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Features of combustion of gas-generating solid compositions based on high-enthalpy dispersants

A. F. Zholudev,[a] M. B. Kislov,[a] I. S. Averkov,[a,b] D. V. Dashko,[c] V. V. Raznoschikov,[a,b] D. B. Lempert,[a★] and L. S. Yanovskiy[a,b,d]

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: lempert@icp.ac.ru
[b] P. I. Baranov Central Institute of Aviation Motors,
2 ul. Aviamotornaya, 111116 Moscow, Russian Federation.
Fax: +7 (495) 362 0064. E-mail: averkov@ciam.ru
[c] Special Design and Technology Bureau "Technolog,"
33a prosp. Sovetskii, 192076 St. Petersburg, Russian Federation.
Fax: +7 (812) 700 3637. E-mail: info@sktb-technolog.ru
[d] Department of Chemistry, Lomonosov Moscow State University,
Build. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation

The features governing the high-rate thermal transformation (combustion without air access) of several dispersants (high-enthalpy N-heterocyclic compounds) were experimentally studied. The quantitative regularities of the combustion of both individual dispersants and their mixtures with isoprene rubber and ammonium perchlorate were examined. The dependences of consumption of individual dispersants on the nitrogen pressure, enthalpy of formation of the dispersants, and oxygen supply coefficient of the dispersant were determined. The dependences of the combustion rate on the contents of isoprene rubber and ammonium perchlorate were experimentally determined for the fuel compositions based on each dispersant. The results of the study can be used for the formation of optimal gas-generating fuel compositions.

Key words: solid compositions, fuel, dispersant, high-enthalpy nitrogen-containing compounds, combustion rate.

The studies on manufacturing solid gas-generating compositions are actively pursued at the present time.[1—3] A number of requirements is imposed on these compositions, among which are a high volume heat of combustion, a high density, a low content of the condensed phase in the gas-generation products, and a high degree of removal from the gas-generation chamber. Several works have recently been published on the possibility of fabrication of solid compositions based on the high-enthalpy compounds (organic polynitrogen substances). These compounds can be used as dispersants without external oxidants. The results of studying the possibility of practical use of new high-enthalpy polynitrogen components were published.[4,5] The systems approach was applied in these works to study the efficiency of application and formation of preliminary gas-generating compositions by high-level criteria.[6] The present work describes the experimental study of the features of combustion of the solid compositions containing the earlier described polynitrogen compounds as dispersants.[4]

Experimental

In the present work we disclose results of experimental studies of the combustion of solid gas-generating compositions,[4] the formulations of which were determined by theoretical calculations. The following characteristics were studied:

— ability of the compositions to stable combustion without air access;

— dependence of the combustion rate u on pressure P ($u = u_0P^\nu$, where ν is the pressure coefficient characterizing the pressure dependence of the combustion rate);

— influence of additives of isoprene rubber SKI-3 and ammonium perchlorate (AP) on the combustion rate;

— combustion temperature;

— gas generation upon the combustion of the compositions in the absence of an external oxidant.

The following substances were chosen as the main components: isoprene rubber SKI-3[7,8] C_5H_8 (enthalpy of formation $\Delta H^\circ_f = -913$ kJ kg^{-1}, density 0.91 g cm^{-3}), AP,[9] and four high-enthalpy dispersants,[10—16] the main energy properties of which are presented in Table 1. The combustion of individual dispersants, their binary mixtures with AP or SKI-3, and ternary mixtures dispersant + SKI-3 + AP was studied.

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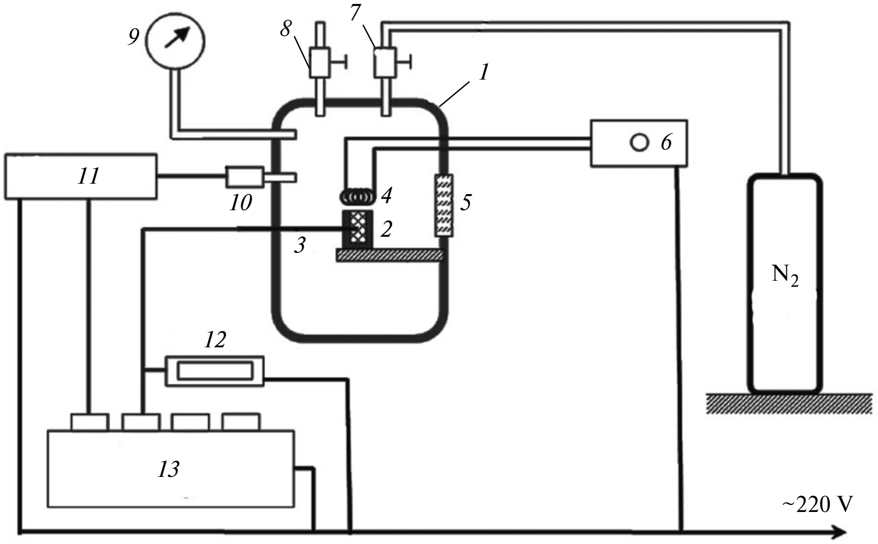
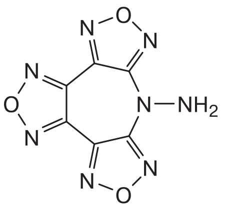
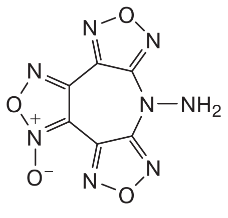


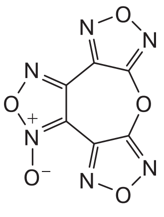
Fig. 1. Scheme of the experimental setup: *1*, Crawford bomb ($V = 3$ L); *2*, studied mixture; *3*, thermocouple; *4*, nichrome glower; *5*, watch window, *6*, transformer; *7*, pressure reducer; *8*, dump valve; *9*, reference manometer; *10*, DD-10 pressure sensor; *11*, ID-2I pressure indicator; *12*, voltmeter; and *13*, N117 12-channel oscillograph.



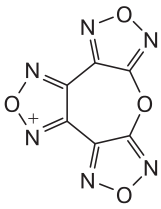
L-40



L-43



L-44



L-45

Experimental procedure. The experimental setup presented in Fig. 1 was used to study the combustion of the compositions without air access.

The setup represents a 3-L Crawford bomb[5] in which a constant nitrogen pressure (20—60 atm) was initially developed. The maximum admissible pressure in the bomb was 100 atm. A beaker with the studied mixture is placed inside the bomb, and a nichrome glower is mounted above the beaker to initiate the combustion process. Once a voltage of 14 V is fed (from the laboratory automated transformer) to the glower, the glower is heated to ~1300 °C with fractions of second. A plexiglass watch window 5 cm in width is forseen in the bomb for visual monitoring. After the sample ignited, voltage feeding to the glower was stopped. Chromel—alumel or tungsten—rhenium thermocouples were used to measure the combustion temperature, depending on the expected temperature. The outlet signal from the thermocouple (emf to 50 mV) came to the voltmeter and in parallel to one of 12 channels of an N117 oscillograph, which allowed

Table 1. Main properties of the dispersants

Compound	Empirical formula	H_V[a] /MJ L^{-1}	α[b]	ρ[c] /g cm^{-3}	ΔH°_f/kJ kg^{-1} (see Ref. 16)
7*H*-Tris([1,2,5]oxadiazolo)[3,4-*b*:3′,4′-*d*:3″,4″-*f*]-azepin-7-amine (L-40)	$C_6H_2N_8O_3$	27.838	0.23	1960	3081
7*H*-Tris([1,2,5]oxadiazolo)[3,4-*b*:3′,4′-*d*:3″,4″-*f*]-azepin-7-amine-1-oxide (L-43)	$C_6H_2N_8O_4$	26.034	0.31	1970	2805
Oxepino[2,3-*c*:4,5-*c*′:6,7-*c*″]tris-([1,2,5]oxadiazolo)-1-oxide (L-44)	$C_6N_6O_5$	23.69	0.42	1960	2084
Oxepino[2,3-*c*:4,5-*c*′:6,7-*c*″]tris-([1,2,5]oxadiazole) (L-45)	$C_6N_6O_4$	25.544	0.33	1960	2302

[a] Volume heat of combustion of the substance in oxygen.
[b] Oxygen supply coefficient equal to O/(2C + 0.5H).
[c] Density.

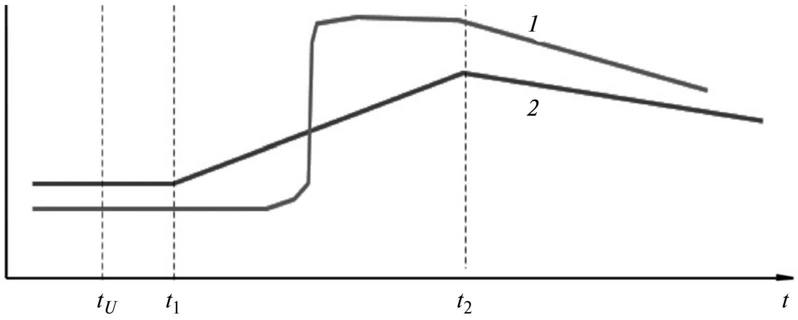


Fig. 2. Typical experimental oscillograms: *1*, signal from the thermocouple; and *2*, signal from the pressure sensor (t_U, t_1, and t_2 are moments of voltage supply and combustion onset and end, respectively).

continuous signal monitoring. The pressure was also monitored with a measuring system including a DD-10 inductive pressure sensor (with a control pressure of 40 atm), an ID-2I converter (pressure indicator), and an N117 oscillograph. The typical oscillogram is shown in Fig. 2.

The compositions containing SKI-3 were prepared as follows. Isoprene rubber SKI-3 was preliminarily dissolved in toluene, heptane, or hexane, and then a target amount of a dispersant was added, as well as AP was introduced if necessary. To ensure a complete vaporization of the solvent, the obtained mixture was dried in draft hood to a constant weight. After this, the mixture was pressed in a hydraulic press with the channel (diameter 8 mm) and a pressure force of the plunger of 2.7 t (at an oil pressure of 100 atm). The pressed cylindrical material (weight 0.7—1 g and height 8—13 mm) was placed in a beaker made from an asbestos-cement pipe. "Armoring" was preliminarily made: the beaker was covered inside with epoxide resin with the additive of 10% hardener (polyethylene—polyamine), and the same composition was deposited on the lateral surfaces of the tested composition.

After the epoxide resin was solidified, the assembled beaker was drilled on one side with a drill 1 mm in diameter at the center of the height to a depth of 4—5 mm, and the thermocouple for combustion temperature detecting was placed in this hole. The mixtures containing no SKI-3 were prepared similarly but without using organic solvents.

For voltage feeding to the nichrome glower in the Crawford bomb, the transformer was switched-on for fractions of second up to ignition. The pressure in the bomb was monitored during combustion using the oscillograph. Knowing the height of the sample (h) and time of its combustion (τ), the combustion rate was calculated: $u = h/\tau$.

The experiments on the combustion of the same 15 compositions in a nitrogen atmosphere at 40 atm showed that the scatter of combustion rate values ranged from 5 to 10%, which characterizes an appropriate reproducibility of the data.

Results and Discussion

The experimental data on the combustion parameters of the studied compositions determined by the law of combustion $u = u_0P^{\nu}$ are presented in Tables 2—5.[17]

It is found from the experimental results that the solid residues of the gas-generation products are dispersed powders. Therefore, it can be expected that the degree of removal of the condensed phase from the gas-generation chamber would be optimal and the phase itself would manifest high reactivity and degree of afterburning in flowing air.

Figures 3—6 show that the AP additive makes it possible to accelerate combustion for the compositions based on L-40 and L-45. At the same time, the combustion rate is nearly independent of the AP content for compositions L-43 and L-44. For all tested compositions, an increase in the SKI-3 content decreases the combustion rate, which should be expected for mixtures based on dispersants with

Table 2. Combustion rate (u) and pressure coefficient (ν) of the compositions based on dispersant L-40 at 20 and 60 atm

L-40	AP	SKI-3	P/atm	u/mm s^{-1}	ν
	%				
100	0	0	20	1.34	0.88
			60	3.51	0.88
90	10	0	20	2.30	0.55
			60	4.23	0.55
80	10	10	20	1.70	0.52
			60	3.02	0.52
90	0	10	20	1.48	0.53
			60	2.65	0.53
90	5	5	20	1.77	0.70
			60	3.83	0.70
80	0	20	20	0.92	0.51
			60	1.62	0.51
70	0	30	20	0.73	0.56
			60	1.35	0.56
60	0	40	20	0.71	0.34
			60	1.03	0.34
70	10	20	20	1.3	0.52
			60	2.3	0.52
60	10	30	20	0.88	0.54
			60	1.6	0.54
50	10	40	20	0.62	0.44
			60	1.0	0.44

Table 3. Combustion rate (u) and pressure coefficient (ν) of the compositions based on dispersant L-43 at 20 and 60 atm

L-43	AP	SKI-3	P/atm	u/mm s^{-1}	ν
	%				
100	0	0	20	3.1	0.69
			60	6.6	0.69
90	10	0	20	3.73	0.71
			60	8.1	0.71
80	0	20	20	2.7	0.60
			60	5.2	0.60
70	0	30	20	2.4	0.46
			60	4.0	0.46
70	10	20	20	3.1	0.40
			60	4.83	0.40
60	0	40	20	1.9	0.53
			60	3.4	0.53
40	10	50	20	0.85	0.58
			60	1.6	0.58
50	0	50	20	1.0	0.48
			60	1.7	0.48

Table 4. Combustion rate (u) and pressure coefficient (ν) of the compositions based on dispersant L-44 at 20 and 60 atm

L-44	AP	SKI-3	P/atm	u/mm s^{-1}	ν
	%				
100	0	0	20	2.75	0.98
			60	8.1	0.98
80	0	20	20	3.2	0.71
			60	7.0	0.71
70	0	30	20	2.9	0.29
			60	4.0	0.29
60	0	40	20	1.9	0.53
			60	3.4	0.53
50	0	50	20	1.8	0.095
			60	2.0	0.095
40	10	50	20	1.3	0.41
			60	2.05	0.41

low α values. When the SKI-3 content in the L-40 or L-45 compositions reaches 40%, combustion becomes unstable and ceases completely. This limit is higher for the compositions with L-43 and L-44 and is equal to 50%. The sensitivity of the combustion rate to pressure is relatively high (their pressure coefficient ν is not lower than 0.5) and is observed for all tested compositions.

The combustion rates of individual dispersants measured without air access and their properties are presented in Table 6.

The study of the combustion rates u of the dispersants shows that u depends on $\Delta H^\circ{}_f$ and α: u increases with an increase in $\Delta H^\circ{}_f$ and α. To reveal how $\Delta H^\circ{}_f$ and elemental composition of the dispersant affect u, we determined the coefficients of the empirical equation $u = p_1 + p_2\Delta H^\circ{}_f + p_3\alpha$ using the known speedy descent algorithm to find coefficients p_i. It is elucidated that at a pressure of 20 atm the following equation is fulfilled:

$$u\ (\text{mm s}^{-1}) = -12.4 + 0.00291 \cdot \Delta H^\circ{}_f + 22.4\alpha, \qquad (1)$$

where $\Delta H^\circ{}_f$ is expressed in kJ kg^{-1}, whereas at 60 atm the following equation is valid:

$$u\ (\text{mm s}^{-1}) = -23.3 + 0.00502 \cdot \Delta H^\circ{}_f + 50.3\alpha. \qquad (2)$$

The correlation coefficient r for Eqs (1) and (2) is higher than 0.999, and the divergences between the values cal-

Table 5. Combustion rate (u) and pressure coefficient (ν) of the compositions based on dispersant L-45 at 20 and 60 atm

L-45	AP	SKI-3	P/atm	u/mm s^{-1}	ν
	%				
100	0	0	20	2.0	0.87
			60	5.2	0.87
90	10	0	20	2.68	0.89
			60	7.1	0.89
80	0	20	20	1.1	0.67
			60	2.3	0.67
75	10	15	20	1.84	0.53
			60	3.28	0.53
70	0	30	20	—	—
			60	1.45	—
60	0	40	20	—	—
			60	0.75	—
60	10	30	20	0.8	0.88
			60	2.1	0.88

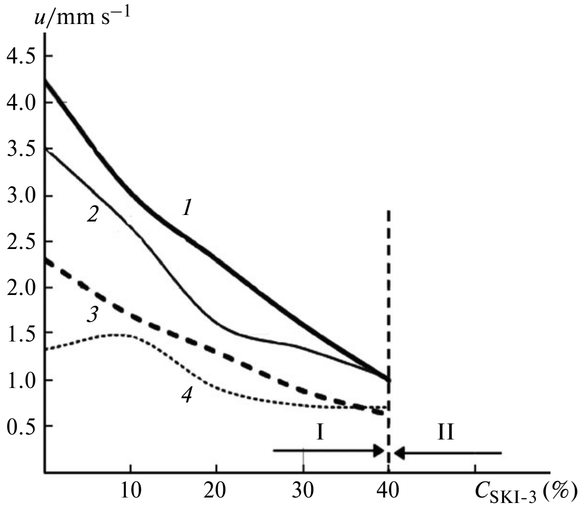


Fig. 3. Combustion rates (u) of the compositions L-40 + SKI-3 + + AP *vs* contents of SKI-3 ($C_{\text{SKI-3}}$) and AP at different pressures: (*1*) 10% AP, P = 60 atm; (*2*) 0% AP, P = 60 atm; (*3*) 10% AP, P = 20 atm; and (*4*) 0% AP, P = 20 atm (here and in Figs 4—6: I is stable combustion, and II is unstable combustion).

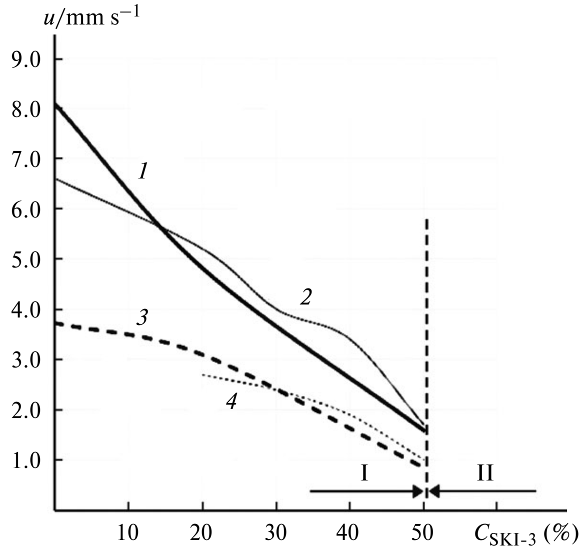


Fig. 4. Combustion rates (u) of the compositions L-43 + SKI-3 + + AP *vs* contents of SKI-3 ($C_{\text{SKI-3}}$) and AP at different pressures: (*1*) 10% AP, P = 60 atm; (*2*) 0% AP, P = 60 atm; (*3*) 10% AP, P = 20 atm; and (*4*) 0% AP, P = 20 atm.

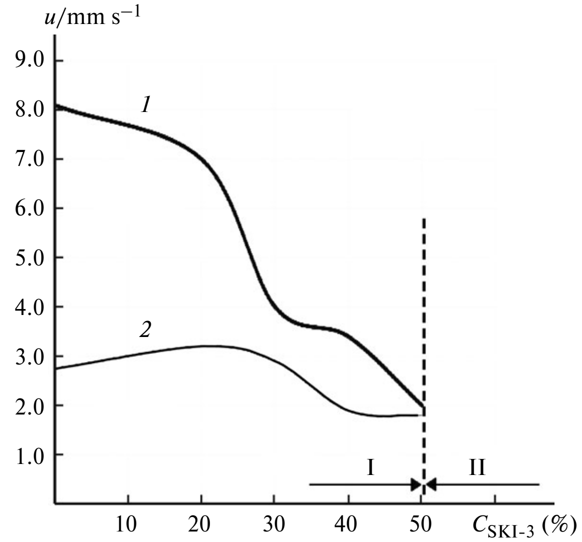


Fig. 5. Combustion rates (u) of the compositions L-44 + SKI-3 + + AP *vs* contents of SKI-3 ($C_{\text{SKI-3}}$) and AP at different pressures: (*1*) 0% AP, P = 60 atm; and (*2*) 0% AP, P = 20 atm.

Table 6. Combustion rates of individual dispersants

Dispersant	$\Delta H^{\circ}_{\text{f}}$ /kJ kg^{-1}	α	u/mm s^{-1}		ν
			20 atm	60 atm	
L-40	3081	0.230	1.34	3.51	0.88
L-43	2805	0.308	3.10	6.60	0.69
L-44	2084	0.420	2.75	8.10	0.98
L-45	2302	0.333	2.00	5.20	0.87

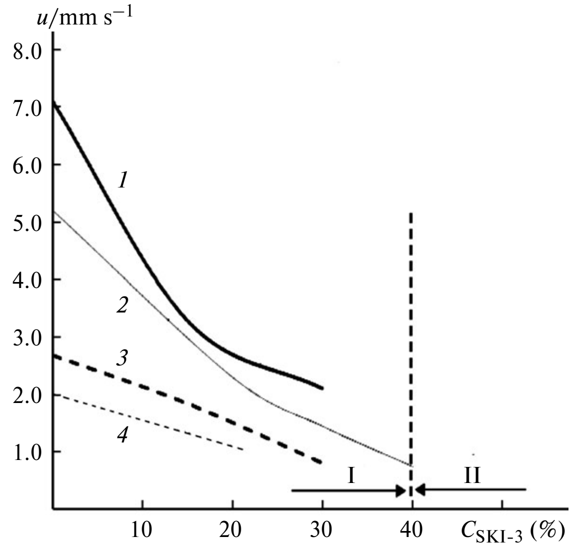


Fig. 6. Combustion rates (u) of the compositions L-45 + SKI-3 + + AP *vs* contents of SKI-3 ($C_{\text{SKI-3}}$) and AP at different pressures: (*1*) 10% AP, P = 60 atm; (*2*) 0% AP, P = 60 atm; (*3*) 10% AP, P = 20 atm; and (*4*) 0% AP, P = 20 atm.

culated by Eq. (1) and found experimentally are 0.35 mm s^{-1} on the average and do not exceed 0.44 mm s^{-1}. For the calculation by Eq. (2), these deviations are 0.24 mm s^{-1} on the average and do not exceed 0.30 mm s^{-1}.

Thus, it is found that an increase in α by 0.1 and an increase in $\Delta H^{\circ}_{\text{f}}$ by approximately 750 kJ kg^{-1} give nearly the same increase in the combustion rate.

The equation relating the ν values to $\Delta H^{\circ}_{\text{f}}$ and α for the studied dispersants is as follows:

$$\nu = 2.02 - 0.000317 \cdot \Delta H^{\circ}_{\text{f}} - 1.0775\alpha, \qquad (3)$$

where the correlation coefficients r are higher than 0.995. The ν values calculated by Eq. (3) differ from the experimentally obtained values (see Table 6) by 0.08 on the average (at a maximum deviation of 0.105). It is seen that an increase in both $\Delta H^{\circ}_{\text{f}}$ and α leads to a decrease in the pressure coefficient ν.

Thus, Eqs (1)—(3) make it possible to preliminarily estimate the combustion rates and pressure coefficients ν of other dispersants for which the $\Delta H^{\circ}_{\text{f}}$ and α values lie in the ranges 2300—3100 kJ kg^{-1} and 0.23—0.42, respectively.

As for the quantitative influence of AP and SKI-3 on the combustion rate of the compositions, a certain regularity is observed: the introduction of AP increases the combustion rate and the addition of SKI-3, on the contrary, decreases the rate. As can be seen from Tables 2—5 and Figs 3—6, these are only the main tendencies, since the found dependences are nonlinear.

The dependences of the consumption rate of the compositions on the contents of SKI-3 and AP were obtained for each dispersant.

Table 7. Coefficients k_i in the equation $u = k_1 + k_2(AP) + k_3R$ at 20 and 60 atm

Dispersant	20 atm			60 atm		
	k_1	k_2	k_3	k_1	k_2	k_3
L-40	1.70	0.032	−0.032	3.55	0.040	−0.074
L-43	3.60	0.011	−0.049	7.26	0.015	−0.110
L-44	3.12	—	−0.020	8.50	—	−0.130
L-45	2.10	0.051	−0.057	5.4	0.075	−0.130

The processing of the experimental data listed in Tables 2—5 shows that the dependence of the combustion rate of the compositions "dispersant + AP + SKI-3" at 20 atm can be described by the equation

$$u = k_1 + k_2(AP) + k_3R, \quad (4)$$

where AP and R (rubber) are the contents of AP and SKI-3 (in %), respectively.

For the compositions based on L-40 at 20 atm, the combustion rate can be described by the equation $u = 1.7 + 0.032 \cdot (AP) - 0.032R$. The u values calculated by this equation differ from the experimental values by 0.15 mm s^{-1} on the average (*i.e.*, by 12% on the average) at a maximum deviation of 0.34 mm s^{-1}. The equation $u = 3.55 + 0.040 \cdot (AP) - 0.074R$ is valid for the same compositions at 60 atm. The u values calculated by this equation differ from the experimentally obtained values by 0.2 mm s^{-1} on the average (*i.e.*, by 9%) at a maximum deviation of 0.45 mm s^{-1}.

The dependence $u = 3.58 + 0.011 \cdot (AP) - 0.049R$ at average and maximum deviations of 0.26 and 0.5 mm s^{-1}, respectively, was obtained for the compositions based on L-43 at 20 atm. For the same compositions at 60 atm, the dependence is described by the equation $u = 7.26 + 0.015 \cdot (AP) - 0.110R$ at average and maximum deviations of 0.35 and 0.7 mm s^{-1}, respectively.

The compositions based on L-44 are characterized by only one experimental point with the nonzero AP content and, hence, the equations can be presented only for the compositions based on L-44 with isoprene rubber. For a pressure of 20 atm, one can write the equation $u = 3.12 - 0.020R$ at average and maximum deviations of 0.35 and 0.5 mm s^{-1}, respectively. For a pressure of 60 atm, we have $u = 8.5 - 0.13R$ at average and maximum deviations of 0.44 and 1.0 mm s^{-1}, respectively.

For the compositions based on L-45 at 20 atm, we have the relation $u = 2.1 + 0.051 \cdot (AP) - 0.057R$ at average and maximum deviations of 0.1 and 0.12 mm s^{-1}, respectively, whereas for a pressure of 60 atm we have $u = 5.4 + 0.075 \cdot (AP) - 0.13R$ at average and maximum deviations of 0.45 and 1.0 mm s^{-1}, respectively.

Attempts to determine the dependences of coefficients k_i on $\Delta H^\circ{}_f$ and α of the dispersants gave no reasonable result. Undoubtedly, these dependences are much more complicated than linear relations. Therefore, for the preliminary development of the compositions that should satisfy the requirements imposed on combustion rates, the k_i values presented in Table 7 should be used for each of four studied dispersants.

Let us consider the conditions for the formation of the process with two-stage combustion of the compositions in which the first stage is gasification with dispersion and the second stage is the afterburning of the formed products in flowing air. It is necessary that the thermal conversion products at the first stage would contain gases that serve not only as a fuel but also as a carrier of dispersed solid combustible products from the gas-generation chamber. It can be assumed that, under other equivalent conditions, the larger the volume (or molar amount) of the gaseous products of thermal conversion in the gas-generation chamber, the higher the degree of removal of dispersed products. The corresponding calculated data are presented in Table 8.

It is seen that the molar amount of gaseous products of thermal conversion increases slightly on going from the individual dispersant to its mixtures with AP and SKI-3.

The main conditions of the stable consumption of the specific composition is the need to achieve the value of T_{ad} not lower than 1500 K at 50 atm. The AP-based compositions with the SKI-3 content not higher than 27.5% and the compositions based on L-40 and L-43—L-45 with the SKI-3 content not higher than 40% (Fig. 7) satisfy this conditions. However, the AP-based compositions containing not more than 27.5% SKI-3 are characterized by H_v not higher than 13 MJ L^{-1}, whereas the compositions based on dispersants L-40 and L-43—L-45 with the iso-

Table 8. Characteristics of combustion of the compositions: T_{ad} (K) is adiabatic temperature, V (mol kg^{-1}) is the volume of generated gas, and z is the mass fraction of the condensed phase

Burnt sample	L-40			L-43			L-44			L-45		
	T_{ad}	V	z	T_{ad}	V	z	T_{ad}	V	z	T_{ad}	V	z
Individual dispersant	3080	34.2	0	3000	36.1	0	3600	34.05	0.043	3470	32.6	0.104
Dispersant : AP = 9 : 1	2760	36.8	0	3060	38.5	0	3420	36.8	0	3080	34.7	0
Dispersant : SKI-3 = 9 : 1	2470	36.6	0.175	2500	38.3	0.11	2560	36.4	0.058	2530	34.6	0.13
Dispersant : SKI-3 : AP = 8 : 1 : 1	2420	39.2	0.135	2460	40.6	0.08	2510	39.0	0.035	2470	37.2	0.095

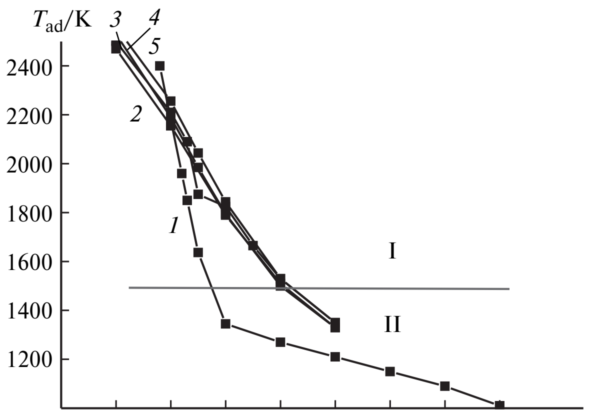


Fig. 7. Dependence of the adiabatic conversion temperature of a mixture of isoprene rubber SKI-3 with AP (*1*) and with dispersants L-40 (*2*), L-43 (*3*), L-44 (*4*), and L-45 (*5*) at a pressure of 5 MPa on the SKI-3 content in the mixture.

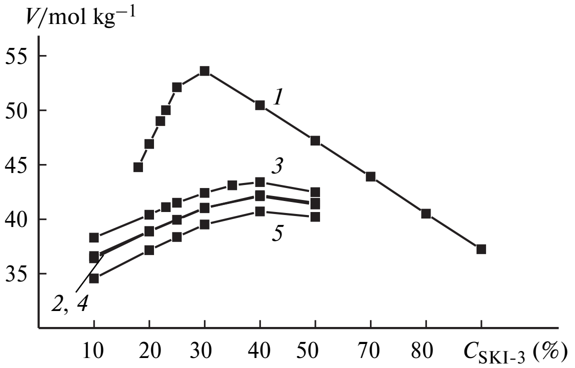


Fig. 9. Amount of gaseous products (V) of the thermal conversion of a mixture of isoprene rubber SKI-3 with AP (*1*) and with dispersants L-40 (*2*), L-43 (*3*), L-44 (*4*), and L-45 (*5*) at a pressure of 5 MPa in an airless medium on the content of SKI-3 in the mixture.

prene rubber content not higher than 40% is characterized by a value nearly twice as large: H_v = 25—32 MJ L^{-1} (Fig. 8). However, the yield of the gas phase for three last compositions does not exceed 40—44 mol kg^{-1}, whereas for the compositions with AP the gas generation value reaches 53 mol kg^{-1} (Fig. 9).

In addition to the calculations, the volumes of gaseous combustion products were experimentally determined. For this purpose, the sample that initially was at room temperature in a specified geometric volume at a specified initial nitrogen pressure was burned, the system was cooled to room temperature, and the volume of generated gases was calculated from the pressure increase. The gas generation volumes close to the calculated values were obtained for the combustion of individual dispersants (see Table 8). However, when a binder was added to the dispersant, the experimentally determined volume of gaseous combustion products turned out to be substantially lower than the calculated value. This can easily be explained by the fact that the introduction of even 10% isoprene rubber to the dispersants sharply (by 500—1000 K) decreased T_{ad}; *i.e.*, combustion occurred with a significantly lower rate and was characterized by a higher degree of underburning.

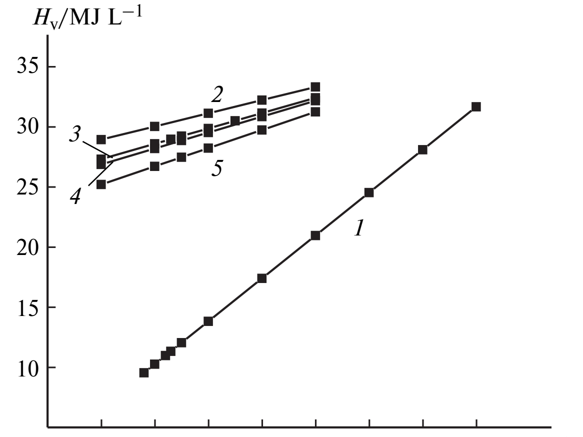


Fig. 8. Heat of combustion of a mixture of isoprene rubber SKI-3 with AP (*1*) and with dispersants L-40 (*2*), L-43 (*3*), L-44 (*4*), and L-45 (*5*) at a pressure of 5 MPa on the SKI-3 content in the mixture.

Further, we intend to study the influence of the dispersion of the components and technology of sample preparation on the combustion rate.

The obtained experimental data make it possible to more precisely determine the character of units in which gas-generating solid compositions are used.

Thus, the experimental data on the combustion rates and pressure coefficients of the polynitrogen compounds (dispersants) and the related compositions containing AP (from 0 to 10%) and isoprene rubber SKI-3 (from 0 to 50%) without an external oxidizer in a pressure range of 20—60 atm were obtained.

The relationships of the combustion rates of the studied compositions of the contents of AP and isoprene rubber SKI-3 were determined.

The relationships of the combustion rates of the studied dispersants and the enthalpies of formation and oxygen supply coefficient α were determined. It was shown that in the range of enthalpies of formation 2300—3100 kJ kg^{-1} and at α = 0.23—0.42 under a pressure of 20 atm an increment in the enthalpy of formation per 100 kJ kg^{-1} led to an increase in the combustion rate of the dispersant by ~0.3 mm s^{-1} and an increment in α per 0.02 increased the combustion rate by ~0.45 mm s^{-1}, whereas under a pressure of 60 atm these values increased by 0.5 and 1.0 mm s^{-1}, respectively.

This work was carried out in terms of state assignment (state registration No. AAAA-A19-119101690058-9).

This paper does not contain descriptions of studies on aminals or humans.

The authors declare no competing interests.

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