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ROCKET ENGINES' SOLID PROPELLANTS AND COMBUSTION PRODUCTS

Martin KŘEPSKÝ

Abstract: Rocket technology has shown considerable progress in recent decades. In addition to peaceful use, rockets are used in the military as a means of transporting destructive charges on a target. Any information obtained, even a partial one, could be used to prevent or mitigate a missile threat. Different types of rocket engines are sources of rocket propulsion. One of the factors by which individual types of rockets differ from each other is the type of fuel used. Combustion of rocket fuel creates a flame that is a source of radiation. The article analyzes the composition of different types of solid propellants and their combustion products. It is further considered if combustion products detected via emission spectra can indicate the rocket launch and if it is possible to identify the type of rocket by assignment of emission spectra to known propellant. The recherche of multiple sources is the method used for gathering information concerning rocket propellants. The results of the recherche are the most used propellants' compositions and their combustion products.

Keywords: Rocket engines; Solid propellants; Combustion products; Emission spectrum.

1 INTRODUCTION

In nowadays conflicts, rockets and missiles cause significant numbers of casualties. Timely warning and defensive measures could decrease the casualties when the rockets and missiles are detected. Thus knowing the details i.e. type of the rocket and the trajectory can increase level of protective measures. The rocket engine is one of the limiting factors of trajectory and maximum range.

Structurally, the rocket consists of various parts. One of the main parts that give the rocket propulsion is the rocket engine with different types of fuel. Combustion of the fuel results in the formation of fumes that flow out of the rocket engine nozzle and create the necessary thrust to drive the system. If "exotic" types of rocket fuel such as a nuclear source are omitted, the fuels can be divided into two main groups: liquid propellants and solid propellants. The existence of a hybrid propulsion method, i.e. a combination of liquid and solid rocket fuel components, is possible.

A flame emitting optical radiation is created during the chemical reactions taking place as part of the burning process. Combustion is a chemical reaction where fuel is oxidized with the help of an oxidizing agent. The spectral distribution of optical radiation intensities at different wavelengths depends on the chemical composition of substances and the burning conditions. The objective of the article is to find out whether rocket solid propellants of different chemical structure effect combustion products and what is the composition of the products. If composition of combustion products differs, the differences will be affecting emission spectra. The analysis of obtained emission spectra could provide supplementary information to air defence process.

Solid propellants can be divided according to different criteria. The basic division can be into homogeneous solid propellants and heterogeneous solid propellants. Further breakdown by chemical composition is given below.

2 HOMOGENEOUS SOLID PROPELLANTS

In the case of homogeneous solid propellants, the propellant grains are usually of larger dimensions than the dimensions of the grains of ordinary gunpowder. In terms of chemical composition, it is nitrocellulose, which absorbs a certain amount of nitroglycerin and other additives. Sometimes these propellants are called double-base propellants. Because both components, nitrocellulose and nitroglycerin, are hydrocarbons containing a significant amount of oxygen, the mixture acts as both a fuel and an oxidizer. The next stage of improving the properties of these mixtures is the addition of explosive components such as nitramines, e.g. RDX or HMX. Furthermore, part of the nitrocellulose can be replaced by another binder, most often a polymer, which gives the mixture elastic properties that increase the resistance of the propellant grain [1, p. 493 – 494].

The composition of nitroglycerin gunpowder-based rocket fuels of different origins in World War II. is shown in Table 1 [2, pp. 405 – 407]. Other energy components than nitroglycerin are added into the mixture e.g. German Giessling Pulver or Nebelwerfer mixtures. The percentages in brackets given for nitrocellulose express the nitrogen content by weight.

3 HETEROGENEOUS SOLID PROPELLANTS

Heterogeneous solid propellants are formed by a mixture of powdered metal, most often aluminum, and inorganic oxygen-rich salts, such as ammonium perchlorate, joined together by a liquid polymer binder, which is then cured. Common heterogeneous mixtures contain 60-72 % ammonium perchlorate and up to 22 % aluminum powder. Organic binder - polymer is represented in 8-16 %. Further modification of these mixtures can be achieved by adding the already mentioned nitramines (RDX, HMX) or nitroglycerin. The nitramines increase the performance parameters of the mixture. Part of the ammonium perchlorate and polymer can be replaced by other high-energy substances [1, p. 493 – 494]. For the sake of extensiveness and to maintain clarity, the compounds of the individual components of solid propellants are not listed in full. An illustrative list is given in Table 2 [1, p. 514 – 515]. The components that can affect the composition of combustion products are listed above all.

Probably the oldest heterogeneous mixture used as a fuel is a mixture of asphalt and potassium perchlorate called galcit 53. Asphalt, as a mixture of hydrocarbons, performed the function of fuel in the mixture, and perchlorate supplied the oxygen needed for its combustion [2, pp. 405 – 407]. Asphalt was later replaced by polymer binders such as Thiokol or polymethyl methacrylate (PMMA). The conditions imposed on these binders are high mechanical resistance and elasticity. The most used oxidizing agents in heterogeneous mixtures are potassium nitrate, ammonium nitrate, potassium perchlorate and ammonium perchlorate. Some properties of heterogeneous solid propellant based on PMMA – potassium perchlorate are listed in Table 3 [2, p. 405 – 407].

Tab. 1 Composition of World War II. rocket fuels based on nitroglycerin gunpowder

Name of propellant	Composition of propellant	
	Name of item	[% wt.]
Soviet Union (I.P.)	Nitrocellulose (13,75 % N)	52,2
	Nitroglycerin	43,0
	Diethyl phthalate	3,0
	Diphenylamine	0,6
	Potassium nitrate	1,1
	Nigrosin	0,1
Soviet Union (I.P.N.)	Nitrocellulose (13,25 %)	51,5
	Nitroglycerin	43,0
	Diethyl phthalate	3,0
	Centralite	1,0
	Potassium sulfite	1,25
	Soot	0,20
	Candela wax	0,05
Soviet Union (Slow burning gunpowder)	Nitrocellulose (12,2 %)	56,5
	Nitroglycerin	28,0
	Dinitrotoluene	11,0
	Centralite	4,4
	Candela wax	0,1
Great Britain	Nitrocellulose	41,0
	Nitroglycerin	50,0
	Centralite	9,0
Germany (Giessling Pulver)	Nitrocellulose	28,0 – 30,0
	Trinitrotoluene	50,0 – 52,0
	Diethylene glycol dinitrate	17,0 – 18,0
	Centralite	0,5
	Diphenylamine	0,5
Germany (Nebelwerfer)	Nitrocellulose	63,0
	Diethylene glycol dinitrate	35,0
	Centralite	0,5
	Wax	0,2
	Graphite	1,2
Japan	Nitrocellulose	60,0
	Nitroglycerin	27,0
	Nitronaphthalene	7,0
	Centralite	3,0
	Potassium sulfite	3,0

Source: [2].

Tab. 2 Overview of typical components of heterogeneous solid propellants

Item	Content [%]	Abbreviation	Chemical substance
Oxidizers	0 - 70	AP AN KP KN ADN	Ammonium perchlorate Ammonium nitrate Potassium perchlorate Potassium nitrate Ammonium dinitramide
Metal fuels	0 - 30	Al Be Zr	Aluminum Beryllium (experimental only) Zirconium (also burn-rate modifier)
Fuels/binders polybutadiene type	5 - 18	HTPB etc.	Hydroxyl-terminated polybutadiene
Fuels/binders polyether or polyester type	0 - 15	PU etc.	Polyurethane polyether or polyester
Curing agents or crosslinkers	0,2 – 3,5		
Burn-rate modifiers	0,2 – 3,0	FeO	Ferric oxide Oxides of Cu, Pb, Zr, Fe Alkaline earth carbonates Alkaline earth sulphates Metallo-organic compounds
Explosive filler	0 - 40	HMX RDX NQ	Octogen Hexogen Nitroguanidine
Plasticizers	0 – 7		
Energetic plasticizer (liquid)	0 - 14	NG DEGDN TEGDN TMETN	Nitroglycerin Diethylene glycol dinitrate Triethylene glycol dinitrate Trimethylolethane trinitrate
Energetic fuel/binder	0 - 15		
Processing aid, stabilizers, etc.	< 0,5		Lecithin

Source: [1].

Tab. 3 Properties of heterogeneous solid propellants based on PMMA – potassium perchlorate

Composition of propellant [% wt.]		Density [g.cm^{-3}]	Heat of combustion [kJ.kg^{-1}]	Temperature of flame [K]	Burn-rate under the pressure [cm.s^{-1}]		
PMMA	$KClO_4$				30 atm	50 atm	100 atm
20,0	80,0	1,88	3 349,44	3750	1,41	-	-
22,5	77,5	1,88	3 483,42	3770	1,43	2,34	5,48
25,0	75,0	1,86	3 596,46	3778	1,38	2,33	-
30,0	70,0	1,82	3 466,67	3518	1,17	2,12	-

Source: [2].

It can be seen from Table 3 that by reducing the oxidizing agent in favor of the fuel, there is first a slight increase in the burning rate and then, at a certain concentration, its decrease. As the pressure in the combustion reaction zone increases, the burning rate will increase. Compared to nitrocellulose and nitroglycerin-based propellants, the burning temperature of the PMMA – potassium perchlorate mixture is much higher. The temperature of combustion has significant effect on radiation characteristics. The comparison of radiation source's and known sample's temperature difference is a possible way for rocket recognition. The difference of combustion temperatures for the mixtures of same amount of oxidizer (80 % AP) and different fuel is depicted in Tables 3 and 4.

Another advantage of heterogeneous mixtures is higher chemical stability, unlike propellants based on smokeless powders, which contain components subject to decomposition reactions, especially at elevated temperatures. Some other examples and compositions of solid propellants are given in Table 4 [3, p. 212].

Tab. 4 Comparison of some properties of solid propellants

Propellant	Components	Density [10^{-3}, kg.m^{-3}]	Heat of combustion [MJ.kg^{-1}]	Temperature of combustion [K]
Diethylene glycol-based propellant (dg)	Diethylene glycol, nitrocellulose, additives	1,55 – 1,60	3,726	2390
Nitroglycerin based propellant (ng)	Nitroglycerin, nitrocellulose, centralite, additives	1,61	5,149	3160
Galcit propellant	Potassium chlorate, asphalt (75/25)	1,74	-	1970
---	Ammonium nitrate, rubber, catalysator (80/18/2)	1,55	-	1720
---	Ammonium perchlorate, fuel, additives (80/20)	1,72	-	2790
---	Ammonium perchlorate, polyurethan	-	-	3300

Source: [3].

Contrary to the previous information, potassium chlorate and not potassium perchlorate is used as an oxidizing agent in Galcit propellant.

4 PRODUCTS OF COMBUSTION

Rocket propellant composition determines combustion products. The following text describes the major changes of combustion products content based on reactants.

At concentrations of ammonium perchlorate above 70 % in the mixture, the combustion products contain significant amounts of H_2O and O_2. Hydrochloric acid is also present in gas products in the range of 10 – 20 % mol. (exceptionally it exceeds 14 % for common fuels). The other products, CO, CO_2 and H_2, tend to decrease. Change of ammonium perchlorate content in the examined range of 60 – 100 % mol. does not affect the amount of nitrogen (5 – 10 % mol.) in the flue gas. In the second case, when the mixture contains RDX instead of ammonium perchlorate, the waste products contain C, CO, CO_2, H_2, H_2O and N_2. Above 80 % RDX content, there is a decrease in C, CO and H_2 and an increase in CO_2 and H_2O [1, pp. 503, 505].

Combustion products of solid propellants composed of ammonium perchlorate and polybutadiene-based fuel terminated with a hydroxyl group (Hydroxyl Terminated Polybutadiene - HTPB) at pressure lower than atmospheric form a mixture of 16 stable elements and compounds. Those products are HCl, H_2O, CO, NH_3, CO_2, HClO, NO, O_2, H_2, NO_2, N_2, C_4H_6, C_2H_2, ClO_2, Cl_2, and HCN [4, pp. 342 – 343].

In the case of RDX burning (at pressure lower than atmospheric), the products are HCN, NO, H_2O, HNCO, H_2, N_2, CO, CO_2, N_2O, NO_2, when the first-mentioned HCN and NO further react together and their concentrations reduces. Combustion of HMX at atmospheric pressure then provides similar products HCN, NO, H_2O, N_2, CO_2, NO_2 and CH_2O [4, pp. 343 – 344].

When burning, the substance ammonium dinitramide (ADN) produces the fumes listed in Table 5. The different composition of the fumes depends on the distance from the burning surface and the ambient pressure. ADN mixed with HTPB then provides waste products with the composition shown in Table 6 [4, p. 345, 347, 349]. It is worth noting the differences in the composition of the combustion products of ADN at a pressure of 6 atm (Tab. 5) and the final combustion products (Tab. 6). This difference can be attributed to other reactions taking place at a greater distance from the combustion zone.

Tab. 5 ADN combustion products

p = 6 atm, distance from the burning surface L = 4,4 mm							
Items	NH_3	NO	N_2O	N_2	HNO_3	H_2O	ADN
Content [%]	0,07	0,23	0,28	0,10	0,02	0,30	0,00
p = 3 atm, distance from the burning surface L = 0,2 mm							
Items	NH_3	NO	N_2O	N_2	HNO_3	H_2O	ADN
Content [%]	0,08	0,19	0,24	0,08	0,08	0,30	0,03

Source: [4].

Tab. 6 Combustion products of ADN and mixtures of ADN and HTPB

Composition	p [atm]	T [K]	NH_3	H_2O	N_2	NO	N_2O	CO_2
ADN/HTPB (97/3)	1	2370	0,01	0,35	0,13	0,26	0,18	0,06
ADN	6	1420	0,00	0,45	0,11	0,25	0,20	---

Source: [4].

In the case of nitroglycerin alone, the explosive decomposition can be expressed as follows:

$$32\ C_3H_5(ONO_2)_3 \rightarrow 96\ CO_2 + 80\ H_2O + 6\ NO + 45\ N_2 + 5\ O_2 \quad (1)$$

During the reaction, the explosion heat of 6,091.79 kJ.kg^{-1} is released, the specific gas volume V_0 is 715 l.kg^{-1} and the explosion temperature is 4250°C [5, p. 27]. Nitrocellulose with a nitrogen content of 13.1 % decomposes according to the equation below [5, p. 175].

$$2\ (C_{24}H_{29}O_9(ONO_2)_{11} + C_{24}H_{30}O_{10}(ONO_2)_{10}) \rightarrow 36\ CO_2 + 47\ CO + 4\ CH_4 + 39\ H_2O + 2\ C_2H_2 + 3\ HCN + 3{,}5\ H_2 + 18{,}5\ N_2 + 2\ NH_4HCO_3 \quad (2)$$

Similar compositions of the combustion products of the compounds contained in rocket propellants are shown in Table 7. Only the main components of the combustion products are shown. In the case of nitrocellulose, the difference in the composition of the combustion products is largely influenced by the different amounts of nitrogen in the original composition. In the case of nitroglycerin, in contrast to Table 7, CO is not listed as a product of the reaction in the decomposition equation, and on the contrary, NO is listed as a product of nitrogen oxidation [6, p. 21]. In addition to nitrocellulose, nitroglycerin, ammonium perchlorate and ammonium nitrate, some other compounds are listed in Table 7.

Tab. 7 Combustion products NC, NG, AP, AN

	Composition [moles/mole]								
	O_2	H_2O	CO	CO_2	H_2	N_2	HCl	Cl_2	OH
NC (12,6 % N)		0,225	0,147	0,128	0,116	0,111			
NG	0,069	0,280	0,107	0,275	0,014	0,181			0,041
TMETN		0,263	0,357	0,096	0,140	0,136			
TEGDN		0,110	0,397	0,063	0,335	0,079			
DEGDN		0,253	0,365	0,079	0,190	0,111			
AP	0,287	0,377				0,119	0,197	0,020	
AN	0,143	0,571				0,286			
NP	0,750					0,125		0,125	
RDX		0,226	0,246	0,082	0,089	0,326			
HMX		0,227	0,246	0,082	0,089	0,326			

Source: [6].

The values of the composition of the combustion products of various solid propellants of the ICT Thermodynamic Code calculation model are shown in Table 8 [7, p. 154].

Tab. 8 Combustion products of various solid propellants according to the ICT Thermodynamic Code calculation model

Type of propellant	Environment Pressure [MPa] Temperature [K]	Composition [% wt.]							
		CO_2	H_2O	N_2	CO	H_2	Cl	OH	HCl
Nitramine (85 % HMX, 15 % binder)	inert 10 MPa 2293 K	5,931	9,132	32,551	49,946	2,421			
	air 0,1 MPa 1227 K	27,700	10,111	62,168	0,001	0,000			
Double-based solid propellant (50 % NC (13.3 % N), 35 % NG, 11 % Triacetin, 2 % Centralite, 2 % CuO)	inert 10 MPa 2508 K	21,790	17,215	13,332	45,021	1,008			
	air 0,1 MPa 1317 K	37,832	10,746	50,743	0,013	0,000			
Heterogenous solid propellant (80 % AP, 10 % Al, 10 % binder)	inert 10 MPa 3470 K	8,362	20,720	9,509	14,724		2,332	1,487	22,166
	air 0,1 MPa 1909 K	19,647	18,089	34,100	0,228		0,261	0,034	15,492

Source: [7].

Modeling of chemical reactions was carried out for two different states of the surrounding environment. In the case of modeling reactions in air, subsequent reactions occur, which correspond to a change in the composition of the waste products, e.g. a decrease in CO and an increase in CO_2 by subsequent oxidation, the formation of N_2, in the case of heterogeneous solid propellants, a decrease in the content of Cl radicals. The resulting permeability of double-based solid propellant emissions is higher than that of heterogeneous solid propellant. The spectral dependence of the transmittance of double-based solid propellant emissions shows a decrease at wavelengths of 4.25 µm (CO_2 absorption), in the range of 4.70 – 4.90 µm (CO absorption) and below 3.00 µm (H_2O absorption). On the contrary, heterogeneous solid propellant shows permeability only in the range of 8.00 µm – 10.0 µm [7, p. 155].

The emission spectrum of the double-based solid propellant also differs from the heterogeneous one. The double-based solid propellant shows higher values of the spectral dependence of the intensity of the emission spectrum compared to the values of the heterogeneous solid propellant in the infrared region. This difference is caused by the different number of particles produced in the combustion gases. In the case of the infrared part of the spectrum, these are CO_2 and H_2O particles [8, p. 188].

In the case of solid propellant with the highest useful values, it is a heterogeneous solid propellant based on a mixture of ammonium perchlorate and aluminum powder. Mixtures of ammonium perchlorate and aluminum have a significant disadvantage in the amount of waste products produced, where a significant part consists of Al_2O_3 as a product of oxidation [9, p. 84 – 85].

5 CONCLUSION

Comparison of information provided in multiple free-accessible sources was used to list the main combustion products of solid rocket fuels.

Based on the above-mentioned different types of solid propellants, it is possible to identify the typical components used in individual mixtures. In the case of double-based mixtures, it is nitrocellulose and nitroglycerin with the main combustion products H_2O, CO_2 and N_2. In the case of nitroglycerin, then O_2. In nitramines (RDX and HMX), in addition to the previous ones, CO is also represented. Heterogeneous perchlorate-based solid propellant produces Cl radicals or an HCl compound. The waste products of mixtures containing powdered metal, e.g. Al, contain oxides of these metals. The combination of these products in exhaust depends on the original solid propellant composition (qualitative and quantitative). On the contrary, some emission spectrum implies the combustion products of propellants. The surrounding atmosphere must be considered for its effects on observation. If the emission spectrum is detected and the surrounding conditions are known, it would be possible to determine the original substances. If the original composition of rocket propellant is known the reverse approach can be utilized to identify the rocket by its combustion products.

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Dipl. Eng. Martin **KŘEPSKÝ**
JCBRN Defence COE
Víta Nejedlého
682 01 Vyškov
Czech Republic
E-mail: martin.krepsky@unob.cz

Martin KŘEPSKÝ, born in 1980, is absolvent of Military Academy in Brno (2003) and University of Pardubice (2021). After the graduation from Military Academy he has been assigned to different command and training posts of the Armed Forces of the Czech Republic. His interest is in optoelectronic means of detection and identification of chemical agents.