

---

---

COMBUSTION, EXPLOSION,  
AND SHOCK WAVES

---

---

## Initial Stage of the Explosion of Ammonium Nitrate and Its Powder Mixtures

B. S. Ermolaev, A. A. Sulimov, V. E. Khrapovskii, and V. A. Foteenkov<sup>†</sup>

*Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia*

*e-mail: boris.ermolaev@yahoo.com*

Received September 13, 2010

**Abstract**—There is an obvious contradiction between the statistics of the devastating explosions that take place with the participation of ammonium nitrate and explosive properties of this material determined in standard tests. Pure ammonium nitrate does not burn under normal conditions and has a very low sensitivity to conventional mechanical and thermal stimuli. So far, ammonium nitrate has been detonated only by using high explosives. Causes of accidental explosions involving large masses of ammonium nitrate are likely to be found in a nonconventional behavior of ammonium nitrate. These changes may arise due to different chemical or physical factors, such as those associated with the presence of active additives, crushing of particles, etc., and lead to acceleration of the process at the initial stage of explosion. This work is devoted studying the convective burning and the initial stage of deflagration-to-detonation transition in dry and wet mixtures of ammonium nitrate with various, largely combustible additives. Experiments were conducted on loose-packed charges in a constant-volume bomb and by using the method of the critical bed height with recording pressure–time diagrams by a piezoelectric sensor. Ammonium nitrate of two different types was used: granular and powdered. The fuel additives were charcoal and aluminum powder, whereas the additives inhibiting the combustion of ammonium nitrate were water and monosodium salt of phosphoric acid. In addition, finely dispersed mixture of four components (ammonium nitrate, aluminum, powdered sugar, and TNT in a proportion of 76 : 8 : 12 : 4) was used. The experiments in the constant-volume bomb were supplemented by numerical simulations, which made it possible to obtain a better understanding of the convective burning of the test mixtures and to evaluate the possibility of using a constant-volume bomb to collect quantitative information on the intensity of the combustion of the mixture at the initial stage of the explosion.

*Keywords:* ammonium nitrate mixtures, combustion, detonation.

**DOI:** 10.1134/S1990793111030195

### INTRODUCTION

In the modern history of the production and handling of explosive materials, the most destructive accidental explosions have been associated with ammonium nitrate [1, 2]. However, there is an apparent contradiction between the statistics of explosions taking place with the participation of ammonium nitrate and the explosive properties of this material as determined by standard tests [3]. Pure ammonium nitrate does not burn under normal conditions and has a very low sensitivity to conventional mechanical and thermal stimuli. Up to now, there is no method of detonating ammonium nitrate other than transferring detonation from another HE. So far, nobody has been able to offer a science-based scenario that would link the picture of the explosion to the conditions and properties of ammonium nitrate, even for the most well known explosions in Oppau and Texas City [1]. Causes of accidental explosions involving large masses of ammonium nitrate should be sought in changes in its

usual behavior. These changes may be due to different chemical or physical factors, such as those associated with the presence of active additives [4], for example, a diminishment of particles, which leads to an acceleration of the initial stage of the explosion. This kind of information is also of interest for assessing the explosion safety in the production of a new generation of ammonium nitrate-based rocket propellants and for developing measures aimed at limiting the possibility of use of ammonium nitrate in terrorist activities.

To characterize the propensity of energetic materials to explosive development of combustion, two types of trials are traditionally performed: constant-volume bomb tests and deflagration-to-detonation transition test, with charges placed in a long steel tube [3]. The readings, the pressure growth in the bomb on the pressure–time diagram, and the length of predetonation-run distance are used for comparison with similar quantities measured for other materials and for constructing a series reflecting the relative explosiveness of the test material [5]. To gain insight into the phenomenon without performing complex comprehensive

---

<sup>†</sup> Deceased.

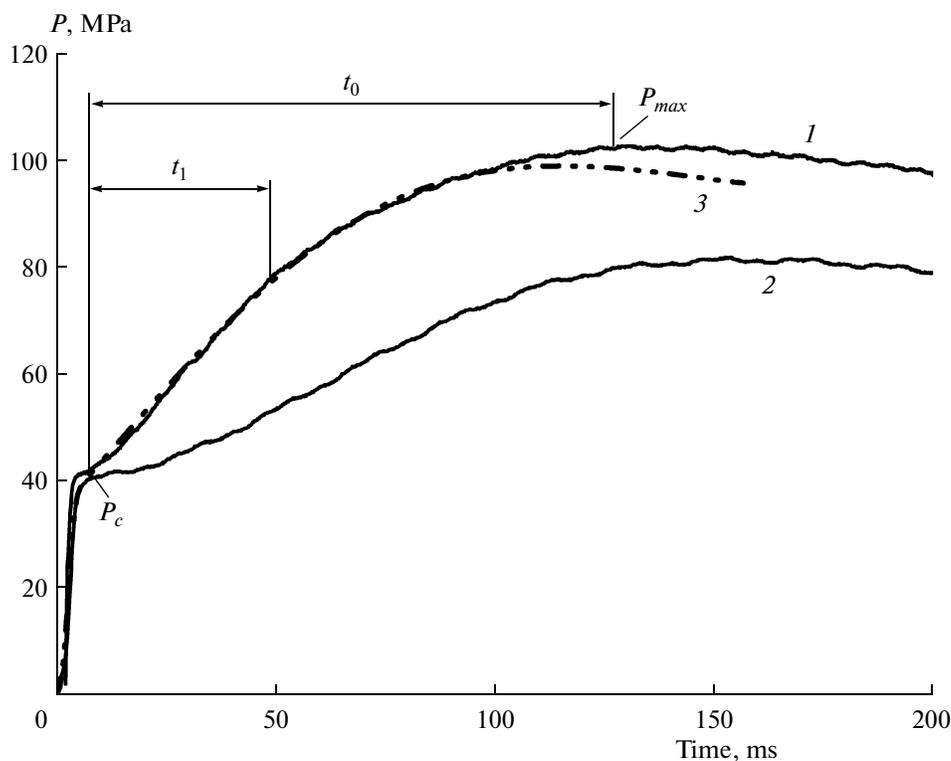


Fig. 1. Pressure–time diagram for the combustion of various samples in a constant-volume bomb: (1) industrial ammonium nitrate (1–2 mm), (2) agricultural ammonium nitrate (3–4 mm), and (3) calculated diagram for industrial ammonium nitrate.

measurements, it was proposed to use numerical simulation. Theoretical models [6–10] designed to analyze deflagration-to-detonation transition and convective burning have been developed and tested by many authors and demonstrated to be realistic.

In the present work, an approach that includes experiments simple enough for implementation and an analysis thereof using numerical simulations was used to study the initial stage of the explosion in dry and wet mixtures of ammonium nitrate with different, largely combustible additives. Experiments were performed in a constant-volume bomb and in a steel tube according to the method described in [11, 12], which, in addition to allowing measuring the length of the predetonation section, can be used to determine the critical conditions of explosion (the critical pressure and critical bed height of the test material).

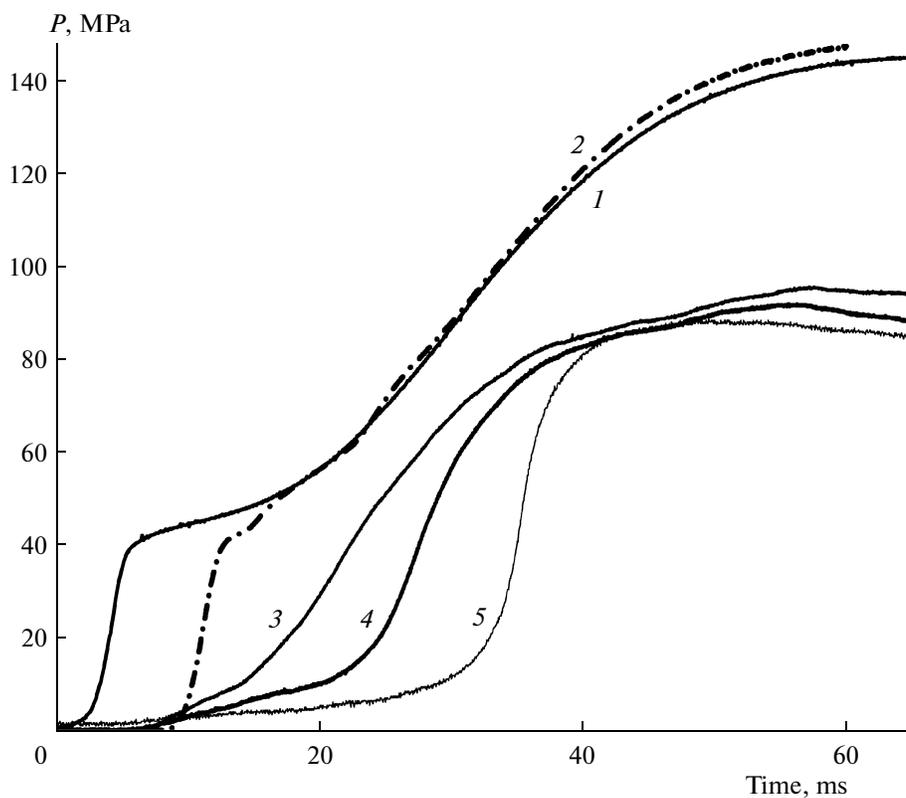
In the experiments, we used industrial-grade ammonium nitrate produced in France in the form of 1- to 2-mm porous spherical granules with a gravimetric density of  $\sim 700$  kg/m<sup>3</sup> as well as agricultural ammonium nitrate in the form of 3- to 4-mm granules with a density of 850 kg/m<sup>3</sup>. Granules were used in their original form or crushed to isolate 0.25–0.63-mm and <250- $\mu$ m fractions. The fuel additives were charcoal and aluminum powder, while the additives suppressing the combustion of ammonium nitrate were water and two monosubstituted salts of phosphoric acid: (NH<sub>4</sub> · H<sub>2</sub>PO<sub>4</sub>) and (K · H<sub>2</sub>PO<sub>4</sub>). In addition, we

studied a fine mixture of four components: ammonium nitrate, aluminum and sugar powder, and TNT in a proportion of 76 : 8 : 12 : 4, below referred to as mixture T. This mixture was studied in [13] in the course of development of testing methods. In numerical simulation, we used a theoretical model developed earlier for analyzing the convective burning of heterogeneous mixtures in a constant-volume bomb [9, 10].

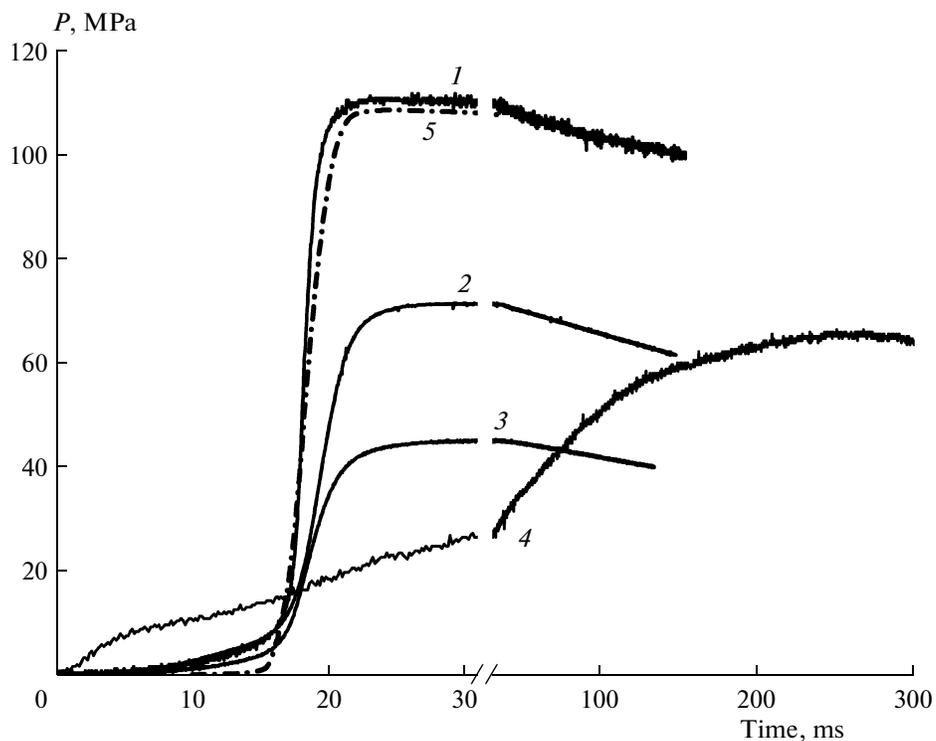
## 1. EXPERIMENTS IN THE CONSTANT-VOLUME BOMB

Experiments were performed in an 80-ml bomb at a loading density of 0.05–0.18 g/cm<sup>3</sup>. The test mixture was placed in a steel cup, 16 or 20 mm in inner diameter and 70 mm in height, and ignited at the upper, open end with a portion of crushed black powder from a Nichrome spiral. The weight of the igniter ranged from 0.5 to 2 g, ensuring that the pressure it created was slightly higher than the pressure of failure of layer-by-layer burning of the mixture [4]. The pressure was measured with a T-6000 piezoelectric transducer to an accuracy of  $\pm 8\%$ .

Typical pressure–time ( $P-t$ ) are shown in Figs. 1–3. The properties of the diagrams are characterized by three points: point  $P_c$ , the beginning of intense pressure growth caused by the convective burning of the mixture (after burnout of the igniter);  $(dP/dt)_{max}$ , the point of maximum pressure rise rate; and  $P_{max}$ , the



**Fig. 2.** Pressure–time diagram for the combustion of various samples in a constant-volume bomb: (1) ammonium nitrate (1–2 mm) with 18% ADS-4, (2) calculated diagram for this mixture; (3–5) mixtures of 16% charcoal with ammonium nitrate of various dispersities: (3) 1–2 mm, (4) 0.25–0.63 mm, and (5) < 0.25 mm.



**Fig. 3.** Pressure–time diagram for the combustion of mixture T in a constant-volume bomb at various weights (lengths) of the charge: (1) 10 g (66 mm), (2) 7 g (47 mm), (3) 5 g (33 mm), (4) 6 g of mixture T + 2% water, and (5) simulation results for 10-g charge of mixture T.

**Table 1.** Experimental results on the combustion of pure ammonium nitrate (AN) and mixtures thereof in a constant-volume bomb at a charge diameter of 20 mm

Composition	Properties of the charge: mass (g)/length (mm)/density (g/cm <sup>3</sup> )	Measurement results			
		$P_c/P_{max}$ , MPa	$(dP/dt)_{max}$ , MPa/ms	$t_0$ , ms	$t_1$ , ms
Industrial AN (1–2 mm)	8/36/0.71	42/102	0.95	125	39
Agricultural AN (3–4 mm)	8/30/0.85	42/82	0.44	130	71
Industrial AN (1–2 mm) + 16% charcoal	8/31/0.84	9/96	4.8	43	10.6
AN (0.25–0.63 mm) + 16% charcoal	8/37/0.71	10/92	7.5	36	9
AN (<0.25 mm) + 16% charcoal	8/35/0.75	7/88	18.4	25	11

point of maximum pressure (end of combustion). Under the same experimental conditions (primarily, at the same loading density), the quantity  $(dP/dt)_{max}$  is a measure of the intensity of combustion, whereas  $P_c$  is the pressure at which convective burning arises.

The measured values of these parameters, along with the time intervals that separate these points (the duration of combustion of the mixture  $t_0$ : from point  $P_c$  to  $P_{max}$ ; the duration of the progressive stage of combustion  $t_1$ , from  $P_c$  to  $(dP/dt)_{max}$  are listed in Tables 1 and 2. These experimental data led us to the following conclusions.

(1) Ammonium nitrate in the form of porous granules burns steadily in a constant-volume bomb at pressures above 40 MPa. At a loading density of 0.1 g/cm<sup>3</sup>, industrial ammonium nitrate burns at a maximum pressure rise rate  $(dP/dt)_{max}$  of ~1 MPa/ms, whereas agricultural ammonium nitrate burns about twice as slowly.

(2) Finely dispersed combustible additives greatly facilitate the ignition and intensify combustion of ammonium nitrate granules. A mixture containing 16% charcoal is characterized by a failure pressure of 9 MPa and  $(dP/dt)_{max} \sim 5$  MPa/ms. Addition of aluminum powder ASD-4 (at 2, 8 or 18%) acts generally weaker, showing lower values of  $(dP/dt)_{max}$  and higher of  $P_c$  than those characteristic of charcoal. The greatest effect of aluminum additives is observed for the stoichiometric mixture, with 18% aluminum.

(3) Grinding of ammonium nitrate granules facilitates the development of combustion in mixtures with combustible additives, increasing the pressure growth rate. At the same time, no trends in  $P_c$  were observed.

(4) A mixture prepared from crushed ammonium nitrate with additives of powdered sugar, aluminum, and TNT (mixture T) ignites easier and burns much more intensely than the mixture of ammonium nitrate with charcoal. When the length of the charge (loading density) was increased one and a half times, the pres-

sure rise rate increased sixfold, reaching 60 MPa/ms for a charge length of 60 mm.

(5) Moistening mixture T by adding of 2% water to the dry mixture dramatically slows down the process of burning. The failure pressure doubles, whereas the pressure growth rate drops more than tenfold. At 5% moisture, the mixture burns in the bed-by mode over the entire pressure range covered (up to 60 MPa).

(6) Addition of potassium salt of phosphoric acid slows down the burning of ammonium nitrate–aluminum mixtures, but the inhibitory effect is markedly inferior to the action of moisture. Ammonium salt, against expectations, caused an increase in the intensity of burning.

## 2. EXPERIMENTS ON DEFLAGRATION-TO-DETONATION TRANSITION IN STEEL TUBES

Since the standard deflagration-to-detonation tests of pure ammonium nitrate and mixtures thereof with combustible additives in thick-walled steel tubes produced no detonation [3, 5], we changed the experimental arrangement to obtain information on the initial stage of explosion development. Experiments were carried out in steel tubes with an inner diameter of 16 or 32 mm and a length of 400 mm. The tube was installed vertically on the closed bottom end, whereas the upper end was opened. The igniter cap and a portion of black powder (0.25–2 g) were placed on the bottom of the tube. The tube had an orifice near the bottom for accommodating a piezoelectric quartz pressure sensor. The material to be tested was poured into the tube to form a bed of a given height  $H$ . The experiments were performed with two mixtures based on fine sodium nitrate: a mixture with 16% charcoal and sensitized mixture T.

This experimental arrangement and its relation to explosion safety were considered in [11, 12]. The test result depends on the height of the bed. At a small bed

**Table 2.** Experimental results on the combustion of ammonium nitrate–aluminum mixtures and mixture T activated by TNT additive in a constant-volume bomb at a charge diameter of 16 mm

Composition	Properties of the charge: mass (g)/length (mm)/density (g/cm <sup>3</sup> )	Measurement results			
		$P_c/P_{max}$ , MPa	$(dP/dt)_{max}$ , MPa/ms	$t_0$ , ms	$t_1$ , ms
AN (1–2 mm) + 18% ADS-4	8.4/ 56/0.72	45/135	3.6	38.5	19.4
AN (0.25–0.63 mm) + 18% ADS-4	7.1/65/0.53	50/136	5.5	19	8
AN (0.25–0.63 mm) + 18% ADS-4 + 10% KH <sub>2</sub> PO <sub>4</sub>	7.3/58.2/ 0.61	44/113	4.3	44	12
AN (0.25–0.63 mm) + 18% ADS-4 + 10% (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	6.9/50.1/ 0.66	38/127	44.0	18.6	0.2
Mixture T	6 /40/0.75	5/56	10.5	21	5
Mixture T	8/53/0.75	5/81	31	18	4
Mixture T	10/60/0.75	5/111	60	9.5	4.2
Mixture T + 2% water	6/40/0.75	11/66	1.2	250	14

height, the charge burns quietly, without explosion, although some burning material is ejected from the tube through the upper open end and burns out on the base. A typical pressure–time diagram (Fig. 4) first rises smoothly, passes through a maximum, and then descends. With increasing bed height, the result changes little as long as the bed height does not exceed a certain critical height  $H^*$ . In this case, burning goes over into explosion (for typical high explosives, detonation accompanied by the destruction of the tube). At a bed height larger than  $H^*$ , the initial, smooth behavior of the pressure–time diagram gives way to a succession of sharp peaks with an amplitude of several hundred MPa. As a result, a wave process arises, which, judging by the amplitude of the pressure can be classified as low-speed detonation.

The parameters measured at the critical conditions:  $H^*$  and the maximum pressure  $P^*$ , and the time of rise  $t^*$  to the maximum pressure in the  $P(t)$  dependence recorded at the bottom of the tube can be recommended for a realistic assessment of the propensity of large masses of explosive materials to explode. The experimental results are illustrated in part in Figs. 4 and 5. The results obtained can be recapitulated as follows.

(1) The tests conducted with mixture T in a steel tube 16 mm in inner diameter and 400 mm in length yielded the critical bed height of ~275 mm and a critical pressure of ~7.3 MPa. In experiments with mixture bed height less than  $H^*$ , the burning occurred without explosion, with most of the burning mixture being ejected into the atmosphere. The pressure rise time was ~15–20 ms, while the pressure at the maximum

varied from 2.0 to 5.5 MPa, depending on the mixture bed height. In experiments with a bed height larger than  $H^*$ , it took a shorter time for the process of burning to transform into an explosion, with a rapid pressure rise in the combustion zone to 250 MPa.

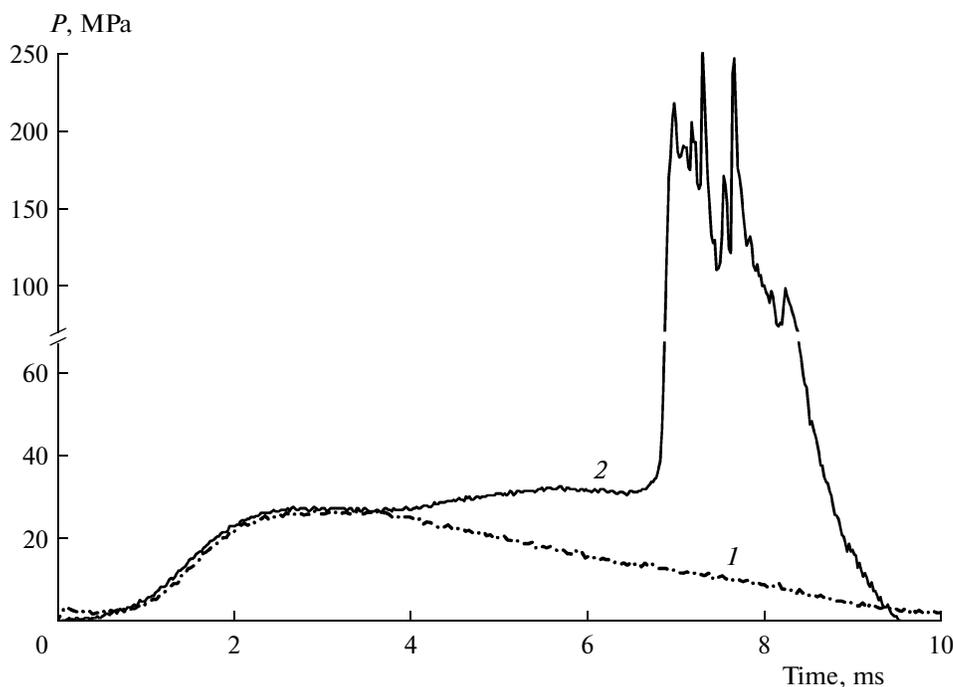
(2) As the weight of the igniter was increased from 0.25 to 2 g of black powder, the critical bed height reduced to 126 mm, the pressure rise time decreased slightly, and  $P^*$  remained at about the same level.

(3) As the charge diameter was changed from 16 to 32 mm, the critical bed height for the 2-g igniter increased almost twofold, to 240 mm. Extrapolating the dependence of the critical height on the charge diameter to a diameter of 200 mm (at which the existing data are indicative of a weakening of this dependence [12]), we obtained a value of about 1.5 m. This gives a rough estimate of the height of a heap or pile for which burning can transform into an explosion.

(4) Experiments carried out with a mixture of ammonium nitrate (0.25–0.63-mm grain size) with 16% charcoal in a tube with a diameter of 16 mm gave a higher value of  $P^*$  (~27 MPa) and higher values of  $H^*$  (>320 mm) as compared to mixture T.

### 3. ANALYSIS OF COMBUSTION IN BOMB MANOMETRIC

The simulations were performed using a computer program we developed earlier based on a model of the convective burning of porous heterogeneous materials in a constant-volume bomb; for details, see [9, 10]. The model equations are written in the Eulerian form in the one-dimensional approximation within the



**Fig. 4.** Pressure–time diagram obtained in critical bed height tests of a mixture of ammonium nitrate (0.25–0.63 mm) with 16% charcoal at bed heights of (1) 320 and (2) 510 mm.

framework of the mechanics of two-phase reacting media [14]. The model considers convective burning that propagates through a porous cylindrical charge of length  $L$  placed in a strong (steel) cup. The open end of the charge, covered with the igniter, communicates with the cavity of the bomb. The process begins with the burning of the igniter, which causes an increase in pressure in the cavity. The combustion products penetrate deep into the charge, initiating convective burning. As the charge burns, gaseous products outflow into the cavity of the bomb, carrying particles dispersed from the burning charge.

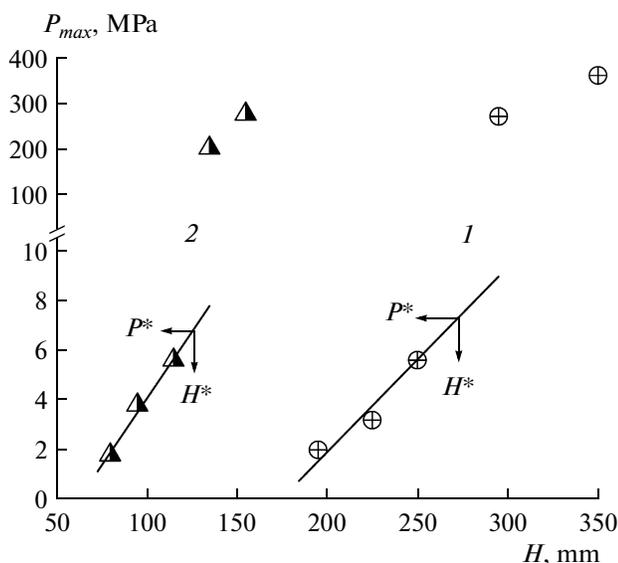
The porous charge is prepared from a two- to three-component heterogeneous mixture based on a dispersed oxidizer, in this case, ammonium nitrate. Particles of ammonium nitrate are regarded as the carrier component, which defines the structure of the charge, defining, with account of the porosity, the permeability, pore diameter, and specific surface area. The other two components (aluminum powder and any additive, such as a sensitizing agent, TNT, or combustible liquids) are distributed in a thin layer over the surface of the carrier component particles. The model takes into account the following processes: the filtration of flow of gas in the pores of the charge, convective heating and ignition of the pore surface; burning of carrier component particles, diffusion combustion of aluminum, combustion of the third component; deformation and motion (compaction or dispersion) of the solid phase under the influence of local pressure peaks;

burnout of dispersed particles in the cavity of the bomb; and heat transfer to the walls of the bomb.

To describe these processes and perform calculations, it is necessary to know a large number of input parameters. Although some of them for ammonium nitrate and mixtures thereof are poorly known, the calculations in general managed to achieve good agreement with the results of experiments in constant-volume bombs, which was achieved by selecting the particle diameter and burning rates of the components. The corresponding particle diameters of ammonium nitrate turned out to be in their natural range, limited by the upper and lower particle diameters of the used fractions, whether original or crushed product. The particle size of aluminum (ASD-4) was  $9\ \mu\text{m}$ . To calculate the burning rates, we used the corresponding data from the literature.

The input parameters of the model for the combustion products were determined from the results of thermodynamic calculations, which were performed using the TDS program [15] for solving the problem of combustion at constant volume and energy with the use of the equation of state of an ideal gas. More information and a comparison of the simulation results with the experimental data are given below.

**Pure ammonium nitrate.** According to thermodynamic calculations, the heat of combustion of ammonium nitrate is 1.47 MJ/kg, combustion temperature, 1560 K, impetus 0.57 MJ/kg, and polytropic exponent 1.24. Experimental data on the ignition and combus-



**Fig. 5.** Dependence of the maximum pressure on the bed height for mixture T and the method for determining the critical parameters (a tube with an inner diameter of 16 mm and (1) 0.25-g and (2) 2-g black powder igniters). The symbols represent experimental data; the lines, a linear interpolation over the subcritical segment.

tion of ammonium nitrate are very scarce. Based on measurements of the rate of layer-by-layer burning of pressed ammonium nitrate samples with catalytic additives [16] in a constant-pressure bomb, we performed calculations using the burning rate law  $U_p$  (mm/s) =  $0.6 [P(\text{MPa})]^{0.53}$ , which gives a burning velocity of 7 mm/s at 100 MPa. The temperature of ignition of ammonium nitrate in the combustion wave was set to be 800 K. The calculations were performed for industrial ammonium nitrate with a grain diameter of 2.2 mm and for agricultural product with a particle size of 3.5 mm.

**Mixture of 82% ammonium nitrate and 18% aluminum.** The burning of this mixture was considered in the two-component mixture approximation with a two-step reaction, involving the burning of ammonium nitrate and the combustion of aluminum particles in the products of its decomposition. The thermodynamic characteristics and the burning rate of ammonium nitrate are given above. The composition of combustion products was selected in a simplified form: 57 mol %  $\text{H}_2\text{O}$ , 29%  $\text{N}_2$  and 14%  $\text{O}_2$ . For the mixture, according to calculations, the heat of combustion is equal to 6.5 MJ/kg, combustion temperature 3946 K, the impetus 1.07 MJ/kg, polytropic exponent 1.145, and fraction of liquid alumina in the combustion products 33.6 wt %. The burning rate of aluminum particles  $U_{\text{Al}}$  was determined by differentiating the empirical equations from [17], which determines the burning time of aluminum particles  $t_b$  as a

function of their initial diameter  $d_{0,\text{Al}}$  and the oxidizing activity of the gaseous medium  $X_{\text{ef}}$ :

$$t_b = \frac{d_{0,\text{Al}}^n}{C_1 X_{\text{ef}}}$$

The respective formula for the burning rate reads as

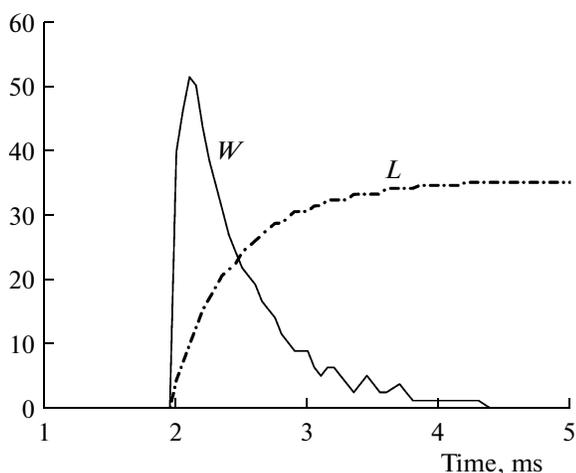
$$U_{\text{Al}} = \frac{C_1 X}{2nd_{\text{Al}}^{n-1}}$$

Here, the particle diameter and oxidative activity of the gaseous medium are the local quantities, which vary with time.

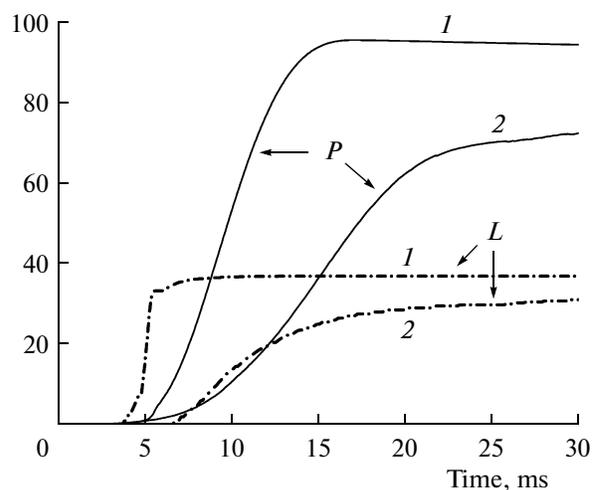
Selection of the coefficients encounters certain difficulties because of a strong scatter in the empirical data on the burning time, especially for fine aluminum particles, with a size smaller than 10  $\mu\text{m}$  [17, 18]. The calculations were performed at  $n = 1.5$ ,  $C_1 = 0.045 \text{ cm}^{1.5}/\text{s}$ ,  $d_{0,\text{Al}} = 9 \mu\text{m}$ , and  $X_{\text{ef}} = 0.5$  [18] for the above decomposition products of ammonium nitrate. The reference burning time of particles with a diameter of 9  $\mu\text{m}$  in this atmosphere is 1.2 ms. The ignition temperature was set equal to the melting point of aluminum.

**Mixture T.** The process of burning was treated in the three-component mixture approximation: a mixture of ammonium nitrate with sugar was considered as a monopropellant, whereas aluminum and TNT, as additives. The thermodynamic characteristics for mixture T were as follows: the heat of combustion, 4.4 MJ/kg; combustion temperature, 2580 K; impetus, 1.01 MJ/kg; and polytropic exponent, 1.17. For the monopropellant, heat of combustion is equal to 3.2 MJ/kg; the approximate composition of the products of combustion: 61%  $\text{H}_2\text{O}$ , 11%  $\text{CO}_2$  and 1%  $\text{O}_2$ ;  $X_{\text{ef}} = 0.4$ ; the burning rate and ignition temperature were assumed to be the same as those for the mixture of ammonium nitrate with charcoal. The heat of combustion of TNT is set equal to 3.2 MJ/kg, the ignition temperature 700 K, and the rate of layer-by-layer burning  $U_p$  (mm/s) =  $0.65P$  (MPa). The characteristics of combustion and ignition of aluminum particles remained unchanged—only the initial particle size was set equal to 4  $\mu\text{m}$ .

**Moistened Mixture of 84% ammonium nitrate and 16% charcoal.** The combustion of the dry mixture was considered in the monopropellant approximation. In thermodynamic calculations, we assumed that charcoal has the chemical formula  $\text{C}_6\text{H}_2\text{O}$  and the enthalpy of formation of 100 kJ/mol. The content of ash and moisture were disregarded. According to these calculations, the heat of combustion of the mixture is 3.6 MJ/kg, combustion temperature 2614 K, impetus 0.95 MJ/kg, and polytropic exponent 1.21. Based on results reported in [16], the layer-by-layer burning velocity of the mixture was written in the form  $U_p$  (mm/s) =  $1.25[P(\text{MPa})]^{0.53}$ , which yields a burning velocity of 14 mm/s at 100 MPa. In modeling the combustion of the moistened mixture, we assumed that the added water is localized in the near-surface layer the ammonium nitrate particles and that it evaporates



**Fig. 6.** Calculated time history of the flame front position ( $L$ , mm) and convective burning velocity ( $W$ , m/s) for pure ammonium nitrate (1–2 mm).



**Fig. 7.** Calculated time histories of the pressure ( $P$ , MPa) and the flame front positions ( $L$ , mm) for a (1) dry and (2) wetted (with 3% water) mixtures of ammonium nitrate (0.25–0.63 mm) with 16% charcoal.

completely at the stage of convective heating ahead of the combustion wave. The calculations were performed for a mixture containing crushed ammonium nitrate with a particle diameter of 0.3 mm.

The simulation results, along with experimental data, are shown in Figs. 1–3 and 6, 7 and in Table 3. The simulation results can be summarized as follows.

(1) Since the pressure rise rate in the bomb is mainly determined by the density of loading and intensity of combustion, the model's ability to reproduce the experimental pressure diagram is an encouraging confirmation of the hypothesis underlying the model. According to this hypothesis, the intensity of combustion can be rather accurately estimated from the initial surface area of particles, defined by their diameter, and from the layer-by-layer burning rate law formulated based on the available data.

(2) For ammonium nitrate with original grains and mixtures based on it, convective burning has a number of specific features, which are due to the high permeability of the bed and the fact that, before beginning to burn, the bed is noticeably compacted under the influence of the high pressure created by the igniter. The example displayed in Fig. 6 for pure ammonium nitrate shows that the flame speed, reaching a value of ~50 m/s, decreases rapidly due to pressure equalization along the length of the charge. The time during which combustion spreads throughout charge is ~2 ms, which constitutes only a small fraction of the total burning time of the charge  $t_0$ .

(3) Although crushed ammonium nitrate mixtures burn more intensively, providing a higher pressure rise rate (approximately inversely proportional to particle size), but the rate of convective burning decreases and

**Table 3.** Simulation results on the combustion of ammonium nitrate and mixtures thereof in a constant-volume bomb

Composition	Measurement results				
	$P_c/P_{max}$ , MPa	$(dP/dt)_{max}$ , MPa/ms	$W_{max}$ , m/s	$t_0$ , ms	$t_1$ , ms
Industrial AN (1–2 mm), calculated at $d_0 = 2.2$ mm, $U_{100} = 8.8$ mm/s	42/101	1.0	48	100	16
Agricultural AN (3–4 mm), calculated at $d_0 = 3.5$ mm, $U_{100} = 6.7$ mm/s	42/85	0.46	7.5	200	44
Mixture T, 10 g	1/109	36	32	9	3.6
AN (0.25–0.63 mm) + 18% ADS-4	43/146	3.4	18	45.3	16
AN (0.25–0.63 mm) + 16% charcoal	1/95.6	13	46	9.2	17.2
AN (0.25–0.63 mm) + 16% charcoal + 3% water	2/76	6	5.4	15.2	47

Note:  $W_{max}$  is the maximum convective burning velocity.

more uniformly changes along the length of the charge. The stage of convective burning is a significant portion (one-quarter to one half) of the total time of burning of the charge.

(4) The addition of combustible components also increases the intensity of burning, but to a lesser extent than the pulverization of the ammonium nitrate. Using mixture T, as an example, we examined the effect of the charge length (density of loading) and showed that, as the pressure rise rate 100 MPa/ms is approached, which can be roughly interpreted as the threshold of an explosion, the rate of convective burning increases, producing a significant (up to 30–50%) difference between the pressure in the combustion wave and in the bomb.

(5) In accordance with the experimental data, the simulation results predict a strong retarding effect of small additives of water. The effect is mainly determined by a high heat of vaporization of water, which, being absorbed on the surface of ammonium nitrate granules, greatly impedes the ignition and, consequently, reduces the rate of convective burning. In addition, water vapor, entering the pores ahead of the combustion front, promotes pressure equalization. As a result, the convective combustion wave does not reach the end of the charge, and the charge partially burns in the regime of layer-by-layer burning.

## CONCLUSIONS

A high stability of ammonium nitrate to external physical stimuli makes the standard test methods unsuitable for estimating the explosiveness of this substance. Researchers are forced to look for unconventional ways, in particular, placing hopes on numerical simulations of explosions, refining the available models and collecting input information needed for the calculations.

In this study, information obtained by measurements on pure ammonium nitrate in a constant-volume bomb and its mixtures with various additives was complemented by numerical simulations of the process and experiments on elongated charges, which gave information about the initial stage of the development of the explosion from the combustion zone. The following results were obtained.

It was shown that the loose-packed bed of pure ammonium nitrate granules can burn in the convective mode at pressures above 40 MPa. The intensity of gas formation in the combustion wave can be assessed with a reasonable accuracy if the product of the layer-by-layer burning rate of ammonium nitrate and the surface area of the granules are known.

In the presence of a combustible additive, the burning rate is higher, while the threshold pressure at which convective burning arises is lower (these effects are more pronounced for charcoal and weaker for aluminum additives, because of a high thermal conductivity of the latter, a factor that impedes ignition).

Phosphorus-containing additives, usually recommended as a means for suppressing the explosive decomposition of ammonium nitrate, affect the combustion of mixtures differently, and in any case, much weaker as compared to the effectiveness of moisture, which greatly impedes convective burning, mainly due to the large heat of vaporization. Additionally, water vapor, entering the pores ahead of the combustion front, promotes a more rapid equalization of pressure. As a result, convective burning does not reach the end of the charge and, therefore, it partially burns out in the layer-by-layer mode.

For pulverized ammonium nitrate, the burning of the mixture is enhanced, but the threshold pressure required to initiate convective burning remains essentially the same. As the length of the charge (see experiments with mixture T in Table 2) is increased, the pressure rise rate increases rapidly, approaching 100 MPa/ms, a value that usually signifies the hazards of explosion.

Tests carried out with two mixtures in a steel tube with an open upper end face and combustion being initiated near the closed bottom end showed that, at a height of the mixture bed lesser than some critical value  $H^*$ , burning occurs without an explosion, with most of the burning mixture being ejected into the atmosphere. If the bed height exceeds  $H^*$ , the process of combustion transforms into an explosion, with the formation of a low-speed detonation wave and a rapid increase of the pressure in the combustion zone to several hundred MPa. The critical bed height varies depending on the power of the initiator and the tube diameter, whereas the pressure that is achieved at  $H^*$  or the critical pressure  $P^*$  is independent of these parameters. Its magnitude was  $\sim 7$  MPa for mixture T and approximately 27 MPa for a mixture of pulverized crushed ammonium nitrate (0.25–0.63 mm) with 16% charcoal, which is higher than the pressure at the beginning of the convective burning measured for these mixtures in the constant-pressure bomb.

Numerical simulations, after refinement (selecting) of the mean grain size and the burning rate law of ammonium nitrate that would provide agreement with experimental data made it possible to examine the characteristics of convective burning. For coarse ammonium nitrate and mixtures thereof, convective burning starts at a high rate, which, however, decreases quickly due to equalization of the pressure along the charge length. The time during which combustion spreads throughout the entire length is short compared to the total burning time of the charge. For mixtures with crushed ammonium nitrate, the duration of the stage of convective burning takes from one third to one half of the total burning time of the charge, while the convective burning rate increases with the pressure in the combustion wave, which can be 30–50% higher than the instantaneous pressure in the bomb.

## ACKNOWLEDGMENTS

The authors are grateful to S. G. Andreev (Moscow State Technical University), who initiated a series of studies that are included in the present paper and participated in the discussion of the results.

This work was supported by the Russian Foundation for Basic Research, project no. 09-03-00229.

## REFERENCES

1. V. Marshall, *Major Chemical Hazards* (Ellis-Horwood, Chichester, UK, 1987; Mir, Moscow, 1989).
2. G. S. Biasutti, *History of Accidents in the Explosive Industry* (Published by the author, Vevey, Switzerland, 1985).
3. *Recommendations on the Transport of Dangerous Goods. Manual of Test and Criteria*, 2nd ed. (United Nations, New York, 1990).
4. B. S. Ermolaev, A. A. Sulimov, A. A. Borisov, et al., *Khim. Fiz.* **26** (7), 50 (2007).
5. A. F. Belyaev, V. K. Bobolev, A. I. Korotkov, A. A. Sulimov, and S. V. Chuiiko, *Deflagration-to-Detonation Transition in Condensed Systems* (Nauka, Moscow, 1973) [in Russian].
6. M. R. Baer and J. W. Numziato, *Int. J. Multiphase Flow* **12**, 861 (1986).
7. A. K. Kapila, R. Menikof, J. B. Bdzil, et al., *Phys. Fluids* **13**, 3002 (2001).
8. B. S. Ermolaev, A. A. Belyaev, and A. A. Sulimov, *Khim. Fiz.* **23** (1), 62 (2004).
9. B. S. Ermolaev, A. A. Belyaev, and A. A. Sulimov, *Khim. Fiz.* **24** (1), 79 (2005).
10. A. A. Borisov, B. S. Ermolaev, P. V. Komissarov, et al., *Pulsed and Continuous Detonations*, Ed. by G. Roy, S. Frolov, and J. Sinibaldi (Torus Press, Moscow, 2006), p. 91.
11. B. S. Ermolaev, V. A. Foteenkov, B. A. Khasainov, et al., *Fiz. Goreniya Vzryva*, No. 5, 102 (1990).
12. B. S. Ermolaev, S. E. Malinin, A. A. Sulimov, et al., RF Patent No. 2037814, *Byull. Izobret.* No. 2 (1995).
13. S. G. Andreev, A. I. Chernov, and V. Yu. Sychev, *Khim. Fiz.* **27** (8), 61 (2008).
14. R. I. Nigmatulin, *Dynamics of Multiphase Media* (Nauka, Moscow, 1972; Hemisphere, New York, 1990).
15. S. B. Viktorov, S. A. Gubin, I. V. Maklashova, et al., *Khim. Fiz.* **24** (12), 22 (2005).
16. A. P. Glazkova, *Catalysis of Combustion of Explosive Matters* (Nauka, Moscow, 1976) [in Russian].
17. P. F. Pokhil, A. F. Belyaev, Yu. V. Frolov, et al., *Combustion of Metal Powders in Active Media* (Nauka, Moscow, 1972) [in Russian].
18. K. P. Brooks and M. W. Beckstead, *J. Propuls. Power* **11**, 769 (1995).