ENVIRONMENTALLY FRIENDLY ADN-BASED SOLID ROCKET PROPELLANT WITH GOOD BALLISTIC CHARACTERISTICS

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ABSTRACT

Further progress in solid rocket propulsion is not possible without some drastic breakthrough. At the same time a development of new solid rocket propellants based on new environmentally friendly ingredients with high enthalpy of formation is not possible without understanding of mechanism and chemistry of combustion. Ammonium dinitramide (ADN)-based propellants are environmentally friendly. These propellants have higher specific impulse than AP-based propellants. For these reasons there is great interest in the combustion properties of ADN propellants; this is especially true as they differ considerably from the combustion properties of AP making prior knowledge of AP propellant design of little use. This paper contains results of experimental investigations, on the basis of which the composition of environmentally friendly ADN-based solid rocket propellant with good ballistic characteristics (high specific impulse, weak dependence of the burning rate on pressure) was proposed. Effective catalyst (CuO) and inhibitor (Pb_3O_4), addition of which allowed to obtain weak dependence of the burning rate on pressure ($\nu \sim 0.5$), have been found. It has been established that place of action of CuO catalyst is condensed phase. The effect of additives (HMX, RDX, AP, ammonium nitrate, aluminum of different fractions), initial temperature and also of the molecular weight of polymer on the burning rate has been studied. Two types of polycaprolactone (PCL) with molecular weight of 10000, PCL(10000), and 1250, PCL(1250), were used as a binder. It has been shown that the molecular weight of polymer influence on the burning rate. Besides, flame structure and combustion mechanism of ADN-based composite solid propellants have been studied by microthermocouple technique, probe mass spectrometry and videotape recording. A torch non-stationary regime of combustion and multizone flame structure have been established. Three zones of chemical reactions in flame of ADN/PCL(1250) propellant have been detected. Vapor of ADN, products of decomposition of the oxidizer and binder, and also products of their interaction have been observed near the burning surface. Complete composition of combustion products in luminous flame zone was also determined. It was established that burning rate of ADN/PCL(1250) propellant (as in the case of pure ADN and ADN/HTPB propellant) is controlled by reactions in condensed phase. Computer modeling of chemical reactions in the dark flame zone using experimental data on composition and temperature of species near the burning surface has been conducted. The calculated temperature and concentration of species in flame have been compared with experimental data. Obtained data on flame structure of ADN/PCL propellant can be used for development of combustion model of this propellant.

Key Words: solid rocket propellant, ammonium dinitramide (ADN), polycaprolactone, specific impulse

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
L	= width of the reaction zone
L_l	= distance from the burning surface
m	= mass burning rate
P	= pressure
q	= heat feedback from gas into condensed phase
q_m	= heat of melting
Q	= heat release in the reaction layer of the condensed phase
r_b	= burning rate
T	= temperature
T_o	= initial propellant temperature
T_s	= burning surface temperature
β	= temperature sensitivity
λ	= coefficient of heat conductivity of gas phase
ν	= pressure exponent
φ	= temperature gradient in gas phase close to the burning surface
Φ	= heat release rate in the gas phase

INTRODUCTION

Ammonium dinitramide (ADN) is a powerful chlorine-free oxidizer, which can replace ammonium perchlorate (AP) in solid rocket propellants. Since the combustion products of ADN-based propellants are not toxic, these propellants are environmentally friendly and investigation of them is of great interest. ADN-based propellant is convenient system for investigation of mechanism and chemistry of composite solid rocket propellant combustion, because of simplicity of 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 the 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, which are devoted to the study of the combustion characteristics and combustion mechanism of the composite ADN-based propellants and sandwiches with different type of binder such as hydroxyl-terminated polybutadiene (HTPB),[7,8] glycidyl azide polymer (GAP),[8,9] paraffin,[3,10] poly(diethyleneglycol-4,8-dinitraza undeconate) (ORP-2A)/nitrate ester (NE) and polycaprolactone polymer (PCP)/NE.[11]

One of the objectives of the study of propellant combustion mechanism is the development of a combustion model, which 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[12]. 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, George 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. 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.[3] However, even small amounts of organic additives (~1%) result in a reduction of both burning rates and their scatter in this pressure range.[4,13] On the contrary, 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.[4]

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/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, initial temperature and addition of different additives on the burning rate and pressure exponent ν, (4) 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 (m.p.) of ADN is 365-367 K. Two types of PCL with different molecular weights of 10000 (PCL(10000)), and 1250 (PCL(1250)) were used. The former polymer at room temperature is flake (m.p. 333 K) and the latter one is a waxy solid (m.p. 309-321 K). Fine crystalline powder of ADN with an average particle size of ~ 40 μm was used for preparation of the composite propellants. Non-cured 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. The sides of the strands were inhibited with a thin layer of the vacuum silicone grease. Density of strands was 1.58 g/cm^3. 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. Accuracy of measurement of the burning rate was equal ±5%. The system containing a massive copper block with a cylindrical cavity for the strand was used for investigation of the temperature sensitivity of the propellant burning rate. Copper block had two thin splits for observation of moving burning surface during combustion. Copper block was cooled by vapor flow of liquid nitrogen or heated by hot water. The temperature of the block was controlled using copper-constantan thermocouple.

Aluminum is commonly used as an additive to solid rocket propellants for improving performance. In this study, aluminum powder with spherical particles ~ 15 μm were used. However ammonium dinitramide can not oxidize aluminum as effectively as ammonium perchlorate[2,14]. In order to increase completeness of oxidation of aluminum in ADN-based propellants, ultrafine aluminum can be used. Electro-exploded aluminum (ALEX) with particle size of ≤ 0.1 μm was used in this study. Specific surface area of ALEX powder was ~ 12 m^2/g.

Probe mass spectrometry is the most effective and universal method for investigation of solid propellant flame structure.[15] It allows detecting all the stable species present in the flame and also to determine their concentrations and their spatial distributions. Flame structure has been studied at 0.1 MPa of argon using the set-up with molecular beam sampling system combined with TOFMS.[16] Temperature profiles in gas phase of propellant flame at 0.1 MPa were measured by WRe(5%)-WRe(20%) thermocouples (thickness of 100 μm) covered by a thin layer of Ceramobond-569. 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.

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(10000) propellants over a pressure range of 4-8 MPa are shown in Fig. 1. Parameters A and ν of the dependence of the burning rate on pressure $r_b=AP^{\nu}$ (r_b in mm/s, P in MPa) are given in Table 1. The St_b(10000) has a high pressure dependence exponent (ν = 1). Replacement of PCL(10000) 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. 1 and Table 1). The possible reason of observed difference in burning rate of these two propellants is considered in chapter discussion.

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)		St_b(10000)	
		A	ν	A	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% 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

Influence of initial temperature. Burning rate dependencies on the initial temperature (T_o, °C) were studied for St_b(1250) and St_b(10000) propellants at pressures of 4 and 8 MPa. 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(10000). The maximum initial temperature did not exceed the melting point of the corresponding polymer. Temperature sensitivity of the propellants (β, %/K) was defined using the formula $\beta=d(\ln(r_b))/dT$. Absolute error in the measurement of β was ±0.15%/K. The decrease of the initial temperature from -20°C to -50°C did not change the burning rate of the propellants under investigation at pressures of 4 and 8 MPa. Besides, combustion instability took place at temperature of -50°C, i.e. possibly these conditions are close to the combustion limit of the ADN/PCL composite propellant. In the temperature range of -20°C to +20°C β for St_b(10000) is larger than β for St_b(1250) and is equal to 0.7-0.8 and 0.5-0.6 %/K respectively. 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(10000) 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. Addition of 2%CuO to St_b(1250) and St_b(10000) propellant increased the burning rate of these propellants at 4 MPa (Fig. 1) and practically did not 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 1.23 times and of St_b(10000) by 1.38 times at 4 MPa. At addition of 2% CuO parameter ν decreased by 1.6 times: to 0.44 for St_b(1250) and to 0.60 for St_b(10000) (Table 1). Addition of 1%CuO similar to addition of 2%CuO resulted in the increase of the burning rate of St_b but in less degree. The burning rate of St_b(1250) increased by 1.15 times and of

$St_b(10000)$ 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.

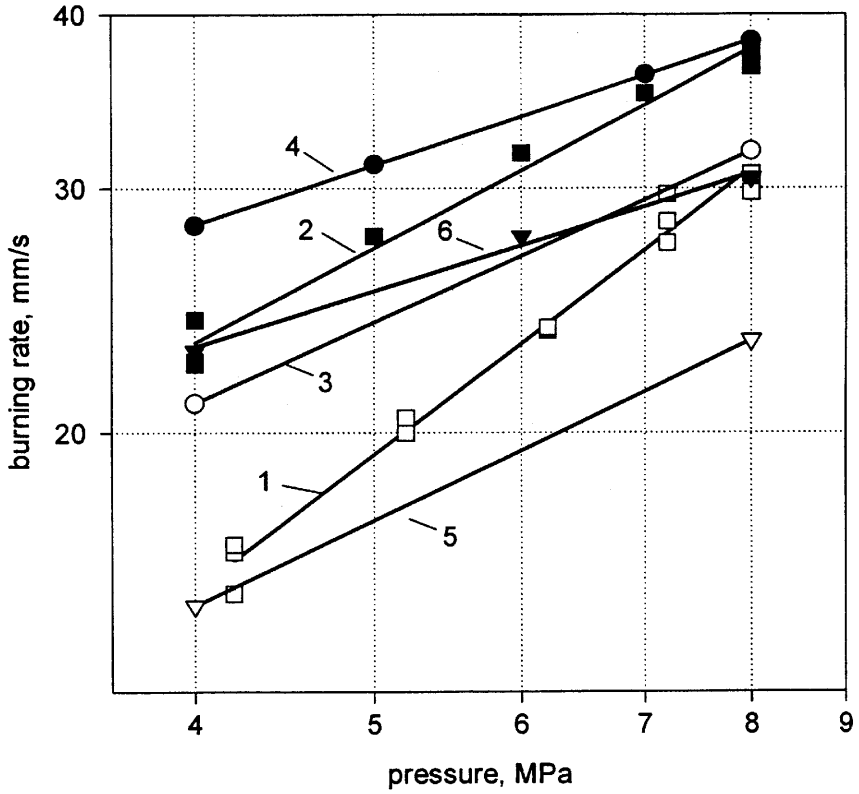

Figure 1. The dependence of propellant burning rate on pressure:
1 (□) - $St_b(10000)$; 2 (■)- $St_b(1250)$; 3 (○) - 98% $St_b(10000)$ +2% CuO;
4 (●) - 98% $St_b(1250)$+2% CuO; 5 (▽) - 98% $St_b(10000)$ +2% Pb_3O_4;
6 (▼) - 98% $St_b(1250)$+2% Pb_3O_4.

The main ingredient of 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 the 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. It is noticeable that the burning rates of 98%ADN+2%CuO mixture are less than the lower boundary of observed scatter of the burning rates of pure ADN. Pressure exponent for 98%ADN+2%CuO mixture in pressure range of 4-8 MPa is negative (similar to additive[4] of Cu_2O), i.e. 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 may indicate a difference in mechanism of action of CuO in these two cases.

As it is shown in Fig. 1 a decrease in the burning rate of both baseline propellants took place upon addition of 2%Pb_3O_4 at 8 MPa. When the initial pressure was decreased from 8 MPa 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.

Addition of 10% of ammonium nitrate (AN) or 10% AP to $St_b(10000)$ resulted in a decrease of the burning rate at a pressure of 8 MPa and had almost no effect at 4 MPa, parameter ν decreased to 0.84 (AN) and 0.73(AP). 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). It is noteworthy that propellants with additives of AN and AP have a positive oxygen balance and propellants with additives of RDX or HMX have a negative one.

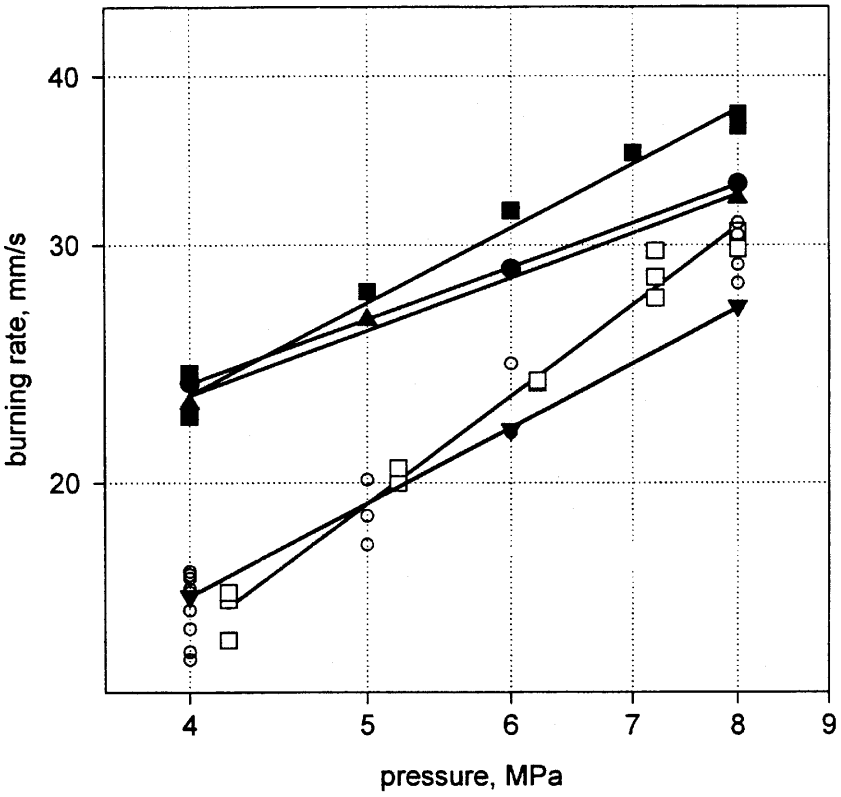

Figure 2. The dependence of propellant burning rate on pressure: (□) - $St_b(10000)$; (○) – 90% $St_b(10000)$ +10% Al; (■) - $St_b(1250)$; (▼) – 90% $St_b(1250)$ + 10% ALEX; (●) – 88% $St_b(1250)$ + 10% ALEX + 2% CuO; (▲) – 90% $St_b(1250)$ + 10% Al.

Addition of 10% Al to $St_b(10000)$ did not change parameter ν but resulted in worse reproducibility of the data on the burning rate (Fig. 2). 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. 2 addition of fine aluminum slightly decreased the burning rate of the propellant at 8 MPa and did not effect 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. Subsequent addition of 2%CuO resulted in a significant increase of the burning rate up to the burning rate of the propellant with 10%Al additive. So, simultaneous addition of ALEX and CuO to the propellant may allow one to reach the optimal characteristics of the propellant (high burning rate, high calculated specific impulse, low ν).

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".[17] 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 decrease of specific impulse. Combination of two additives (10%ALEX and 2%CuO) gives both high specific impulse and low parameter ν.

Besides, specific impulse for AP/PCL propellant of stoichiometric composition was calculated. The specific impulse of this propellant is less than that of ADN/PCL by 12.9 s and is equal to 234.6 s.

Thermal Structure of Propellant Combustion Wave at 4MPa. Mechanism and Place of Action of CuO Catalyst.
Temperature of the propellant burning surface was determined by a method of "slope break" on the temperature profile[18] in several experiments. In Fig. 3 the part of initial profile (showing "slope break") near the burning surface for $St_b(10000)$ is presented. We took into account the time response of the thermocouple using procedure described in Ref.[18] when processing the experimental data. Correction for surface temperature was equal to ~ 70 K. Corrected temperature profiles are shown in Fig. 3. Mean value of burning surface temperature (T_s) of $St_b(10000)$ was equal to 630±10 K. It is close to estimation of T_s for pure ADN (640K)[6] at 4 MPa. The thickness of the thermal layer in the condensed phase (CP) was ~ 180 μm, and width of the reaction zone in the flame, L, for $St_b(10000)$ was ~ 150 μm. The temperature gradient near the burning surface, φ, was ~ 1.9×10^7 K/m. The addition of 2%CuO to St_b resulted in the increase of T_s by 70 K (Fig. 3) 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 equation $q=-\lambda(T)\varphi/m$, where λ - coefficient of heat conductivity of gas phase (4.2×10^{-2} W/m K) and m - mass burning rate. Heat release in the reaction layer of the CP, Q, was calculated using the formula $Q=C(T_s-T_o)-q+q_m$, where C - coefficient of specific heat of CP (1.26×10^3 J/kg K), q_m - heat of melting (1.34×10^5 J/kg), T_o – initial temperature (293 K). The values of λ, C, q_m were taken 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 - coefficient of specific heat of gas phase (1.39×10^3 J/kg K).[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 2). As a result the burning rate increased. The obtained data indicate that reactions in the CP control the burning rate of ADN-based propellant. Accuracy of data presented in Table 2

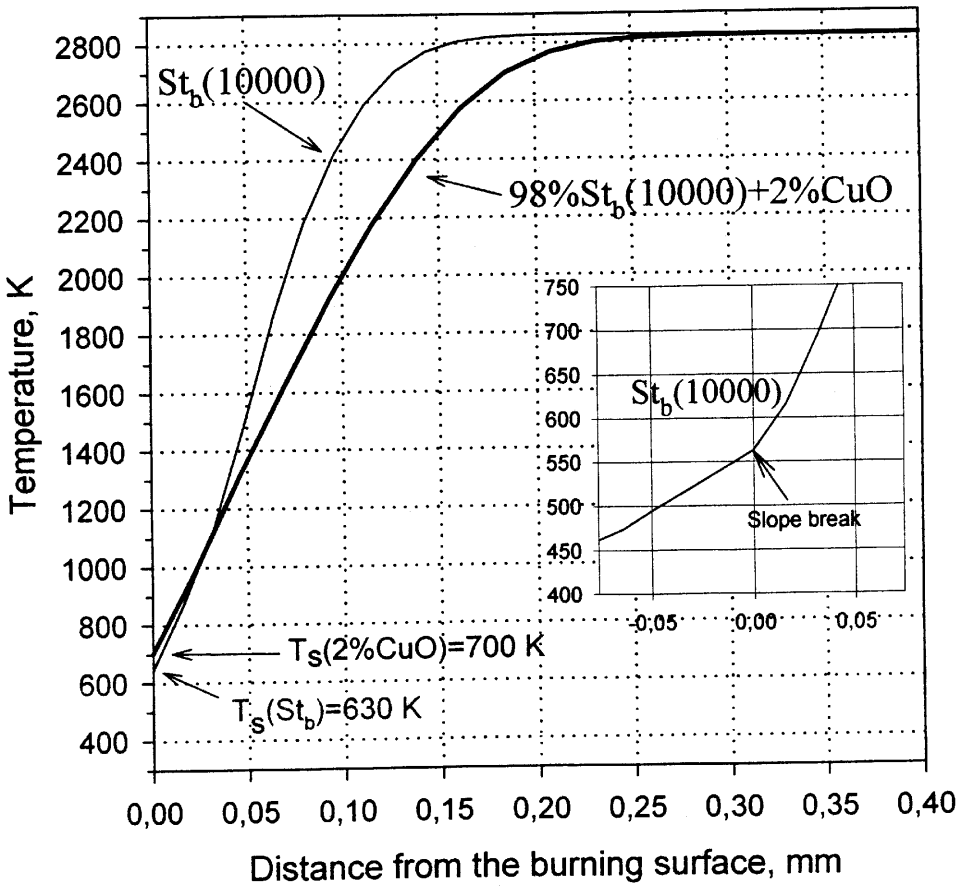

Figure 3. Corrected temperature profiles in combustion wave of $St_b(10000)$ and $98\%St_b(10000)+2\%CuO$ propellants at 4 MPa.

is equal to ± 10% for φ, ± 15% for q, ± 5% for Q, ± 5% for m and ± 15% for Φ. Data obtained show that place of action of CuO catalyst is CP.

Table 2
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	-

Flame Structure of St_b(1250) Propellant at 0.1 MPa

Experiments showed that St_b(10000) propellant burned without visible flame at 0.1 MPa. Brown residue (apparently, undecomposed polycaprolactone) remained on strand holder after experiment. Temperature of combustion products was ~ 670 K, which is close to that of pure ADN[5] at 0.1 MPa. So, one can suppose that at 0.1 MPa only ADN burns whereas PCL(10000) only melts and partially decomposes. Replacement of PCL(10000) by PCL(1250) resulted in the appearance of the visible flame. However, flame did not cover the whole burning surface of strand. Separate jets of flame moving over the strand burning surface during the combustion were observed. 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 processes, which take place on the propellant surface during combustion. Following processes should be noted (see Fig. 4): 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 in large spots (c, d), arrows show the direction of fusion; 3) appearance of two torches over large spots, diameter of which is ~ 1 mm (e); 4) one of torches lift-off (f); 5) complete disappearance of one torch (g). These spots are probably drops of liquid undecomposed PCL on the surface of ADN. Fusion of small drops of PCL in bigger drops is caused by less 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 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 0.1MPa, which confirm the conclusion regarding torch combustion of this propellant, are presented in Fig. 5. Curve 1 in Fig. 5 corresponds to the case when the thermocouple moved from the torch to the burning surface. Abrupt fallings of temperature on curve 1 are connected with changing of torch location with respect to thermocouple. Curve 2 corresponds to the case when the thermocouple moved to the burning surface from the dark zone. Abrupt increase of temperature at the distance of about 2 mm relates to torch appearance near the burning surface. 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 existence of three zones in the flame (Fig. 5): 1) the narrow dark zone adjacent to the burning surface (width of the zone ~ 0.2-0.3 mm), where the temperature grew from ~ 600 K to ~ 1150 K, 2) the dark zone (width of the zone ~ 0.5 to ~ 3 mm), where the temperature slightly increased from 1150 K to 1450 K, 3) the luminous zone (torch), where the temperature increased to 2600 K at the distance of 4-8 mm.

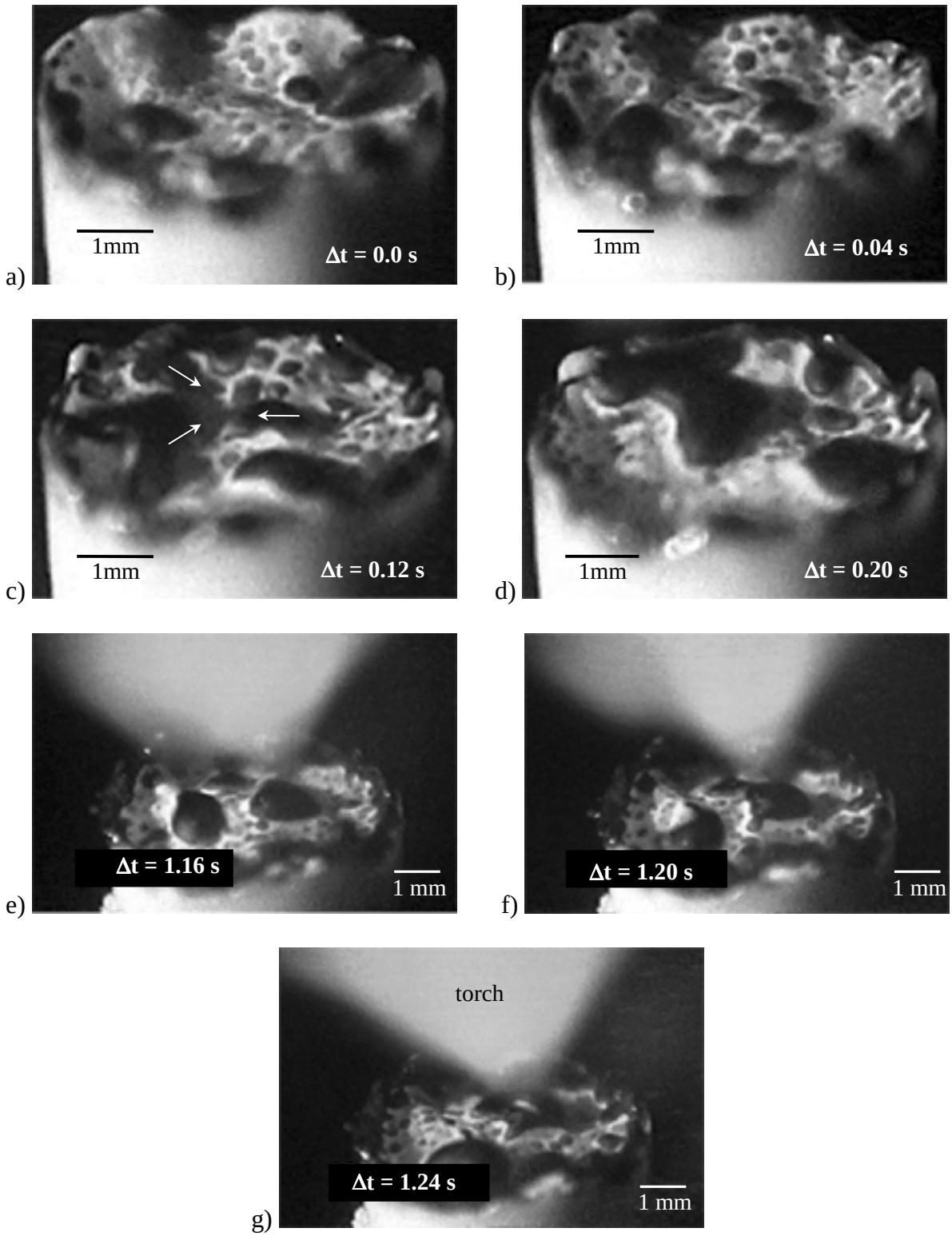

Figure 4. Video images of the burning surface of propellant $St_b(1250)$ at 0.1 MPa.

Compositions of the combustion products in the luminous and dark flame zones of $St_b(1250)$ propellant are presented in Table 3. Temperature of the combustion products in luminous zone, which is equal to 2600 K, is slightly less than the calculated equilibrium temperature[17] (2695 K), i.e. 100% completeness of combustion is not achieved. Presence of NO in combustion products confirms this conclusion. The element 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.

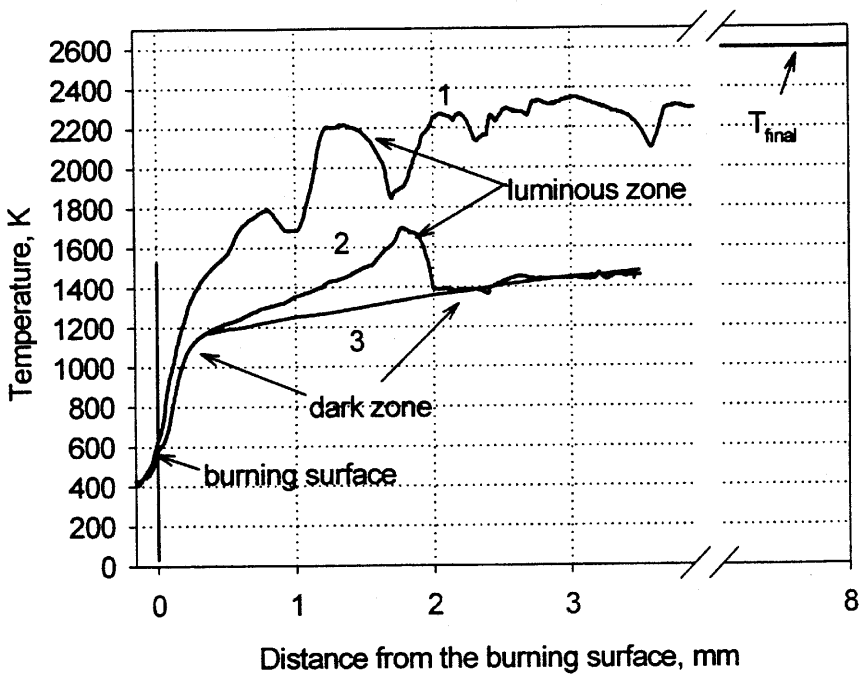

Figure 5. Temperature profiles in flame of propellant ADN/PCL(1250) at 0.1 MPa.

Besides, we have obtained peaks of the following unidentified masses in 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 are responsible for decomposition products of PCL.

Table 3

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

	Dark zone (exp)	Pure ADN dark zone at $L_1 \sim 4$mm (0.6 MPa)[5]	Dark zone of propellant far from surface (exp)	Dark zone of propellant far from surface (modeling)	Luminous zone (exp)	Thermod. calc.[17]
T, K	~1120	~920	~1400	1410	~2600	2695
H_2O	0.32	0.31	0.38	0.38	0.39	0.4
N_2	0.11	0.1	0.15	0.15	0.32	0.34
N_2O	0.2	0.28	0.2	0.19	0	0
NO	0.2	0.23	0.15	0.16	0.1	0.01
NH_3	0.04	0.07	0.01	0.01	0	0
HNO_3	0.01	0.02	0	0	0	0
H_2	0.01	-	0.01	0	0.03	0.03
CO	0.02	-	0.01	0.01	0.02	0.05
CO_2	0.08	-	0.09	0.08	0.12	0.09
O_2	0.01	-	0.01	0.01	0.02	0.03

DISCUSSION

Analysis of Table 1 shows that using different additives we can influence on 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 reduces. Addition of nitramines in amount of 10% allows to decrease parameter ν and slightly increase specific impulse. For propellant with high specific impulse and low parameter ν additive of 10%ALEX+2%CuO can be used.

Temperature sensitivity for pure ADN over the pressure range of 4-6 MPa and temperature range of –50 to +20°C is less than that for ADN/PCL propellant and is equal to 0.3-0.4%/K. But temperature sensitivity for pure ADN over the range of +20 to +80°C is larger than for the ADN/PCL propellant and is equal to 1.5-1.6%/K.[6] So, while ADN is the main ingredient in the model St_b propellant, nevertheless, there is no correlation between temperature sensitivity for ADN and the ADN-based composite propellant.

Processing of temperature profile of both propellants (St_b(10000) 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(10000) increased Q, so 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 less than that of pure ADN. As it was shown earlier, even small amounts (~ 1%) of organic fuel (plasticizer, rubber) significantly decrease the burning rate of pure ADN[4] contrary to the influence of additives of binder on the burning rate of AP. Additive of fuel probably inhibits 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 effectiveness of inhibition of ADN decomposition reactions in CP likely depends on these properties. The rate of pyrolysis of PCL(1250) is significantly higher than that of PCL(10000). Experiments on combustion of St_b propellants at 0.1 MPa described above confirm this conclusion. The difference between the rate of pyrolysis of PCL(10000) and PCL(1250) could be a reason of their different influence on the burning rate of propellant. Slower pyrolysis of PCL(10000) 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(10000) propellant. The effect of inhibition of ADN decomposition in condensed phase by minor additives of hydrocarbon fuels was discussed earlier.[4] The addition of fuel in amount of only 1% resulted in significant decrease of the burning rate of ADN at 0.1 MPa. The following increase of fuel content up to 5% did not effect much on the burning rate. 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 at the addition of hydrocarbon fuel can be explained solely by heat loss for evaporation/decomposition of the fuel. 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 HTPB in the amount of 3% and 7% had almost the same burning rates at 0.6 MPa (~7.3 mm/s and ~7.5 mm/s respectively), which is less than the burning rate of pure ADN by 3 times 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. 4), takes place. It results in variation of oxidizer/fuel ratio in gas phase near the burning surface. One can assume, that space near small drop is filled mainly by products of decomposition of oxidizer. Deficiency of carbon-containing products in dark zone confirms this statement. Thus, invisible lean diffusion flame (dark zone - Table 3) with low temperature of products occurs near the small drops of fuel. Fusion of several small drops of partially decomposed PCL in big one takes place on the burning surface (Fig. 4 c) during the combustion. Intense flow of products of gasification and/or decomposition of fuel exists over the big drop. An interaction of products of decomposition of oxidizer with it resulted in appearance of luminous diffusion flame directly over the drop. Lifetime of drop (after appearance of the torch) is equal ~ 0.1 s. The presence of luminous torch with high temperature of combustion products over the drop leads to increase of heat feedback from gas phase to the burning surface and increase of temperature of the drop. As a result, increase of decomposition rate of the drop occurs. Volume and thickness of the drop decrease during the combustion. The shape of the drop changes from near hemispherical to more flat form. Then, some drops fall into smaller drops under the influence of flow of

oxidizer decomposition products from under the drop, and the torch disappears or exists over the rest part of the drop.

It was obtained 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 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. Ratio between them is not given here, but this ratio corresponds to the ratio of this peaks in the mass spectrum of ADN vapor.[5] The comparison of combustion products composition of St_b(1250) in dark flame zone with that of pure ADN at 0.6 MPa at a distance from the burning surface L_1 ~ 4 mm (Table 3) 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 narrow (dark) flame zone of propellant (~ 0.3 mm at 0.1 MPa) mainly the same reactions as in the dark zone adjacent to the burning surface of pure ADN at 0.6 MPa occur. Temperature in dark zone of propellant is higher than that 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 narrow zone near the burning surface.

Using the composition of combustion products in the dark zone near the burning surface as a boundary condition, the modeling of the dark flame zone was conducted. Code PREMIX[19] was used. For calculations a mechanism containing developed earlier mechanism of chemical reactions in ADN flame[20] and consisting of 144 reactions for 34 species was used. Calculations with initial temperature of 1040 K gave temperature profile (curve 3, Fig. 5). It coincides with part of experimental profile (curve 2, Fig. 5) corresponding to the dark zone. Besides, the composition of combustion products obtained in calculations (corresponding to the temperature of 1410 K) coincides with experimentally measured composition of combustion products in the dark zone far from the burning surface (Table 3). So, the second (dark) flame zone of St_b(1250) propellant was simulated. In this zone the consumption of HNO_3, NH_3 and partial consumption of NO with formation of H_2O and N_2 take place. Similar reactions occur in the dark zone of pure ADN flame at 0.6 MPa.[5]

Accordingly experimental results 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.[21] 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 skeleton contains a large amount of agglomerates with 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. Besides, in the case of addition of CuO to St_b(10000), larger increase of the burning rate in comparison with St_b(1250) is caused by larger accumulation of products of pyrolysis of PCL(10000) at the burning surface. However, the main mechanism of action of CuO catalyst relates to chemical reactions with it. Mentioned mechanism of increase of the burning rate due to the accumulation of the catalyst on the burning surface and the increase of thermal conductivity of near-surface layer is additional one to the main mechanism.

CONCLUSIONS

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 flame. CuO catalyst at 4 MPa increases the rate of reactions and heat release in the condensed phase and in 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 composition of baseline propellant by minor additives of CuO or Pb_3O_4 and using of

polymers with different molecular weights allowed 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. Besides, 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 composition of ADN-based propellants. Data obtained can be used for development of combustion model of ADN-based propellants.

ACKNOWLEDGMENT

This work was supported by the US Army Aviation and Missile Command under the Contract DAAHO1-98-C-R151.

REFERENCES

1. Pak, Z., "Some Ways to Higher Environmental Safety of Solid Rocket Applications," AIAA Paper 93-1755, 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, Vol. 185, Progress in Astronautics and Aeronautics, AIAA, Reston, VA, 2000, pp. 185-206.
3. Fogelzang, A.E., Sinditskii, V.P., Egorshev, V.Y., et al., "Combustion Behavior and Flame Structure of Ammonium Dinitramide," Proceedings of the 28-th International Annual Conference of ICT, Fraunhofer Institut Chemische Technologie, Karlsruhe, 1997, pp. 99-(1-14).
4. Strunin, V.A., D'yakov, A.P., and Manelis, G.B., "Combustion of Ammonium Diniramide," Combustion and Flame, Vol. 117, 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, 1999.
7. Korobeinichev, O.P., and Paletsky, A.A., "Flame Structure of ADN/HTPB Composite Propellants," Combustion and Flame, Vol. 127, 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, 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 5-th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials, Stresa, 2000, pp. 492-501.
12. Parr, T., and Hanson-Parr, D. M., "Solid Propellant Diffusion Flame Structure," Proceedings of the Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1996, pp. 1981-1987.
13. Sinditskii, V.P., Fogelzang, A.E., Egorshev, V.Y., et al., "Combustion Peculiarities of ADN and ADN-based Mixtures," Proceedings of the 5-th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials, Stresa, 2000, pp. 502-512.
14. 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 5-th International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials, Stresa, 2000, pp. 381-396.

15. 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, Vol. 185, Progress in Astronautics and Aeronautics, AIAA, Reston, VA, 2000, pp. 335-354.
16. Korobeinichev, O.P., Kuibida L.V., Paletsky, A. A., and Chernov, A.A., "Study of Solid Propellant Flame Structure by Mass-Spectrometric Sampling," Combust. Sci. Tech., Vol. 113-114, 1996, pp.557-572.
17. Belov, G.V., ASTRA Code, ver. 2/24, MSTU, Moscow, 1990 (in Russian).
18. Zenin, A.A., "Experimental Investigation of the Burning Mechanism of Solid Propellants and Movement of Burning Products", Ph.D. Dissertation, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, USSR, 1976 (in Russian).
19. Kee, R., et al., Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Sandia National Laboratories Report No. SAND85-8240, 1994.
20. Korobeinichev O.P., Bolshova T.A., and Paletsky A.A., "Modeling the Chemical Reactions of Ammonium Dinitramide (ADN) in a Flame", Combustion and Flame, Vol.126, 2001, pp. 1516-1523.
21. 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.

Questions/Comments:
Reviewer No. 2

1. *In the experimental part (p.3), there is no particle size of PCL flakes indicated, neither diameter of the charge, nor a method of the charge preparation and inhibition of back surface.*
2. *The measured temperature sensitivity is changed from 0 to 0.9 %/K when changing the temperature interval from -50 ÷ -20 C to -20 ÷ 20 C. Such improbable growth is most likely connected with burning rate data scattering, which is characteristic of burning ADN at that pressure range.*
3. *From the chemical point of view a fuel additive can not inhibit monomolecular decomposition reaction of ADN, which defines combustion of ADN. Fuel consumes a portion of heat released at the surface molten layer to decomposition/evaporation and thus reduces the burning rate (see how the molecular weight of a binder influences the burning rate). The absence of a direct correlation between amount of fuel added and effect obtained can be explained by the burn rate data scattering or by some physical reasons (for example, by emerging of luminous flame, see Fig.4)*

Author's Reply:

1. *The average size of PCL (only for 10.000) flakes at room temperature was about 0.2-0.5 mm in diameter, but it did not play any role during preparation of the propellant mixture, because during mixing of the propellant ingredients the PCL was molten.*
2. *The growth of the temperature sensitivity of the propellant burning rate was not connected with pure ADN burning rate data scattering at that pressure range. It is known that small addition of fuel decreases and stabilizes burning rate of ADN temperature sensitivity of burning rate for many propellant ingredients [A.I. Atwood et al. "Burning Rate of Solid Propellants Ingredients, Part 2: Determination of Burning Rate Temperature Sensitivity", JPP, Vol. 15, № 6, 1999, pp. 748-752] slightly changes at negative temperatures (in Celsius) and significantly increases at positive temperatures. Analogous dependence was obtained in our investigation for the ADN/PCL propellant, therefore the value of temperature sensitivity coefficient abruptly increased when changing temperature interval from -50 ÷ -20 °C to -20 ÷ 20 °C.*
3. *Processes taking place in condensed phase are very complicated. When we say "reaction of ADN decomposition" we mean not only the reaction monomolecular decomposition of ADN, but the whole process taking place in condensed phase, including the formation of gasification products. It is known that decomposition products of ADN accelerate its decomposition. In the case of propellant the part of ADN decomposition products reacts and/or absorbs by fuel (or decomposition products of fuel). As a result decomposition rate of ADN decreases [Strunin, V.A., d'yakov, A.P., and Manelis, G.B., "Combustion of Ammonium Dinitramide," Combustion and Flame, Vol. 117, 1999, pp. 429-434]. Therefore not only heat loss for vaporization and decomposition of fuel accounts for the observed decrease of burning rate, but also inhibition of ADN decomposition by fuel.*

Questions:
Reviewer No. 3

1. *For burning rate measurements please specify if it is a single data point or an average of data points. If so, how many measurements were made and what is the standard deviation?*
2. *Is there any chemical evidence for the fact that the brown residue is polycaprolactone?*

Author's Reply:

1. *The number of burning rate measurements was from 2 to 5 for each pressure value. We showed several points on the plot when it was necessary. In many cases the values of burning rate were enough close to each other and were shown like one point on the plot. Accuracy of measurement of the burning rate was equal to ±5%.*
2. *We did not conduct special experiments to confirm that brown residue was polycaprolactone. But we know that there is no any residue after experiments on combustion of pure ADN.*

Question:
Dr. Alain Davenas, SNPE, France

1. *What was the particle size of ADN you used in your formulations?*
2. *Do you know of any studies about the effect of ballistic modifiers incorporated inside the ADN particles to see if there is any difference as compared to ballistic modifiers outside the ADN particles?*

Author's Reply:

1. *We used crystalline powder of ADN with average particle size 40 μm.*
2. *No ballistic modifier was used.*

Follow-Up Comment:
Dr. May L. Chan, NAWC, USA
This is in response to the question asked by Dr. Alain Davenas regarding the effects of internal vs. external ballistic modifiers of AND particles. Yes, I have incorporated various burning rate catalysts (Fe_2O_3, CuO, Pb_2O_3, etc.) inside AND particles by a prilling method. I found there is no major difference in burning rate effects whether the catalysts existed inside or outside of the ADN particles (prills).

Question:
Mr. Max Calabro, EADS-LV, France.
For civilian applications, there is a need for low burning rates (say, below 7 mm/s at 7 MP) and clean combustion products. Do you believe it Is it possible to reach these goals by using ADN and/or other ingredients?

Author's Reply:
I believe that burning rate can be decreased by the addition of some polymers and subsequent polymerization.

Follow-Up Comment:
Prof. S.R. Chakravarthy, Indian Institute of Technology Madras, India
This is in response to the question asked by Mr. Max Calabro regarding the formulation of propellants with new ingredients that have burning rates not exceeding 7 mm/s at 7 MPa, but still giving higher specific impulse and lower HCl emissions. I have worked on propellants AP-ADN combinations, while at Georgia Tech, and found that bimodal propellants with fine (30 μm) ADN and coarse (300 μm) AP particles give similar burning rates as all-AP propellants, but offers higher specific impulse and lower (not zero) HCl emissions. The data were presented at the 1997 JANNAF Combustion Meeting and 1998 Joint Propulsion Conference in Cleveland, OH, both in the USA; the corresponding paper has been accepted for publication in Propellants, Explosives & Pyrotechnics (PEP).