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Study of Combustion Characteristics of Ammonium Dinitramide/Polycaprolactone Propellants

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This paper is devoted to the investigation of main characteristics and mechanism of combustion of the composite solid-rocket pseudopropellant based on ammonium dinitramide and polycaprolactone. Experimental data on the dependence of the burning rate on pressure in the pressure range of 4–8 MPa for ammonium dinitramide/polycaprolactone propellant with different additives and with polycaprolactone of different molecular weight are presented in the paper. The dependence of propellant burning rate on particle size of oxidizer and initial temperature has been also investigated. Composition of the combustion products of the propellant at pressures of 4 MPa using two different systems of sampling has been determined. The temperature profile in the combustion wave of some propellants has been obtained with aid of thin flat thermocouples. Temperature of the final combustion products of the propellant without additive and for some propellants with additive has been determined by a thermocouple method. Also the influence of a CuO catalyst on temperature profile has been investigated. Flame structure of ammonium dinitramide/polycaprolactone propellant at 0.1 MPa has been studied. Data obtained elucidating combustion mechanism and place of action of catalyst are discussed.

Nomenclature

A	=	factor in pressure dependence of the burning rate
C	=	coefficient of specific heat of condensed phase
C_p	=	coefficient of specific heat of gas phase at constant pressure
D_{mn}	=	mean size (diameter)
m	=	mass burning rate
P	=	pressure, MPa
Q	=	heat release in the reaction layer of the condensed phase
q	=	heat feedback from gas into condensed phase
q_m	=	heat of melting
r_b	=	burning rate, mm/s
T	=	temperature
T_s	=	burning surface temperature
T_0	=	initial propellant temperature, °C
β	=	temperature sensitivity, %/K
λ	=	coefficient of heat conductivity of gas phase
ν	=	pressure exponent
Φ	=	heat-release rate in the gas phase
φ	=	temperature gradient in gas phase close to the burning surface

Introduction

AMMONIUM dinitramide (ADN) is a powerful chlorine-free oxidizer, which can replace ammonium perchlorate (AP) in solid-rocket propellants. Because the combustion products of ADN-based propellants are not toxic, these propellants are environmentally friendly, and investigation of them is of great interest. An ADN-based propellant is a convenient system for investigation of the mechanism and chemistry of composite solid-rocket propellant combustion because of the simplicity of the oxidizer. (ADN molecule contains only three elements: H, N, and O.) Important physicochemical properties and combustion characteristics of ADN and ADN-based propellants were published for the first time in Ref. 1. ADN has a higher heat of formation than AP, the common oxidizer of solid-rocket propellant; therefore, ADN-based propellants have higher specific impulse than AP-based propellants.[1,2] The study of the combustion mechanism of pure ADN was the subject of several investigations.[3–6] It was found that the burning rate of ADN is controlled by reactions in the condensed phase. A multizone flame structure was also established. At present, however, there are only a few papers that are devoted to the study of the combustion characteristics and combustion mechanism of composite ADN-based propellants and sandwiches with different types of binder such as hydroxyl-terminated polybutadiene (HTPB),[7,8] glycidyl azide polymer,[8,9] paraffin,[3,10] poly(diethyleneglycol-4,8-dinitraza undeconate) (ORP-2A)/nitrate ester, (NE)[11] polycaprolactone polymer/NE,[11] and polybutadiene polymer.[12]

One of the objectives of the study of propellant combustion mechanism is the development of a combustion model that can predict combustion characteristics of solid propellants. The development of a combustion model describing composite solid propellant requires information on propellant flame structure. As a model of composite solid propellant, sandwiches based on oxidizer and binder are used. Flame structure of ADN-based sandwiches with various energetic and nonenergetic binders has been investigated in Ref. 13. Results showed either no or insignificant effects of diffusion flames on the processes controlling the propellant burning rate in the pressure range from 0.1 to 1.4 MPa. However, the burning rates of sandwiches such as ADN/(ADN/HTPB)/ADN and ADN/PBAN/ADN increased nearly 1.5-fold with the pressure increase from 1.5 to 7 MPa (data of Ed. Price, Georgia Tech. University, USA). This suggests a possible influence of the ADN-binder diffusion flames on the burning rate of sandwiches. It has been shown in Ref. 7 that the reactions in the condensed phase control ADN/HTPB propellant combustion.

The most important combustion characteristics of a rocket propellant in terms of practical application are specific impulse, burning rate r_b, parameter ν in dependence of the burning rate on pressure ($r_b = AP^{\nu}$), sensitivity of propellant burning rate to initial temperature, and composition and temperature of combustion products. It is not known at present what factor does determine the burning rate of ADN-based propellants. Combustion instability of pure ADN takes place in the pressure range of 2–10 MPa (Ref. 3). However, even

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small amounts of organic additives (~1%) result in a reduction of both burning rates and their scatter in this pressure range.[4,14] In contrast, the addition of Cu_2O (2%) leads to an increase in the burning rate at pressure 0.1–2 MPa followed by a decrease above 4 MPa (Ref. 4). As it is shown in Ref. 12, the shape of the particles of ADN influences the burning rate of propellant. Ballistic characteristics of propellant are better in the case of more spherical shape of ADN prills. Parameter ν values of 0.40 and 0.11 in pressure range of 3.4–5.1 MPa were obtained for different propellants with spherical prills of ADN. In the case of less spherical prills, parameter ν was equal to 0.67. Thus, the microstructure of oxidizer influences the ballistic characteristics of an ADN-containing propellant, that is, variation of such parameters as uniformity of particle size distribution and shape of the oxidizer particles allows the tailoring of the propellant burning rate and parameter ν.

The chemical mechanism of combustion of ADN-based propellants is not well understood. The objective of this research was the comprehensive experimental investigation of the combustion mechanism of ADN/polycaprolactone (PCL) propellants by study of 1) pressure dependence of the burning rate in the pressure range of 4–8 MPa; 2) temperature profile in the propellant flame at 4 MPa; 3) the influence of molecular weight of PCL, particle size of ADN, initial temperature and addition of different additives on the burning rate and pressure exponent ν; 4) composition of final combustion products for ADN/PCL propellant; 5) temperature of final combustion products for propellants with and without additives; and 6) flame structure of ADN/PCL propellant at 0.1 MPa.

Experimental

The ADN used in this study was synthesized at the Zelinsky Institute of Organic Chemistry Russian Academy of Science. It contains 2% of ammonium nitrate as an impurity. The melting point (mp) of ADN is 365–367 K. Two types of PCL with different molecular weights: 10000 [PCL(10000)] and 1250 [PCL(1250)] were used. The former polymer at room temperature is flake (mp 333 K), and the latter one is a waxy solid (mp 309–321 K). Fine crystalline powdered ADN with an average particle size of ~40 μm was used for preparation of the composite propellants. Propellant strands with bimodal ADN oxidizer were also prepared. The bimodal oxidizer consisted of two fractions (~40 and ~300 μm) in equal amount (by mass). Uncured ADN/PCL propellant of stoichiometric composition St_b consisted of 89.08 wt% ADN and 10.92 wt% PCL. It was prepared by mixing the ingredients in a vessel filled with dry air at a temperature slightly exceeding the melting point of the polymer. Strands with diameter of 6 mm and length of 10–12 mm were prepared by pressing the propellant mixture under a pressure of ~390 MPa. Density of strands was 1.58 g/cm^3. Addition of x% additive to St_b means that in this propellant mass fractions of St_b and additive are equal to (100-x)% and x%, respectively. The sides of the strands were inhibited with a thin layer of high vacuum silicone grease. Measurement of the burning rate at high pressures (4–8 MPa) was conducted in a combustion chamber of constant volume in argon by two methods: by pressure control during the combustion process and by videotape recording of movement of the burning surface through the combustion chamber windows.

Aluminum is commonly used as an additive to solid-rocket propellants for improving performance. In this study aluminum powder with spherical particles ($D_{10} = 4.2$ μm, $D_{30} = 5.8$ μm, $D_{43} = 15.0$ μm) was used. The content of metal in virgin aluminum particles was equal to 97.8 ± 0.9%. However ammonium dinitramide cannot oxidize aluminum as effectively as ammonium perchlorate.[2,15] To increase completeness of oxidation of aluminum in ADN-based propellants, ultrafine aluminum can be used. Electroexploded aluminum (ALEX) with particle size of $\leq$0.1 μm was used in this study. Specific surface area of ALEX powder was ~12 m^2/g, and the mass fraction of oxide film on the surface of ALEX was ~6%. To prevent oxidation of ALEX by atmospheric oxygen, it is stored as a mixture with transformer oil. Extraction of ALEX from the viscous mixture of ALEX/transformer oil was done by multiple washings of this mixture with hexane.

CuO powder with particle size of ~2–5 μm and specific surface area of 33.6 m^2/g was used. Particles of Pb_3O_4 powder were of ~1–3 μm size with specific surface area of 1.6 m^2/g.

Sampling of the combustion products of the St_b(10,000) propellant was carried out using one-stage and two-stage sampling systems. One-stage sampling at 4 MPa was conducted using a probe made of stainless steel with an internal angle of 40 deg and inlet orifice diameter of 170 μm. A propellant strand was located at the distance of 8–10 mm along the axis of probe. In the case of aluminized propellants, the strands were situated perpendicularly to the probe axis. Such strand location allowed sampling of combustion products before clogging of the inlet orifice by condensed combustion products occurred. Combustion products, sampled by the probe, were conducted through the 6-mm-diam tube and through a three-way tap into the glass receiving vessel at atmospheric pressure. To indicate the beginning and end of the passage of combustion products through the vessel, a flowmeter was used. Filling of the vessel by combustion products was carried out during the time of strand burning (0.4–1.0 s). Sampled combustion products were isolated in the vessel with aid of inlet and outlet taps. The volume of sampled products for GC analysis comprises ~2–7% of overall volume of vessel. GC analysis allowed quantitative determination of the content of gaseous combustion products such as N_2, CO_2, CO, H_2, NO, and O_2. As it will be shown in the following, the one-stage sampling system does not allow precise sampling and the saving of all of the combustion products. The formation of shocks inside the probe takes place as the gas flow through the orifice in probe from the area with high pressure to the area with low pressure. An increase in reaction rates, caused by heating of gas as it crosses the shock, can change the composition of combustion products. To improve freezing of combustion products during sampling, a two-stage sampling system was designed. This system (Fig. 1) consists of two chambers. A more thorough description can be found in Ref. 16. Chamber 1 is located between the probe and the skimmer, whereas chamber 2 is between the skimmer and the diaphragm. Gas flows through the probe with inner opening angle of 90 deg and diameter of orifice of 0.12 mm from the chamber 1 to 2. The large opening angle of probe and pumping of chamber 2 provide free expansion of gas and abrupt freezing of sampled gas. The skimmer with orifice of 1.2 mm and internal opening angle of 36 deg is located at a distance of 1.9 mm from the probe orifice before Mach disk. Such location of the skimmer prevents heating of sampled gas and consequently changing of its composition. In Fig. 2 an image of probe in cross section and

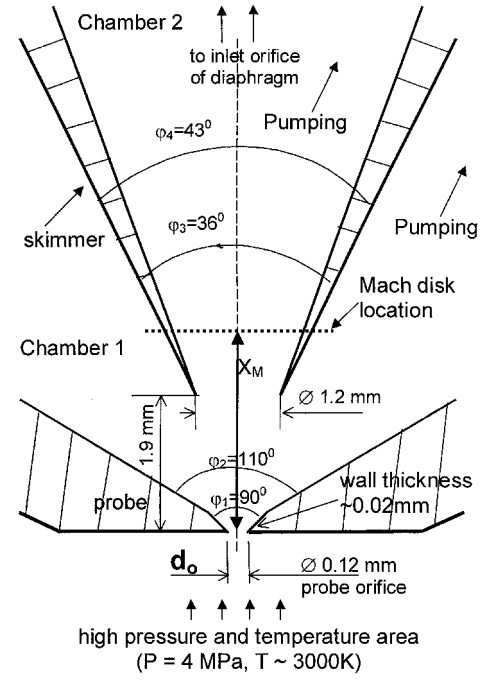


Fig. 1 Two-stage sampling system at high pressure and temperature.

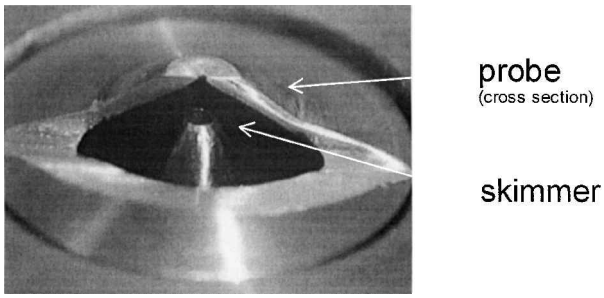


Fig. 2 Image of probe in cross section and skimmer.

skimmer is presented. Sampled gas flows through the skimmer in chamber 2 and then through the diaphragm with diameter of 40 μm in chamber of mass-spectrometer's analyzer ($P \sim 2 \times 10^{-6}$ torr). The quantitative determination of CO and N_2 is one of the main problems of analysis of combustion products by time-of-flight mass spectrometer (TOFMS) because both of these gases contribute to the peak with mass 28. Two types of experiments were conducted. In the first one the combustion products directly entered the inlet system of TOFMS. In the second one a flow of oxygen was added to sampled combustion products in chamber 2 and resulting mixture passed through the layer of granules of CuO catalyst heated to a temperature around 870 K. In this case CO oxidized to CO_2. Oxidation of CO allows us to get rid of its contribution to the peak with mass 28. The joint processing of data from both experiments makes the determination of concentrations of CO and N_2 in combustion products possible.

Probe mass spectrometry is the most effective and universal method for investigation of solid propellant flame structure.[17] It allows the detection of all of the stable species present in the flame and also the ability to determine their concentrations and their spatial distributions. Flame structure has been studied at 0.1 MPa of argon using a setup[18] with molecular beam sampling system combined with TOFMS. Calibrations[5] were conducted for N_2, O_2, CO, CO_2, N_2O, NH_3, NO, HNO_3, and H_2O. Calibration for water was conducted by vaporization of a drop of water in argon flow. Accuracy of measurement of species mole fractions in the range of 0.1–0.4 (H_2O, N_2, N_2O, NO, and CO_2) was ~10%. For species with mole fractions less than 0.1, the error was 20–30%. The temperature of the final combustion products was measured by Π-shaped WRe(5%)–WRe(20%) thermocouples with a shoulder length of ~3 mm, made of wire of 100 μm in a diameter. The thermocouples were located at a distance of ~2–5 mm from the strand surface. The error in determination of the temperature of the final combustion products was equal to ±25 K. Temperature profiles in the propellant combustion wave at 4 MPa were measured by ribbon WRe(5%)–WRe(20%) thermocouples (thickness of 13–15 μm and width of ~140–150 μm) embedded in the strand.

Results

Burning Rate

Influence of Polycaprolactone Molecular Weight

Data on the dependence of the burning rate r_b on pressure for St_b(1250) and St_b(10,000) propellants over a pressure range of 4–8 MPa are shown in Fig. 3. Parameters A and ν of the dependence of the burning rate on pressure $r_b = AP^{\nu}$ are given in Table 1. The St_b(10,000) has a high pressure dependence exponent ($\nu = 1$). Replacement of PCL(10,000) in the propellant by a polymer with the same structure and chemical composition, but with lower molecular weight (1250) and lower melting point, led to the increase of the burning rate (by 1.5 times at 4 MPa and by 1.2 times at 8 MPa) and to the decrease of parameter ν to 0.7 (Fig. 3 and Table 1). The possible reason of observed difference in burning rate of these two propellants is considered in the discussion section.

Influence of Particle Size of ADN

It was shown that particle size of oxidizer influences the burning rate of St_b(10,000). The parameter ν for propellant with bimodal oxidizer decreased to 0.72 in comparison with propellant on base of fine oxidizer ($\nu = 1.0$) within a pressure range of 3–8 MPa. Values of the burning rate for propellant with bimodal oxidizer are very close to propellant with fine oxidizer. However, for St_b(10,000) propellant with fine oxidizer there are two regions with different parameter ν in the pressure range 2–8 MPa, whereas propellant with bimodal oxidizer has one parameter ν within a pressure range of 3–8 MPa (Fig. 4).

Table 1 Calculated specific impulse at 4 MPa and parameters of pressure dependence of the burning rate for St_b-based propellants at 4–8 MPa

Propellants	Specific impulse, s	St_b(1250) A	St_b(1250) ν	St_b(10,000) A	St_b(10,000) ν
90% St_b + 10% Al	255.3	11.67	0.50	——	~1.0
90% St_b + 10% ALEX	255.3	6.16	0.71	——	——
88% St_b + 10% ALEX + 2% CuO	252.3	12.0	0.49	——	——
90% St_b + 10% RDX	249.3	——	——	9.63	0.54
90% St_b + 10% HMX	249.3	——	——	8.40	0.57
St_b	**247.5**	**8.74**	**0.70**	**3.79**	**1.00**
99% St_b + 1% CuO	245.7	12.29	0.55	7.29	0.69
98% St_b + 2% Pb_3O_4	244.7	12.92	0.42	6.22	0.64
98% St_b + 2% PbO	244.7	——	——	7.01	0.70
98% St_b + 2% PbO_2	244.7	——	——	5.41	0.82
98% St_b + 2% CuO	243.9	15.30	0.44	9.10	0.60
90% St_b + 10% AN	242.2	——	——	4.60	0.84
90% St_b + 10% AP	241.6	——	——	5.62	0.73

Table 2 Burning rate r_b at different initial temperatures T_0 °C

Propellant	P, MPa	T_0, °C −50	−20	+20	+30	+50
St_b(1250)	4	18.9	18.4	23	24.1	——
	8	31.1	31.3	37.5	39.1	——
St_b(10,000)	4	——	11.5	15.2	——	19.9
	8	21.9	21.9	30.3	——	29.6

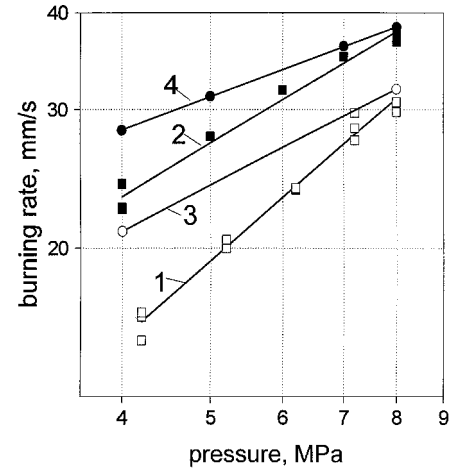


Fig. 3 Dependence of propellant burning rate on pressure: 1 (□), St_b(10,000); 2 (■), St_b(1250); 3 (○), 98% St_b(10,000) + 2% CuO; and 4 (●), 98% St_b(1250) + 2% CuO.

Influence of Initial Temperature

Burning-rate dependencies on the initial temperature T_0, for St_b(1250) and St_b(10,000) propellants at pressures of 4 and 8 MPa are presented in Table 2. The minimum temperature studied for both propellants was −50°C, and the maximum ones were +30°C for St_b(1250) and +50°C for St_b(10,000). The maximum initial temperature did not exceed the melting point of the corresponding polymer. Temperature sensitivity of the propellants β was defined using the formula $\beta = d[\ln(r_b)]/dT$. Absolute error in the measurement of β was ±0.15%/K. Temperature sensitivity of the burning

Table 3 Temperature sensitivity β over different temperature ranges

Propellant	P, MPa	Temperature range, °C			
		−50 to −20	−20 to +20	+20 to +30	+20 to +50
St_b(1250)	4	≤0.15	0.56	0.47	——[a]
	8	≤0.15	0.45	0.42	——[a]
St_b(10,000)	4	——[a]	0.69	——[a]	0.89
	8	≤0.15	0.81	——[a]	≤0.15

[a]Did not measure in experiment.

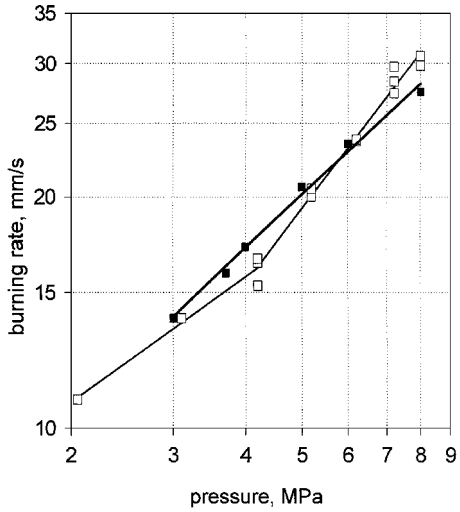


Fig. 4 Dependence of propellant burning rate on pressure: 1 (□), St_b(10,000); and 2 (■), St_b(10,000) with bimodal ADN.

rate over different temperature ranges at 4 and 8 MPa is presented in Table 3.

The decrease of the initial temperature from −20–−50°C did not change the burning rate of the propellants under investigation at pressures of 4 and 8 MPa (Table 2). Besides, combustion instability took place at temperature of −50°C, that is, possibly these conditions are close to the combustion limit of the ADN/PCL composite propellant. In the temperature range of −20–+20°C β for St_b(10,000) is larger than β for St_b(1250) and is equal to 0.7–0.8 and 0.5–0.6 %/K, respectively (Table 3). A further increase of temperature of St_b(1250) to +30°C had little change on β at pressures of 4 and 8 MPa. With an increase of initial temperature of St_b(10,000) propellant to +50°C, β slightly increased to ∼0.9%/K at 4 MPa pressure and decreased to practically zero at 8 MPa.

Influence of Different Additives on the Burning Rate

CuO and Cu_2O. Addition of 2%CuO to St_b(1250) and St_b(10,000) propellant increased the burning rate of these propellants at 4 MPa (Fig. 3) and practically had little effect on the burning rate at 8 MPa. Qualitatively, the effect of CuO on the burning rate of the propellant does not depend on the properties of the polycaprolactone used. Quantitatively, the effect of an additive on the burning rate is characterized by ratio of the burning rates of propellant with and without an additive. Addition of 2%CuO resulted in the increase of the burning rate of St_b(1250) by a factor of 1.23 and of St_b(10,000) by 1.38 at 4 MPa. At addition of 2% CuO parameter ν decreased by a factor of 1.6: to 0.44 for St_b(1250) and to 0.60 for St_b(10,000) (Table 1). Addition of 1%CuO resulted in effects similar to the addition of 2%CuO: an increase of the burning rate of St_b, but in a lesser degree. The burning rate of St_b(1250) increased by 1.15 times and of St_b(10,000) by 1.26 times at 4 MPa. Addition of both 1%CuO and 2%CuO did not change the burning rate of St_b at 8 MPa.

The main ingredient in the propellants under investigation is ADN (89.08%). Therefore, the effect of the addition of CuO on ADN burning rate has been explored. Combustion of pure ADN over the pressure range of 2–8 MPa is unstable.[3] Our investigation confirmed this fact. However, addition of 2%CuO to pure ADN resulted in stabilization of ADN combustion. Burning rates of the 98%ADN + 2%CuO mixture at pressures of 4–8 MPa are compared with those for pure ADN in Fig. 5. The burning rates of 98%ADN + 2%CuO mixture are beneath the lower boundary of the observed scatter of the burning rates of pure ADN. The pressure exponent for 98%ADN + 2%CuO mixture in the pressure range of 4–8 MPa is negative [An effect similar to that attained by adding of Cu_2O (Ref. 4).], that is, the burning rate of this mixture decreases with the increase of pressure from 4 to 8 MPa. The different influence of CuO on the burning rate of pure ADN at 4–8 MPa and that of the St_b propellant might indicate a difference in the mechanism of action of CuO in these two cases.

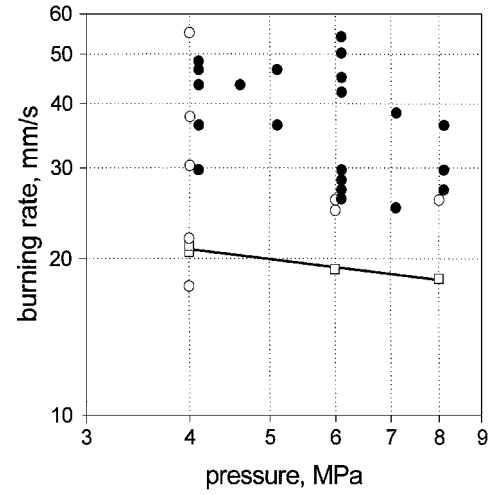


Fig. 5 Dependence of the burning rate of ADN + catalyst mixture on pressure: □, 98%ADN + 2%CuO; ○, ADN (our data); and ●, ADN (Ref. 3).

Addition of 2%Cu_2O promoted combustion of St_b(10,000) at pressure of 4 MPa and decreased parameter ν similar to addition of 1%CuO. During the pressing of the mixture of 98%St_b(1250) with 2%Cu_2O, ignition and burning of this mixture took place; therefore, experiments with 98%St_b(1250) + 2%Cu_2O propellant were not conducted.

PbO and PbO_2. Propellants with additive of PbO and PbO_2 have been also investigated. The effect of 2%PbO on the burning rate of St_b(10,000) at an initial pressure of 4 MPa is less than the effect of 2%CuO. Addition of PbO to St_b(1250) in the amounts of 1 and 2% resulted in nonsteady combustion at the initial pressure of 4 MPa. The burning rate at this pressure varied ∼2 times during the combustion of one strand. Addition of 2%PbO_2 to St_b(10,000) did not particularly influence the pressure dependence of the burning rate (Table 1).

Pb_3O_4. As it is shown in Fig. 6, a decrease in the burning rate of both baseline propellants took place at an initial pressure of 8 MPa upon addition of 2%Pb_3O_4. When the initial pressure was decreased from 8 to 4 MPa, the influence of Pb_3O_4 on the burning rate decreased. Addition of a mixed catalyst, 2%Pb_3O_4 + 2%CuO, did not result in the expected combined effect of the individual catalysts: increase of the burning rate at 4 MPa (CuO) and decrease of the burning rate at 8 MPa (Pb_3O_4). The effect of this composite additive turned out to be very close to that of 2%CuO. In this case Pb_3O_4 played a passive role, at best.

Other Oxidizers and Cyclic Nitramines. The effect of different additives in the amount of 10% to St_b(10,000) propellant has been studied. In Table 1 the parameters of the dependence of the burning rate on pressure over a pressure range of 4–8 MPa for propellants based on St_b(10,000) are shown.

Addition of 10% AN or 10% AP to St_b(10,000) resulted in a decrease of the burning rate at a pressure of 8 MPa and had almost no effect at 4 MPa and parameter ν decreased to 0.84 (AN) and

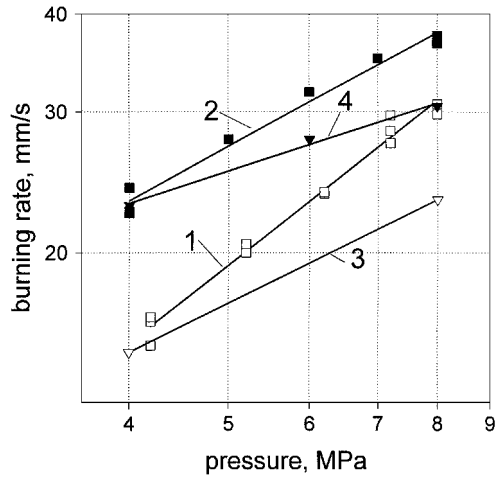


Fig. 6 Dependence of propellant burning rate on pressure: 1 (□), St_b(10,000); 2 (■), St_b(1250); 3 (▽), 98% St_b(10,000) + 2% Pb_3O_4; and 4 (▼), 98% St_b(1250) + 2% Pb_3O_4.

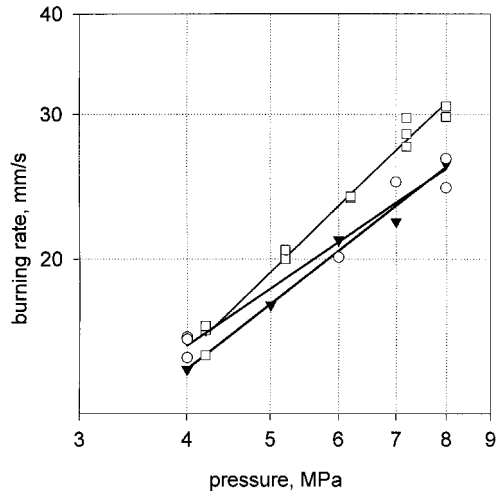


Fig. 7 Dependence of propellant burning rate on pressure: □, St_b(10,000); ▼, 90% St_b (10,000) + 10% AN; and ○, 90% St_b(10,000) + 10% AP.

0.73(AP) (Fig. 7). Addition of 10% RDX or 10% HMX led to an increase of the burning rate at 4 MPa pressure and did not effect the burning rate at 8 MPa. Addition of cyclic nitramines decreased ν to 0.57 (HMX) and 0.54 (RDX) (Fig. 8). Propellants with additives of AN and AP have a positive oxygen balance, and propellants with additives of RDX or HMX have a negative one.

Aluminum. Addition of 10% Al to St_b(10,000) did not change parameter ν, but resulted in worse scatter of the data on the burning rate (Fig. 9). Parameters of the dependence of the burning rate of St_b(1250) propellant with additives of 10%Al (or ALEX) and 10%ALEX + 2% CuO are presented in Table 1.

As it shown in Fig. 9, addition of fine aluminum slightly decreased the burning rate of the propellant at 8 MPa and did not affect it at 4 MPa. At the same time addition of ALEX in the same amount (10%) to St_b(1250) propellant strongly decreased the burning rate over the pressure range of 4–8 MPa and did not change parameter ν. Use of ultrafine aluminum (ALEX) in propellants is necessary to achieve more complete oxidation and the concomitant increase in specific impulse. Subsequent addition of 2%CuO resulted in a significant increase of the burning rate up to that of the propellant with 10%Al additive. Simultaneous addition of ALEX and CuO to the propellant might allow one to reach the optimal characteristics of the propellant (high burning rate, high calculated specific impulse, low ν).

Table 4 Temperature of the final combustion products of St_b(10,000)-based propellants at 4 MPa

Propellant	T_{calc}, K	T_{exp}, K	ΔT, K
St_b	2960	2870	90
98% St_b + 2% PbO_2	2950	2915	35
98% St_b + 2% Pb_3O_4	2950	2910	40
90% St_b + 10% AN	2873	2785	88
90% St_b + 10% AP	2909	2870	39

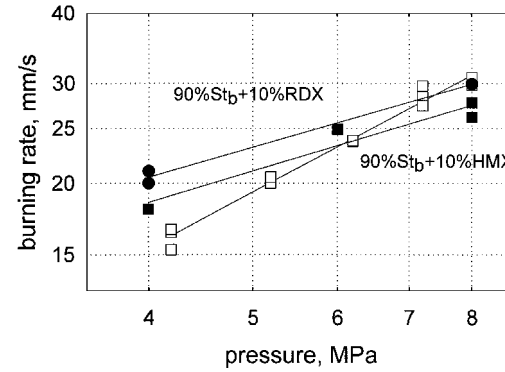


Fig. 8 Dependence of propellant burning rate on pressure: □, St_b(10,000); ■, 90% St_b(10,000) + 10 %HMX; and ●, 90% St_b(10,000) + 10% RDX.

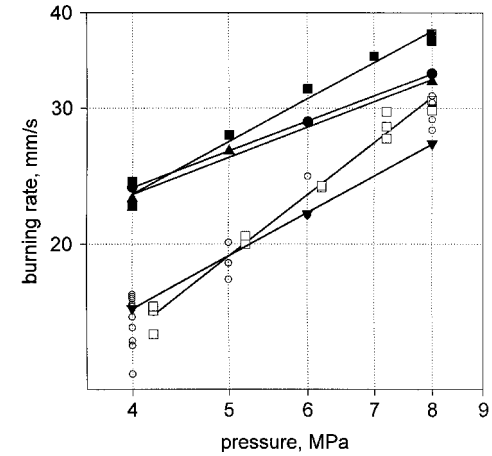


Fig. 9 Dependence of propellant burning rate on pressure: □, St_b(10,000); ○, 90% St_b(10,000) + 10% Al; ■, St_b(1250); ▼, 90% St_b(1250) + 10% ALEX; ●, 88% St_b(1250) + 10% ALEX + 2% CuO; and ▲, 90% St_b(1250) + 10% Al.

Results of Calculations of Specific Impulse

Specific impulse for base propellant (St_b) and also for propellant with additives at 4 MPa and exit pressure of 0.1 MPa was calculated using code "Astra."[19] Results of calculations are presented in Table 1. Addition of such energetic additives as aluminum and nitramines (RDX, HMX) to St_b increases specific impulse. Addition of lead and copper oxides and also oxidizers with less enthalpy of formation (AP, AN) results in a decrease of specific impulse. Combination of two additives (10%ALEX and 2%CuO) gives both a high specific impulse and a low parameter ν.

Specific impulse for AP/PCL propellant of stoichiometric composition was also calculated.[19] The specific impulse of this propellant is less than that of ADN/PCL by 12.9 s and is equal to 234.6 s.

Temperature and Composition of Final Combustion Products

In Table 4 experimental values for the temperature T_{exp} of the final combustion products of St_b(10,000) propellant with and without additives at 4 MPa are presented in comparison with the calculated thermodynamic equilibrium values ($\Delta T = T_{calc} - T_{exp}$). The thermodynamic equilibrium composition of the combustion products and temperatures T_{calc} were calculated with the computer code "Astra."[19] We could not measure the temperature of the final

Table 5 Temperature and concentrations of the final combustion products (percents by volume) of St_b(10,000) and 90%St_b(10,000) + 10%Al propellant at 4 MPa

Propellant	T, K	H_2O	N_2	CO_2	CO	O_2	NO	H_2	OH	H	O
St_b, calc[19]	2960	43.7	34.8	10.5	3.6	1.8	0.9	2.0	2.2	0.2	0.3
St_b, exp[a]	2870	48	35.8	10.9	1.3	1.7	0.6	1.1	——[b]	——[b]	——[b]
90%St_b + 10%Al, calc[19]	3392	34.5	34.4	4.4	9.5	0.8	0.9	9.0	3.6	2.2	0.5
90%St_b + 10%Al, exp[a]	——[b]	41.0	37.0	6.7	6.7	1.4	0.5	6.2	——[b]	——[b]	——[b]

[a]One-stage sampling with following GC analysis. [b]—— was not measured in experiment.

Table 6 Results of processing of temperature profiles in combustion wave of ADN/PCL propellant without and with 2%CuO and of ADN

Propellant	P, MPa	φ, K/m	m, kg/m^2 s	q, J/kg	Q, J/kg	Φ, J/m^{3}s
St_b	4	1.9×10^7	25.3	3.2×10^4	5.4×10^5	6.7×10^{11}
98%St_b + 2%CuO	4	1.3×10^7	36.3	1.6×10^4	6.3×10^5	6.6×10^{11}
Pure ADN[6]	2	10^7	46.4	1.3×10^4	5.5×10^5	——

combustion products for propellants with additives of CuO and Al using uncovered thermocouples. Corrected data for heat loss by radiation[20] are presented in Table 4. In the case of St_b(10,000) propellant at 4 MPa, this radiation correction for cylindrical thermocouples with a diameter of 0.1 mm was equal to ~190 K. Temperature of the final combustion products of St_b(10,000) propellant with radiation correction measured by different thermocouples was equal to 2870 ± 25 K. This temperature is slightly less than the calculated equilibrium temperature [2960 K (Ref. 19)]. The increase of the initial pressure to 8 MPa did not change the temperature of the final combustion products of St_b(10,000).

Final combustion temperatures for the baseline propellant and propellant with AN added are lower than the corresponding calculated thermodynamic equilibrium temperatures by ~90 K. In the case of the additives of AP and lead oxides, experimental and calculated temperatures are consistent with each other (within experimental error). Small additives of PbO_2 and Pb_3O_4 increased experimental temperature value for the baseline propellant by 35 and 40 K, respectively.

Application of the one-stage sampling system with subsequent gas chromatographic (GC) analysis of the composition of the combustion products of St_b(10,000) allowed quantitative determination of such products as N_2, H_2, NO, O_2, CO, and CO_2 (Table 5). With the exception of NO, these combustion products are environmentally friendly. However, the concentration of NO in the combustion products at 4 MPa is less than 1%. Moreover, calculations showed that its concentration decreases to ~0.02% at the nozzle exit at 0.1 MPa (Ref. 19). The largest difference between experimentally determined and calculated equilibrium compositions of combustion products involves the concentration of CO. For more precise determination of the amount of CO in combustion products, a two-stage sampling system was used. Application of this system allowed the determination of the ratio between CO and CO_2 and thus a more precise value of CO concentration, which appeared to be 3.1 ± 0.6%.

In Table 5 experimental and calculated[19] compositions of the combustion products of 90%St_b(10,000) + 10%Al propellant at 4 MPa are presented. We could not measure concentration of H_2O; therefore, the content of H_2O in the combustion products was calculated with aid of material balance equations using the ratio of elements H:N:O:C in the initial propellant. Permanganometric method of analysis of the condensed combustion products[21] showed that ~93% of the initial Al oxidized to Al_2O_3. This fact was taken into account in calculations of the composition of gaseous combustion products of aluminized propellant. According to the thermodynamic calculation, ~99% of the initial amount of aluminum oxidizes to Al_2O_3.

Thermal Structure of Propellant Combustion; Wave Place of Action of CuO Catalyst

To take into account the time response of the thermocouple in the flame when processing experimental data, we used the procedure proposed by Zenin.[22] Corrected temperature profiles for

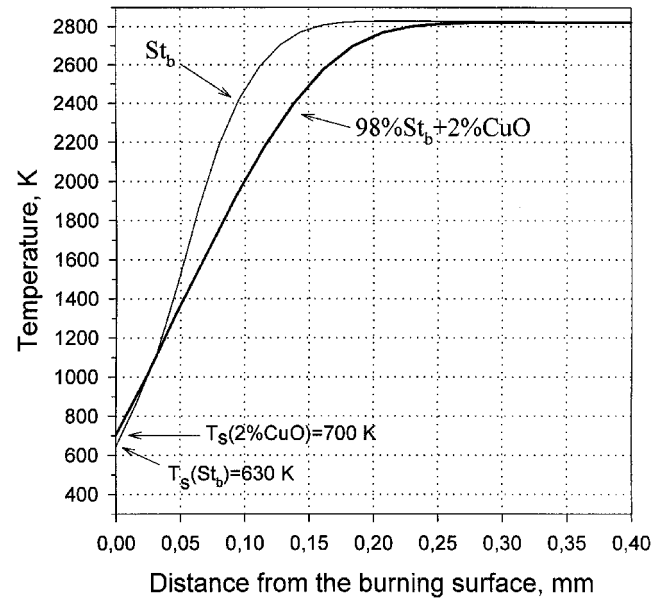


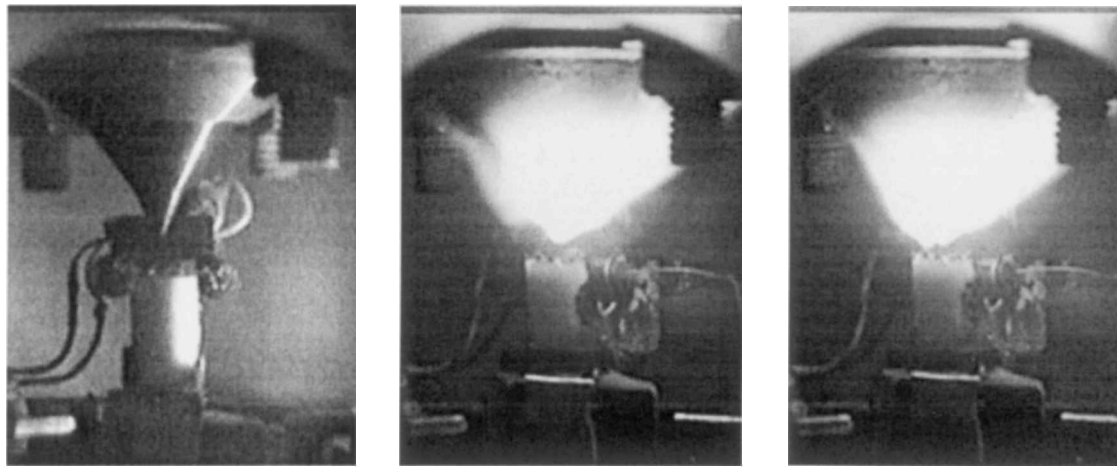
Fig. 10 Corrected temperature profiles in combustion wave of St_b(10,000) and 98%St_b(10,000) + 2%CuO propellants at 4 MPa.

St_b(10,000) and 98%St_b(10,000) + 2%CuO at 4 MPa are shown in Fig. 10. Temperature of the propellant burning surface was determined by a method of "slope break" on the temperature profile[22] in several experiments. Mean value of burning surface temperature T_s of St_b(10,000) at 4 MPa was equal to 630 ± 10 K. It is close to the estimation of T_s for pure ADN (640 K) at 4 MPa (Ref. 6). The thickness of the thermal layer in the condensed phase (CP) was ~180 μm, and L width of the reaction zone in the flame of St_b(10,000) was ~150 μm. The temperature gradient near the burning surface φ was $\sim 1.9 \times 10^7$ K/m. The addition of 2%CuO to St_b resulted in the increase of T_s by 70 K (Fig. 10) and the increase of L by 50 μm at 4 MPa.

Heat feedback q from the flame into the CP by heat conductivity was calculated by the equation $q = -\lambda(T)\varphi$/m, where $\lambda = 4.2 \times 10^{-2}$ W/m K. Heat release in the reaction layer of the CP was calculated using the formula $Q = C(T_s - T_0) - q + q_m$, where $C = 1.26 \times 10^3$ J/kg K, $q_m = 1.34 \times 10^5$ J/kg, $T_0 = 293$ K. The values of λ, C, q_m were the same as in the case of pure ADN.[6] Heat-release rate in the flame was calculated by the approximate formula $\Phi = C_p \varphi m$, where $C_p = 1.39 \times 10^3$ J/kg K (Ref. 6). Addition of 2%CuO to St_b did not change Φ, but decreased q and increased Q by a value of 9.2×10^4 J/kg (Table 6). As a result, the burning rate increased. The data obtained indicate that reactions in the CP control the burning rate of ADN-based propellant. Accuracy of data presented in Table 6 is equal to ±10% for φ, ±15% for q, ±5% for Q, ±5% for m, and ±15% for Φ. Data obtained show that the place of action of the CuO catalyst is in the CP.

Table 7 Concentrations (in mole fractions) of species and temperature in flame of propellant $St_b(1250)$ at 0.1 MPa and of ADN at 0.6 MPa

Flame zone	T, K	H_2O	N_2	N_2O	NO	NH_3	HNO_3	H_2	CO	CO_2	O_2
Luminous zone (exp)	~2600	0.39	0.32	0	0.10	0	0	0.03	0.02	0.12	0.02
Thermodynamic calc.[19]	2695	0.40	0.34	0	0.01	0	0	0.03	0.05	0.09	0.03
Dark zone (exp)	~1120	0.32	0.11	0.20	0.20	0.04	0.01	0.01	0.02	0.08	0.01
Pure ADN dark zone at $L_1 \sim 4$ mm (0.6 MPa) (Ref. 5)	~920	0.31	0.10	0.28	0.23	0.07	0.02	——	——	——	——



a) b) c)

Fig. 11 Video images of combustion of propellant $St_b(1250)$ at 0.1 MPa: a) before the experiment and b) and c) in different times during combustion ($\Delta t = 0.04$ s).

Flame Structure of $St_b(1250)$ Propellant at 0.1 MPa

Experiments showed that $St_b(10{,}000)$ propellant burned without a visible flame at 0.1 MPa. Brown residue (apparently, undecomposed polycaprolactone) remained on the strand holder after the experiment. Temperature of combustion products was ~670 K, which is close to that of pure ADN at 0.1 MPa (Ref. 5). So, one can suppose that at 0.1 MPa only the ADN burns, whereas PCL(10,000) only melts and partially decomposes. Replacement of PCL(10,000) by PCL(1250) resulted in the appearance of a visible flame. However, the flame did not cover the entire burning surface of the strand. Separate jets of flame moving over the strand burning surface during the combustion were observed (Fig. 11). So, the combustion of $St_b(1250)$ at 0.1 MPa has a torch character with formation of separate seats of burning on the burning surface. Video recording of the burning surface with 16-fold magnification revealed the processes that take place on the propellant surface during combustion. The following processes should be noted (see Fig. 12): 1) appearance of sites of darkening on the burning surface (a) with consequent transition of them in small dark spots (b); 2) fusion of these small spots into large spots (c, d), with arrows showing the direction of fusion; 3) appearance of two torches over large spots, the diameter of which is ~1 mm (e); and 4) one of torches lifts-off (f). These spots are probably drops of liquid undecomposed PCL on the molten surface of the ADN. Fusion of small drops of PCL in the bigger drops is caused by the lower melting point of PCL in comparison with ADN.

The measurement of temperature and the determination of combustion product composition were conducted in different experiments. The probe (or thermocouple) during the combustion was located either in the luminous zone (torch) or in dark zone (between torches or far from them). Analysis of the videotape recording allowed the determination of the flame zone, where the probe or thermocouple was located at the moment of measurement.

Results of two experiments on measurement of the temperature profile in flame of $St_b(1250)$ at 0.1 MPa, which confirm the conclusion regarding torch combustion of this propellant, are presented in Fig. 13. Curve 1 in Fig. 13 corresponds to the case when thermocouple was in the torch, and curve 2 corresponds to the case when it was between the torches. The videotape recording showed that a dark zone exists near the burning surface. The width of the dark zone varies from ~1 mm (near bottom of torch) to 3–4 mm (region between torches). Thermocouple measurements revealed the existence of three zones in the flame (Fig. 13): 1) the narrow dark zone adjacent to the burning surface (width of the zone ~0.2–0.3 mm), where the temperature rose from ~600 to ~1200 K; 2) the dark zone (width of the zone ~0.5–~3 mm), where the temperature slightly increased from 1200 to 1450 K; and 3) the luminous zone (torch), where the temperature increased to 2600 K at the distance of 4–8 mm.

Compositions of the combustion products in the luminous and dark flame zones of $St_b(1250)$ propellant are presented in Table 7. Temperature of the combustion products in the luminous zone, which is equal to 2600 K, is slightly less than the calculated equilibrium temperature [2695 K (Ref. 19)], that is, 100% completeness of combustion is not achieved. The presence of NO in combustion products confirms this conclusion. The elemental balance in the luminous zone was in satisfactory agreement (±5%) with that in the propellant. The calculated deficiency of carbon in the combustion products determined in the dark zone is equal to ~50% of the initial amount. This fact indicates that identification of carbon-containing products in the dark zone was incomplete. In addition, we have obtained peaks of the following unidentified masses in the mass spectrum of species near the burning surface of the $St_b(1250)$ propellant: 55, 57, 60, 67, 69, 70, 71, 73, 79, 81, 95, 108, 115. We suggest that masses from 55 to 115 correspond to the decomposition products of PCL.

Discussion

Analysis of Table 1 shows that by using different additives we can influence the specific impulse and burning rate of St_b propellant. Using additives of 2% CuO and 2% Pb_3O_4 parameter ν can be significantly reduced, but at the same time specific impulse also decreases. Addition of nitramines in amount of 10% decreases parameter ν and slightly increases specific impulse. To achieve propellants with high specific impulse and low parameter ν, addition of 10%ALEX + 2%CuO can be done.

Temperature sensitivity of pure ADN over the pressure range of 4–6 MPa and temperature range of −50–+20°C is lower than that for ADN/PCL propellant and is equal to 0.3–0.4%/K. But temperature sensitivity of pure ADN over the range of +20–+80°C is larger than

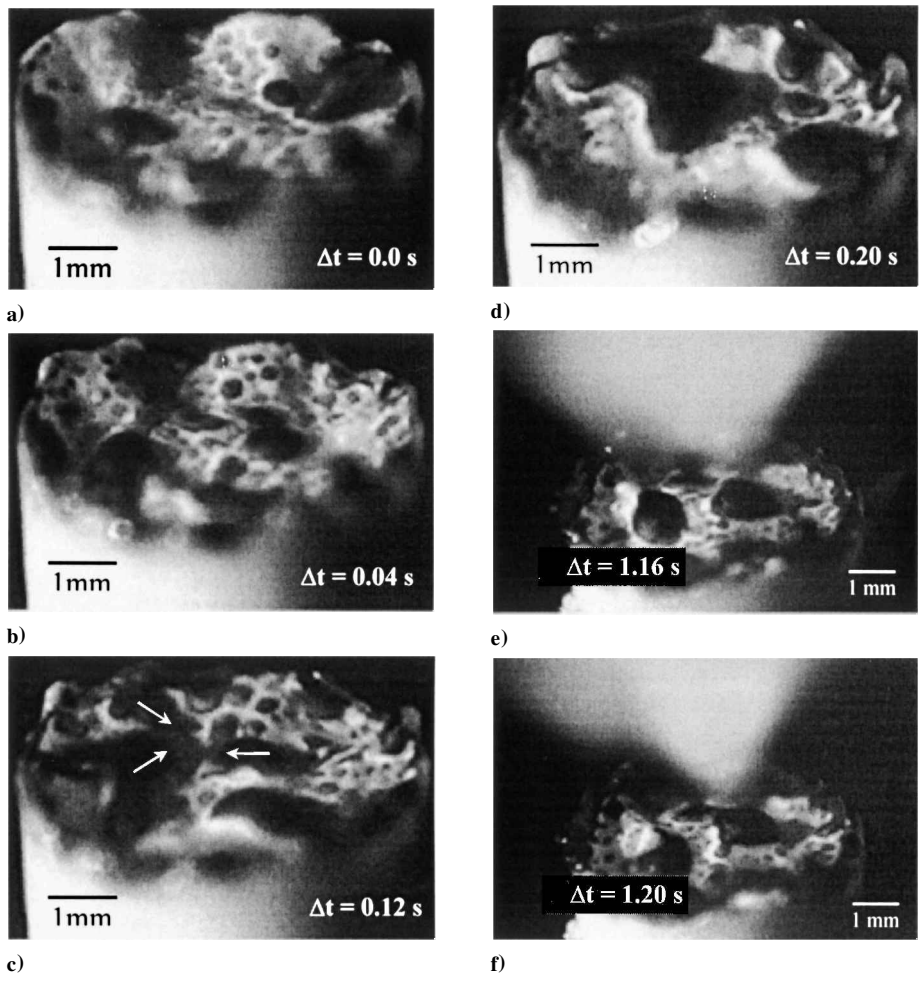


Fig. 12 Video images of the burning surface of propellant St_b(1250) at 0.1 MPa obtained at 16-fold magnification.

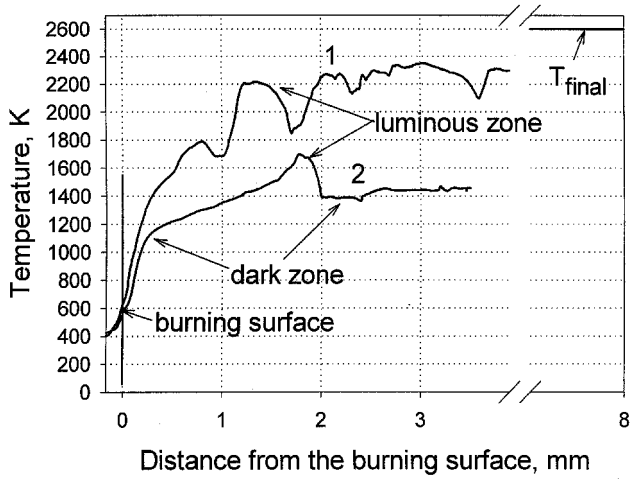


Fig. 13 Temperature profiles in flame of propellant ADN/PCL(1250) at 0.1 MPa.

for the ADN/PCL propellant and is equal to 1.5–1.6%/K (Ref. 6). So, although ADN is the main ingredient in the model St_b propellant, there is no correlation between temperature sensitivity for neat ADN and the ADN-based composite propellant.

Processing of the temperature profiles of both propellants [St_b(10,000) with and without CuO] at 4 MPa showed that heat feedback from flame into CP is small in comparison with Q. Addition of CuO to the St_b(10,000) increased Q, so that the place of action of CuO catalyst is CP. Therefore the reactions in the CP control combustion of the composite propellant as well as in the case of pure ADN.

The burning rate of the composite propellant is lower than that of pure ADN. As it was shown earlier,[4] even small amounts (~1%) of organic fuel (plasticizer, rubber) significantly decrease the burning rate of pure ADN, which is contrary to the influence of additives of binder on the burning rate of AP. Addition of fuel probably inhibits the reactions of ADN decomposition in the CP. The influence of binder properties (molecular weight, melting point) on the burning rate of composite propellant indicates that the effectiveness of inhibition of ADN decomposition reactions in the CP likely depends on these properties. The rate of pyrolysis of PCL(1250) is significantly higher than that of PCL(10,000). Experiments on combustion of St_b propellants at 0.1 MPa just described confirm this conclusion. The difference between the rate of pyrolysis of PCL(10,000) and PCL(1250) could be the reason for their different influence on the burning rate of the propellant. Slower pyrolysis of PCL(10,000) leads to more accumulation of it on the burning surface. As a result of this, reactions of decomposition of ADN become significantly slower in the case of St_b(10,000) propellant. The effect of inhibition of ADN decomposition in the condensed phase by minor additives of hydrocarbon fuels was discussed earlier in Ref. 4. The addition of fuel in the amount of only 1% resulted in a significant decrease of the burning rate of ADN at 0.1 MPa. The subsequent increase in fuel content up to 5% did not affect the burning rate much more. Such a behavior can be explained only assuming that fuel inhibits ADN decomposition. Thus, it is unlikely that the decrease of the burning rate of ADN upon the addition of hydrocarbon fuel can be explained solely by heat loss for evaporation/decomposition of the fuel. A paper devoted to the investigation of ADN/HTPB propellants[7] provides additional confirmation of the prevalence of inhibition over the thermal effect. ADN/HTPB propellants with content of a HTPB in the amount of 3 and 7% had almost the same burning rates at 0.6 MPa (~7.3 and ~7.5 mm/s, respectively), which is

less than the burning rate of pure ADN by a factor of three at this pressure.

Initially, fuel (PCL) and oxidizer (ADN) are distributed uniformly in propellant mixture. During the combustion of $St_b(1250)$ at 0.1 MPa, redistribution of fuel on the burning surface, which is caused by formation of carbon-containing drops (Fig. 12), takes place. It results in variation of oxidizer/fuel ratio in the gas phase near the burning surface. One can assume that space near a small drop is filled mainly by products of decomposition of the oxidizer. The deficiency of carbon-containing products in dark zone confirms this statement. Thus, an invisible lean diffusion flame (dark zone in Table 7) with low product temperature occurs near the small drops of fuel. Fusion of several small drops of partially decomposed PCL into a larger one takes place on the burning surface (Fig. 12c) during the combustion. An intense flow of products from gasification and/or decomposition of fuel exists over the large drop. An interaction between the products of the decomposition of the oxidizer with the fuel decomposition products resulted in the appearance of a luminous diffusion flame directly over the drop. Lifetime of the drop (after appearance of the torch) is equal ~0.1 s. The presence of this luminous torch with high temperature of combustion products over the drop leads to an increase in heat feedback from gas phase to the burning surface and an increase in the temperature of the drop. As a result, an increase in the decomposition rate of the drop occurs. Volume and thickness of the drop then decrease during the combustion. The shape of the drop changes from near hemispherical to a more flat form. Then, some drops divide into smaller drops under the influence of the flow of oxidizer decomposition products from under the drop, and the torch disappears or moves over the remaining part of the drop.

It was discussed earlier that ADN at 0.1 MPa burns without flame (temperature of combustion products ~620 K) and that the combustion products of pure ADN contain ADN vapor.[5] During the investigation of the flame structure of $St_b(1250)$ at 0.1 MPa peaks with 17, 30, 44, and 46 m/z were detected near the burning surface at temperature of ~600 K. The ratio between them is not given here, but this ratio corresponds to the ratio of these peaks in the mass spectrum of ADN vapor.[5] The comparison of combustion products composition of $St_b(1250)$ in the dark flame zone with that of pure ADN at 0.6 MPa at a distance from the burning surface $L_1 \sim 4$ mm (Table 7) shows that the compositions of nitrogen-containing species and the temperatures are close. A similar conclusion was made in the investigation of ADN/HTPB(97/3) propellant[7] and ADN/GAP(82.5/17.5) sandwiches.[9] One can suppose that in the narrow (dark) flame zone of the propellant (~0.3 mm at 0.1 MPa), generally the same reactions as in the dark zone adjacent to the burning surface of pure ADN at 0.6 MPa occur. Temperature in the dark zone of propellant is higher than that of the dark zone of pure ADN by 200 K. This fact can be explained by reactions of interaction between oxidizer and binder and/or their decomposition products with formation of CO and CO_2, which occur in the CP and/or in a narrow zone near the burning surface.

Accordingly, experimental results indicate the conclusions that CuO catalyst acts in the CP. Usually the effect of additives on propellant combustion has a complicated character. Combustion chemistry of ADN-based propellants is closer to that of double-based ones than to that of the other types of propellants. In both cases reactions of nitrogen-containing species in the CP and in the gas phase play an important role. According to Ref. 23, in the case of double-based propellants a significant catalytic effect of CuO appears only when formation of a carbonaceous skeleton and the accumulation of catalyst on the burning surface take place. As this skeleton contains a large amount of agglomerates with the catalyst, the coefficient of thermal conductivity of this skeleton at the burning surface is higher than that of the propellant without additive. As a result, additional heat release appears near the burning surface. This heat release accelerates reactions in both CP and gas phase near the burning surface, and as a consequence the burning rate increases. Additionally, in the case of addition of CuO to $St_b(10{,}000)$ the larger increase of the burning rate in comparison with $St_b(1250)$ is caused by the larger accumulation of products of pyrolysis of PCL(10,000) at the burning surface. However, the main mechanism of action of CuO catalyst relates to chemical reactions with it. The mentioned mechanism of increase of the burning rate caused by the accumulation of the catalyst on the burning surface and the increase of thermal conductivity of the near-surface layer is an additional one to this main mechanism.

Conclusions

Experiments on investigation of combustion of ADN/PCL propellant of stoichiometric composition at 4 MPa were conducted in conditions close to that typical of the combustion chamber of a rocket motor. It was shown that experimentally determined temperature and composition of combustion products are close to that at equilibrium. Thus, it can be stated that experimentally derived specific impulse for this propellant will be close to calculated one.

The comprehensive study of the combustion of ADN/PCL propellant showed that the burning rate of this propellant is controlled by both oxidizer and binder. Reactions of ADN decomposition are responsible for heat release in the condensed phase. On the one hand, PCL inhibits the reactions of ADN decomposition in the condensed phase. This leads to a decrease of the burning rate. On the other hand, reactions between decomposition products of PCL with those of ADN result in intensification of gas phase processes in the flame. CuO catalyst at 4 MPa increases the rate of reactions and heat release in the condensed phase and in the gas phase near the burning surface. The mechanism of influence of CuO catalyst on combustion of ADN-based propellants is probably similar to the mechanism of its influence on double-based propellants. Slight modification of the composition of the baseline propellant by minor additives of CuO or Pb_3O_4 and the use of polymers with different molecular weights allowed us to obtain a number of propellant formulations with different pressure dependence of the burning rate at 4–8 MPa.

ADN-based propellants have higher specific impulse than AP-based propellants. Also, the combustion properties of ADN-based propellants differ considerably from those of AP-based propellants making prior knowledge of AP-based propellant design of little use. This fact should be taken into account when tailoring the composition of ADN-based propellants. Data obtained via this tailoring can be used for development of a combustion model of ADN-based propellants.

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References

[1]Pak, Z., "Some Ways to Higher Environmental Safety of Solid Rocket Applications," AIAA Paper 93-1755, June 1993.

[2]Chan, M. L., Reed, R., and Ciaramitaro, D. A., "Advances in Solid Propellant Formulations," *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, edited by V. Yang, T. B. Brill, and W.-Z. Ren, Progress in Astronautics and Aeronautics, Vol. 185, AIAA, Reston, VA, 2000, pp. 185–206.

[3]Fogelzang, A. E., Sinditskii, V. P., Egorshev, V. Y., Levshenkov, A. I., Serushkin, V. V., and Kolesov, V. I., "Combustion Behavior and Flame Structure of Ammonium Dinitramide," *Proceedings of the 28th International Annual Conference of ICT*, Fraunhofer Inst. Chemische Technologie, Karlsruhe, 1997, pp. 99-1–99-14.

[4]Strunin, V. A., D'yakov, A. P., and Manelis, G. B., "Combustion of Ammonium Diniramide," *Combustion and Flame*, Vol. 117, No. 1–2, 1999, pp. 429–434.

[5]Korobeinichev, O. P., Kuibida, L. V., Paletsky, A. A., and Shmakov, A. G., "Molecular-Beam Mass-Spectrometry to Ammonium Dinitramide Combustion Chemistry Studies," *Journal of Propulsion and Power*, Vol. 14, No. 6, 1998, pp. 991–1000.

[6]Zenin, A. A., Puchkov, V. M., and Finjakov, S. V., "Physics of ADN Combustion," AIAA Paper 99-0595, Jan. 1999.

[7]Korobeinichev, O. P., and Paletsky, A. A., "Flame Structure of ADN/HTPB Composite Propellants," *Combustion and Flame*, Vol. 127, No. 3, 2001, pp. 2059–2065.

[8]Parr, T., and Hanson-Parr, D., "Solid Propellant Flame Chemistry and Structure," *Non-Intrusive Combustion Diagnostics*, edited by K. K. Kuo and T. P. Parr, Begell House, New York, 1994, pp. 571–599.

[9]Kuibida, L. V., Korobeinichev, O. P., Shmakov, A. G, Volkov, E. N., and Paletsky, A. A., "Mass Spectrometric Study of Combustion of GAP- and ADN-Based Propellants," *Combustion and Flame*, Vol. 126, No. 3, 2001, pp. 1655–1661.

[10]Weiser, V., Eisenreich, N., Baier, A., and Eckl, W., "Burning Behavior of ADN Formulations," *Propellants, Explosives, Pyrotechnics*, Vol. 24, No. 3, 1999, pp. 163–167.

[11]Chan, M. L., Reed, R., Turner, A., Atwood, A., and Curran, P., "Properties of ADN Propellants," *Proceedings of the 5th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials*, edited by K. K. Kuo and L. T. Deluca, Begell House, New York, 2002, pp. 492–501.

[12]Ramaswamy, A. L., "Energetic-Material Combustion Experiments on Propellant Formulations Containing Prilled Ammonium Dinitramide," *Combustion, Explosion and Shock Waves*, Vol. 36, No. 1, 2000, pp. 119–124.

[13]Parr, T., and Hanson-Parr, D. M., "Solid Propellant Diffusion Flame Structure," *Proceedings of the Twenty-Sixth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1996, pp. 1981–1987.

[14]Sinditskii, V. P., Fogelzang, A. E., Egorshev, V. Y., Levshenkov, A., I., Serushkin, V. V., and Kolesov, V. I., "Combustion Peculiarities of ADN and ADN-based Mixtures," *Proceedings of the 5th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials*, edited by K. K. Kuo and L. T. Deluca, Begell House, New York, 2002, pp. 502–512.

[15]Babuk, V. A., Vassiliev, V. A., and Naslednikov, P. A., "Experimental Study of Evolution of Condensed Combustion Products in Gas Phase of Burning Solid Rocket Propellant," *Proceedings of the 5th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials*, edited by K. K. Kuo and L. T. Deluca, Begell House, New York, 2002, pp. 381–396.

[16]Tereshenko, A. G., Korobeinichev, O. P., Skovorodko, P. A., Paletsky, A. A., and Volkov, E. N., "Probe Method for Sampling Solid-Rocket Combustion Products at Temperatures and Pressures Typical of a Rocket Combustion Chamber," *Combustion, Explosion and Shock Waves*, Vol. 38, No. 1, 2002, pp. 81–91.

[17]Korobeinichev, O. P., "Flame Structure of Solid Propellants," *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, edited by V. Yang, T. B. Brill, and W.-Z. Ren, Progress in Astronautics and Aeronautics, Vol. 185, AIAA, Reston, VA, 2000, pp. 335–354.

[18]Korobeinichev, O. P., Kuibida, L. V., Paletsky, A. A., and Chernov, A. A., "Study of Solid Propellant Flame Structure by Mass-Spectrometric Sampling," *Combustion Science and Technology*, Vol. 113–114, 1996, pp. 557–572.

[19]Belov, G. V., ASTRA Code, Ver. 2/24, Moscow State Technical University, Moscow, 1990 (in Russian).

[20]Fristrom, R. M., *Flame Structure and Processes*, Oxford Univ. Press, New York, 1995, pp. 100–120.

[21]Fedotova, T. D., Glotov, O. G., and Zarko, V. E., "Chemical Analysis of Aluminum as a Propellant Ingredient and Determination of Aluminum and Aluminum Nitride in Condensed Combustion Products," *Propellants, Explosives, Pyrotechnics*, Vol. 25, No. 6, 2000, pp. 325–332.

[22]Zenin, A. A., "Experimental Investigation of the Burning Mechanism of Solid Propellants and Movement of Burning Products," Ph.D. Dissertation, Physical and Mathematical Sciences, Inst. of Chemical Physics, USSR Academy of Sciences, Moscow, 1976 (in Russian).

[23]Denisyuk, A. P., Demidova, L. A., and Galkin, V. I., "The Primary Zone in the Combustion of Solid Propellants Containing Catalysts," *Combustion, Explosion and Shock Waves*, Vol. 31, No. 2, 1995, pp. 161–167.