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# Combustion of binary mixtures of energetic binder with different fillers

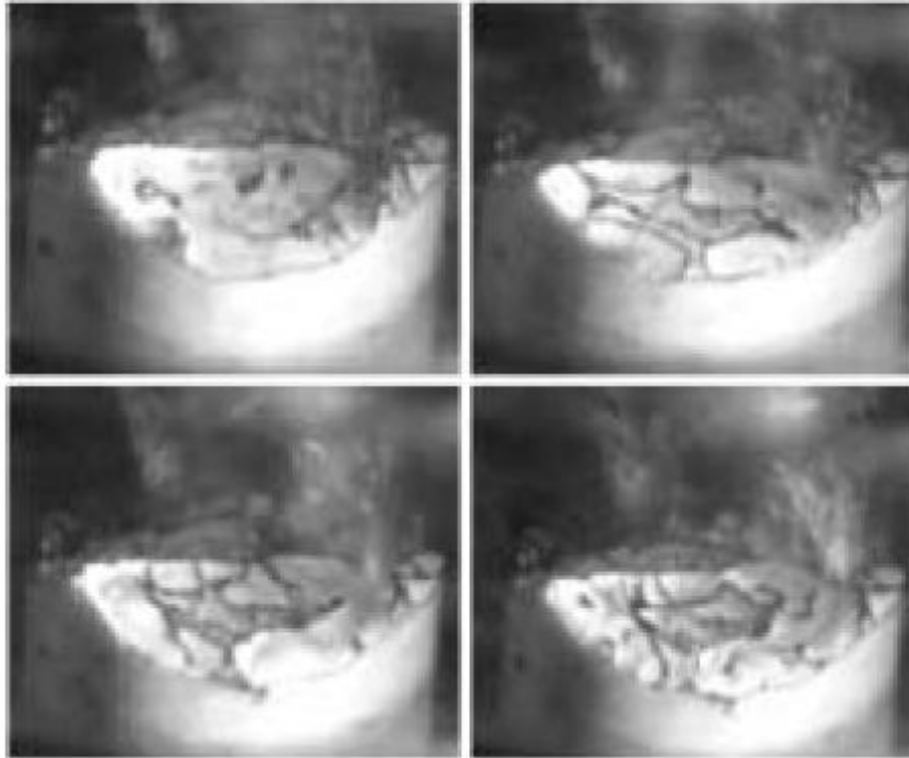
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## Experimental data. Combustion of homogeneous energetic materials

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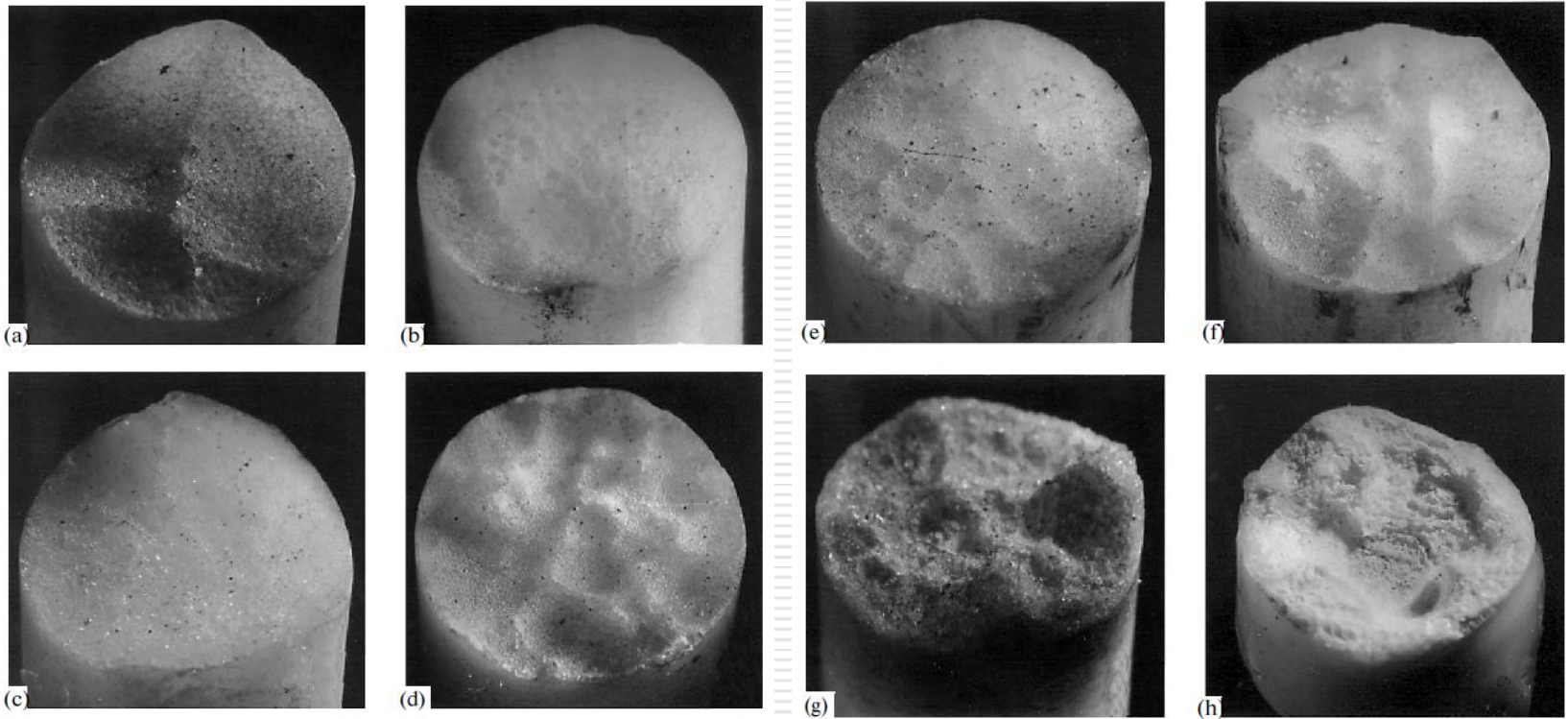


A picture series taken at a time interval of 40 msec and demonstrating the burning of a 10-mm diameter colloxylin specimen under atmospheric pressure. The initial temperature of the specimen was 70°C. Marshakov, Istratov, Puchkov, 2003

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## Experimental data. Combustion of homogeneous energetic materials

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Images of the surfaces of quenched AP samples: (a–g) samples 12 mm in diameter quenched by pressure drop and (h) sample 10 mm in diameter quenched with a coolant spray. The extinction of the samples occurred at the following pressures: (a) ~3, (b) ~7, (c) ~8–9, (d) ~3.5, (e) ~5, (f) ~3.5, (g) ~2.8, and (h) 3.0 MPa. Marshakov, Melik-Gaikazov, 2009

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## Effect of burning surface curvature

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Velocity of normal propagation of premixed flame depends on curvature of its front [Markstein]

$$u = u^0 \left( 1 + \alpha \frac{\kappa}{u^0 R} \right)$$

Analogy: reaction zone in premixed laminar flame and reaction zone in homogeneous condensed energetic materials

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## ZN-theory of non-steady combustion

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In accordance with phenomenological ZN-theory of non-steady combustion on homogeneous condensed energetic materials

$$u = u(p, \varphi)$$

$$u^0 = u^0(p, T_0)$$

$$\varphi = \frac{u^0}{\kappa} (T_s - T_0)$$

$$T_s = T_s(p, \varphi)$$

$$u = u^0(p, T_s(p, \varphi) - \kappa\varphi/u)$$

$$u \frac{dT}{dr} = -\kappa \frac{1}{r} \frac{d}{dr} r \frac{dT}{dr}$$

$$T(r = R) = T_s, \quad T(r = \infty) = T_0$$

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## Solution

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$$\varphi = \frac{u}{\kappa}(T_s - T_0) + \frac{u}{\kappa}(T_s - T_0) \left( \frac{\exp\left(-\frac{uR}{\kappa}\right)}{\frac{uR}{\kappa} \int_R^\infty \frac{1}{r} \exp\left(-\frac{ur}{\kappa}\right) dr} - 1 \right)$$

$$\varphi = \frac{u}{\kappa}(T_s - T'_0)$$

$$T'_0 = T_0 + \Delta T_0$$

$$\Delta T_0 = -(T_s - T_0) \left( \frac{\exp(-\xi)}{\xi \int_{\xi}^{\infty} \frac{1}{\xi} \exp(-\xi) d\xi} - 1 \right)$$

$$\xi = \frac{uR}{\kappa}$$

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## Effect of burning surface curvature

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$$Z = \exp\left(-\frac{2kK_0}{Z}\right)$$

$$Z = \frac{u}{u_N^0}$$

$$K = \frac{1}{2} \left( \frac{1}{\xi_1} + \frac{1}{\xi_2} \right) \quad \xi_{Ni} = \frac{u_N^0 R_i}{\kappa}$$

$$k = (T_s - T_0) \frac{\partial \ln u^0}{\partial T_0} = \beta(T_s - T_0)$$

Combustion of condensed energetic material with curved burning surface at

$$Z_{cr} = 1/e$$

$$2kK_0 > 1/e \approx 0.368$$

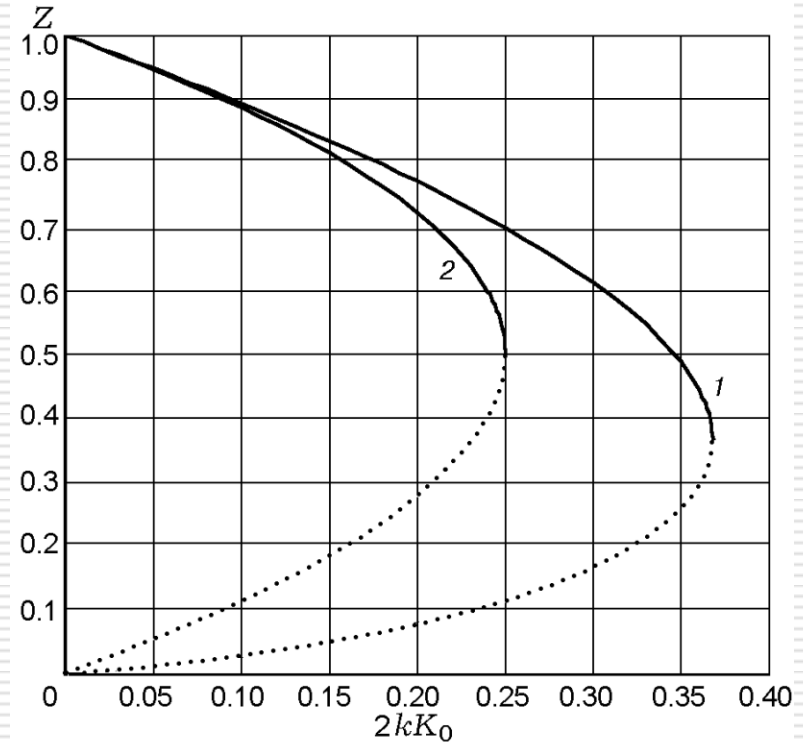
is impossible.

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## Results of calculations

$$u^0(p, T_0) = u_N^0(p) \exp(\beta \Delta T_0)$$

$$u^0(p, T_0) = u_0^0(p) (1 + \beta \Delta T_0)$$



Burning rate of the condensed energetic material with the curved burning surface convex toward the c-phase versus the parameter  $2kK_0$ : solutions for exponential (curve 1) and linear (curve 2) dependences of steady-state burning rate on initial temperature.  $K_0$  – non-dimensional curvature of burning surface.



## Comparison with experimental data

$$Mi = Ru/\kappa$$

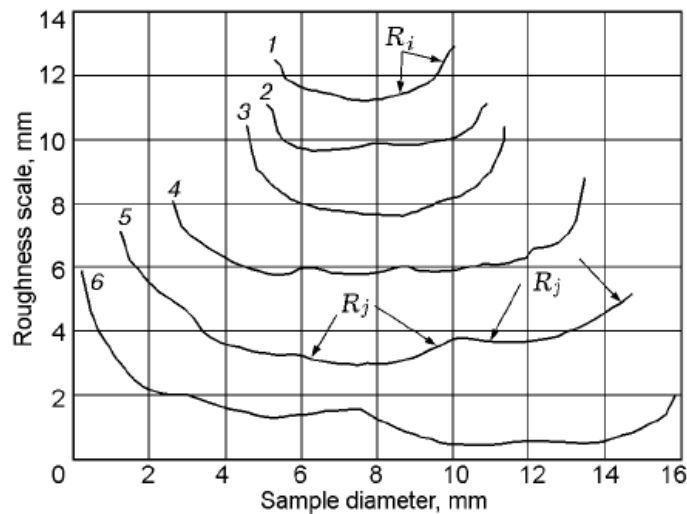
Theoretical critical value of Michelson-Markstein criterion

$$Mi_{cr} = 2ke$$

For example, for powder N, which has  $k = 2 \dots 2.5$  at  $p = 1-5$  atm, one obtains

$$Mi_{cr} = 10.8 \dots 13.5$$

which coincides with experimental data by Marshakov and Istratov



Profiles of quenched burning surfaces of samples of powder NB of various diameters: profiles 1, 2, and 3 refer to the samples of diameter 5, 6, and 7 mm, respectively and profiles 4, 5, and 6 refer to the samples of diameter 11, 14, and 16 mm, respectively, quenched in water;  $R_i$  and  $R_j$  are the surface curvature radii at the wall and at the bottom, respectively. Marshakov, Istratov, 2007

## Critical diameter of combustion

Assuming that quenching of combustion at decreasing of grain diameter is related to overlimited curvature of burning surface

$$R_{cr} = d_{cr} / 2$$

one obtains

$$d_{cr}(p) = \frac{4\kappa k(p)}{u_N^0(p)}$$

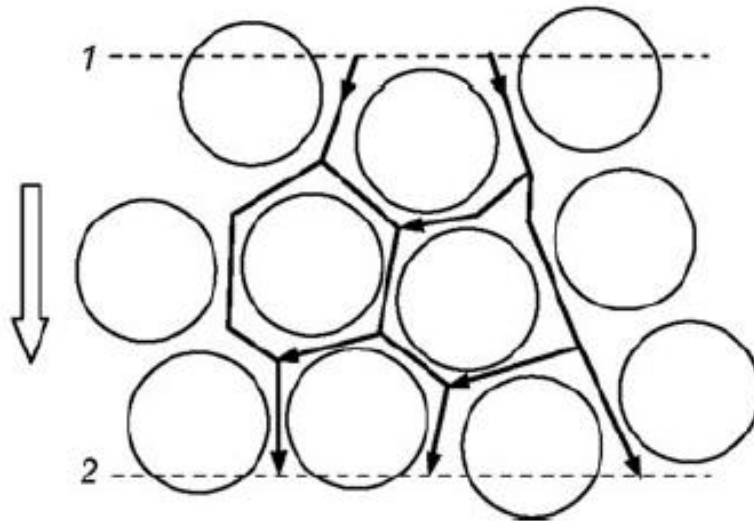
Assuming  $\kappa = 1.5 \cdot 10^{-3} \text{ cm}^2/\text{s}$ ,

$$d_{cr} = 0.15k / u_N^0$$

Energetic material	$k$	$u^0$	Theory	Experiment
Powder N	$k = 2.4p^{-0.1}$	$u_N^0 = 0.047p^{0.67}$	$d_{cr} = 7.7p^{-0.77}$	$d_{cr} = 7p^{-0.74}$
Powder A	$k = 2.4p^{-0.1}$	$u_N^0 = 0.1p^{0.64}$	$d_{cr} = 3.6p^{-0.75}$	$d_{cr} = 6p^{-0.75}$
Powder NB	$k = 2.4p^{-0.1}$	$u_N^0 = 0.09p^{0.65}$	$d_{cr} = 4p^{-0.75}$	$d_{cr} = 6.8p^{-0.76}$
RDX	$k \approx 2.3$	$u_N^0 = 0.037p^{0.82}$	$d_{cr} = 9.3p^{-0.82}$	$d_{cr} = 9.26p^{-0.88}$

## Combustion of binary mixtures with energetic binder

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$$Z = \frac{u}{u_b^0}$$
$$Z_b = \exp\left(-\frac{2kK_0}{Z_b}\right)$$

Diagram of combustion propagation in a mixture along binder layers between filler particles: the light thick arrow indicates the direction of combustion of the mixture as a whole, and the dark arrows show the direction of combustion of the binder layers; 1 and 2 are the initial and final positions of the average burning surface of the mixture as a whole.

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## Basic assumptions

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The basic assumptions of the model are as follows:

- (1) The burning rate of the mixture is determined by the burnup of binder layers between filler particles;
  - (2) The burning rate of the binder in the layers between filler particles differs from the burning rate of the pure binder;
  - (3) Change in the burning rate of binder layers between filler particles is mainly due to the curvature of the burning surface of the binder;
  - (4) The burning rate of particles of the dispersed components is equal to the stationary burning rate of these components as individual substances.
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## Scheme of the system

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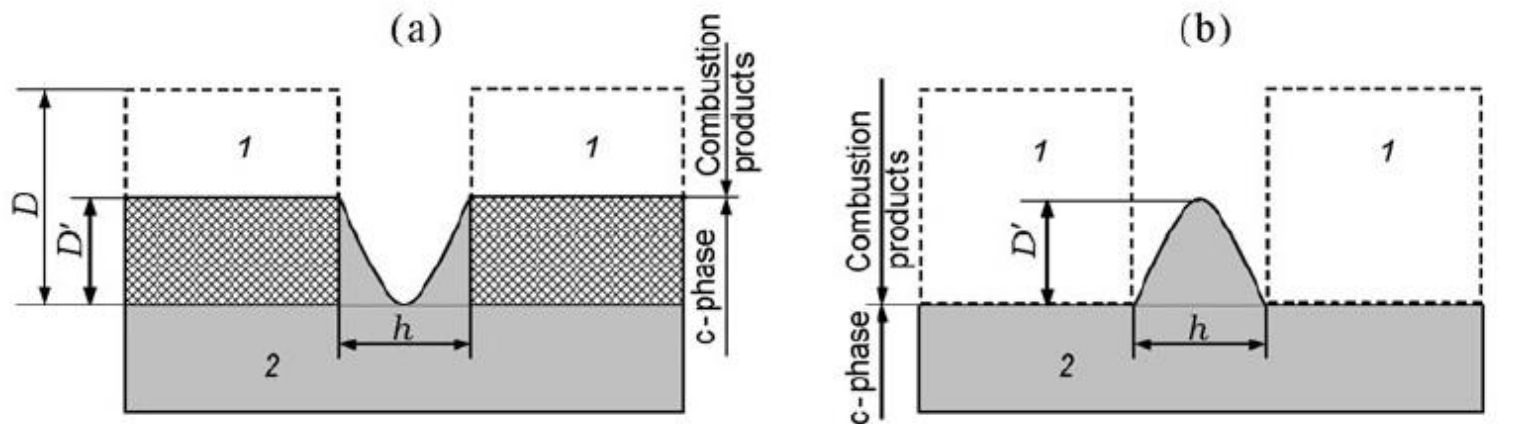


Diagram of burnup of the components in a mixture of a binder and a dispersed filler capable of self-sustained combustion: (1) filler particles; (2) binder; the dashed line shows the initial particle, and the shaded region is the remainder of the particle at the time considered; (a) the binder burns faster than the particle; (b) the binder burns slower than the particles.

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## Ignition delay time of the particles

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$$t_{ign}(h) = t_{ign}^{\infty} (1 - \exp(-\gamma h))$$

$$t_{ign}^{\infty} = C \frac{D^{n+1}}{u_b^*}$$

For ammonium perchlorate

$$t_{ign}^{\infty} = 0.15 \frac{\kappa}{Z_b u_b^2} \left( \frac{u_b D}{\kappa} \right)^{1.7}$$

For HMX

$$t_{ign}^{\infty} = \tau_0^{\infty} \frac{\kappa}{Z_b u_b^2} \left( \frac{u_b D}{\kappa} \right)^{0.6}$$

For CL-20

$$t_{ign}^{\infty} = 1.57 \frac{\kappa}{Z_b u_b^2} \left( \frac{u_b D}{\kappa} \right)^{0.37}$$

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## Parameters of the binders and fillers

Table 1. Parameters of binders used in mixtures

Binder number	Binder composition	$u_b$ , mm/s	$\rho_b$ , g/cm <sup>3</sup>
1	1/1 NG/AzPI	43.6 ( $p = 8$ MPa)	1.500
4	Powder A	15.0 ( $p = 8$ MPa)	1.600
5	NG	12.2 ( $p = 8$ MPa)	1.560
6	NHL	7.0 ( $p = 8$ MPa)	1.472
8	4/1 NHL/DBP	2.9 ( $p = 8$ MPa)	1.379
9	9/1 DNDEG/DBP	2.7 ( $p = 8$ MPa)	1.353
10	AFB3	7.3 ( $p = 4$ MPa) 13.2 ( $p = 10$ MPa)	1.520
11	AGS [15]	$0.159p^{0.513}$ ( $p \leq 21.5$ atm) $0.0784p^{0.748}$ ( $p \geq 21.5$ atm)	1.360
12	AFB1 [16]	16.9 ( $p = 10$ MPa)	1.460
—	HMX	8.0 ( $p = 4$ MPa) 14.7 ( $p = 8$ MPa) 17.7 ( $p = 10$ MPa)	1.960
—	AP particles [1]	$3.8p^{0.45}/D^{0.15}$ ( $p$ in atm; $D$ in $\mu\text{m}$ )	1.950
—	CL-20	30.5 ( $p = 10$ MPa)	2.04

Note: NG is the abbreviation for nitroglycerine, AzPI for azide plasticizer, NGL for nitroglycol, DBP for dibutyl phthalate, DNDEG for diethylene glycol dinitrate, AFB for nitroglycerine urethane binder, and AGS for polyurethane rubber and a plasticizer which is a mixture of nitrate esters.

## Parameters of the mixtures

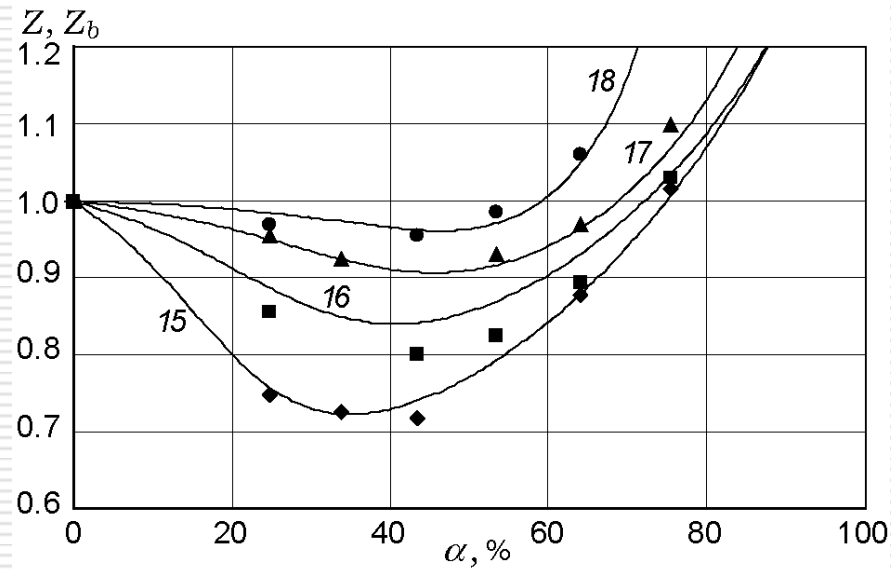
Table 2. Model parameters used in calculations

Variant number	Mixture composition (particle size)	$k_0$	$\sigma$	$\alpha_{\max}$
1	Bin. 1 + SiO <sub>2</sub> (17 $\mu\text{m}$ )	1	1.3	1
2	Bin. 1 + SiO <sub>2</sub> (1000 $\mu\text{m}$ )	1	0.4	0.77
3	Bin. 1 + HMX (20 $\mu\text{m}$ )	1	1.2	1
4	Bin. 1 + HMX (1000 $\mu\text{m}$ )	1	0.9	0.8
5	Bin. 5 + SiO <sub>2</sub> (17 $\mu\text{m}$ )	1.5	1.9	1.2
6	Bin. 5 + SiO <sub>2</sub> (900 $\mu\text{m}$ )	1.5	1.9	1.2
7	Bin. 5 + HMX (20 $\mu\text{m}$ )	1.5	2.9	0.85
8	Bin. 5 + HMX (900 $\mu\text{m}$ )	1.5	1.9	1.2
9	Powder A + SiO <sub>2</sub> (1000 $\mu\text{m}$ )	5	1.5	1
10	Powder A + HMX (40 $\mu\text{m}$ )	5	1.4	0.9
11	Bin. 10 + HMX (8 $\mu\text{m}$ )	1	5	0.87
12	Bin. 10 + HMX (40 $\mu\text{m}$ )	1	2	0.87
13	Bin. 10 + HMX (80 $\mu\text{m}$ )	1	1.6	0.87
14	Bin. 10 + HMX (140 $\mu\text{m}$ )	1	1.4	0.83
15	Bin. 10 + HMX (8 $\mu\text{m}$ )	1	3	0.95
16	Bin. 10 + HMX (40 $\mu\text{m}$ )	1	1.15	0.95
17	Bin. 10 + HMX (80 $\mu\text{m}$ )	1	0.9	0.9
18	Bin. 10 + HMX (140 $\mu\text{m}$ )	1	0.9	0.75
19	Bin. 9 + HMX (20 $\mu\text{m}$ )	1	1.4	1
20	Bin. 8 + HMX (20 $\mu\text{m}$ )	1	1.4	1
21	Bin. 6 + HMX (20 $\mu\text{m}$ )	0.8	2.8	1.1
22	Bin. 8 + SiO <sub>2</sub> (20 $\mu\text{m}$ )	1	1.7	1
23	Bin. 9 + SiO <sub>2</sub> (20 $\mu\text{m}$ )	1	1.8	1.1
24	Bin. 11 + AP (10 $\mu\text{m}$ )	1.2	0.7	0.7
25	Bin. 11 + AP (30 $\mu\text{m}$ )	1.2	0.9	0.9
26	Bin. 11 + AP (200 $\mu\text{m}$ )	1.2	0.75	0.75
27	Bin. 12 + CL-20 (35 $\mu\text{m}$ )	32	1.0	0.9
28	Bin. 12 + CL-20 (350 $\mu\text{m}$ )	32	0.9	0.8



## Calculations vs experimental data for HMX

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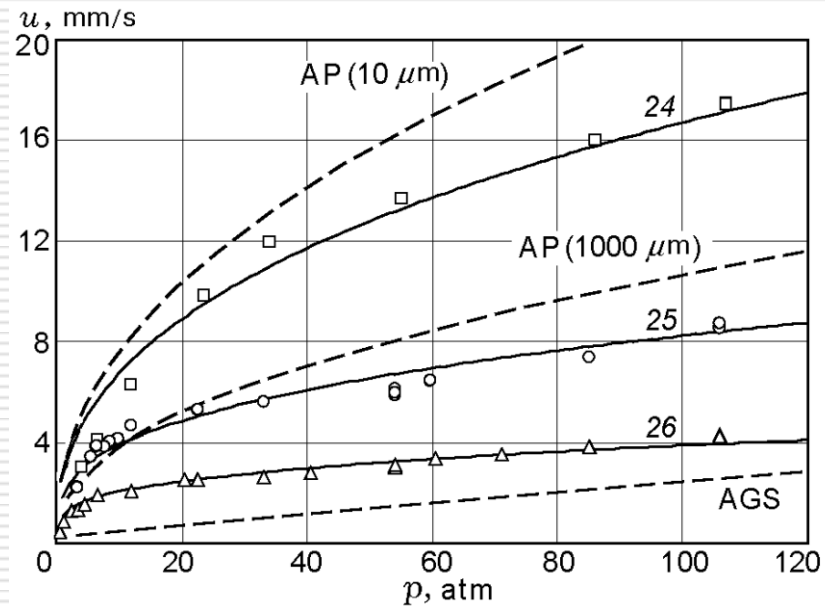


Calculated (curves) and experimental (markers) dependences of the burning rate of mixtures based on energetic binder AFB3 on the volume concentration of the filler at  $p = 10$  MPa.

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## Calculations vs experimental data for AP

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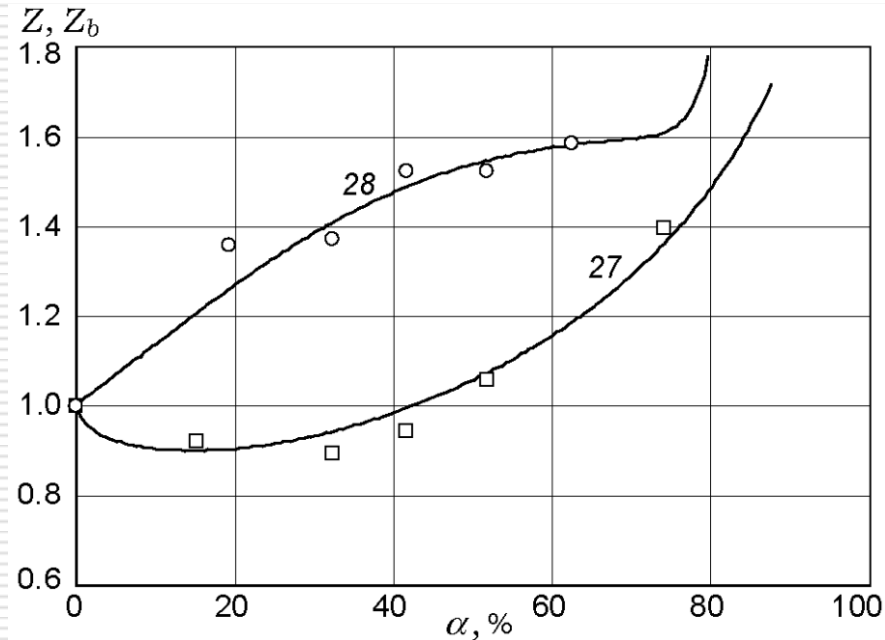


Calculated (curves) and experimental (markers) dependences of the burning rate of mixtures based on energetic binder AGS on the pressure at a volume concentration of the filler in the mixture  $\alpha = 29\%$ ; dashed curves correspond to combustion of the pure binder or individual AP particles of different sizes.

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## Calculations vs experimental data for CL-20

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Calculated (curves) and experimental (markers) dependences of the burning rate of mixtures of energetic binder AFB1 with CL-20 on the volume concentration of the filler at  $p = 10$  MPa.

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## CONCLUSIONS

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- A unified combustion mechanism for mixtures based on energetic binders with inert and active dispersed fillers is proposed.
  - The role of particles of different natures and different sizes reduces to curving the burning surface of the binder layers.
  - A combustion model for mixtures of energetic binders with inert fillers and active fillers was developed.
  - The wide set of available experimental data can be described using the proposed model.
  - Ignition delay of HMX, AP, and CL-20 particles in mixtures with energetic binders plays a crucial role in the burning rate of the mixtures.
  - A unified dependence of the ignition delay of HMX, AP, and CL-20 particles on their size, the burning rate of the mixture, and the thickness of the binder layers was proposed.
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# Thank you for attention!

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