POSSIBLE WAYS TO DEVELOP SOLID PROPELLANTS FOR ECOLOGICAL SAFETY

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ABSTRACT　The large quantity of pollutants, including primerily hydrogen chloride and other propellant combustion products like dioxine and some carcinogens from rocket exhaust, are a serious threat to the atmosphere in which the humankind live. In this paper some ways to develop chlorine- and fluorine-free solid propellants and the new type of oxidizers with superior properties are discussed. From the viewpoint of putting the energy, chemical stability and combustion regularity in the important place, the author proposes that ammonium nitrate, hydrazine nitrate, ammonium dinitramide and hydrazine nitroform would be suitable oxidizers to substitute ammonium perchlorate and HMX in solid propellants. The thermodynamic calculation for some model formulations were made and compared with those of some conventional propellants. The results obtained therefrom may be taken as a basis to develop the ecologically safe propellant.

KEYWORDS　rocket exhaust, pollutant, chlorine-free propellant, thermodynamic calculation.

1　INTRODUCTION

It is well-known that the combustion products of conventional solid rocket propellants comprise a great quantity of pollutants, primarily hydrogen chloride and other chlorine-containing compounds, carbon monoxide, etc.. Some propellants, furthermore, yield highly toxic beryllium and fluorine compounds. The concentration of the pollutants at the nozzle can be evaluated by thermodynamic calculation on the basis of the chemical composition of the propellant and stationary work conditions of the engine. The pollutant exhaust at the nozzle is scarcely investigated. It can be assumed, however, the incompletely oxidized dioxines and other carcinogens are likely formed at the stage of engine ignition and extinguishment. The main source of the pollutants in the

combustion products is the ammonium perchlorate (NH_4ClO_4), which is the main oxidizer in conventional solid propellants.

A substantial decrease in environmental damage from solid rocket propellants could be achieved if the formulations do not contain chlorine, fluorine or beryllium. A further improvement of environmental safety is possible if all metals (e. g. aluminum) are eliminated from propellants.

Resent years, two types of propellants free of chlorine and fluorine are widely used and studied, e. g. the propellants based on nitrocellulose (double-base propellant) and octogen, and their advantages and disadvantages are well known.

There exist other directions to develop fluorine- and chlorine-free propellants by exploring new type of oxidizers with superior properties.

The major problems which should be solved for this purpose are the energy of the propellant, chemical stability and regularity of its combustion. The cost, technology, composition of particular formulations, mechanical characteristics etc. are also important. However, without solving the first three problems, the attempt to solve the further problems are useless. On this work we consider the following components such as NH_4NO_3, hydrazine nitrate ($N_2H_5NO_3$), ammonium dinitramide [$NH_4N(NO_2)_2$, ADN], and hydrazine nitroform [$N_2H_5C(NO_2)_3$] to be suitable to substitute NH_4ClO_4 and HMX. The data of boranehydrazine ($BH_3N_2H_4$) and $NaClO_4$ are also listed in Table 1. Since the combustion product of $NaClO_4$ is non-toxic NaCl, it is an ecologically safe oxidizer. The high-energy chlorine-free compound like hydrazine azide ($N_2H_5N_3$), hydroxyammonium nitrate (NH_4ONO_3) and hexanitroethane [$C_2(NO_2)_6$] are not suitable for solid propellants because of their thermal instability (Table 2).

Table 1　Heat of formation (ΔH) measured for some compounds

Compound	ΔH/(kJ/mol)	density ρ/(g/cm³)
NH_4ClO_4	−2499.5	1.95
HMX	322.4	1.92
$NH_4N(NO_2)_2$	−1130.4	1.82
$N_2H_5NO_3$	−2767.5	1.68
NH_4NO_3	−4567.8	1.73
$N_2H_5C(NO_2)_3$	−410.3	1.90
$NaClO_4$	−3098.2	2.53
$B_2H_6N_2H_4$	−1409.2	0.94
$BH_3N_2H_4$	−975.5	0.95

Table 2　Thermal stability of three compounds

Compound	$k = f(T)$/ (s⁻¹)	$\tau_{0.1\%}$
$N_2H_5N_3$	$10^{8.0}\exp(-24000/RT)$	2 years
$C_2(NO_2)_6$	$10^{16.5}\exp(-35800/RT)$	6.85 months
NH_4ONO_3	$10^{4.6}\exp(-16500/RT)$	1 day

Here k is the rate constant of decomposition according to initial rate, $\tau_{0.1\%}$ is the time of 0.1% decomposition at 20℃ (impurities disregarded).

2 THERMODYNAMIC CALCULATION OF SEVERAL FORMULATIONS

For comparative thermodynamic calculations we use a model hydrocarbon matrix (HM) with composition $CH_{1.65}$ having $\Delta H = -376.8$ kJ/kg and $\rho = 0.92 g/cm^3$, and high-energy matrix (AM) (nitrocellulose + nitroglycerine) with composition $C_{20.833}H_{27.87}O_{36.792}N_{9.495}$, $\Delta H = -2616.75$ kJ/kg and $\rho = 1.62$ g/cm³.

These are not the best matrices but they, nevertheless, can be used to comparatively analyze the different oxidizers. The model fuel formulations had the following thermodynamic characteristics calculated for pressure of 4.0 MPa in combustion chamber and 0.1 MPa at the nozzle.

The results of thermodynamic calculations presented in Table 3 show that energy of the formulations based on $NH_4N(NO_2)_2$ and $N_2H_5C(NO_2)_3$ are higher not only than NH_4ClO_4-based propellants but those based on HMX, and the temperatures in combustion chamber and at the nozzle are lower than those of conventional propellants. The energy of $N_2H_5NO_3$ is intermediate between those of NH_4ClO_4 and HMX. The formulations based on NH_4NO_3 and $NaClO_4$ have expectedly low energy. However in some cases low cost and availability of these components, accompanied with certain other advantages may make them reasonable to be used.

The unicomponent propellants $BH_3N_2H_4$ and $BH_3N_2H_4BH_3$ are exceptional. The reaction of chemical combustion proceed predominantly according to the scheme $B_2H_6N_2H_4 \longrightarrow 2BN + 5H_2$. This results in high energy release at very low temperatures in the chamber and at the nozzle. The disadvantages of these propellants are low density and lack of binder. They can be used in the form of hard pressed blocks, especially, in the case where energy release is of primary importance, e.g. in a spacecraft.

The composition of combustion products substantially differs from that of NH_4ClO_4-based propellants. Table 4 presents the calculated concentrations of main components of combustion products at the nozzle.

Obviously the use of chlorine-free oxidizers results in chlorine- and hydrogen-chloride-free combustion products. This also excludes possible formation of chlorinated dioxines. The substitution of NH_4ClO_4 by $NaClO_4$ results in a substantial decrease of chlorine and HCl in the combustion products.

The noteworthiness is the substantial decrease in the concentration of nitrogen oxides in combustion products. High concentrations of hydrogen and carbon monoxide do not comprise an environmental threat, since combustion products can mix with air and burn out. But the author has not known any quantitative data on what fraction of carbon monoxide and hydrogen survive in the rocket exhaust and how atmospheric pressure and particular design of the rocket engine affect the process.

Table 3　Results of thermodynamic calculation for several formulations

Oxidizer	Formulation matrix wt%	Fuel wt%	Specific momentum $I/(s)$	Density $\rho/(g/cm^3)$	Temperature in chamber $T_{ch}/(K)$	Temperature at the nozzle $T_{out}/(K)$
NH_4ClO_4	HM-10%	Al-20%	250.8	1.84	3616	2520
NH_4ClO_4	HM-10%	—	240.3	1.76	2998	1902
HMX	AM-22%	Al-20%	257.4	1.95	3702	2548
$NH_4N(NO_2)_2$	HM-10%	Al-20%	262.0	1.76	3583	2331
$NH_4N(NO_2)_2$	HM-11%	—	249.0	1.64	2967	1580
$N_2H_5NO_3$	HM-11%	Al-20%	254.0	1.65	2913	1766
$N_2H_5NO_3$	HM-12%	—	215.6	1.53	1955	932
NH_4NO_3	HM-11%	Al-20%	244.6	1.68	2884	1799
NH_4NO_3	HM-12%	—	204.6	1.56	1876	921
$N_2H_5C(NO_2)_3$	HM-10%	Al-20%	265.0	1.81	3578	2360
$N_2H_5C(NO_2)_3$	HM-11%	—	253.6	1.70	3073	1604
$NaClO_4$	HM-15%	Al-20%	224.9	2.05	3650	2608
$NaClO_4$	HM-15%	—	211.2	2.00	3080	2034
		$BH_3N_2H_4$	249.6	0.95	1562	758
		$B_2H_6N_2H_4$	278.0	0.94	2114	1176

Table 4　Combustion products of different formulations

Oxidizer	Formulation matrix wt%	Fuel wt%	Combustion products/(mol/kg)										
			Al_2O_3	Cl_2	HCl	CO	CO_2	N_2	NO	H_2	H_2O	BN	NaCl
NH_4ClO_4	HM-10%	Al-20	3.70	0.2	5.73	6.69	0.54	2.98	2×10^{-3}	9.78	4.98	—	—
NH_4ClO_4	HM-10%	—	—	0.6	7.62	0.77	6.46	3.83	8×10^{-1}	0.48	17.0	—	—
HMX	AM-22%	Al-20	3.70	—	—	12.4	0.04	8.87	2×10^{-1}	10.4	0.22	—	—
$NH_4N(NO_2)_2$	HM-10%	Al-20	3.70	—	—	6.88	0.36	1.3	6×10^{-1}	13.2	3.92	—	—
$NH_4N(NO_2)_2$	HM-11%	—	—	—	—	3.55	4.40	14.3	2×10^{-6}	4.5	16.4	—	—
$N_2H_5NO_3$	HM-11%	Al-20	3.70	—	—	7.71	0.24	10.9	8×10^{-7}	22.2	2.53	—	—
$N_2H_5NO_3$	HM-12%	—	—	—	—	3.21	5.37	13.9	—	16.2	13.9	—	—
NH_4NO_3	HM-11%	Al-20	3.70	—	—	7.28	0.67	8.62	3×10^{-4}	17.6	6.2	—	—
NH_4NO_3	HM-12%	—	—	—	—	2.03	6.61	11.0	—	11.3	17.8	—	—
$N_2H_5C(NO_2)_3$	HM-10%	Al-20	3.70	—	—	11.0	0.1	9.56	1×10^{-4}	14.6	0.73	—	—
$N_2H_5C(NO_2)_3$	HM-10%	—	—	—	—	8.2	4.61	12.2	1×10^{-6}	6.91	11.8	—	—
$NaClO_4$	HM-15%	Al-20	3.65	5×10^{-2}	1.07	—	—	—	—	7.1	0.45	—	4.15
$NaClO_4$	HM-15%	—	—	3×10^{-3}	0.25	—	—	—	—	0.46	5.33	—	6.55
—	—	$BH_3N_2H_4$	—	—	—	—	—	10.8	—	76.1	—	33.5	—
—	—	$B_2H_4N_2H_4$	—	—	—	—	—	—	—	87.7	—	21.8	—

3 STABILITY OF PROPELLANTS

Generally speaking，when the formulation is correctly composed and the components do not mutually react，the stability of the fuel is controlled by the stability of the major component，the oxidizer. This is confirmed by numerous studies on kinetics performed in Chernogolovka Institute of Chemical Physics (CICP) and in a number of laboratories in the world. The rate of thermal decomposition of the propellant usually equals the decomposition rate of the least stable component. The heat effect of decomposition may enhance due to secondary reactions of the active species in decomposition products and other constituents in a propellant.

The kinetic studies in CICP showed that the ammonium and hydrazonium cations in ionic salts are quite stable but less stable than the analogous salts of alkali metals. The mechanism of thermal decomposition of the ammonium and hydrazonium salts is much similar to each other and can be elucidated with the simplest representative of the class，ammonium nitrate.

A common feature of ammonium and hydrazonium salts is their fast proton transfer according to the scheme.

$$BH^+ A^- (s) \xrightarrow{k_{ps}} B(s) + HA(s) \tag{1}$$

Where B is ammonia or hydrazine，HA is acid (nitric，perchloric，etc.)，BH^+ is ammonium or hydrazonium cation，A^- is anion of the respective acid，and k_{ps} is the equilibrium constant in solid phase.

Since both acids and bases here are relatively strong，the equilibrium in reaction (1) is mainly shifted to the left and equilibrium concentration of B and HA are low. The equilibrium vapor concentration of acid and base over the surface of solid (liquid) salt corresponds to the equilibrium concentration B(s) and HA(s).
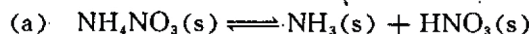
$$p_B = k_{gB}B(s) \qquad p_{HA} = k_{gHA}HA(s) \tag{2}$$

The presence of the vapor and，hence，vaporization (sublimation) of the salts，plays an important rolé in the combustion.
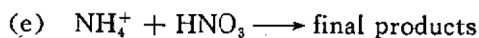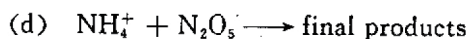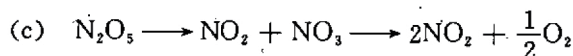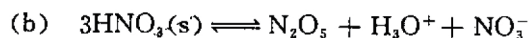
Hydrazine and respective acids are unstable compounds to decompose. In the simplest case the rate of decomposition is determined by the concentration of reactants

$$W = k_1 C_{B(s)}^n + k_2 C_{HA(s)}^m$$

Where k_1 and k_2 are the rate constants of decomposition of B(s) and HA(s) respectively，n and m are the reaction orders. Additional reactions can also occur，namely，interaction of the primary products of decomposition with the fresh ions of acid and base formed according to reaction (1)，and reactions between the primary products.

For example，in decomposition of ammonium nitrate，the following principal reactions must occur：

(a) $NH_4NO_3(s) \rightleftharpoons NH_3(s) + HNO_3(s)$

(b)　$3HNO_3(s) \Longleftrightarrow N_2O_5 + H_3O^+ + NO_3^-$

(c)　$\dot{N}_2O_5 \longrightarrow NO_2 + NO_3 \longrightarrow 2NO_2 + \dfrac{1}{2}O_2$

(d)　$NH_4^+ + N_2O_5 \longrightarrow$ final products

(e)　$NH_4^+ + HNO_3 \longrightarrow$ final products

The reactions (a) and (b) are fast and the rate of decomposition W can be expressed as follows:

$$W = k_1 C_{N_2O_5} + k_2 C_{NH_4} + C_{N_2O_5} + k_3 C_{NH_4} + C_{HNO_3}$$

At temperature $T > 220\,℃$, the third reaction will prevail; at lower temperatures, the second and the first in less extent.

Thus, the stability of ammonium and hydrazine salts is governed primarily by the acid-base equilibrium (1), i. e. the stability of the acid and base formed therefrom, and also by the presence of additional reaction paths, like in ammonium nitrate.

The common feature of all the ammonium and hydrazonium salts considered is their high sensitivity to the acidity of the salt (stoichiometry), high susceptibility to admixtures capable of shifting the acid-base equilibrium (in particular water content). Since the reaction is a complex one, its temperature dependence is determined by the combination of the equilibrium and rate constants. All these constants have different activation energies or (equilibrium constants) heats of reaction. In effect, the limiting reaction can change in different temperature range, and the apparent activation energy experiences corresponding changes. Therefore, the estimation of low-temperature stability requires a special analysis.

The stability of $NaClO_4$ is determined by the stability of ClO_4^- anion. Decomposition of boranehydrazine, hexanitroethane and HMX proceed via different mechanisms. The time of 0.1% decomposition at $20\,℃$ and parameters of apparent rate constants are summarized in Table 5.

Table 5　Thermal decomposition parameters of components at 20 ℃

Compound	$\lg A/(s^{-1})$	$E(kJ/mol)$	$\tau_{0.1\%}/(a)$
NH_4ClO_4	8.0	125604	7×10^3
β-HMX	11.2	158679.7	3.8×10^7
$NH_4N(NO_2)_2$	13.7	151562.2	6.65×10^2
$N_2H_5NO_3$	12.2	159098.4	4×10^5
NH_4NO_3	14.4	197617.0	1.5×10^{10}
$N_2H_5C(NO_2)_3$	18.0	180032.4	3.8×10^3
$NaClO_4$	13.0	251208.0	10^{21}
$BH_3N_2H_4$	11.6	127697.4	15
$B_2H_6N_2H_4$		10048.3	2

The data are given without account of possible effect of admixtures on the initial de-

composition rate. In certain case, a given rate constant is the estimation of stability obtained from measuring the molten salts because the little decomposition rate in solid state can not be directly measured. It should be kept in mind that the transition from liquid to solid may decrease the rate constant by the factor of $10 \sim 10^4$ due to the stabilization effect of the crystalline lattice. With respect of this point, the data in Table 5 are rather approximate estimation.

From the viewpoint of stability, all the compounds presented in Table 5 can be used in solid propellants. To make a desired formulation, it is required for more studies to search for components that will not deteriorate the stability of these oxidizers.

4 COMBUSTION

Extensive experimental and theoretical studies on combustion of solid propellants were done in CICP and other laboratories in different countries, which allowed to establish the following common regularities of combustion.

(1) The chemical reactions controlling the combustion rate and regularities of the process are localized in the near-surface layer of the solid phase. (The combustion of HMX and HMX-based formulations needs a special discussion).

(2) The controlling stage in kinetics of chemical reactions is the decomposition of oxidizer in solid phase.

(3). Addition to decomposition of oxidizer, the sublimation and dispersion of oxidizer, thermal decomposition and oxidation of the matrix occur in condensed phase.

(4) The rate of oxidizer decomposition is controlled by the temperature of the surface.

(5) The temperature of the surface is governed by the heat effect of decomposition, the dispersion fraction of sublimated matter, the heat of evaporation and the degree of the matrix oxidation in solid, the heat capacity of the fuel, the heat effect, the degree of decomposition and evaporation of the fuel. The heat flux from gas is usually not a governing factor.

Since some of the aforementioned processes (sublimation degree of fuel oxidation, etc.) depend on pressure, the surface temperature and hence the combustion rate depend on pressure too.

Therefore, the data on combustion of main oxidizers are the primary parameters to decide whether a designed formulation can be used. The combustion of NH_4ClO_4-based systems can be realized from a simpler system without sublimation of oxidizer and the heat effect related to oxidation of matrix. The boranehydrazine complex is a unicomponent system and analysis of the effect of other components is not required .

Table 6 presents the experimental data on combustion of the studied compounds, compared to those from theoretical calculation. The calculation was made on the basis of

independently measured kinetic and thermophysical parameters.

Table 6　Combustion parameters of different components

Compound	$p/(MPa)$	Experimental/Calculated		
		$r/(cm/s)$	n	$\sigma \times 10^3/(K^{-1})$
NH_4ClO_4	4.0	0.5/0.3	0.7/0.47	2/2.9
NH_4NO_3	7.0	0.4/0.34	0.85/1.03	—/—
$N_2H_5NO_3$	5.0	0.8/0.70	0.82/0.90	3.1/2.5
$NH_4N(NO_2)_2$	2.0	1.8/1.5	0.7/0.82	—/—
HMX	4.0	0.9/2.7	0.9/0.8	—/—
$BH_3N_2H_4$	4.0	0.5/0.56	0.5/0.5	—/—

Here r is combustion rate, n is pressure index, and σ is the temperature coefficient.

It can be seen that the experimental values well agree with the calculated ones except of HMX, and regularities of the combustion of ammonium perchlorate do not substantially differ from those of other compounds considered. The data presented show that these compounds from the viewpoint of their combustion characteristics can constitute a basis for propellants which meet the requirements of aerospace industry.

Naturally, the combustion rate, its dependence on pressure and initial temperature can experience changes upon transition from pure oxidizer to mixed solid propellants.

It was already mentioned afore that the presence of a fuel is revealed via changing heat effect and temperature of the oxidizer decomposition. The main effect is envisaged by experiment as follows:

(1) Composition and reactivity of oxidizer decomposition products.

(2) Reactivity of the fuel in oxidation and thermal decomposition.

(3) The particle size in the system, which affects the ratio of oxidation and decomposition rates and the heat transfer in solid.

Fig. 1 illustrates the calculated dependence of the combustion rate on the ratio of oxidation and decomposition rates.

The figure also presents the dependence of the combustion rate on the reactivity of the oxidizer decomposition products with respect to fuel. It can be seen that for highly reactive fuel the combustion rate of propellant can remarkably increase or equal to that of the pure oxidizer.

The particle size can have a strong and diverse effect on combustion.

When reactivities of the oxidizer decomposition products and the fuel in oxidation reaction are high, the surface of interphase contact and, hence, the oxidation degree of binder will increase due to the particles diminished. This results in increasing the heat effect of solid phase combustion, higher surface temperature and combustion rate (Fig. 2, curve 1). When the reactivity is low and fuel strips the oxidizer of heat, thus de-

creasing the temperature of oxidizer decomposition, the combustion rate of propellant decreases with diminishing the particle size (Fig. 2, curve 2). In general cases both branches of particle size-combustion rate dependence should be observed (the dash line presents the resulted dependence). In experiment, however, because reactivity changes dramatically from one reaction system to another, for a particular oxidizer-fuel pair only one branch can usually be obtained, either decrease or increase of the combustion rate with diminishing the particles size.
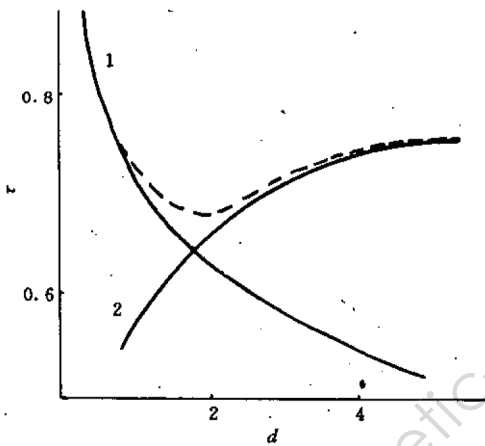

Fig. 1 The dependence of combustion rate on the ratio of the oxidizer decomposition and fuel oxidation rate: (1) mixed fuel, (2) pure oxidizer.
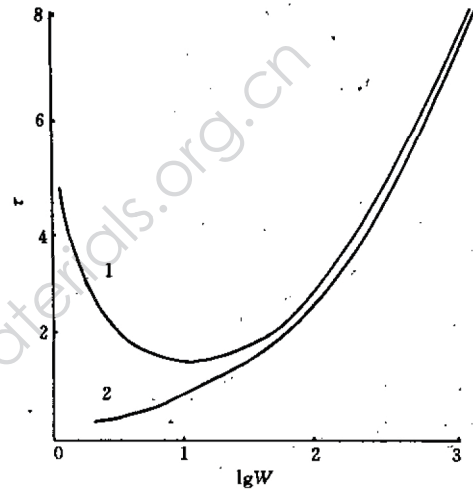
Fig. 2 The dependence of combustion rate on the particle size of oxidizer: (1) chemically reacting oxidizer and fuel, (2) heat exchange only.

5 CONCLUSION

It is impossible to work out a comprehensive rule to guide the development of the practical propellant formulations because of the diversity in properties of the different compositions. Nevertheless, the general behavior of the compounds considered in this paper may be taken a basis for the composite solid rocket propellant behavior.

The propellants that can be developed on the basis of the afore considered compounds are inherently more environmentally safe than those based on ammonium perchlorate. The energy of the possible formulations are diverse from each other and provide the possibility to develop propellants with higher energy than those based on HMX and ammonium perchlorate. The stability and principal combustion characteristics of the systems considered meet the requirements of aerospace industry.

According to the practical application, the propellant characteristics should be optimized to meet the requirements for the special purposes. The application scope of possi-

ble propellants based on these systems is determined not only by the performance of the propellant per se but also by the cost and technological requirements to the characteristics which affect the particular use. These problems need a specific consideration.

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研制生态安全的固体火箭推进剂的可能途径

摘要　本文叙述了常规火箭推进剂燃烧时产生大量污染环境,危及人类生存的有害物质,如一氧化碳和含氯化合物等致癌物。为研制生态安全的推进剂,如果不首先考虑推进剂的能量高、化学安定性和燃烧特性俱佳的氧化剂,企图进一步解决其它问题就无意义。当然成本、工艺性和力学性能因素亦很重要。在探索研制配方时,可考虑选用硝酸铵、硝酸肼、二硝酰胺、硝仿肼等氧化剂取代 NH_4ClO_4 和 HMX。

为此,本文着重介绍了由七种氧化剂组成的配方并进行了热力学计算,结果表明以 $NH_4N(NO_2)_2$ 及 $N_2H_5C(NO_2)_3$ 为基的配方的能量均高,而其燃烧室和喷管温度则分别低于以 NH_4ClO_4 和 HMX 为氧化剂的推进剂燃烧产生的高温。就上述氧化剂热分解参数而言,在 20℃ 下,热分解 0.1% 所需时间,以 $NaClO_4$ 的为最长;以 $NH_4N(NO_2)_2$ 的为最短。其顺序为:

$$NaClO_4 > NH_4NO_3 > \beta\text{-HMX} > N_2H_5NO_3 > NH_4ClO_4 > N_2H_5C(NO_2)_3 > NH_4N(NO_2)_2。$$
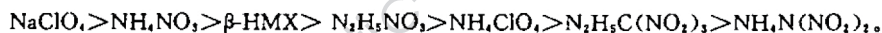
文中对上述氧化剂的燃烧速率、压力指数和温度系数分别进行了实测和计算,除 HMX 外,所得两值均较一致,还介绍了燃烧速率与氧化剂产物分解比例和燃料氧化率的关系曲线等。文中还介绍了 $N_2H_5NO_3$、$C_2(NO_2)_4$、NH_4ONO_2、$BH_4N_2H_4$ 等高能无氯氧化剂的热分解参数。

结论指出:由于配方中各组分的性质不同,不可能为研制有实用价值的推进剂配方拟订综合准则。但本文提到的氧化剂的综合行为,可能作为研制性能优于 NH_4ClO_4 或 HMX 的推进剂配方的基础,以达到使用要求。

关键词　火箭排出物　污染　无氯固体推进剂　热力学计算