CONVECTIVE BURNING OF TERNARY ALUMINUM–AMMONIUM PERCHLORATE–NITROMETHANE MIXTURES

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Introduction

Explosions of aluminum-rich materials can be more beneficial than detonation of conventional energetic materials under certain conditions not only because oxidizer–aluminum mixtures are usually more energetic than homogeneous explosives but also because expanding explosion products are capable of entering the reaction with the ambient medium (air or water) to release large amount of additional heat. To produce intense pressure pulses, the charges must either detonate or burn in a fast deflagration mode, which in some situations can be even more efficient because provides better conditions for mixing of the products with ambient oxidizer than does detonation. Significant drawbacks of aluminum–oxidizer mixtures are that their combustion products contain small amount of gaseous components and that without appropriate additives it is hard to fabricate dense mechanically strong charges with controlled porosity. Thus, optimal compositions should contain additives that serve as both a gasprovider and binding (compacting) component. Dense ternary mixtures with no additives of high explosives are extremely hard to detonate, therefore convective burning is virtually the only regime that can provide fast pressure buildup in the charge. Unfortunately, information about studies of convective burning of ternary mixtures is lacking; therefore, the present work is an attempt to develop a model of this burning regime* in mixtures with liquid gasprovider (nitromethane (NM)) and to verify it experimentally.

Theoretical Model and Computer Code

Convective burning was simulated using a physical approach resting on the mechanics of two-phase reacting fluids [1]. The model was a modified version of model [2]. It included three exothermic chemical reactions (burning of ammonium perchlorate (AP), NM vapor, and aluminum in combustion products of AP and NM). The reaction rates were expressed by the phenomenological laws of AP and Al combustion and a global Arrhenius type formula for decomposition of NM vapor.

Basic notions of the model. Geometry of the problem is illustrated in Fig. 1. A cylindrical premixed porous AP/Al/NM charge of a preset length was placed in the channel of a combustion chamber. One of the butt channel ends was closed with a plug, the other was open and connected to a bomb volume in which an igniter was positioned. The charge to be studied was a porous body, mechanical behavior of which was distinguished by hysteresis depending on the strain sign. Under compression, the charge behaved as an ideal plastic body whereas under stretching stress exceeding a certain limiting value, the charge was capable of dispersion. The structure units were AP particles of mean diameter d_{ko}. Aluminum particles (either flakes about 1 μm thick or spheres several microns in diameter) were much finer and coat AP particles with a thin uniform layer. The reacting mixture comprised 6 components: AP, NM, Al particles (coating AP particles and in aggregates), and also gaseous combustion products and a dispersed product of aluminum oxidation. Aluminum particles were oxidized in the diffusion combustion regime by the gaseous products of nitromethane and AP combustion. Some fraction of the products of mixture combustion

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*A specific regime of burning of porous energetic materials in which heat is transferred from the combustion products by convection is usually called convective burning. The combustion products penetrate inward the charge through pores to preheat and ignite the energetic material at pore surface. The properties of convective burning, which precedes all detonation-like processes in solids make it fairly attractive for using in various pulse pressure sources.

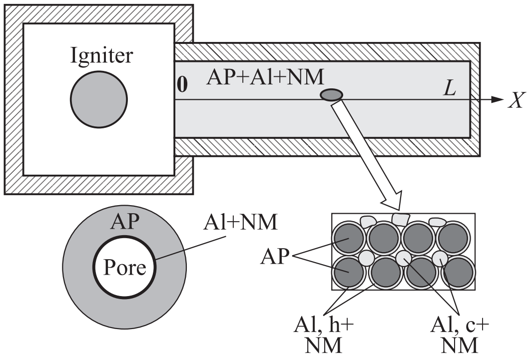

Figure 1 Schematic specifying geometry of the problem solved and schematic of unit cell used to analyze preheating and ignition of condensed components of the mixture

penetrated through pores inward the charge to preheat the pore surface. The available data on the surface temperature in burning charges of AP and compositions based on it (500–600 °C according to [3]) were used. Conditions for ignition of Al particles varied depending on a particle size according to the literature data [3, 4]. Nitromethane burning included an evaporation stage, NM burned in the gas phase in a flame controlled by an Arrhenius-type reaction.

The cell is also shown in Fig. 1. The size of the cell and its layers were assessed using the AP particle size, charge porosity and ratio of the components with the aid of well-known formulas. The analysis reduced to solving the heat conduction equation in the layers of condensed components under the appropriate initial and boundary conditions. The sequence of the events to be analyzed looked as follows. The unreactive preheating stage rapidly ended up to launch NM evaporation; however, the pore surface temperature remained low; therefore, NM evaporation during some period of time was accompanied by unreactive preheating of AP and Al particles. Inasmuch as heat conductivity of Al was very high, only a thin AP layer near the pore surface was preheated by the instant when the pore surface temperature attained the AP ignition temperature. Unreactive Al preheating kept going after AP ignition. Although the composition of gaseous products varied depending on the burnt NM and AP fractions and on the fraction of oxidized Al, for simplicity, the model assumed that all the gas properties except for oxygen content could be specified by constant averaged values. Aluminum oxide in the α-Al_2O_3 phase formed as fine particles, the temperature and velocity of which were assumed identical to the appropriate values of the gas. The charge was ignited with a primer placed in the volume adjacent to the open combustion chamber end.

The processes resulting in ignition of Al aggregates was not analyzed assuming that ignition of Al particles in the cell immediately launched burning of aggregates. The bomb volume into which the gases and dispersed particles were discharged was treated as a well-stirred reactor. Ammonium perchlorate and Al particles entering the volume after charge dispersion were assumed to burn at an initial rate specified by the diameter they have had when crossed the volume boundary. Nitromethane, if not had evaporated, burned at a preset rate in the layer-by-layer regime. Parameters of the gas phase were specified by the equation of state and also by the mass and energy conservation equations for the gas in the bomb volume. The initial and boundary conditions corresponded to the one-dimensional approximation to the problem on initiation and burning of a cylindrical charge placed in a strong enclosure closed at one end and joined to a plenum chamber at the other. Igniter — a propellant charge — was mounted in the plenum chamber. The tailoring conditions at the dispersion front reduced to continuity of all variables characterizing the state and motion of the reacting mixture. The boundary conditions at the open charge end approximately reproduced exit of a stream tube into unconfined volume and differred, depending on the direction of the flow of reacting mixture.

Results of numerical modeling and discussion. Below, the most important properties and the input parameters are shortly considered. The NM boiling point was slightly lower than 100 °C, heat of evaporation was 0.63 MJ/kg. The burning rate of liquid NM was 0.23 cm/s at 10 MPa and was a linear function of pressure. At pressures below 1 MPa, when the mixture began to burn in the constant volume bomb, NM decomposed in a layer-by-layer combustion wave within a wide zone whose size exceeded the pore size in the propellant. Therefore, in the present model of convective burning, conversion of NM was considered as a process consisting of two phases: evaporation under action of the convective heat flux and thermal decomposition of NM vapor. According to literature data [5–7], decomposition of NM vapor obeys an overall first-order kinetic equation with an activation energy of 50–57 kcal/mol. Keeping in mind discrepancies in the form of equations for the rate constant, the value 51.2 kcal/mol was chosen for the activation energy and $5.8 \cdot 10^{13}$ s^{-1} for the preexponential factor.

Layer-by-layer AP burning in the presence of fuels is distinguished by quite high burning velocities, narrow flame zones, and pressure exponent in the burning law equal to about 0.5. However, because of the lack of appropriate data for burning of AP/Al/NM mixtures, the choice of the burning velocity equation for them is somewhat uncertain. Therefore, an expression that yielded a layer-by-layer burning velocity of 1 cm/s at 10 MPa was used. The ignition temperature was set at 850 K.

Fine Al particles in AP-based propellants burn violently and the reaction starts virtually at the AP surface. Burning times of fine Al flakes used in experiment were presumably shorter than 1 ms [8]; however, the particle size can increase due to agglomeration, particularly at such a high Al content as in the compositions considered. Inasmuch as the empirical burning law incorporated in the model was derived for spherical particles, a diameter of an equivalent spherical particle (imitating flakes in terms of burning time) was assumed to be equal to 3.6 μm, the exponent of diameter and burning rate constant in the burning law were set at 1.5 and 0.045, respectively. These values of the input parameters yielded 0.3 ms for the burning time of a single particle in the products of AP decomposition. The calculated burning time of Al particles in the products of NM decomposition was several times longer because their oxidative ability was much lower than that of AP combustion products and because the content of oxidizing gases reduced in the course of Al burning. Input parameters of the problem pertaining to the charge pore structure were chosen with a great degree of arbitrariness because of their uncertainty. Particle diameter was assumed equal to 0.12 mm, the pore diameter was calculated using the particle diameters and charge porosity. The thickness of Al layer on the AP particle surface h_{Al} was set equal to 3 μm, which amounted to 25 % (wt.) of the Al available in a charge with Al/AP = 1 : 1. The ratio of mixture components and some properties of the charge and

Table 1 Example of calculation and experimental results

	Variant	Mixture: Al/AP+% (wt.) NM	$W_{\max}$, m/s	$(dP/dt)_{\max}$ MPa/ms	$P_{v\max}$ MPa	$t_{\rm cb}$, ms; (t^*, ms)
Exp.		1/1+18		1.8	10.4	(44)
		1/1+18		4.5	26	(12)
		2/1+18		2.2	15.1	(28)
Calculation	1	1/1+15.2	25.4	3.7	16.3	5.5 (13.2)
	2	1/1+10	174	3.2		0.47
	3	2/1+18	2.54	1.0	15.6	27.2 (35.2)
	4	1/1+10	53.5	5.05	> 11.3	10.5

$W_{\max}$ is the maximum convective burning velocity, $(dP/dt)_{\max}$ is the maximum pressure rise rate in the combustion chamber, $P_{v\max}$ is the maximum pressure in the bomb, $t_{\rm cb}$ is duration of the convective burning propagation stage, t^* is the time measured from the beginning of convective burning to the pressure maximum in the bomb.

components were varied in computations. The bomb chamber volume (632 cc), charge weight (12 g), and diameter (1.2 cm), as well as the igniter parameters remained constant in all calculations. Brief information about the input parameters is listed in Table 1 which presents also the calculation results.

Computations revealed two major mechanisms of flame propagation through the ternary mixtures considered. If the temperature of the combustion products penetrating through pores inward the unburned mixture was low and concentration, volatility, and ignition temperature of the liquid phase were high, its gasifying cooled the penetrating products and hindered filtration due to flow choking in pores. The ignition front of the liquid phase laged behind the AP/Al ignition front. As a result, this convective burning mode was extremely slow, therefore was discarded from further consideration. The burning mode of interest was that in which ignition of the vaporized liquid phase led the flame. Calculations suggest that depending on the initial mixture properties, it seems expedient to distinguish four diverse burning regimes:

1. **Convective burning spreading at moderate velocities** (most appropriate for practice). Figure 2 displays the results of calculations for an equi-weight Al/AP mixture with a 15.2 % (wt.) NM additive (variant 1). Convective burning spreaded through the charge at

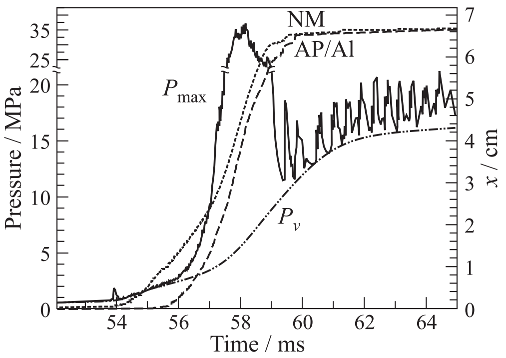

Figure 2 Time histories of the pressure in the bomb and of the maximum pressure in the convective burning wave and trajectories of ignition fronts of NM and AP/Al. Variant 1

an average velocity of about 20 m/s, the maximum burning velocity being close to 25.4 m/s. The chronology of events was as follows. Charge started burning at 49.8 ms (it was nitromethane which was ignited) and the flame penetrated in pores inward the charge through 5 or 6 particle diameters. At 53.9 ms, AP and Al particles started burning at the open charge end, 0.1 ms later convective burning started: the NM ignition front broke through inward the charge along the pores and attained a velocity of nearly 9 m/s. Propagation of the fronts inward the charge was attended by a progressive pressure rise in the bomb volume, the difference between the peak pressure at the wave front and pressure in the bomb attained 30 MPa. The front velocity increased to 25.4 m/s in the second charge half while the distance between the fronts diminished to 0.7 cm, the pressure rise rate in the bomb volume increased to its maximum of 3.7 MPa/ms. Front velocity dropped drastically over the last few millimeters of the charge length (after 58.8 ms), the pressure rise rate and difference between the peak pressure in the burning wave and pressure in the bomb appreciably lowered. Pressure in the bomb kept rising until 67.4 ms (not shown) attaining 16.26 MPa, after which it started decreasing because of cooling of the combustion products. Fluctuations of the peak pressure of nearly regular nature deserve special discussion. They were observed in all regimes of convective burning.

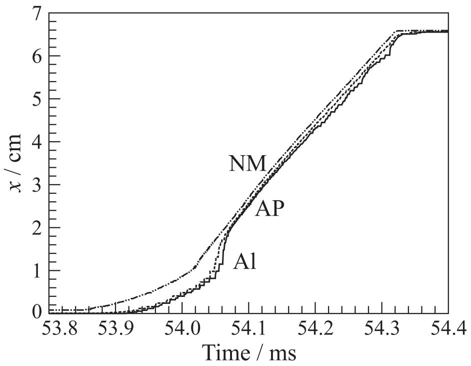

Figure 3 Trajectories of the fronts of NM, AP and Al ignition. Variant 2: Al/AP = 1/1 +10 % (wt.) NM; d_0 = 0.12mm; φ_0 = 23.5%; W = 174 m/s; $(dP_v/dt)_{\max}$ = 3.18 MPa/ms; and $P_{v\max} > 8.5$ MPa

2. Fast convective burning. Calculations were made for an equi-weight Al/AP mixture. Compared to the previous variant, the NM additive and aluminum layer thickness $h_{\rm Al}$ were reduced about 1.5-fold and amounted to 10 % (wt.) and 2 μm, respectively. The charge porosity, initial density, and length were 23.5%, 1.57 g/cm^3, and 6.6 cm, respectively. In addition, the equivalent diameter of burning Al particles was increased to 7.4 μm and Al ignition temperature to 945 K. As seen from Fig. 3, after some acceleration stage, the flame front accelerated up to 174 m/s and the ignition fronts of all the components nearly merged, NM self-ignited immediately after it evaporated. The amount of unburnt material ejected into the bomb volume was even greater than in the moderate burning regime.

3. Slow convective burning. Doubling Al concentration and increasing NM content to 18 % (wt.) decreased the burning velocity to 2.54 m/s.

4. Convective burning spreading jumpwise. Apart from the above-considered regimes in which the combustion wave propagated through the charge more or less uniformly, though at dissimilar velocities, calculations also revealed some situations in which combustion

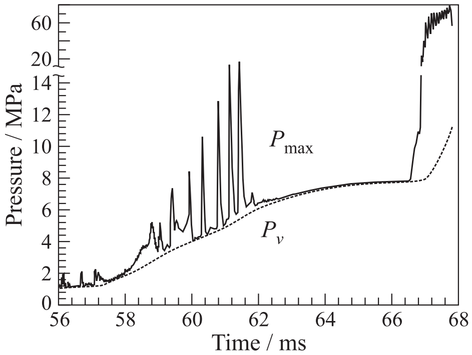

Figure 4 Time histories of the pressure in the bomb and maximum pressure in the unsteady convective burning wave. Variant 4

wave spreaded jumpwise, rather than evenly, with jumps separated by pauses. This calculation performed for an Al/AP = 1/1 + 10 % (wt.) NM mixture is exemplified in Fig. 4. The charge density, porosity, and length were 1.3 g/cm^3, 32.8%, and 8.2 cm, respectively, and h_{Al} = 3.0 μm. Obviously, the pore surface in the charge portion ahead of the stopped flame front was slowly preheated during the pause, in addition, the excess gas filling pores flowed out in the bomb volume to reduce the counterpressure impeding gas filtration. This provided favorable conditions for the second jump, the considerable pressure rise in the wave also favored burning intensification in the second jump.

The calculations show the following results and assumptions:

First, vaporized liquid component flowing in pores condensed there decreasing thereby gas permeability of the charge; in addition, some liquid phase can be picked up by the gas flow to move it inward the mixture; this together with pressure buildup ahead of the flame front in the last charge portions would slow down the burning process with time and even stop flame propagation, which must be taken into account properly in further development of the model.

Second, clogging pores with liquid could also be responsible for the jumpwise burning mode. Indeed, long lasting pause was a stage at which burning spreaded in the layer-by-layer mode, releasing the pressure and preheating the mixture layer adjacent to the combustion products would result in reignition, fast pressure buildup, and drastic flame acceleration, because the layer was preconditioned.

Third, although distinguishing moderate, fast and slow convective burning modes was somewhat conditional, it was accounted for by relative positions of the ignition fronts and flow reversal point in the charge. When the flow reversal point was localized ahead of the AP and Al ignition fronts, the energy released by the chemical reactions of mixture components was only partially spent to preheat gas portions that permeated in pores and drove the spreading wave. As a result, the convective burning velocity was low.

At high convective burning velocities, the pressure peak and, correspondingly, the gas flow reversal point set in behind the AP and Al ignition fronts. The pressure in the wave attained values exceeding 100 MPa. Therefore, for practical purposes, moderate convective burning velocity values at a 30–50 m/s level may turn out preferable to keep the pressure in the charge no higher than a few tens of megapascals that do not destroy the enclosure. Calculations performed for Al/AP = 1/1 mixtures demonstrated that moderate charge densities (in the 1.3–1.5 g/cm^3) and optimal NM content (about 10%) favored high convective burning velocities.

Experimental Study of Mixture Burning in a Constant Volume Bomb

Pressed or loose packed cylindrical samples with a height-to-diameter ratio of 5:1 and greater, to warrant transition to the convective burning regime, were burned in a cylindrical 614 cm^3 bomb capable of withstanding a pressure that did not exceed 40 MPa to check main results of calculations. Sample was placed in a metal capsule fixed at the bomb casing (as shown in Fig. 5). The charge was ignited by electrically fused wire with 1.2 g of ground black powder. The process was monitored with a tensoresistive pressure gauge. In processing the pressure–time histories, the maximum pressure in the bomb, pressure rise time, the maximum pressure rise rate, and average burning velocity were assessed. The dependence of these parameters on the composition (Al/AP ratio 1:1, 2:1, 3:1, and 4:1, NM content from 0 to 30 % (wt.), density (from 1 to 1.9 g/cm^3) and porosity (from 0.4% to 46.2%), and initial pressure in

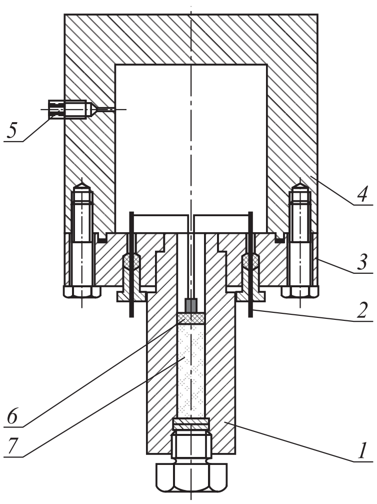

Figure 5 Schematic of the constant volume bomb: *1* — load capsule, *2* — electrodes, *3* — cover, *4* — casing, *5* — pressure gauge, *6* — black powder, and *7* — sample studied

the bomb was analyzed. Aluminum particles were flakes $10 \times 10 \times 1$ μm in average size, AP particles were less than 125 μm in size, charges were 12 mm in diameter.

Experiments in a constant volume bomb furnished the following results. The maximum burning rates were observed in charges with 1:1 and 2:1 Al/AP ratios of densities in the 1.3–1.5 g/cm^3 range. Further increase in the density of 1:1 and 2:1 mixtures to 1.7 g/cm^3 drastically decreased the maximum pressure attained after charge burning: from 260 to 104 bar (1:1 mixture) and from 151 to 37 bar (2:1 mixture). In Al richer mixtures, the dependence of the burning characteristics on charge density was flatter. An increase in the Al content in the mixture and in its density reduced the burning rate because of greater losses to preheating inert material and of lower gas permeability of the charges. Burning of 3:1 and 4:1 Al/AP mixtures was virtually unaffected by variation of the NM content, whereas the burning velocity of 2:1 mixtures increased with NM concentration, which indicated that contribution of NM decomposition to the burning process in this mixture was significant. The optimal amount of NM at which mixtures burned fast and had reasonably great density (up to 1.5 g/cm^3) was 18%. As the NM content increased, the dependence of the maximum pressure in the bomb on the Al/AP ratio got steeper that again emphasized the importance of NM decomposition in the mechanism of convective burning propagation. Replacement of AP by an inert material supported the inference that NM played a leading role in convective burning of the charges studied, which was consistent with numerical modeling. As the initial pressure increased, the burning velocity diminished significantly, but this was associated with the dynamic pressure rise procedure used at the initial stage (by burning an auxiliary charge in the bomb), which resulted in charge compaction. As the initial charge porosity increased, the maximum pressure and pressure rise rate at elevated initial pressures increased, which supported the supposition that a dynamic increase in the initial pressure reduced the charge porosity.

Concluding Remarks

1. Four various convective burning regimes were distinguished: (*i*) convective burning with moderate velocities (in the one–two tens of meters per second range); (*ii*) fast convective burning at a propagation velocity at a level of 100 m/s and above; (*iii*) slow convective burning at a velocity of several meters per second, and (*iν*) convective burning spreading jump-wise with front propagation phases separated by pauses.

2. Fast convective burning was observed in AP/Al = 1/1 mixtures at moderate charge densities in the 1.3–1.45 g/cm^3 range and h_{Al} values close to 3 μm.

3. Nitromethane content was varied from 1 to 18 % (wt.). The convective burning velocity dependence on this parameter showed a maximum at a 10 percent NM additive.

4. Variation of an AP particle diameter affected the convective burning velocity insignificantly (its effect was compensated for by the proportional reduction of parameter h_{Al}). However, at a 60-micron particle

size, convective burning spreaded only through some charge portion and jump-wise burning regime was possible.

5. Two major mechanisms of flame propagation through ternary mixtures were revealed. The mechanizm of practical interests providing reasonably high charge burning and pressure rise rates was that in which ignition of the vaporized nitromethane led the flame. Experiments confirmed predictions of numerical modeling.

Acknowledgments

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References

1. Nigmatulin, R. I. 1987. *Dynamics of multiphase media*. Moscow: Nauka.
2. Sulimov, A. A., and B. S. Ermolaev. 1977. *Chemical Physics Reports* 16(9):1573.
3. Pokhil, P. F., A. F. Belyaev, Yu. V. Frolov, V. S. Logachev, and A. Korotkov. 1972. *Combustion of powdered metals in active media*. Moscow: Nauka.
4. Dokhan, A., E. W. Price, J. M. Seitzman, and R. K. Sigman. 2003. The ignition of ultra-fine aluminum in ammonium perclorate solid propellant flames. AIAA Paper No. 2003-4810.
5. Andreev, K. K. 1966. *Thermal decomposition and burning of explosives*. Moscow: Nauka.
6. Borisov, A. A., S. M. Kogarko, and G. I. Skachkov. 1967. Thermal decomposition of nitromethane. *Combustion Explosions Shock Waves*.
7. Kelzenberg, S., N. Eisenreich, W. Eckl, and V. Weiser. 1999. Modeling nitromethane combustion. *Propellants Explosives. Pyrotechnics* 24(3): 189–94.
8. Glazkova, A. P. 1976. *Catalysis of burning of explosives*. Moscow: Nauka.