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Combustion of Ammonium Dinitramide, Part 1: Burning Behavior

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The paper presents a detailed analysis of the ammonium dinitramide (ADN) combustion behavior depending on organic and inorganic additives, material of the surrounding shell, and the sample cross-section size. In spite of the fact that ADN is an oxidizer, combustible surroundings have been found to exert practically no effect on the burning rate of ADN pressed strands. In contrast, minor amounts of organic and inorganic admixtures were shown to have a strong effect on ADN burning behavior, extending considerably the pressure limit of sustained combustion to the vacuum area. Within the pressure range of 1–10 MPa, a decrease in the strand cross-section size leads to a decrease in the ADN burning rate, accompanied by a notable burning-rate data scatter. The main reason for the observed combustion behavior is assumed to be a dominant role of exothermic condensed-phase decomposition reactions in burning of ADN. A descriptive mechanism has been proposed to explain the influence of small amounts of different substances added to ADN on its combustion behavior and the low-pressure limit of self-sustained burning.

Nomenclature

c_p = average specific heat of the condensed phase
L_m = heat of melting
m = mass burning rate/mass evaporation rate
n = pressure exponent
p = pressure
r_b = burning rate
T_s = surface temperature
T_0 = initial temperature
σ_p = burning-rate temperature sensitivity

I. Introduction

CURRENTLY there is a continuing interest in the combustion of chlorine-free oxidizers. Ammonium dinitramide (ADN), a peculiar representative of this type of energetic material, was first synthesized in the Soviet Union in 1971[1,2] and then independently in the USA in 1991.[3–5] ADN is an ionic salt of ammonia and dinitramidic acid, and it is considered as an environmentally friendly oxidizer that can offer higher performance than conventional ammonium perchlorate (AP) and ammonium nitrate (AN). Dinitramide-anion-containing compounds present a new class of energetic materials, which combustion behavior has investigated recently. Practical application of these kind of materials obviously requires a detailed knowledge of their burning characteristics.

There have been published results on ADN burning-rate characteristics over a wide pressure range obtained in several leading research laboratories.[6–18] The burning-rate characteristics measured by different researchers have been noted to differ substantially. Such is the case for the low-pressure limit of ADN-sustained burning and behavior of the burning-rate–pressure dependence within the 4–10 MPa pressure range. As ADN has a positive oxygen balance, any combustible impurities, material of a surrounding shell, and sample cross-section size can be presumed to influence the burning rate and its dependence on pressure. The present paper is devoted to a detailed analysis of the effect of the preceding factors on ADN combustion properties.

II. Experimental

A. Sample Preparation

ADN was used for burning-rate experiments as obtained by a technique given in Ref. 19 followed by recrystallization from 95% water ethanol (1 g of ADN in 1.5 ml of ethanol). Precipitated ADN crystals were dried in vacuum at 60°C for 3 h. The needle-shaped ADN crystals had a melting point 93–95°C. UV-spectrophotometric analysis indicated 0.4% of ammonium nitrate as an impurity. Density of the single crystals was 1.83–1.84 g/cm^3 (Refs. 20 and 21).

The combustion behavior of ADN was studied in the form of both pressed strands and single crystals. To clear up possible effects of strand diameter, density, and side-surface inhibitor on burning-rate characteristics, different types of ADN strands were employed: ADN pressed into quartz tubes with an internal diameter of 8.5 mm to the density of 1.54 g/cm^3; ADN pressed into Plexiglas® tubes with internal diameters of 7 or 4 mm to the density of 1.75–1.79 g/cm^3, ADN-pressed pellets of 12 mm diam and 1.75 g/cm^3 density, and thin pressed plates of 0.5 mm in thickness, 1.5–2 mm in width, and 7–10 mm in length with density of 1.77 g/cm^3. Because the densities of the samples are dependent on the preparation conditions, the mass burning rates are used when comparing different samples.

ADN single crystals 0.3–0.5 mm in thickness, 2–3 mm in width, and 10–15 mm in length were grown by slow evaporation of saturated ethanol solution at room temperature. The side surface of ADN-pressed pellets was inhibited by coating with perchlorovinyl resin. ADN single crystals were coated with a thin film of polychlorotrifluoroethylene or immersed into perhalocarbon oil.

To obtain ADN containing 0.2% of paraffin, thoroughly grinded ADN (particle size less than 60 μm) was treated with a solution of the required amount of paraffin in pentane or chloroform and dried in air with stirring followed by keeping under vacuum for some time.

To obtain ADN containing additives of soot and silica gel (a highly porous, noncrystalline form of silicon dioxide), powdered ADN (particle size less than 60 μm) was thoroughly mixed with the required amount of the additive. The surface area of these additives was about 300 m^2/g.

An ADN-supersaturated solution containing 10% of water was prepared in quartz tubes just before burning tests.

B. Burning-Rate Measurements

Burning-rate measurements were carried out in a constant-pressure window bomb of 1.5-liter volume. The pressure range

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studied was 0.1–36 MPa. Measurements in the subatmospheric region were conducted in a vacuum chamber of 40-liter volume. A slit camera was used to determine the character of the combustion process as well as the burning-rate values. At pressures below 0.6 MPa, backlighting was used as the luminosity of ADN combustion was too weak to record the burning process. At elevated pressures the brightness of ADN gas flame increased, making measurements possible without backlight. The accuracy of the measurements was ±3%.

C. Analysis of Condensed Products of ADN Combustion

A preliminary weighed ADN sample of about 0.5 g was burned at atmospheric pressure on an fluoroplastic film under a sintered disc filter funnel. Once burning was complete, the condensed combustion products were collected on a filter funnel. The film was weighed, and an increase in the total weight was calculated. The condensed combustion products thus collected were first dried and then dissolved in water so that a solution of 8–12 mg/l concentration could be obtained. The contents of dinitramide and nitrate anions were determined with UV-spectrophotometry using adsorptions at $\lambda = 200$ and 284 nm (Ref. 22). In the case of reduced pressures, only analysis of condensed combustion products that collected on the top edge of tube was performed.

D. Effect of Initial Temperature on the Burning Rate

Burning-rate measurements at different initial temperatures were conducted with samples of ADN pressed into 7-mm i.d. Plexiglas tubes at atmospheric pressure. The samples were kept in a thermostat or refrigerating chamber ($T_0 = 251$ K) for 1 h before being burned. To cool down to $T_0 = 195$ and 77 K, the samples were kept in solid carbon dioxide for 30 min or in liquid nitrogen for 15 min, respectively.

III. Results

ADN burns without any luminous emission at low pressure, forming copious white vapors, which condense as a fine white powder inside the tube and on the cold surfaces of the bomb. As the pressure increases, small "flamelets" emanating from local reaction sites are observed.[23] Above 1–2 MPa, the gases become almost transparent, a luminous flame appears, and the condensed products of combustion are not observed. Nevertheless, photographic records frequently reveal segments without luminescence, suggesting that the flame is not very stable, often exhibiting random patterns. It has been observed that the burning-rate data display a considerable scatter, especially in the pressure range below 10 MPa.

Burning-rate characteristics measured by different researchers differ substantially. Thus, the burning rate r_b vs pressure p curves found in Refs. 7, 9, and 10 reveal a maximum at 4–5 MPa followed by a decrease, and then, after 8–10 MPa, the burning rate increases again. The $r_b(p)$ dependence looks like that of a commonly used oxidizer, ammonium perchlorate (AP),[24] but ADN demonstrates significantly higher burning rates as compared with AP. In other Refs. 11 and 14, the $r_b(p)$ dependence of ADN was described by a straight line.

According to Glazkova (unpublished data cited in Ref. 25), Strunin et al.,[10] Zenin et al.,[12] and Korobeinichev et al.,[15] ADN is capable of sustained burning at atmospheric pressure, whereas according to Denisiuk et al.[7] ADN does not burn at pressures below 0.5 MPa. The authors of Ref. 26 also claimed that ADN started to burn at pressures between 0.2 and 0.3 MPa. In a study on laser-induced deflagration of ADN, it was shown that ADN-pressed samples of 4 to 9 mm diam extinguished immediately upon removal of laser heating at pressures 0.01–0.3 MPa (Ref. 8). These apparent contradictions are probably connected with a presence of some impurities in the ADN. For example, an admixture of AN, typically occurring in ADN samples, was shown in Ref. 10 to reduce the burning rate of ADN.

The carefully measured low-pressure limit of combustion of recrystallized ADN pressed into 7-mm i.d. Plexiglas tubes was found to be 0.2 MPa (Ref. 16). We failed to obtain self-sustained burning of pure ADN at atmospheric pressure either by decreasing the sample density to 1.35 g/cm^3 or by increasing the sample diameter to 12 mm. A sample 12 mm in diameter and 14 mm in height, having a density of 1.67 g/cm^3, burned through a length of about 8 mm and extinguished. Even at an initial temperature of 80°C, samples of pure ADN were incapable of complete burning at atmospheric pressure. Samples of molten ADN at a temperature of 100°C, however, were often capable of complete burning with the rate varying from 6.7 to 9.1 mm/s.

Table 1 Burning-rate law for pure ADN pressed into 7-mm i.d. Plexiglas tubes

Pressure interval, MPa	Burning-rate law: $r_b = bp^n$, mm/s	
	b	n
0.2–5.8	18.98	0.60
5.8–10	213.18	−0.80
10–36	9.06	0.60

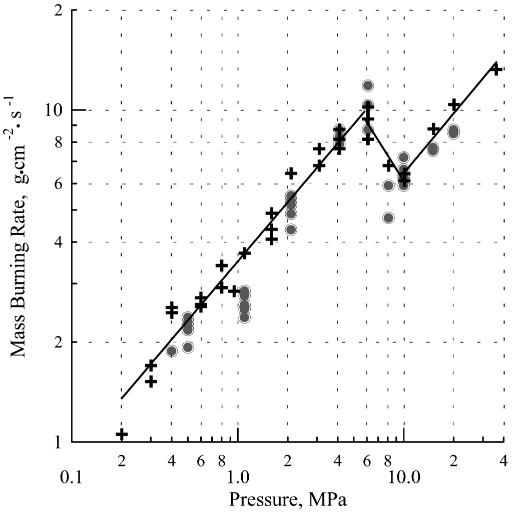

Fig. 1 Effect of pressure on the mass burning rate of ADN pressed into 7-mm combustible Plexiglas tubes with density of 1.79 g/cm^3 (+) and 8.5-mm noncombustible quartz tubes with density of 1.54 g/cm^3 (light points).

An excess of oxygen in the ADN molecule can be thought to make the burning rate of the pressed strands sensitive to the composition of the confinement shell because of possible interaction with combustibles. To examine the effect of a combustible shell on the burning-rate characteristics of ADN pressed strands, thick-walled quartz tubes were employed, allowing the samples to be pressed to the maximum density as low as 1.54 g/cm^3. A comparison of the burning rate of ADN pressed into combustible Plexiglas tubes and noncombustible quartz tubes showed an insignificant distinction between them (Fig. 1).[9] It can be concluded, therefore, that a combustible shell covering pressed ADN strands has little influence on the burning rate. The burning-rate law for recrystallized ADN pressed into 7-mm i.d. Plexiglas tubes, covering all of the pressure range studied, is given in Table 1. The $r_b(p)$ curve for pure ADN with its maximum and minimum of the burning rate is very similar to those obtained earlier in Refs. 7 and 10.

An utterly peculiar phenomenon was noted in the combustion of ADN pressed into 4-mm i.d. Plexiglas tubes.[9] Within the pressure interval of 2–10 MPa, the burning rate was variable through the length of the strands (there were regions on the photographic records, in which the burning rate dropped practically to zero), and its value might vary by more than two times at the same pressure. For example, the burning rate ranged from 26 to 54 mm/s at 6 MPa (Fig. 2). Within the pressure interval of 0.2–2 MPa and 10–36 MPa, the combustion process is quite stable. Experimental data points for these intervals lie on straight lines and coincide with the 7-mm strands.

A further decrease in the cross-section size of the ADN strands (when using thin pressed plates 0.5 mm in thickness, 1.5–2 mm

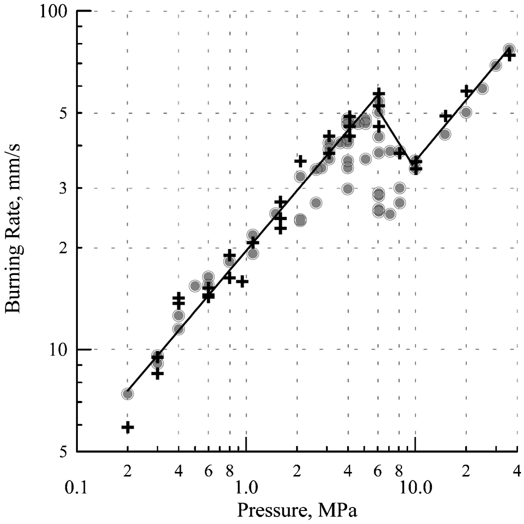

Fig. 2 Comparison of burning rates of ADN pressed into 4-mm Plexiglas tubes (light points) and ADN pressed into 7-mm Plexiglas tubes (+ and —). Density of both types of the samples is 1.79 g/cm^3.

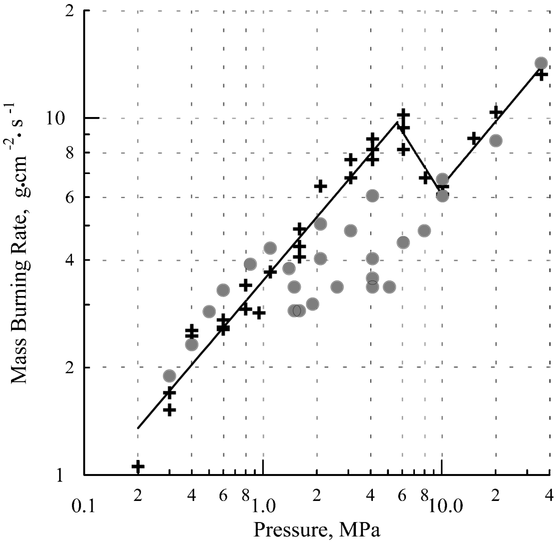

Fig. 3 Comparison of combustion of ADN pressed into thin plates (light points) and 7-mm Plexiglas tubes (+ and —).

in width, and 7–10 mm in length) leads to even more increased data scatter with a general decrease in the burning rate at 1–10 MPa (Fig. 3).[16] Within the pressure interval of 0.2–1 MPa and 10–36 MPa, the experimental data points coincided with data for strands of ADN pressed into 7-mm Plexiglas tubes. Comparable burning rates with noticeable data scatter were also obtained by Atwood et al.[11] for ADN pellets approximately 3.7 mm in thickness, 6.4 mm in width, and 12.8 mm in height. A decrease in the burning rate as the ADN sample diameter changed from 7 to 5 mm was also observed in Ref. 10 at pressures above 3 MPa. The authors of Ref. 18 studied combustion of ADN obtained from different sources in the form of thin lamina (0.350–0.375 mm) and, because of appreciable scatter in the data, could only conclude that the ADN self-deflagration rate was not strongly dependent on pressure in the range of 0.69–10.34 MPa. Data points from this work are located below the $r_b(p)$ dependence for 7-mm pressed strands.

The appearance of a region of strongly pronounced data scatter is obviously a result of the decrease in the strand diameter and is evidence of combustion instability at these pressures. In the case of ADN single crystals, the combustion instability area is emphasized very distinctly: the crystals are simply incapable of sustained burning within the pressure range of 2–10 MPa (Fig. 4).[9] Attempts at igniting an ADN crystal at these pressures led to cracking it to form small splinters, and the combustion process ceased. The absence of ADN single crystal combustion in this region is concluded to be connected to crystal splitting, rather than the small size of the crystal, because ADN-pressed plates of similar sizes are capable of combustion at these pressures (Fig. 5). The type of single crystal coating material (polychlorotrifluoroethylene or perhalocarbon oil) did not influence the burning rate. A single run was conducted to measure the burning rate crosswise to the crystal, which did not show a different value.

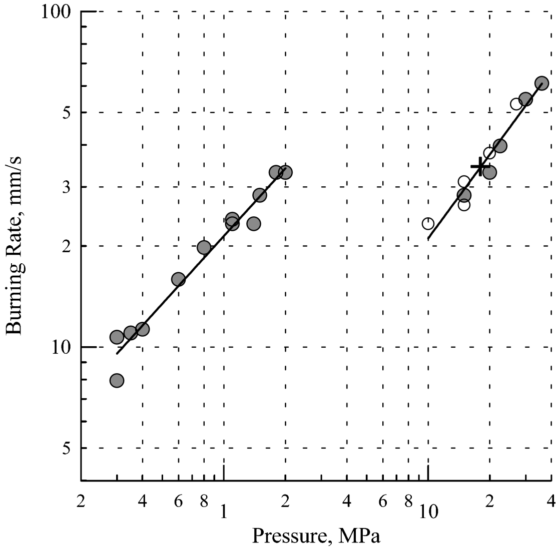

Fig. 4 Effect of pressure on the burning rate of ADN single crystals coated with polychloro-trifluoroethylene (light points); immersed into perhalocarbon oil (open points). The cross is the burning rate measured across to the crystal.

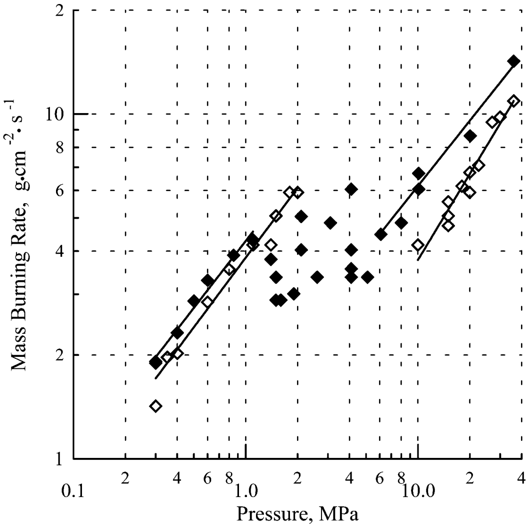

Fig. 5 Comparison of combustion of ADN single crystals (open points) and pressed plates (black points).

Yet another peculiarity of combustion of ADN single crystals is the lower values of burning rates in the pressure interval of 10–36 MPa as compared with those obtained for ADN pressed strands and ADN thin pressed plates (Fig. 5). Cracking ADN crystals at ignition and combustion is caused by thermal impact and is likely responsible for the lack of burning in the region of combustion instability (2–10 MPa) and for decreased burning rates at higher pressures.

The presence of extremely insignificant amounts of organic admixtures had an amazing effect on the ADN burning-rate characteristics. An addition of only 0.2% of paraffin to crystalline ADN

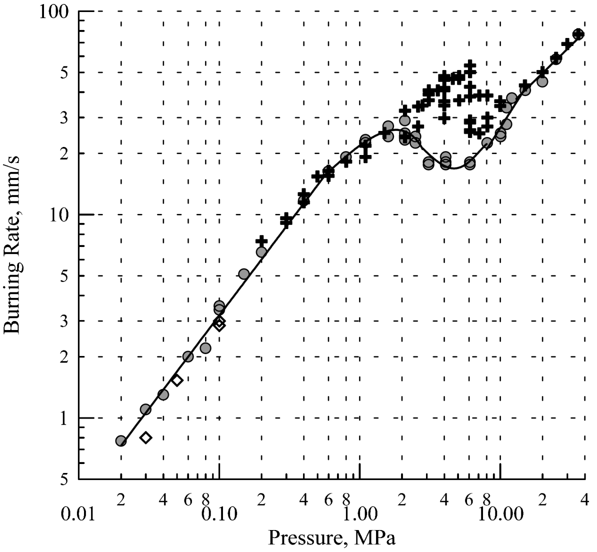

Fig. 6 Comparison of combustion of pure ADN (black points) and ADN doped with paraffin (light points) or halogencarbon oil (□) as 4-mm pressed strands with average density of 1.79 g/cm^3.

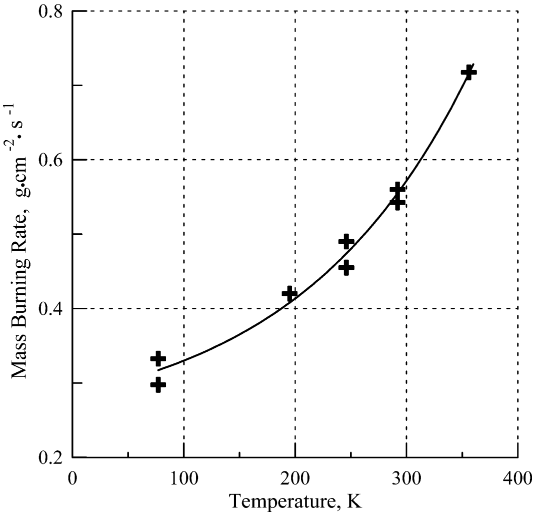

Fig. 7 Effect of initial temperature on the burning rate of paraffin-doped ADN at 0.1 MPa.

appeared to expand a low-pressure limit of ADN sustained combustion from 0.2 to 0.02 MPa (Fig. 6). Within the pressure intervals of 0.2–2.1 and 15–36 MPa, the burning rate of ADN + 0.2% paraffin coincides well with that of pure ADN. Within the pressure range of unstable combustion of pure ADN (2–10 MPa), the burning rate of ADN + 0.2% paraffin is slightly less, and no marked scatter in the data is observed. On straight sections of the $r_b(p)$ curve, 0.02–0.6 MPa and 12–36 MPa, the burning rate can be described by the following laws: $r_b = 28.89p^{0.96}$ and $r_b = 6.58p^{0.67}$, respectively.

The mixture of ADN with 0.2% of paraffin pressed into 7-mm Plexiglas tubes was capable of sustained burning at atmospheric pressure even at an initial temperature as low as the boiling point of nitrogen (77 K, Fig. 7; Ref. 27). Thus, differences in the low-pressure limit of ADN sustained combustion observed by different authors can be caused by the presence of extremely insignificant amounts of organic impurities in the ADN.

The effect of a small paraffin additive on the ADN burning-rate characteristics could be explained by the fact that paraffin apparently shows itself as an alternative fuel, which is more readily oxidizable than NH$_3$. However, the lower-pressure limit of ADN combustion turned out to be reduced by addition of not only paraffin but perhalocarbon oil also (Fig. 6), which could hardly be regarded as a readily oxidizable fuel. At the same time, an addition of 0.2% of soot instead of paraffin, which usually stabilizes combustion, failed to prolong the lower-pressure limit. This fact allows a conjecture to be made that the effect of some minor additives on the ADN lower-pressure limit is connected with physical reasons rather than chemical ones.

Table 2 Analysis of ADN combustion products (unreacted ADN/formed AN ratio in the solid residue at different pressures)

	ADN/AN ratio for combustion of	
Pressure, MPa	Pure ADN	ADN + 0.2% Paraffin
0.025	——	30:70
0.05	——	15:85
0.1	——	6:94
0.3	3:97	<1:99
0.6	<1:99	<1:99

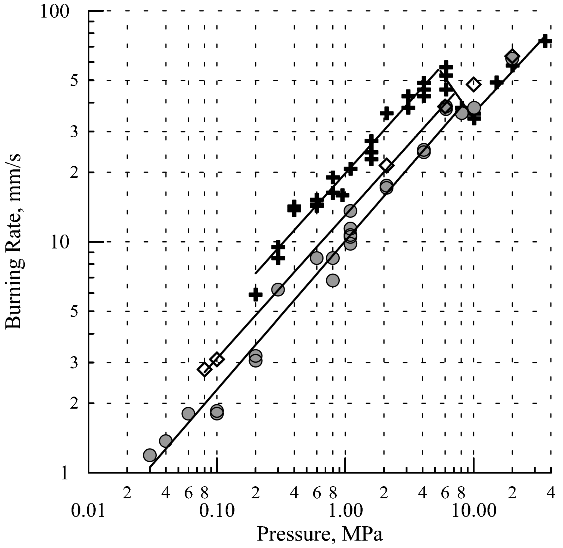

Fig. 8 Comparison of combustion of pure ADN (+) and ADN with 1.5% additive of soot (◇) and SiO$_2$ (light points).

The physical reasons are supported by the following experimental fact: an addition to ADN of either 1.5% of soot or 1.5% of silica gel leads to a decrease in the lower-pressure limit of combustion. However, a comparison shows (Fig. 8) that noncombustible SiO$_2$ is able to decrease the limit to a greater extent than easily oxidizable soot.

In parallel with a decrease in the low-pressure limit of combustion, a significant effect of the additives on a position of the local maximum on the $r_b(p)$ curve within the interval of 2–10 MPa can be noted, or its disappearance at all (see Figs. 6 and 8). An extreme sensitivity of ADN burning rate to different additives in the area of local maximum was pointed out by Denisiuk et al.[7]

Combustion of paraffin-doped ADN at subatmospheric conditions is characterized by the lack of a luminous flame and the formation of copious condensed-phase products. Combustion of paraffin-doped ADN at atmospheric pressure results in the formation of as much as 47 weight percent of condensed-phase products. The amount is reduced to 37 weight percent after drying. In the studies on ADN decomposition,[28–32] it was found that ammonium nitrate is a major condensed-phase product. A carryover of small droplets of a liquid substance to the gas phase has been observed at combustion ADN in Ref. 8 and attributed to molten AN. We have found that the condensed residue after ADN combustion at low pressures consists of a mixture of AN and ADN, with the ADN content increasing as the pressure decreases. At atmospheric pressure, the ADN content of the residue after combustion of ADN + 0.2% paraffin has been determined to be around 6% by weight (Table 2 and Fig. 9). Taking this into account, one can estimate a proportion of ADN converted

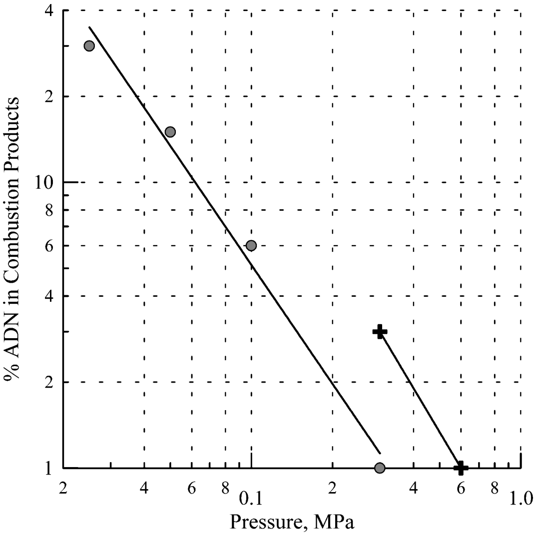

Fig. 9 Effect of pressure on ADN content in the condensed combustion products of neat ADN (+) and paraffin-doped ADN (light points).

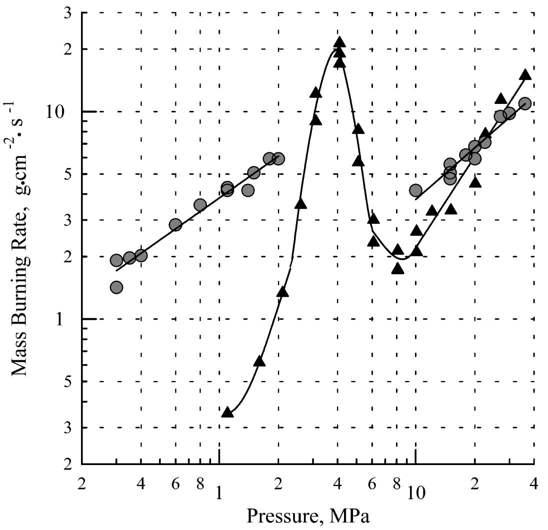

Fig. 10 Comparison of combustion of single crystals of ADN (light points) and 90% solution of ADN in water (▲).

into AN during combustion: it is equal to 57% (by mole). This result is in a good agreement with the findings of Oxley et al.,[32] who observed 0.59 mole of ammonium nitrate formed in decomposition of one mole of neat ADN. The presence of initial ADN in the combustion products is thought to be a result of dispersion of the condensed substance from the burning surface, rather than formation of the salt from gaseous ammonia and acid. The latter is quite permissible for AN, but improbable for ADN because of a very low thermal stability of dinitramide acid.[31]

Very interesting results were observed with ADN water solutions. The 90% supersaturated ADN solution begins to burn at 1 MPa at a rate less than the burning rate of neat ADN at this pressure. As the pressure increases, however, the burning rate of the solution rises very rapidly and has a maximum at 4 MPa, surpassing the neat ADN (Fig. 10). As with ADN monocrystals, in this case the combustion instability area is distinguished very distinctly. However, the turbulent combustion of the supersaturated water solution reveals a local maximum on the burning rate vs pressure curve in this area, whereas the crystals are incapable of sustained burning within the same pressure range.

IV. Discussion

Three segments on the $r_b(p)$ curve can be distinguished when all of the burning-rate data for ADN pressed strands are taken into account: the first one from 0.2 to 5.8 MPa is the burning-rate growth with pressure, the second one from 5.8 to 10 MPa is the burning-rate decrease, followed by increasing burning rate again at the third segment (10 to 36 MPa). Combustion of ADN within the pressure interval of 2–10 MPa is accompanied by a notable burning-rate data scatter, which is indicative of ADN combustion instability.

On the first segment, the burning rate is obviously determined by reactions occurring in the condensed phase. The burning at low pressures proceeding without a luminous flame and accompanying by intensive dispersion of the condensed material supports this hypothesis. Analogous suggestions have been made in Refs. 7, 10, and 12. This suggestion is also supported by values of the burning-rate temperature sensitivity $\sigma_p = \partial\, \ell n\, \dot{m}/\partial T_0$ for paraffin-doped ADN at 0.1 MPa, which increases from $2.2 \cdot 10^{-3}$ K^{-1} to $4 \cdot 10^{-3}$ K^{-1} when temperature grows from 77 to 355 K (Fig. 11). The increase in σ_p with T_0 is generally typical for combustion with the leading reaction in the condensed phase.[33,34] These values of σ_p prove to be close to σ_p, calculated on the assumption of condensed-phase predominance, $\sigma_p = 1/(T_s - T_0 + L_m/c_p)$. In the calculation, T_s was used to be 614 K at 0.1 MPa (taken from Ref. 9), L_m as 20 cal/g, c_p as 0.49 cal/g K (an estimate based on the heat capacity of AN[35]).

In the pressure interval of 10–36 MPa, a bright flame is visible just above the surface of the burning strand; therefore, it is logical to assume that reactions occurring in the gas phase make a significant contribution to the burning rate on the third segment of the $r_b(p)$ curve.

The second segment on the $r_b(p)$ curve is transitive. The amount of heat released in the condensed phase is limited. According to DSC[32] and dynamic microcalorimetric studies,[36] the thermal effect of the condensed phase reaction is about 50 kcal/mole, and, consequently, the temperature increase in the condensed phase is limited by the heat of reactions proceeding in it. Because the surface temperature grows with pressure, there comes a point when the heat released in the condensed phase becomes insufficient for warming up it to the surface temperature, while the heat flux from the gas phase is still not enough to warm up and evaporate the condensed phase. Because of lack of heat, the combustion process becomes unstable and assumes an oscillatory mode, that is, when the fast but energy-limited heat-release process in the condensed phase has to adapt itself to the slow but energy-rich heat-release process in the gas phase.

The measurements of ADN burning rate at various pressures and initial temperatures were carried out in various works.[11,12] In Ref. 12, the measurements were carried out at 123, 293, and 353 K in the

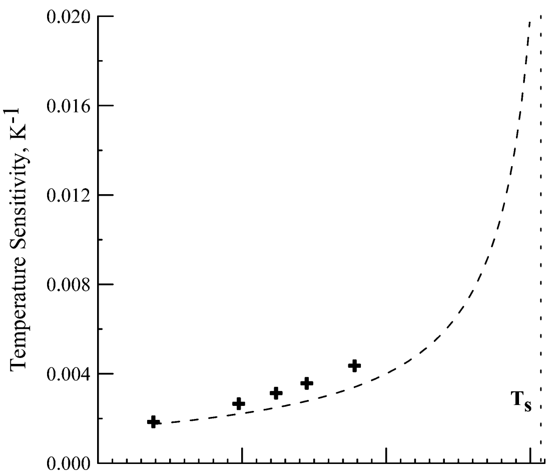

Fig. 11 Comparison of experimental (+) and calculated (—) burning-rate–temperature sensitivity for paraffin-doped ADN at 0.1 MPa.

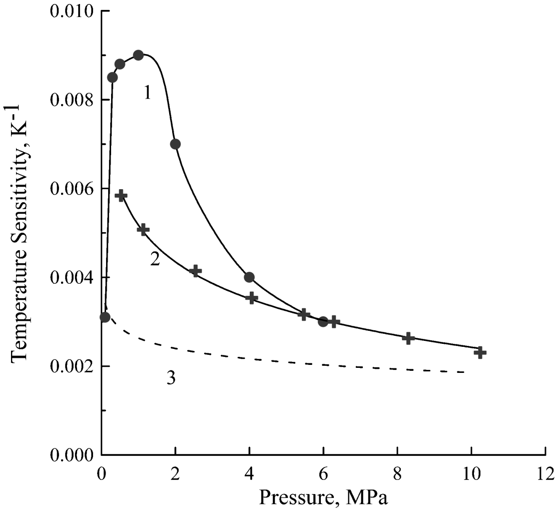

Fig. 12 Comparison of experimental temperature sensitivities of ADN burning rate measured at 123–298 K (1) and at 298–348 K (2) with calculated one (3).

pressure interval of 0.1–6 MPa; in Ref. 11 at 293 and 348 K in the interval of 0.7–10.3 MPa. Our burning-rate data obtained at atmospheric pressure[27] are in a good agreement with data of Ref. 12 up to $T_0 = 353$ K. At higher initial temperatures, samples of ADN containing small amounts of ammonium nitrate as an impurity begin to melt that can result in a substantial increase in the burning rate because of turbulization of the burning surface. Therefore, only the data obtained in the interval 123 to 293 K were taken from Ref. 12. Temperature sensitivities of ADN burning rate calculated on the basis of data of Refs. 11 and 12 are presented in Fig. 12. The differences in the results are caused not only by significant scatter in the ADN burning rates in the interval of 2–8 MPa, but also by the variation in the initial temperatures. Experiments carried out at 123 K resulted in a sharp decrease in the burning rate that was reflected in the value of σ_p. As can be seen from the Fig. 12, the calculated temperature sensitivity increases sharply with pressure, and, in the interval of 0.3–6 MPa, both of the experimental curves are considerably higher than the theoretical curve. The large magnitudes of the temperature sensitivity might be indicative of the thermal instability of combustion in this pressure region.

An important role in the combustion of ADN belongs to dispersion, a widespread phenomenon in the burning of materials with their heat release dominated by the condensed phase.[37,38] Decomposition of the material in the condensed phase accompanied by formation of gaseous products leads to agitation of the molten reaction layer and droplet entrainment into the gas, making the reaction layer and adjacent gas-phase zone nonhomogeneous. Carryover of spherical liquid droplets into the gas phase during ADN deflagration was observed in many studies. Some of the larger droplets are over 200 μm in diameter.[23]

The dispersion phenomenon plays a double role. On the one hand, within the pressure region of unstable combustion (2–10 MPa), dispersion of the condensed phase supports the combustion, facilitating removal of the condensed products from the surface and compensates for the deficient heat feedback from the gas. On the other hand, at the vicinity of low-pressure deflagration limit of ADN, dispersion hinders the burning progress because of increased heat losses in the reaction layer. The irregular nature the dispersion is apparently responsible for the scatter in the experimental data observed at low pressures. The degree of dispersion (and, consequently, data scatter) can be assumed to attain its maximum in the transitive pressure region when the combustion suffers from a deficiency in the condensed-phase heat production, accompanied by molten layer thickening. Decreasing the ADN strand cross section (diameter) leads to increased heat losses and, as a result, to an increased data scatter, which is probably most pronounced when the scale of the disturbance and the sample size become comparable.

It is assumed that the addition of such organic substances as paraffin or halogencarbon oil, which are capable of extending the low-pressure limit of ADN sustained combustion and decreasing the data scatter, influence dispersion on the surface. The stabilizing effect of such fuels can hardly be explained by elimination of possible thermal deconsolidation of the material caused by thermal stresses in the crystalline sample, which was suggested in Ref. 11 as an explanation of ADN burning-rate data scatter.

It can be presumed that the effect of organic additives on the ADN burning behavior is caused by changes in the surface tension and viscosity of the highly polar melt layer as is the case, for example, when oil is added to water. The phenomenon shows itself in the reduction of the amplitude of the molten surface layer oscillations by partitioning of the large-scale perturbations into smaller ones that, in turn, result in decreasing the size of the particles being ejected into the gas phase. If the ADN/AN ratio in the condensed combustion products is compared for samples of pure and 0.2% paraffin-doped ADN at the same pressures, one can find a larger relative content of ADN for the pure material (Fig. 9, Table 2).

In the transitional area, dispersion of the ADN surface layer facilitates the removal of the condensed-phase products from the surface, thus compensating for the deficient heat feedback from the gas. Suppression of the dispersion in this case results in a lowering of the burning rate. At low pressures, when reactions in the condensed phase play a dominant role, an intense agitation of the reaction layer can account for inability of pure ADN to burn below 0.2 MPa. An organic additive suppresses molten surface layer oscillations, conditioning it for stationary burning.

Another way to reduce the data scatter can be in the addition of high-porosity and/or superfine components, which could be able to increase the viscosity of the molten surface layer by structuring it, and thus suppressing the surface oscillations. Such was the case with polymethylmethacrylate and SiO_2, both capable of reducing the ADN burning rate in the transitional area.[7] Results of our work also show that both soot and silica gel decrease the pressure limit of ADN combustion (Fig. 8). It confirms the hypothesis that hydrophilic silica gel capable of absorbing ADN melt reduces the pressure limit of ADN combustion better than hydrophobic soot.

Combustion behavior of ADN single crystals[9] and the supersaturated water solution[16] is in line with the preceding reasoning. There appears to be an additional complicated property in combustion of single crystals: thermal deconsolidation with formation of small splinters, which usually accompanies the combustion of single crystals,[39] rendering sustained combustion impossible within the critical, sensitive-to-heat-loss area. Replenishment from gas-phase reactions at higher pressures (>8–10 MPa) revives combustion of the crystals, but they still burn slower than thin pressed plates.

An addition of 10% of water to ADN clearly defines the critical combustion area as well. Liquid energetic materials are known to be able to easily change their combustion regime from laminar to turbulent one, which is conditioned by the Landau–Andreev instability effect,[40] that is, by hydrodynamic disturbance of the liquid–vapor interface under the effect of flowing-off gases. The disturbance appears and progresses after the burning rate has reached a critical value, which depends on the viscosity and surface tension of the liquid. This is the case with the supersaturated water solution of ADN. It starts burning at the turbulent regime as evidenced by a very strong pressure dependence of the burning rate (the pressure exponent, $n > 3$ in the interval of 1.1–4 MPa). However, as pressure increases, the phenomenon observed in combustion of solid ADN reveals itself. A point is reached when heat generated in the condensed phase is no longer sufficient to warm up the condensed material to the constantly increasing surface temperature, followed by evaporation/dissociation from the surface. As a result, an intensity of flowing-off gas decreases, and turbulization scale is reduced. A sharp decrease in the burning rate occurs, giving rise to a local maximum on the burning rate-pressure curve within the critical pressure region.

At pressures above 8–10 MPa, the role of gas-phase reactions increases, resulting in cessation of the burning-rate drop. The pressure dependence of the burning rate at high pressures is still strong

($n \sim 1.4$), but combustion velocities are rather small, close to the theoretical critical values, suggesting only a low degree of hydrodynamic disturbance at the surface.

V. Summary

Detailed burning-rate measurements in the constant-pressure bomb have shown the following peculiarities of ADN combustion:

1) In spite of the fact that ADN is an oxidizer, combustible surroundings have been found to exert practically no effect on the burning rate of ADN pressed strands. In contrast, even minor amounts of organic admixtures to ADN turned out to have a strong effect on the burning behavior, extending considerably the pressure deflagration limit from 0.2 MPa to the vacuum area (0.02 MPa) changing substantially the burning rate vs pressure dependence within the area of 1–10 MPa.

2) Within the pressure range of 1–10 MPa, a decrease in the strand cross-sectional size leads to a decrease in the ADN burning rate, accompanied by a notable burning-rate data scatter. Within this pressure range, the burning rate of strands with diameter of 4 mm or less can differ by more than two times at the same pressure. Small amounts of organic substances added to ADN appeared to suppress the scatter and strongly affect the burning rate. A similar effect is exerted by non- and low-volatile additives. A peculiarity of ADN single crystal combustion over this pressure interval is incapacity for burning because of cracking of the crystals at ignition. At the same time, a 90% solution of ADN in water demonstrates a local maximum of the burning rate, which is two times as much as the burning rate of pure ADN.

3) Burning of both neat and doped ADN at low and subatmospheric pressures occurs with no visible flame, but is accompanied by formation of considerable amounts of condensed products consisting of AN–ADN mixture, with the ADN content increasing as the pressure decreases. The proportion of ADN converted into AN during combustion at atmospheric pressure (57%) is close to that observed in slow thermal decomposition of ADN.

4) The main reason for the observed combustion behavior is assumed to be a dominant role of exothermic condensed-phase decomposition reactions in burning of ADN. The ADN surface temperature is controlled by the reaction of salt dissociation and grows with pressure. Because the amount of heat released in the condensed phase is chemically limited, combustion of ADN occurs at the limit of condensed-phase energetics, starting from the pressure of 1 MPa and ending by 10 MPa, where the gas-phase chemistry begins to play a perceptible role in combustion. Because of the condensed-phase location of the primary heat source, burning is accompanied by significant dispersion of the molten surface layer consisting of initial ADN and AN, the only condensed decomposition product. The maximum degree of dispersion (and, correspondingly data scatter) is obviously attained at critical pressures, when a deficiency in heat generated in the condensed phase results in a thickening of the reaction layer. On the one hand, dispersion of the condensed phase backs up the combustion within the pressure region of unstable combustion (1–10 MPa), facilitating removal of the condensed products from the surface and compensating for deficient heat feedback from the gas. On the other hand, at the vicinity of the low-pressure limit of ADN deflagration, an intense agitation of the reaction layer can account for inability of pure ADN to burn below 0.2 MPa. Suppression of large-scale perturbations of the reaction layer by means of the action of nonpolar admixtures on the polar molten layer or by addition of high-porosity and/or superfine components capable of increasing the viscosity of the molten surface layer by structuring it results in decreasing the lower-pressure limit of deflagration and reduces both burning rates and their scatter in the pressure interval of 1–10 MPa.

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