propellants of different type and application are described – metal-free compositions containing an oxidizer and a fuel-binder only; compositions containing additionally an energetic compound (Al, Be, Mg, B), metal hydrides (AlH_3, BeH_2, $B_xN_yH_z$). A considerable attention is attracted to analysis of oxidizers (ammonium perchlorate, hydroxylammonium perchlorate, ammonium dinitramide etc) because oxidizer occupies the greatest mass fraction in propellant and mostly that is the oxidizer that determines energetic characteristics of the propellant. The main principles of the using of different kinds of binder are considered. It was shown that the competence to choose the binder to the given oxidizer can increase considerably the energetic characteristics even without creation of new compounds. Ways to optimize solid composite propellants destined for missile complexes of different mass characteristics are described. Different ways to further development of solid composite propellants are presented – optimization of formulations basing on accessible components; creation of new more effective binders, having additional functions of oxidizer or gasifying component etc. Ecological problems of solid composite propellants are also a topic of the paper. Ways to decrease ecological danger while solid composite propellants using are investigated.

Keywords: solid composite propellants, specific impulse, density, ballistic effectiveness, oxidizers, binders, metal hydrides, gas generating compositions

Introduction

In the middle of the 20th century the energetic level of solid composite propellant (SCP) has been increasing considerably every decade up to 70-80

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years, but later it seemed that energy had already approached to the maximal possible value. The fact is that the growth of energy capacity of chemical material is connected with the degradation of many operating characteristics – thermal stability decreases, impact sensitivity and friction sensitivity increase, compatibility of compounds reduces, probability of combustion becoming a detonation decreases, the cost increases drastically etc. So, when we try to increase energetic characteristics we must be ready to a compromise – energy growth against definite degradation of other performances.

Rocket flight range and mass of the useful load depend mainly on specific impulse (Isp) value (though many other parameters are influenced too), and this dependence is very considerable. For example, when the specific Isp is increased from 255 to 260, (i.e. of about 2%), useful load is increased by 10% at the same flight range. Such result should be noted as significant achievement both for military and non-military rockets.

Specific impulse, together with the content of combustion products can be nowadays easily calculated with computers if the element content and enthalpy value of propellant, and the pressure in the combustion chamber and nozzle section are known. When we compare different types of propellant, we do not compare experimental parameters, but the theoretical (i.e. calculated) ones, because experimental determination is very expensive (the sample mass must be at least several kg) and even impossible when there is a lack of any compound. The calculation of Isp is a regular procedure using current computers and necessary software. It was shown that the difference between the calculated and real Isp values is 4-6% and this difference depends much more on the type of rocket engine than on the type of propellant.

Basic chemical content and basic components of SCP

The major chemical elements from which one can create a real SCP are H, O, F, C, N, and Cl. The most important for thrust creation give H, O and F atoms. The value of specific impulse increases as the enthalpy of the composition or pressure in the combustion chamber increases. The specific impulse usually also increases if the percentage of H, O or F grows. However in real SCP one cannot exclude C and N, because without them it's impossible to create molecules in solid state. It is very useful to take notice that a simple presence of high energetic components in composition does not guarantee a high value of Isp, the optimal ratio among components is always necessary.

Oxidizer is one of the most important components of SCP because it takes the greatest mass fraction in propellant and mostly that is the oxidizer that determines energetic characteristics of the propellant. Solid composite propellant contains always a fuel-binder (for achievement of necessary physico-mechanical characteristics). This binder often plays function of combustible – when the heat of its oxidation by the oxidizer brings the main input to the total combustion energy. The introduction of metal (Be, Al, B, sometimes Mg) into composition is one of ways to increase the Isp value because of high combustion heat of these metals. There is another kind of component, which can be named neither oxidizer nor fuel because these components play the both functions – actually they may be named "gas generating components". Cyclotetramethylene tetranitroamine (octogen or HMX) is the most well-known and most used substance of this type.

Requirements to solid composite propellants, a compromise among basic properties

While in liquid-propellant rocket engines all components are kept in tanks and are injected with pumps into the combustion chamber, solid-propellant rocket engines look simpler – the propellant fills up almost entirely the whole interior of the rocket body and burns from the surface. But this simplicity requires many specific properties for the propellant to be fulfilled. Since the propellant is subjected to much tension during acceleration – it has to be both strong and elastic, it has to burn uniformly with a given rate, the combustion rate has not to depend considerably on the pressure (in the formula $U=A\cdot P^{\nu}$, where U is combustion rate, P – pressure, the exponent $\boldsymbol{\nu}$ usually must be lower than 0.6), otherwise during the combustion a sharp increase in pressure is possible and consequently the destruction of the rocket body. It is necessary to prevent the possibility of combustion becoming a detonation. Other restrictions include: low hygroscopicity, enough thermal stability, rather low impact and friction sensitivity, not too high temperature in the combustion chamber (< 3800-3900 K) and a lot of other restrictions. All these restrictions hamper developers of new more powerful compositions. For example, a substitution of any hydrazonium salt (as oxidizer) for its ammonium analogue would definitely increase the Isp value, however it would significantly degrade thermal stability, impact sensitivity and compatibility of components. Introducing of the most effective elements (beryllium, active fluorine) into the propellant formulation damages the environment. Increasing of the enthalpy of formation increases the Isp ($\delta Isp/\delta\Delta H_f \approx 0.06$ s/(kcal/kg)), but herein the thermal stability usually decreases etc.

Density and ballistic effectiveness

The density is one of the important properties determining ballistic effectiveness of propellant. It happens often that density is in a compromise with specific impulse. As draft estimation one uses some special functions for comparing ballistic characteristics of propellants with different Isp and density values. One of these functions is a so-called ballistic effectiveness (Ef_n) of the propellant on the n^{th} stage of the multistage rocket complex. Ef_n can be written as $Ef_n = Isp \cdot d^a$, where *d* is the density, the value of the exponent "*a*" depends on the mass characteristics of the rocket complex and the definite stage number "n". Usually for three-staged rocket complexes the values *"a"* are the following: ~0.6 for the first stage, ~0.4 for the second, and ~0.2 for the third one. Thus, on the upper stages the density has less influence on the ballistic effectiveness. For example if we have five different compositions, where the first has Isp = 260 with d = 1.95; the second – Isp = 270 with d = 1.8; the third – Isp = 275 with d = 1.7; the forth – Isp=295 with d = 1.0, and the fifth Isp = 230 with d = 2.3, the best composition for the first stage is #1; for the second stage - #2; for the third stage -#3. Though the composition #4 is of the highest Isp value its low density makes it less effective than ## 1-3 on all stages. Thus, developing ballistic effectiveness of SCP, we have to find the best way of using the SCP under investigation, that is on what stage of the rocket complex this SPC can provide the maximal growth of rocket flight range or mass of the useful load.

The simplest SCP – binder+oxidizer

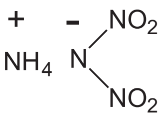
The set of oxidizers is not too large, we can divide them conditionally on three basic categories: a) oxidizers free of halogen; b) perchlorates; and c) oxidizers containing active fluorine.

Oxidizers of type "a" are ecological safe, of type "c" – are very dangerous ecologically, oxidizers of the type "b" occupy the intermediate position – they are wide used though their combustion product (hydrogen chlorine) damages environment.

a) SCP basing on halogen-free oxidizers

The cheapest oxidizer of this type is ammonium nitrate (AN). It has the best element content, however its too low enthalpy of formation (-1080 kcal/kg) makes it low effective as oxidizers for SCP. In Table 1 several oxidizers are represented to give an outline about Isp values and difference among Isp values of different compositions. All Isp values represented in this paper are calculated by assumption that the combustion chamber pressure is 40 atm and nozzle section pressure is 1 atm. Dimension of a Isp value is (kg-force)·(kg-mass)$^{-1}$·s (that is Isp is the resultant thrust by propellant burning with the rate 1 kg/s), or simply “s”. All compositions represented in this paper contain at least oxidizer and a binder with the optimal content of the binder, but in condition that binder percentage is not lower than 18-20 volume % (that is about 8-10 mass% for compositions with total density ~1.8 and binder density ~0.9) otherwise it’s impossible to produce a composite with satisfactory physico-mechanical properties. Actually in binary compositions (oxidizer+binder) a binder is necessary not only as a binder itself, but as a combustible too. In binary compositions simple hydrocarbon binders may be rather optimal.

Table 1. Energetic characteristics of SCP basing on the most important NOH-oxidizers

Oxidizer	ΔH_f, [kcal/kg]	d, [g/cm^3]	Additional info	Composition, mass [%%]	Isp, s	d, [g/cm^3]
NH_4NO_3	-1080	1.725	m.p. 160 °C, stable	12%CH* 12%PMVT** 10%CH +20%Al	211 220 246	1.57 1.60 1.70
$N_2H_5NO_3$	-661	1.685	m.p. 71 °C, hygro-scopic	11%CH 12%PMVT 17%Act *** 15%Act +20%Al 12%PMVT+20%Al 10%CH +20%Al	219 230 240.5 256.5 255.5 255	1.54 1.62 1.64 1.78 1.7 1.67
$NH_4N(NO_2)_2$  ADNA	-270	1.82	m.p. ~89 °C, enough stable	12%CH 12%PMVT 10%CH +20%Al 15%Act +20%Al 12%CH +13%Be 15%CH +13%Be 34%Act +13%Be 34%Act +14%Be	247 250 262 264 281 293 291 294.5	1.63 1.72 1.76 1.86 1.63 1.34 1.42 1.40
$N_2H_5N(NO_2)_2$	-52	1.80	m.p. 76-80 °C, hygro-scopic	12%CH 16%PMVT 19%Act 10% CH +20%Al	251 255 241.3 267	1.62 1.70 1.64 1.75
$C(NH_2)_3N(NO_2)_2$	-229	1.71	m.p. 135-139 °C, enough stable	10%CH 18%Act 17%Act +20%Al	208 233 255	1.58 1.67 1.80

*-CH – hydrocarbon binder (#1, Table 3); ** PMVT - polymethylvinyltetrazole (#2, Table 3); *** Act- active binder (#3, Table 3).

The most interesting among NHO-oxidizers is ammonium dinitramide (ADNA). It was first synthesized in the former USSR in 1972 (however first published in 1992 [1]). ADNA is enough stable and compatible with many compounds and nowadays it is used in real compositions. ADNA is almost the best oxidizer for SCP for upper stages while because of its rather low density it is not enough powerful for first stage SCP, where ammonium perchlorate (see below) is more appropriate.

b) SCP basing on perchlorates

Table 2. Energetic characteristics of SCP basing on some perchlorates

Oxidizer	ΔH_f, [kcal/kg]	d, [g/cm^3]	Additional info	Formulation, mass [%%]	Isp, s	d, [g/cm^3]
NH_4ClO_4	-597.5	1.95	stable	10%CH* 20%Act*** 18%PMVT** 9%CH+20%Al	240 204 238 250	1.75 1.83 1.78 1.86
NH_3OHClO_4	-494	2.07	m.p. 89 °C, hygroscopic	13%CH 20%Act 21%PMVT 9%CH+20%Al	250 204 247 253.5	1.77 1.92 1.82 1.94
$N_2H_5ClO_4$	-320	1.94	m.p. 137 °C, hygroscopic, high impact sensitivity .	9%CH 10%CH 26%Act 9%CH+20%Al	251 246.5 240 259	1.76 1.74 1.70 1.86
$N_2H_6(ClO_4)_2$	-297	2.21	hygroscopic, high impact sensitivity	12%CH 9%CH+20%Al	251 254	1.88 2.02
$C(NH_2)_3ClO_4$	-465	1.75	m.p. 240 °C, stable, hygroscopic	18%Act 15%Act+20%Al	226 246.4	1.70 1.82
$C(NHNH_2)_3ClO_4$	-116.5	1.56	high imp. sensit., m.p. 132 °C.	18%Act 15%Act+20%Al	233.5 255	1.54 1.69
NO_2ClO_4	65	2.22	extremally reactive	20%CH 14%CH+20%Al	261 258	1.72 1.91

*-CH – hydrocarbon binder (#1, Table 3); ** PMVT - polymethylvinyltetrazole (#2, Table 3); *** Act- active binder (#3, Table 3).

Among all perchlorates (Table 2) only ammonium perchlorate (AP) is really used (we consider only oxidizers free of metal, because mostly metal salts are considerably less effective). Nitronium perchlorate (NP) is the best energetic oxidizer, but it is so much chemical active, that it can not be used in mixture with any other compound. Hydroxylammonium perchlorate (HAP), hydrazine monoperchlorate (HMP), and hydrazine diperchlorate (HDP) are much more effective than AP, especially for lower stages (because of high density). However these high-density oxidizers have some serious drawbacks – they are less thermostable than AP, less compatible with other compounds, and, finally, they are too hygroscopic. In IPCP RAS methods of thermal stabilization of HAP, HMP, HDP have been found [2], methods of stabilizing mixtures of HAP with some compounds have been developed [3], but the hygroscopicy cannot be decreased yet.

c) Oxidizers containing active fluorine

The fluorine is a more active oxidizer than oxygen is, i.e., the heat of H_2O formation is much lower than the heat of HF formation. There are some inorganic oxidizers with active fluorine (e.g. $FClO_4$, some complex salts $(NF_4)_aMeF_x$) but their physical and chemical properties do not allow us to use them in SCP. The only real way to introduce active fluorine into molecule is using of >N-F or $-NF_2$ groups because if fluorine is introduced with a component containing C-F bond no power increase is gained because of high energy of the C-F bond. Nowadays many NF_2-derivatives of organic substances are known, some of them are used in energetic compositions. If such compounds are used as oxidizer it's possible to create SCP with Isp 280 and even higher. However these substances have some serious drawbacks – they are not ecologically soft, and their impact and friction sensitivity are rather high.

SCP, containing metals

Only four metals (Be, Al, B and Mg) can increase the Isp of the pair binder+oxidizer. The effectiveness of metal is due to the great heat of their oxidation into oxides. In case of other metals the heat of their combustion does not compensate the loss of gas fraction in combustion products. The effectiveness of metal introduction falls with the range Be→Al→B→Mg, and it depends much on the oxidizer enthalpy. In Figure1 the dependence of the Isp growth (dIsp) while metal introduction on oxidizer enthalpy is demonstrated. dIsp = Isp_{Me} - Isp_0, where Isp_{Me} is the Isp value of the optimal composition metal+oxidizer+hydrocarbon binder; Isp_0 is the Isp value of the optimal binary formulation oxidizer+hydrocarbon binder. Circlets on the figure represent very different oxidizers, with different oxygen balance, organic and inorganic, real and designed. That's why all circlets for each metal do not represent an absolute straight lines. However, the tendency is evident – effectiveness of metal introduction falls with the growth of the oxidizer enthalpy. Magnesium introduction may be useful only if ΔH_f of the oxidizer is rather low (see Figure 1), while the introduction of beryllium is useful until ΔH_f of oxidizer is about +600-800 kcal/kg. However Be-containing SCP are extraordinarily toxic because of BeO toxicity, that's why their development ended about 30 years ago. Regardless the introduction of other metals always decreases the Isp values, some metals with high density (Zr, Ti) can be useful in definite cases – when the propellant density is of higher importance (see above), that is when the exponent *a* in the formula $Ef_n = Isp \cdot d^a$ is 0.7-0.8 and higher.

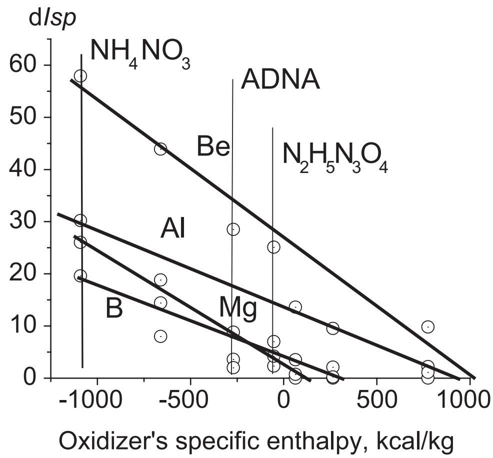


Figure 1. The dependence of the dIsp on value of CNHO-oxidizer enthalpy [4].

Optimal binders

We found that though binder does not occupy a big fraction in the composition (usually 9-12 mass % if binder density is 0.9-1.0 and about 20-25 mass % if the density is high, up to 1.5-1.55) the choice of binder type is very important for the maximal energy achievement. Element content of the binder has to compensate excess or lack of oxygen in the leftover formulation (the summary of compounds except binder). Thus, if binary formulation contains a binder and an oxidizer with a high oxygen balance α ($\alpha = O/(2C+0.5H)$), e.g. ADNA or HAP, the best binder is usually a simple hydrocarbon binder, because it contains a lot of hydrogen. As soon we begin to add so called gasifying component, e.g.

HMX, the *α* value of the mixture oxidizer + HMX begins to decrease and the hydrocarbon binder can not any longer secure maximal energetic potential, that is kept in these compounds – we have to use more “active” binders with higher *α* values. Because of the same reason active binders are necessary if the formulation contains metal hydrides (see below). Thus, when we study a new compound (mainly oxidizer, gasifying or energetic compound) we have to test formulations with different kinds of binder. For example, in our investigations we use a listing like that represented in Table 3. Binder #2 is a representative of high-enthalpy binders, binder #4 is a representative of binders with a middle *α* value, but higher enthalpy and hydrogen content than #3. In some cases such binders as #4 may become the optimal binders among all other types.

Gasifying compounds

Actually we may consider a gasifying compound as a part of a binary oxidizer. The best of gasifying compounds is widely used well-known HMX. Though gasifying compound is not usually a good oxidizer itself, its mixture with the main oxidizer can be more effective than if the main oxidizer is used alone. For example in the system 15.5 mass % (20 volume %) active binder + 20 mass % Al +AP + HMX the maximum value of Isp is 260.5 at 57% HMX, while in the system 10 mass % (20 volume %) hydrocarbon binder + 20% Al +AP + HMX the maximum value of Isp is 254 at 25% HMX.

Table 3. Energetic properties of some binders

#	Name, formula	ΔH_f, [kcal/kg]	d, [g/cm^3]	α
1	Hydrocarbon, $C_{73,17}H_{120,9}$	-94	0.91	0
2	Polymethylvinyltetrazole, $C_{37,34}H_{56,007}N_{32,69}O_{2,32}$	+300	1.28	~0
3	“Active”, containing 20% polyvinylmethyltetrazole, nitroglycerine with some additives. $C_{18,96}H_{34,64}N_{19,16}O_{29,32}$	-181	1.49	0.53
4	Polyvinylmethoxydiazen-N-oxid, $C_3H_6N_2O_2$	-14	1.31	0.22

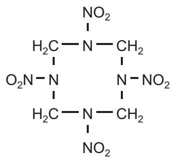
SCP with metal hydrides

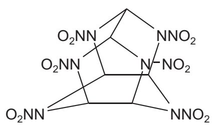
Introduction of metal hydrides (BeH_2, AlH_3) in SCP offers great opportunity to increase Isp values. In Table 3 it’s evident that Isp values can be increased on 10-15 s using the same oxidizer, because hydrides serve not only as metal fuel, but as a rich source of hydrogen too. However new SCP with hydrides required new binders – so called “active binders” (see above). If in propellants oxidizer+binder and oxidizer+binder+metal a binder was necessary not only as properly binder, but as a fuel (in system oxidizer+binder) and a gas source (both quoted systems) too, in the presence of hydride SCP has already a powerful heat source as well as a gas source. So, binder is not energetically necessary any more. However so long as a polymer binder is still necessary, it has to possess new function, namely to serve as oxidizer too. So, new “active” binders, containing NO_2, ONO_2, NNO_2 groups etc have been created. Simultaneously active binders may serve as energetic component if they contain high energetic functional fragments, e.g. N-heterocycles. The creation of new SCP with metal hydrides was a great step in development of high energy SCP. Isp value of the composition containing 25% AlH_3, 25% active binder and ADNA is 276-277 (d = 1.64), of the composition containing 14% BeH_2, 34% active binder and ADNA is 293.5 ($d \approx 1.40$). However AlH_3 and especially BeH_2 have low density (1.48 and ~0.7 g/cm^3 respectively), therefore the SCP density is lower than in similar SPC with free metals. Thus, SCP with BeH_2 is energetically useful only for upper stages (really for the third stage only) when the exponent “*a”* in the formula $Ef_n = Isp \cdot d^a$ is 0.2 and lower; with AlH_3 – if the exponent *“a”* is ~0.4 and lower, i.e. for the second and third stages. Moreover, BeH_2 has the same obstacle than free Be has, this is an extraordinary high toxicity of the combustion product (BeO).

SCP basing on high-enthalpy oxidizers

This kind of SCP is not used yet because though many organic oxidizers with ΔH_f +500 kcal/kg and even higher are known, their application in SCP is limited by many factors (high impact and friction sensitivity, sometimes low thermal stability, high price, etc). The first relatively high-enthalpy component that has been widely investigated during last 15 years or so is hexanitrohexaazaisowurtzitane (CL-20, ΔH_f=+185 kcal/kg, d = 2.044 [5]). Propellants containing aluminum, active binder, CL-20, and AP are a bit more effective on the lowest stage (Isp~258 at Pc:Pa = 40:1, d =~2.00; combustion temperature 3970 K; temperature of products leaving nozzle section 2770 K) than the similar propellant containing HMX instead of CL-20. Actually this higher effectiveness is the result of higher density of CL-20 against HMX.

There are many organic substances (containing mainly high-enthalpy N-heterocyclic frame with fragments-oxidizers, such as NO_2, NNO_2, $C(NO_2)_3$, etc) that can be used as high-enthalpy oxidizers ($\Delta H_f > 500$ kcal/kg), e.g. ditrinitromethylfuroxane (DTNMF, $\Delta H_f = +570$ kcal/kg); 1,2,5-oxodiazolo-[3,4-*e*]-[1,2,3,4]-tetrazine 4,6-dioxide (ODATDO, $\Delta H_f = +730$ kcal/kg); 5-(3-nitro-furoxan-4-yl)-1H-[1,2,3]triazolo[4,5-c]-furoxan inner salt (NFTAF, $\Delta H_f = +760$ kcal/kg) [6, 7]. Using such oxidizers with appropriate binders it's possible to accomplish Isp values up to 268-270s.


HMX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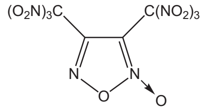
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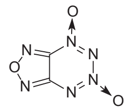
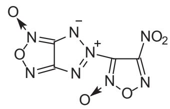

ODATDO


NFTAF

Anyway propellants with such new oxidizers as DTNMF, NFTAF or ODATDO will cost much more than propellants basing on accessible PA and HMX. Moreover, as it was already remarked, further increasing of energy power of solid composite propellants is connected with an appreciable aggravation of other properties (impact and friction sensitivity, thermal stability etc).

Anyway such high-enthalpy oxidizers are still rather promising, moreover they do not need metals (see above) and therefore they have no loss of Isp because of biphasic combustion products. This loss is the difference between real Isp value and the calculated one. The reason of so-called "biphasic loss" is the following: when in combustion products there is a solid phase some extra heat is carried away from the nozzle section with these solid particles – they are a bit superheated in comparison with the gas phase because the thermal equilibrium between solid and gas phase can not be established during so small time when combustion products expand trough nozzle. Thermodynamic calculation of Isp does not include this kind of thrust loss, therefore if calculated Isp values of two different formulations are equal, but the first formulation contains metal while the second does not, it means that other characteristics being equal the second formulation procures higher real thrust. Actually biphasic loss depends on solid particles dimension and of the rocket engine type and may average 5% or so.

Ways for Further Solid Composite Propellants Development

Recently the geopolitical situation changed considerably because of the cold war end. Therefore the creation of cost-to-cost ballistic missiles and their propellants have not such a great importance while the portion of SCP civil applications grows constantly in importance.

- If we estimate briefly the attained energy level of SCP that are being actually produced it is evident that the most powerful are the following ones:
- propellants based on aluminum, HMX (~55%) and active binder - Isp~260 at Pc:Pa = 40:1, d = 1.91; combustion temperature (Tc) = 3780 K; temperature of products leaving nozzle section (Ta) = 2550 K – this kind of propellant is the most effective on lower stages because of high density;
- propellants based on aluminum hydride, ADNA and active binder (Isp~276 at Pc:Pa = 40:1, d = 1.64; Tc = 3550 K; Ta = 2330 K), this kind of propellant is the most effective on upper stages;
- propellants basing on CL-20 (see above) that are developed recently are more effective on the lowest stage only because of its higher density, on upper stages HMX is more effective.

SCP basing on new high-enthalpy oxidizers (see above) have rather higher Isp values, but this kind of propellants is not developed yet, and in any case they will cost much higher than propellants with PA, HMX, ADNA. Moreover, further increasing of SCP power is attended with an appreciable aggravation of other properties. For example, application of high-enthalpy CHNO-substances (> +500 kcal/kg) would decrease the stability; would degrade impact and friction sensibility, would increase values of exponent ν in combustion law $U = A \cdot P^{\nu}$. Anyway maybe SCP of this type (with high-enthalpy CHNO-substances) can be used too, but this perspective is too far.

In the case of civil applications one puts a considerable accent on ecological problems. The HCl effusion ruins greenery and atmospheric ozone coat. The solution of these problems may be carried by different ways, using chlorine free inorganic (e.g. ADNA, Table 4, #4) or organic oxidizers, e.g. HMX (#3), RDX (hexogen), as well as using propellants containing potassium or sodium salts (e.g. sodium nitrate or hyponitrate) together with AP (Table 4, #15, 16) when equivalent amount of alkaline metal is a bit higher than one of chlorine, thus almost all chlorine undergoes into the most thermodynamically stable alkaline metal chloride [8].

Table 4. Energetic characteristics and concentration of toxic gases and condensed phase in combustion products

#	Propellant	Isp	d [g/cm^3]	Tc, [K]	Ta, [K]	HCl+ Cl_2, [mol/kg]	CO [mol/kg]	Cond. phase, [mass.%]
1	PA+CH*+Al	251	1.84	3610	2520	6	7	38
2	AP+CH	240	1.76	3000	1900	7.8	0.8	0
3	HMX+ Act**+Al	257	1.95	3700	2550	-	12	38
4	ADNA+ CH+Al	262	1.76	3580	2330	-	7	38
5	ADNA+ CH	249	1.64	2970	1580	-	3.6	0
6	$N_2H_5NO_3$+ CH+Al	254	1.6	2910	1770	-	7.7	38
7	$N_2H_5NO_3$+ CH	215	1.53	1950	930	-	3	0
8	NH_4NO_3+ CH+Al	244	1.68	2880	1800	-	7.3	38
9	NH_4NO_3+ CH	205	1.56	1870	920	-	2	0
10	$N_2H_5C(NO_2)_3$+CH+Al	265	1.81	3580	2360	-	11	38
12	$N_2H_5C(NO_2)_3$+ CH	254	1.7	3070	1600	-	8	0
13	$NaClO_4$+ CH +Al	225	2.05	3650	2610	1.1	10	66
14	$NaClO_4$+ CH	211	2.0	3080	2030	0.25	2	44
15	AP+$NaNO_3$+ CH +Al	230	1.96	3665	2650	0.9	4.7	37.7
16	AP:$Na_2N_2O_3$+CH+Al	237	1.94	3675	2600	0.98	5.3	37.7

* CH – hydrocarbon binder, ** Act – active binder

Some new civil applications of solid composite compositions

Multiyear experience of chemists in the area of military propellants creation and production may help to resolve currently some tasks of exceptionally civil application of energetic materials, i.e. in development of gas-generating compositions for airbag inflators. In this task the thrust value is no longer necessary, but quite other attributes become crucial. Moreover, very high energy makes even cardinally worse the characteristics of the top-priority. New propellants must be free of drawbacks of currently used propellants. The main drawbacks are toxic ingredients, presence of toxic gases (CO, NO_x) and solid phase in combustion products, too high combustion temperature, insufficient stability. On the other hand propellants for airbag inflators require much higher thermal stability level than propellants for solid rocket engines do. Main requirements for compositions for airbags and the characteristics that SCP can provide differ much (Table 5). Thus, to improve characteristics of propellants for their application in airbags, we have to decrease their power, that is to decease considerably combustion temperature of stoichiometric formulation (#1, Table 5), and on the other hand we have to increase the stability and combustion rate.

It was shown that it is possible to decrease combustion temperature of stoichiometric formulations (this is $C_aH_bN_xO_{2a+0.5b}$, otherwise combustion products contain either CO or NO_x) by introducing low-enthalpy oxygen-containing groups (-OH, -O-, -COOH, >CO, -COO-, -OCO-COO- etc) into oxidizer containing regular groups-oxidizers ($-NO_2$, $-ONO_2$, $-NNO_2$). Later groups provide high oxygen amount in the formulation while the first ones provide considerable enthalpy decreasing, and consequently – Tc decreasing at minimal oxygen amount decreasing [9].

Table 5. Requirements to propellants for airbags and characteristics that can be reached with accessible SCP.

#	Characteristics	Requirement to propellants for airbags	Characteristics that can be reached with accessible SCP
1	Element ratio	2C+0.5H~ =O (atoms ratio)	No requirements
2	Condensed phase in combustion products	Absence of solid, at least very low amount	Usually 37 mass % of Al_2O_3 if the formulation contains 20% Al. If there is no metal in the formulation – no condensed phase
3	Combustion temperature	~ 2000-2400 K	>2900 K
4	Combustion rate	25-30 mm/s at 200 atm	~10-20 mm/s at 200 atm
5	Exponent *v* in combustion law ($U=A\cdot P^v$)	~0.5-0.6	0.3-0.5
6	Thermal stability	~2 weeks at 110 °C	One week at ~60-70 °C
7	Toxic products and hydrogen content combustion products	No toxics, no HCl, no Cl_2. Low H_2 content, very low CO and NO_x content.	[CO] = 3 mol/kg (even if Tc~1900 K) and higher. [H_2] = 0.5-15 mol/kg. Many HCl if the formulation contains AP.
8	Minimal melt. point of ingredients	110 °C	80 °C
9	Sensitivity to impact and friction	Low	Rather low
10	Requirement to dioxines amount	No data	Accordingly international ecological requirements < 10^{-10} g/m^3

High energetic compositions may be used more widely as gas generating compositions for different goals. Of the most importance are generators producing gases (air, oxygen, nitrogen and other gases) of desired produced gases ratio with a necessary combustion rate.

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