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Combustion of Ammonium Nitrate–Based Compositions, Metal-Containing and Water-Impregnated Compounds

B. N. Kondrikov,* V. E. Annikov,† and V. Yu. Egorshev‡
Mendeleev University of Chemical Technology, 125047, Moscow, Russia
and
L. DeLuca§ and C. Bronzi¶
Politecnico di Milano, 20133 Milan, Italy

Ammonium nitrate (AN), an inorganic solid oxidizer used in rocket propulsion decades ago, has been enjoying a new prosperity. The main reasons favoring its return are that it produces environmentally friendly combustion products, it is very cheap, and it is a safe energetic material. The principal objectives of this work are to improve the general understanding of pure AN combustion, clarify the burning properties of a broad range of AN-based formulations, and elucidate some instability effects of pure AN, as well as AN-based propellant burning. Experiments were performed on several categories of AN-based compositions: neat AN burning as a solid monopropellant, with minor additives to promote decomposition chemical reactions; mixtures of AN with organic substances including trinitrotoluene; solid mixtures of AN with metallic powders; and AN water solutions with an organic fuel (also called water-impregnated compositions). Preliminary results indicate that, up to pressures of the order of hundreds of atmospheres, the main reactions responsible for the heat release occur mostly in the condensed phase. At higher pressures, the gas-phase flame plays an important role in controlling the burning rate.

Nomenclature

d = diameter, cm
E = activation energy, cal/mol
k = thermal conductivity, cal/(cm $\cdot$ s $\cdot$ K)
n = order of reaction
Pe = Peclet number
p = pressure, atm
Q = heat release, cal/g (positive if exothermic)
R = universal gas constant, 1.987 cal/(mol $\cdot$ K)
r_b = burning rate, cm/s
T = temperature, K
u_m = mass burning rate, g/(cm^2 s)
x = space coordinate, cm
α = mass concentration
ν = pressure exponent of ballistic steady burning rate
ρ = density, g/cm^3

Subscripts and Superscripts

cr = critical
ev = evaporation
p = pressure

Introduction

AMMONIUM NITRATE (AN), an inorganic solid oxidizer used in rocket propulsion decades ago,[1-9] has been enjoying a new prosperity.[10-17] AN is hygroscopic and not very energetic; features several crystalline transitions at −16.9°C, +32.3°C, +84.2°C, and +125.2°C; melts with some decomposition at 169.6°C (Ref. 18); does not burn without the help of catalysts; and has a burning rate that is low and little affected by particle size but strongly sensitive to pressure and initial temperature. The ballistic properties can be adjusted by fuel tailoring and blending in a catalyst yet the burning-rate range remains limited.[6,15,16] Because of these overall unfavorable properties and the low flame temperature (1247 K for the monopropellant flame[10-12]), AN has been used mainly in gas generators and other auxiliary power sources. The reasons that have favored its comeback are that it is totally gasifiable, produces clean and smokeless combustion products, can be phase stabilized,[13-17] is very cheap compared with chlorine-free oxidizers, is easily available, and is a safe energetic material. However, notwithstanding the earlier studies and the present renewed interest in AN, the scientific knowledge of combustion properties of AN-based compositions, even under steady-state operating conditions, is far from satisfactory. Thus, the objectives of this work are to improve a general understanding of pure AN combustion, clarify the burning properties of a broad range of AN-based formulations, and elucidate some instability effects of pure AN as well as AN-based propellant burning.

This cooperative investigation covers several categories of AN-based compositions: 1) neat AN burning as a solid monopropellant and with minor additives to promote decomposition chemical reactions and to lower the pressure deflagration limit (PDL); 2) mixtures of AN with organic substances including trinitrotoluene (TNT, $C_7H_5N_3O_6$); 3) solid mixtures of AN with metallic powders; and 4) mixtures of AN water solutions with powdered aluminum and an organic fuel (also called water-impregnated compositions). Points 3 and 4 are elaborated here. Points 1 and 2 are discussed in detail in Ref. 19, correspondingly, only a brief review of these points is included in this paper. The mechanisms of chemical reactions occurring in the combustion wave also are discussed.

Note that the term PDL has both theoretical and experimental significance. In the theory of propellant burning, it results from the intrinsic burning instability as in the Zel'dovich–Novozhilov theory. Mathematically, it is a limit of the steady-state solution of the overall energy equation. Experimentally, the PDL is just the limiting pressure at which a charge of given composition, dimensions, density, etc., begins to burn for a gradual, step-by-step pressure enhancement during the experiments in the combustion bomb (i.e., Andreev–Crawford strand burner). It is in this sense that PDL is used in the present paper.

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*Professor, Engineering Chemical Technology Department, 9 Miusskaya Square.

†Associated Professor, Engineering Chemical Technology Department, 9 Miusskaya Square.

‡Scientist, Engineering Chemical Technology Department, 9 Miusskaya Square.

§Professor, Dip. Energetica, 32 Piazza Leonardo da Vinci. Associate Fellow AIAA.

¶MSc. Candidate, Dip. Energetica, 32 Piazza Leonardo da Vinci.

Preliminary results indicate that up to pressures of the order of hundreds of atmospheres, the leading reactions, i.e., the reactions that are responsible for the main part of thermal flux entering the cold solid substance, proceed mostly in the condensed phase. At higher pressures, the gas-phase flame certainly plays an important role in controlling the burning rate. This study mostly deals with AN-based compositions and operating conditions of the first kind, i.e., with deflagration reactions proceeding preeminently in the condensed phase. A future paper will be devoted primarily to the second type of mechanism, i.e., deflagrations for which chemical reactions in the gas phase are essential for a comprehensive explanation of burning peculiarities.

Burning of AN and AN–TNT Mixtures

Andreev and Glaskova[20–23] were among the first investigators who extensively studied burning of pure AN and AN-based compositions. The main goals of their studies were to clarify mechanisms of burning and elucidate the influence of possible catalysts considered at that time by Andreev as one of the main factors determining safety of AN-based explosives as applied in coal mines.

In room-temperature constant-pressure experiments carried out by Glaskova,[21] neat AN did not burn in glass tubes of large diameter, up to 30 mm, even at 1000 atm. Typical burning rates of AN–catalyst mixtures in a pressure interval from 1 to 1000 atm also are presented in the work.[21] A similar behavior was observed during investigation of AN–TNT 80/20 mixture (denoted hereafter as Am). This composition burns very slowly and also has a very high pressure deflagration limit about 130 atm, which is much lower, however, than for pure AN. The presence of AN deflagration catalysts enhances burning rates of Am and reduces the PDL.

The most effective fuels for AN and AN-based compositions are charcoal and activated carbon; burning of these kinds of mixtures will be the object of a further compilation by the authors. Here, we consider AN–TNT mixtures as model compositions of the oxidizer with an active binder capable of melting, as well as with wood flour and carbon black. In addition to pure AN, a commercial-grade product containing several tenths of a percent of ferrous salts of organic acids was used. This material imparts to AN some kind of water resistance while working as a weak catalyst of the burning reaction. This waterproof material is called ANZ, a water-resistant ammonium nitrate containing 0.2–0.3% $FeSO_4$ and organic acids (so-called ZhV additives). The full compositions and basic characteristics of materials tested are given in Table 1.

Experimental Procedure

The compositions were prepared by mixing AN (at most 100 μm) with TNT (50 μm) and additives in a glass bulb containing a dozen rubber plugs for about 20 min. The mean particle sizes were NaCl ≤ 200 μm, wood flour 10 μm, and carbon black ≤ 1 μm.

Mixtures in a dry powder form were pressed into polymethymetacrylate (PMMA) tubes of 7 mm i.d. × 9 mm o.d. × 20 mm long at a pressure of about 0.2 GPa, giving the specimen practically zero porosity. Glass tubes (12–14 mm) also were used for AmZ burning rate experiments. The relative density of the mixture was about 0.8 in this particular case. Burning-rate measurements were carried out in the constant-pressure bomb at pressures from several atmospheres to 360 atm. A drum photorecorder FR-10 was used to obtain the streak photographs of the combustion process in the course of the burning-rate measurements.

Table 1 Composition and basic characteristics of materials tested

Compound[a]	Component content, % AN	TNT	NaCl	Other[a,c]	u_m, g/(cm$^2\cdot$s), at 30 MPa	T_f,[b] K, at 30 MPa
Am	79	21	——	——	1.2	2609
AmZ	78.7	21	——	~0.3 ZhV additives	1.8	2623
ANZ	99.7		——	~0.3 ZhV additives	0.9	——
Am + NaCl	74.4	18.6	7	——	3.0	2439
Am + NaCl	64	16	20	——	2.3	2232
AmZ + NaCl	63.8	16	20	~0.2 ZhV additives	2.3	2234
Am + 5%WF	76	19	——	5 WF	1.2	2466
Am + 5%CB	76	19	——	5 CB	1.3	2322

[a] AmZ is ANZ–TNT 80/20, CB is carbon black, WF is wood flour.
[b] T_f is the adiabatic flame temperature (calculated).
[c] ZhV additives are $FeSO_4$ + organic acids added to AN during its preparation.

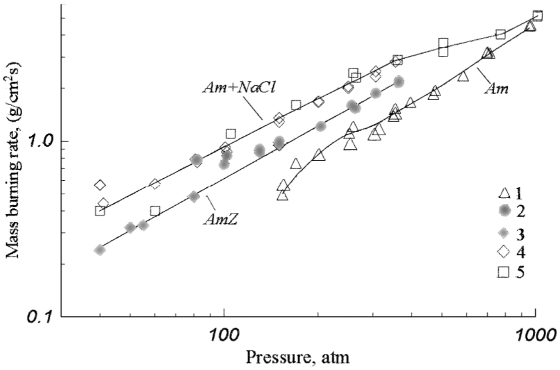

Fig. 1 **Burning rates of Am (1), AmZ (2, 3), and mixture of Am and NaCl 80/20 (4, 5). Compounds 1, 2, 4, and 5 are in PMMA tubes of 7 mm i.d.; 3 is in glass tubes of 12 mm i.d.; 1 and 5 are from Ref. 21.**

Burning-Rate Measurements

Burning rates of Am, AmZ, and their mixtures with NaCl (20%), having oxygen balance close to zero, are shown relative to pressure in Fig. 1. For neat Am, the data collected by Glaskova[21] are reported.

The burning rate of AmZ is about 1.5 times higher than that of AN–TNT. The addition of 20% NaCl leads to further augmentation of about 30–40%. NaCl as a catalyst is so effective that it suppresses the influence of the ferrous salts introduced into AN. Thus, the burning rates of AN–TNT and AmZ with NaCl are almost equal. The mass burning-rate dependence on pressure is about the same for all of the compositions presented in Fig. 1. The only exceptions are for Am at moderate pressures, and Am–NaCl at higher pressures. It appears that the burning rate is directly proportional to pressure up to at least 300 atm. For higher pressures, the effect of NaCl on Am burning becomes weaker, and thus the $u_m(p)$ line of Am–NaCl gets closer to that of the neat Am and almost overlaps it at $p \approx 1000$ atm. The unusually high burning rates of AmZ in PMMA tubes at a low pressure (80–100 atm) probably are connected to a reaction of AN with PMMA walls. Neat Am demonstrates rather peculiar $u_m(p)$ dependence. At high pressure, it is the usual straight line, $\nu = 1$. In the pressure interval from the PDL to about 400 atm, the curve is characterized by a ν-value variation.

Introducing NaCl into the composition sensibly increases burning rates of both mixtures. The maximum increase is reached for 5% NaCl, demonstrating the outstanding influence of chlorine ions on the process. Interaction between NaCl and NH_4NO_3 is considered responsible for the dominant part of heat entering into solid phase.

The influence of other additives on burning of Am and AmZ mixtures is shown in Fig. 2. The addition of 5% WF changes the burning rate of Am very little if one compares the points at the same pressure. The main effect of WF addition consists of the large decrease of PDL and the associated critical-mass burning rate, respectively, from 130 atm and 0.5 g/(cm$^2\cdot$s) to 50 atm and 0.2 g/(cm$^2\cdot$s). Still more pronounced in this respect seems to be the effect of CB. Even added in quantities as small as 5%, it diminishes the mass burning rate of Am at high pressures (at lower pressures, the mass burning rate slightly increases with CB addition) whereas PDL is reduced from 130 to ~2 atm, and the critical-mass burning rate from 0.5 to 0.02 g/(cm$^2\cdot$s). The difference between AN and ANZ-based materials consists in the fact that CB reduces PDL of AmZ less strongly, from 80 to ~20 atm (in the PMMA tubes of 7-mm diam).

The high value of PDL needs special attention. For Am, it is about 130 atm, whereas most common rocket or gun propellants can burn at atmospheric or even subatmospheric pressure. The corresponding mass burning rate is about 0.5 g/(cm$^2 \cdot$ s), 10–20 times larger than those of common propellants at PDLs. Ferrous salts and NaCl seem to diminish the PDL value considerably, but the corresponding critical burning rate at PDL is still extremely high compared with that of the common propellants.

Burning of AN Mixtures with Magnesium

Because pure AN does not burn as a monopropellant,[1] 3% by mass of ammonium dichromate [AD, $(NH_4)Cr_2O_7$] was added as a catalyst to accelerate AN chemical decomposition in a variety of AN-based mixtures.[24–27] AD consists of orange crystals, which decompose under heating. The baseline AN–AD 97/03 composition was examined by Rossi[24] for burning-rate measurements up to 75 atm. To achieve higher performance, magnesium was added in the amounts of 5, 15, and 30%.[17,28,29] The PDL did not decrease appreciably, but burning rates increased with increasing Mg content.[27] Most experiments then were performed with 15% Mg.[26,27]

Experimental Procedure

The samples used for experiments were produced by crushing solid AN and AD crystals in a ceramic mortar. The crushed powders were sieved: the grain size was ≤ 80 μm for both AN and AD; magnesium (≤ 200 μm) was added later for safety. The resulting powders were stored in an oven at 35°C for at least 24 h to dry. Then, by use of a steel matrix and plug, the powders were pressed into small cylindrical pellets to be used as test samples. For the mixture AN–AD–Mg 82/03/15, cylindrical samples of 8.2-mm diam, 25-mm height, and 1.65-g/cm^3 density were prepared. To obtain temperature profiles, fine (≤ 10-μm wire) tungsten-rhenium 80/20–tungsten-rhenium 95/05 thermocouples were embedded into each sample by enclosing the bead between two small pellets and then gluing them together. To avoid flame propagation on the sample sides, the lateral surface of samples was painted with a combustion inhibitor, which dried up in less than 30 min.

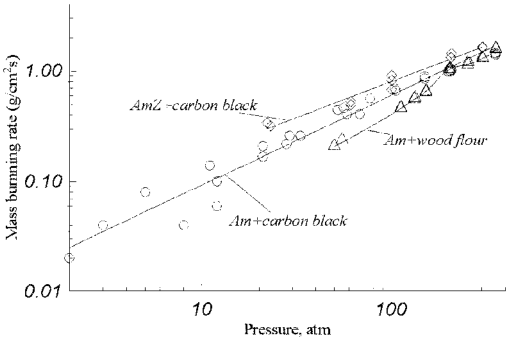

Fig. 2 Influence of CB and WF on burning rates of compositions of Am and AmZ.

Ignition was achieved by electrically heating the upper or lower surface with a nickel–chrome spiral wire. The test bomb was filled with dry nitrogen. Burning-rate measurements were obtained by superimposing a millimeter grid and a timer signal onto the burning-sample image while recording the test. Temperature profiles were recorded on a Nicolet 440 Digital Oscilloscope. Conversion of the voltage profile into a temperature profile was made on a personal computer using Labview 4.0 and then elaborated with a specialized software package.

Burning-Rate Measurements

Burning-rate data were fitted according to both the standard Vieille law and granular diffusion flame (GDF) theory. Data fitting for AN–AD–Mg 82/03/15 over a pressure range from 15 to 46 atm gave the following results in terms of Vielle law (see Fig. 3 and Ref. 27):

$$r_b = (0.072 \pm 0.004) p^{(0.63 \pm 0.02)} \tag{1}$$

The PDL was found to be about 18 atm for samples burning downward and 13 atm for samples burning upward; the burning-rate difference between the two configurations under the same operating pressure was within experimental error. Similar results were obtained in Refs. 24–26. The effect of Mg addition was investigated by Rossi[24] (0 and 15% Mg content) over a pressure range 15–75 atm and by Porricelli[25] (5, 15, and 30% Mg content) over a pressure range 15–50 atm. Tests with the metalized samples showed a systematic increase of the burning rate with increasing Mg load but no appreciable change of the pressure exponent ν (see Fig. 4 and Ref. 25). Analysis of combustion residues by x-ray diffraction revealed the presence of a large amount of MgO as well as $Mg_2C_2O_4$ and carbon obviously originating from the cover of the pellet. Oxidation of Mg during storage tends to reduce the fuel content in aged propellants by covering the Mg particles with MgO.

Temperature Measurements

Temperature profiles (Fig. 5) were handled in two different ways to obtain surface temperature: first, by visually searching for a sudden change of the profile slope; and second, by analytically searching for a peak in the first derivative profile. All prattles were smoothed by a computer implementation of the Savitzky–Golay algorithm[30]; the first derivative of all traces also was computed by

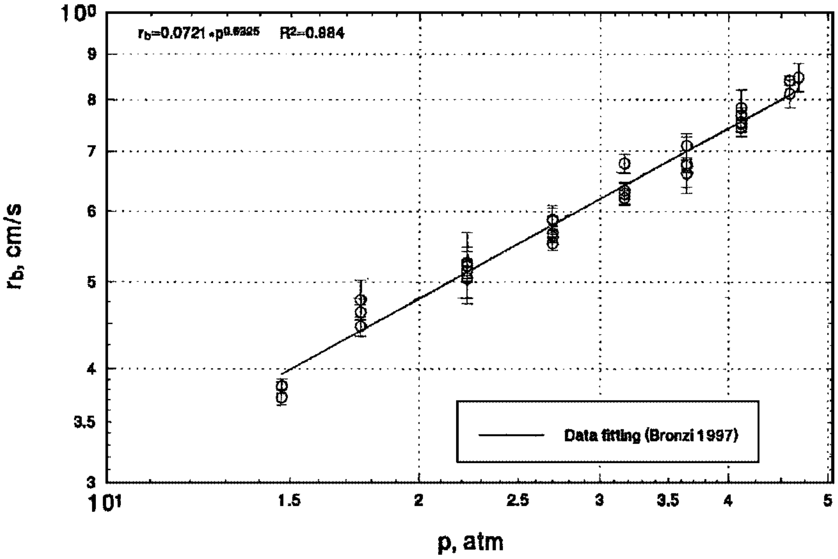

Fig. 3 Steady burning rate relative to pressure of the mixture AN–AD–Mg 85/03/15.

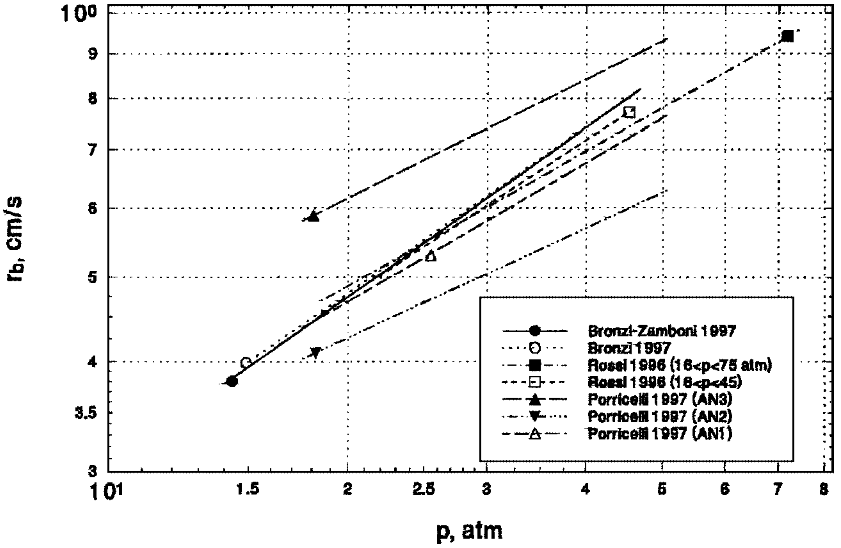

Fig. 4 Influence of magnesium content on the steady burning-rate dependence on pressure of AN–AD–Mg compositions: AN1–plus 5%, AN2–plus 15%, AN3–plus 30% of Mg in the mixture.

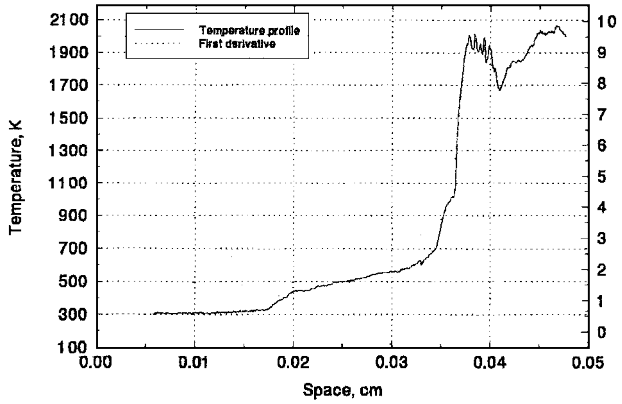

Fig. 5 Steady temperature profile of the mixture AN–AD–Mg 83/03/15 at 27 atm.

the same code. The best curve through surface temperature data for AN–AD–Mg 82/03/15 over a pressure range from 22 to 41 atm gave the following results[27]:

Visual method:

$$T_s = (69 \pm 14)p^{(0.68 \pm 0.06)} \tag{2}$$

Analytical method:

$$T_s = (71 \pm 12)p^{(0.69 \pm 0.05)} \tag{3}$$

Equations (2) and (3) are slightly different, with a systematic increase of the surface temperature predicted by the analytical method compared with the visual method. A thick zone of slow temperature rise between the melting point T_m and surface temperature T_s is observed.

Application of GDF Theory

For this variety of AN-based composite propellants, the classical GDF theory originally developed by Summerfield and co-workers for AP-based propellants[31–34] was applied. This requires a proper reformulation of the underlying semiempirical approach leading again to the standard expression

$$p/r_b = a + bp^{\frac{2}{3}} \tag{4}$$

where the constants a and b, respectively, measure the importance of chemical kinetics and mass diffusion in the gas phase. The GDF theory provides very good fitting of the measured steady-state burning rates for the tested AN–AD–Mg compositions:

$$p/r_b = (770 \pm 60) + (18 \pm 1)p^{\frac{2}{3}} \tag{5}$$

This result points out a strong influence of the chemical kinetics parameter a and indicates that the chemical kinetics processes are slower than diffusion of chemical species. This finding confirms the presence of a relatively thick liquid layer on the combustion surface that allows fast diffusion of reagents. In the experimental temperature profiles, the liquid layer should be visible as a plateau zone having a relatively slow temperature rise immediately before the surface and subsequent sharp temperature rise. However, several investigations reveal poor data reproducibility; that is, for the same operating conditions, temperature profiles do not overlap, except the surface temperature value. This is probably due to heterogeneity of the burning wave[17] and three-dimensional effects, causing the thermocouple bead to sense a different temperature value each time.

Burning of AN Water-Impregnated Compositions

The water-impregnated explosive compounds (WECs) are compositions based on an oxidizer and a fuel, which are fully or partially dissolved in water. Such compounds have been used industrially for about 40 years.[35] Numerous investigations have been dedicated to the study of their detonation, operational, and technological characteristics. In contrast, the combustion of WEC has been left nearly unexplored. The effect of water on the combustion rate of three individual explosives and an AmZ compound in a constant-pressure bomb has been determined by Annikov et al.[36] They showed that water reduces the combustion rate by diluting the explosive and by heat losses due to heating and evaporation. When the water content and operating pressure are sufficiently high, the burning may be made turbulent. Watergel WEC burning was investigated earlier.[37] In the present work, burning of both watergel and water-in-oil compositions is studied. The main interest of this study is connected with the fact that water solutions are characterized by a well-determined condensed-phase temperature dependence on pressure, which is just the boiling point of an AN water solution relative to temperature.

Experimental Procedure

Five types of WECs were investigated (Table 2):

1) exothermic compositions (compounds 1 and 2), containing water, oxidizer, gelling agent and powdered aluminum, for use in electric–hydrodynamic installations;

2) aquanals (compounds 3–5) sensitized with pigment-grade aluminum powder (PAP-2, with a specific surface of 2 m^2/g) and

Table 2 Compositions and some characteristics of WECs

	Content of components, %								Burning rate, mm/s, at a pressure (MPa) of		
Compound no.	H_2O	AN–SN	PG–CP	Fuel[a]	T_f, K	ΔP,[b] MPa	ν	PDL	30	10	PDL
1	15.0	33.0/12.0	0/40	——	3970	1–36	0.8	1.1	6	2.4	0.5
2	15.0	33.0/12.0	4.0/36.0	——	3970	1–36	0.5	0.6	6	3.4	0.7
3	20.0	45.0/15.0	10.0/0	10.0 U	2253	20–36	1.2	20	13	——	6
4	18.0	40.0/13.0	20.0/0	9.0 U	2943	6–18	1.5	6.0	31	13.6	6
						18–36	0.0				
5	15.0	35.0/12.0	30.0/0	8.0 U	3323	2–9	1.5	2.0	33	23.7	2
						9–36	0.3				
6	10.0	44.0/17.0	4.0/5.0	20.0 M	2489	2–36	0.8	2.0	17	7.1	2
7	11.0	48.0/18.0	——	23.0 M	1579	6–36	1.2	4.0	13	3.5	0.6
8	20.0	28.0/9.0	——	43.0 M	1488	5–16	1.5	4.0	——	3.5	0.8
9	10.0	34.0/10.0	5.0/0	41.0 R	2844	0.4–36	1.0	0.4	26	9.1	0.5
10	15.0	60.0/18.0	——	7.0 C	1793	——	——	>36	——	——	——
11	20.0	38.0/0	——	42.0 M	1472	20–36	1.8	20	12	——	6
12	22.0	49.0/17.0	——	11.0 U	1040	——	——	36	——	——	5
13[c]	19.0	42.5/14.0	15.0/0	9.5 U	2442	14–25	1.7	14	21	——	8
						25–36	0.7				
14[c]	19.0	42.5/14.0	1 5.0/0	9.5 U	2442	13 –25	1.6	12	19	——	5
15[c]	19.0	42.5/14.0	15.0/0	9.5 U	2442	13–23	1.6	13	16	——	6
						23–36	0.7				
16	14.5	61.0/14.5	——	10.0 C	1523	16–36	0.8	16	5	——	3
17	14.2	59.6/14.2	——	12.0 C	1377	15–36	1.0	14	5	——	2
18	13.7	57.6/13.7	——	15.0 C	1273	22–36	0.9	21	5	——	3
19	13.2	55.6/13.2	——	18.0 C	1227	30–38	1.1	30	3	——	3
20	12.2	61.1/17.7	——	9.0 I	1742	27–39	1.4	26	4	——	4
21	14.2	43.4/10.4	——	12.0 C/20.0 M	1291	12–36	2.2	11	14	——	1.5

[a] U is carbamide (Urea), M is methylamine nitrate, R is RDX, I is industrial oil (the percentage includes an emulsifier), C is crude oil, PG is pigment-grade aluminum powder, CP is crude powder.

[b] Interval of pressures studied.

[c] These compositions are almost identical except that 14 does not contain $Na_2S_2O_3$ and 15 does not contain $K_2Cr_2O_7$.

nonexplosive organic fuel carbamide (for comparison, the investigation also included compound 12 without aluminum);

3) aquamins containing an active organic fuel, methylamine nitrate, in addition to aluminum (compound 6), or with no aluminum (compounds 7, 8, and 11);

4) water-impregnated explosive sensitized by RDX (compound 9; actually, one of the first types of WECs employed in industry[35]); and

5) waterproof (water-resistant) compounds of the water-in-oil type containing, as a combustible, a mixture of petroleum products (industrial oil, heavy oil, or crude oil) with an emulsifier providing the combustible distribution in the form of a thin film on the surface of the finest oxidizer suspension droplets (compounds 10 and 16–21). With the exception of compound 11, a mixture of ammonium and sodium nitrates (SNs) was used at a 3:1 ratio by mass as oxidizer in all cases. In compound 11, only AN was used.

To prevent separation of the compounds during the storage process, the saltwater solution was always (except for compound 11) gelatinized with polyacrylamide (1.1–1.5%, pulverized granulated product). The cross-linking of polyacrylamide in the gelled solution was performed with potassium dichromate in the presence of sodium thiosulfate. Potassium biphosphate (0.1%) was used to stabilize the aluminum.

Water-in-oil compositions were prepared by adding concentrated AN–SN water solution at approximately 90°C to the mixture of the fuels, i.e., crude oil, or industrial oil, and emulsifier. With very intensive stirring, a substance having the consistency of a dense cream (at viscosity of about several hundred poises) was formed.

Experimental Results

The tests have shown (Table 2) that, for pressures above some limiting value (which varies significantly from compound to compound), all compositions except poremite (10) burn at rates between 0.4–40 mm/s. The specific rates depend on the pressure and the compound composition. Up to 36 MPa, the highest pressure used in our tests, the poremite 10 did not burn, whereas all of the other water-in-oil compositions (16–21) burned with a steady-state rate. An interesting result was obtained with compounds 3–5. Compound 3 burns poorly: PDL = 25 MPa (recall that the aluminum-free, carbamide-containing compound 12 generally did not burn up to 36 MPa). Compounds 4 and 5 burned at lower pressures and much higher rates; the normal burning velocity is higher than for all remaining compounds including composition 9. However, when $r_b \approx 3$ cm/s and pressures are 17 and 11 MPa, respectively, the burning-rate increase rapidly moderates, the value of n drops almost to zero. Only with compound 5 at $p = 35$ MPa is there a tendency for the r_b value to continue to rise.

The PDL and especially the critical burning rate (r_b at PDL) are usually very high for most of the WEC compositions investigated. The exceptions are compositions 1 and 2, containing abnormally big amounts of powdered aluminum, and compositions 7–9 (mostly as to the critical r_b value) containing trimethylenetrinitramine (RDX, $C_3H_6N_6O_6$) or methylamine nitrate (MAN) with no or minor aluminum content. Note that compound 11, which is very similar to compound 8 but with no SN, is characterized by a much higher level of burning instability. The PDL numbers changed from 20 MPa for composition 11 to 4 MPa for composition 8, and the corresponding critical burning rates from 6 to 0.8 mm/s.

Discussion

The main point of this discussion of the experimental data is the very poor burning ability of AN, which does not allow combustion to propagate at a constant pressure below 1000 atm. This behavior also is reflected in the very high PDL of the great majority of AN-based compounds.

Very important parameters of burning instability, at least in the theoretical sense, are the critical values of burning rate at a given diameter of a sample, critical Peclet number

$$Pe = \frac{u_m d_c c_p}{\lambda} \tag{6}$$

or the product $u_m d_c$ [see Table 2: burning rate (mm/s) at p = PDL is virtually $u_m d_c$ kg/(m · s), as $\rho \approx 1.5$ g/cm^3 and $d = d_c \approx 0.7$ cm, at p = PDL]. The theoretically predicted value of $u_m d_c$ for gases[38] and condensed substances burning steadily and stably at the expense of a reaction in the gas phase[39] is 0.1–0.2 kg/(m · s). The actual values for AN-based compositions are, as a rule, 2–6 kg/(m · s), i.e., 10–60 times greater.

Three fundamental observations might be helpful to explain this basic result:

1) A very thick liquid layer on the surface of the solid substance, about 2–20 times thicker than the theoretical Mikhelson preheated layer of the steady-state burning theory, is obtained.

2) A strong influence of NaCl as well as most of the other AN burning catalysts is observed on burning rates along with a weaker influence on PDL and Peclet number.

3) An unusually strong influence of carbonaceous materials, especially CB, on PDL, d_c, Pe^*, and $u_m d_c$ is observed, with minor influence of the materials on burning rates of the corresponding substances per se.

Chemical Mechanisms of AN-Based Mixtures

Thermal decomposition of AN includes a sequence of chemical interactions of equilibrium type, as is usual for the simple inorganic substances. These interactions have been studied extensively during the past four decades.[40–55] They can be written in the radical, molecular, and ionic forms. We use only the set of reactions in the molecular form for the high temperature of the liquid phase. It has been shown[50] that the ionic mechanism of AN decomposition is overtaken at higher temperatures by reactions of the radical type, whereas the molecular form of the chemical equations usually generalizes all sorts of interactions when the specific mechanisms are not understood in regular ionic or radical terms.

In both the gas and liquid states at a high temperature, the following set of reactions is usually suggested:

$$NH_4NO_3 = HNO_3 + NH_3\ (K_1) \tag{7}$$

$$2HNO_3 = N_2O_5 + H_2O\ (K_2) \tag{8}$$

$$N_2O_5 = N_2O_4 + \tfrac{1}{2}O_2\ (K_3) \tag{9}$$

$$NH_3 + N_2O_5 = NH_2NO_2 + HNO_3\ (K_4) \tag{10}$$

$$NH_3 + N_2O_4 = NH_2NO + HNO_3\ (K_5) \tag{11}$$

The main irreversible kinetic equations leading to formation of the products of AN decomposition are

$$NH_2NO_2 \rightarrow N_2O + H_2O\ (k_1) \tag{12}$$

$$NH_2NO \rightarrow N_2 + H_2O\ (k_2) \tag{13}$$

A simple mathematical treatment of the Eqs. (7–13) gives

$$W_{N_2O} = \frac{d[N_2O]}{dt} = k_1 K_1 K_2 K_4 \frac{[NH_4NO_3]}{[H_2O]}$$

$$W_{N_2} = \frac{d[N_2]}{dt} = k_2 K_1 K_2 K_3 K_5 \frac{[NH_4NO_3]}{[H_2O][O_2]^{0.5}} = 2W_{O_2}$$

$$\frac{1}{2} W_{H_2O} = W_{N_2O} + W_{N_2} = W_{AN} = \frac{-d[NH_4NO_3]}{dt}$$

$$\frac{W_{N_2O}}{W_{N_2}} = \frac{k_1 K_4 [O_2]^{0.5}}{(k_2 K_3 K_5)}$$

where k_1 and k_2 are the velocity constants of reactions (12) and (13), and K_1, K_2, etc., are the equilibrium constants of the reactions (7–12).

It is easy to see that AN decomposition is a reaction of the first order relative to $[NH_4NO_3]$ if H_2O and O_2 concentrations are constant. If the stable volatile products, e.g., H_2O, escape from the reaction zone (as is the case during laboratory N_2O preparation), the decomposition is a zero-order reaction. To date, the real values of the constants k_1, k_2, and the relevant equilibrium constants are not known exactly and further study is needed. The rate of the overall reaction, when water evaporation is limited by the small energy evolution, is strongly circumscribed by the process of water formation. All of the expressions for the reaction rates contain concentration of water in denominator.

The main obstacle to the overall process of AN decomposition is reaction (8), which is strongly endothermic and very slow at a moderate temperature. At low pressures, a layer of a solution of NH_4NO_3 and its decomposition products in water is formed at burning of AN-based compounds. The layer thickness increases at low pressure and the resulting unsteady process extinguishes by choking in its own reaction product, water.

All of the known AN burning catalysts predominately increase the velocity of HNO_3 decomposition. For instance, the consequence of the reactions when chlorides are added can be represented by interactions of the type

$$2HNO_3 + NaCl \rightarrow NOCl + NaNO_3 + \tfrac{1}{2}O_2 + H_2O$$

$$NH_4NO_3 + NOCl \rightarrow HCl + H_2O + N_2 + HNO_3$$

$$NaNO_3 + HCl = NaCl + HNO_3$$

$$HCl + HNO_3 = NO_2Cl + H_2O$$

$$NH_4NO_3 + NO_2Cl = N_2O + H_2O + HCl + HNO_3$$

Chlorine oxides are vigorous oxidizers of ammonia, which in turn is a relatively inert fuel formed during the process of AN burning.

In the case of catalysts containing chromium, it might be the simple set of two reactions:

$$2HNO_3 + Cr_2O_3 \rightarrow H_2Cr_2O_7 + N_2 + \tfrac{1}{2}O_2$$

$$2NH_4NO_3 + H_2Cr_2O_7 \rightarrow Cr_2O_3 + 4H_2O + N_2$$

The interactions

$$NaNO_3 + N_2O_3 = NaNO_2 + N_2O_4$$

$$NaNO_2 + NH_4NO_3 = NH_4NO_2 + NaNO_3 \rightarrow N_2 + 2H_2O + NaNO_3$$

accelerate the reaction when SN is present.

All of these reactions proceed preeminently in the liquid phase. The liquid surface temperature and, consequently, the burning rate increase for increasing pressures. At 200–300 atm, which is near the critical pressure of water, the critical conditions at the liquid–gas interface are reached and it is difficult to increase the temperature and the reaction rate in liquid phase.

Carbonaceous materials, CB in particular, react with nitrogen oxides and acids and the resulting heat and CO remove water from the reacting mixture. The water-impregnated layer on the solid-phase surface becomes thinner, and burning becomes more stable. Moreover, a layer of CB on the dry surface of the substance is formed and the problem can be transformed to the Kondrikov–Novozhilov (KN) theoretical model.[56] CB actually is the ingredient of a many-sided action: It reacts, it is able to catalyze the oxidation reactions, it absorbs energy in visible and infrared parts of spectrum, and it forms the solid particles layer. In the long run, all of the effects of CB functioning result in increased burning stability.

TNT is not a catalyst. Consequently, it cannot force AN to burn at least up to 120–140 atm, when the boiling temperature of the AN water solution becomes high enough to induce self-sustaining decomposition of TNT, producing an additional heat release. Under these circumstances, AN–TNT mixtures begin to deflagrate. The distinction between the burning of AN–TNT mixtures and the deflagration of the neat AN compositions is the extended flame that appears after some period of decomposition in the liquid layer. This flame prevents the unconfined growth of this layer. But in contrast to CB specially added, it cannot remove the water excess to reduce the liquid layer to its normal Mikhelson thickness, because of a lack of carbon production. What is still more important, this occurs in the gas-phase flame and not on the surface of the condensed phase.

At pressures greater than the critical point of the water solution, where water evaporates extensively, the equilibrium reaction (8) is displaced to the right side. Therefore, the main obstacle against AN decomposition disappears and something similar to supercritical oxidation takes place. According to our estimates, AN burns in the manometric bomb at about 1500 atm and easily detonates at pressures of the order of several gigapascals.

Burning Mechanism of Water-Impregnated and Metal-Containing Compounds

Burning of WECs, having one phase interface, gas–liquid, can proceed in a simpler way than burning of solid compounds. Thus, the discussion continues with a focus on the behavior of water-impregnated materials.

It was stated that burning rates of WECs are close to the rates previously found for individual nitrocompounds. The $r_b(p)$ curves for nitrocompounds clearly show[57] that the burning mechanisms at $p \approx 30$ MPa are significantly different from those at $p \approx 10$ MPa. When $p \approx 10$ MPa, the leading burning reaction of some nitrocompounds (e.g., tetryl, single-base propellant[58,59]) occurs in the condensed phase. If, in the burning of the WEC materials, the leading reaction also proceeds in the condensed phase, then aluminum oxidation by the water nitrate solutions and decomposition of the nitrates themselves in compounds without aluminum are supposed to occur. The rate of the aluminum oxidation reaction was estimated by Egorshev et al.[37] It is of interest to clarify the influence of pressure and concentration of magnesium on the AN–AD–Mg model propellants burning in terms of the mechanisms proposed for AN–water–Al mixtures. Let us propose that the burning rate depends on some reaction of the AN–AD mixture and on some interaction of AN with Mg. The burning-rate dependence has the overall form

$$r_b^2 = a_1 + b_1 \alpha_m^n \tag{14}$$

where α_m is the mass fraction of magnesium in the mixture, n is the order of reaction of Mg with the oxidizer related to the Mg surface, and a_1, b_1 are constants. Equation (14) follows from the usual Zel'dovich relation for a burning rate at the expense of a reaction in the condensed phase when the reaction consists of two parallel constituents, in this case the decomposition of AN–catalyst and oxidation of Mg particles in the liquid oxidizer. At $p = 50$ atm and $\alpha_m = 0.05$, 0.15, and 0.3, r_b values are 6.2, 7.8, and 9.3 mm/s, respectively (see Fig. 4). Equation (14) gives $a_1 = 18$ mm^2/s, $b_1 = 160$ mm^2/s, and $n = 0.7$. The n value is sensibly less than the value of 1.2 obtained for the AN–water–Al mixtures by Egorshev et al.[37] The theoretical figure of n for particles suspended in oxygen containing media is 1. The difference could be attributed to possible melting and evaporation of a metal in the deflagration reaction zone. This behavior would change the original surface of the metal particles and change the temperature in the reaction zone accompanying a change in the concentration of the metal particles. For increasing α_m, the first factor probably prevails, whereas during combustion of Al-containing mixtures, the temperature rise from the Al concentration increase is the reason for n relative enhancement.

It is well known that for a leading reaction going on in the liquid phase at a temperature close to the boiling point of the liquid, the pressure exponent ν depends on the energy of activation of the reaction and the enthalpy of evaporation of the liquid. The activation energy can be calculated using the simple formula

$$E = 2\nu Q_{\text{ev}} \approx 12 \text{ kcal/mol}$$

In the case of AN–water–Mg composition, $Q_{\text{ev}} \cong 10$ kcal/mol, corresponding to the evaporation heat of the main reaction product of water, $\nu \approx 0.6$. The activation energy is supposed to be lower than that for the AN–Al reaction [17 kcal/mol (Ref. 37)].

Burning of the ammonium nitrate and the methylamine nitrate compositions with no aluminum (compounds 7, 8, and 11 in Table 2) is governed by the nitrate decomposition in the liquid phase. If T_{ev} is determined by water evaporation, one can evaluate the activation energy E for the leading reaction ($E = 2\nu Q_{\text{ev}}$). According to Table 2, the average ν value for compounds 7, 8, and 11 is 1.5 ± 0.3 and, correspondingly, $E = 28.5 \pm 5$ kcal/mol. It was shown by Egorshev et al.[37] that the value k (750 K) $= 2 \times 10^2$ s^{-1} corresponds to the preexponential factor of a bimolecular reaction rate $K_{O_2} \approx 2 \times 10^9$ l/(mol · s) and also practically equals the reaction constant for the AN decomposition (10^2 s^{-1} at 750 K).[60]

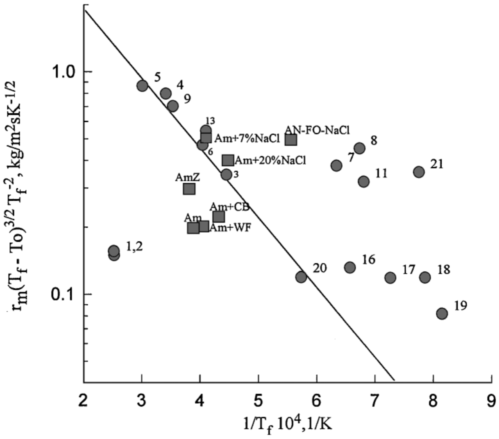

Fig. 6 Dependence of the reduced burning rate of water-impregnated materials at p = 30 MPa vs the calculated inverse of the flame temperature. The straight line corresponds to the same dependence for nitrocompounds (Ref. 57).

In the high-pressure region, the results are generalized easily and the burning mechanisms are simpler.[57] The relation between the velocity and the adiabatic combustion temperature at $p = 30$ MPa is shown in Fig. 6 (based on the data in Table 2) in the same coordinates as used by Kondrikov et al.[57] The straight line in Fig. 6 is taken from Ref. 57 and corresponds to the burning velocity dependence on the flame temperature for nitrocompounds at $p = 30$ MPa. The experimental points for 7 of the 20 WECs capable of steady-state burning, which are mostly those containing pigment-grade aluminum powder, lie with striking accuracy near the straight line for the nitrocompounds. The compositions without pigment-grade aluminum yield points lying either far below (1 and 2), or much higher than the line (7, 8, 11, 16–19, and 21).

The state of substance 20 might be merely a coincidence. For the sequence of substances 16–20, whose burning rates are close to each other, Fig. 6 shows a tendency to move closer to the straight line as the content of fuel in the composition diminishes. Compositions 16–19 containing the crude oil fall in a relatively straight line on Fig. 6 in the order of 18, 15, 12, and 10% of the fuel. It appears as if a leading reaction of these water-in-oil substances proceeds in the condensed phase. Alternatively, the leading reaction is in the first flame, where temperature is connected weakly with the final adiabatic flame temperature and, correspondingly, the placement of points 16–21 in the Fig. 6 plane has no special physical sense. Compound 20 contains 9% fuel and is exactly on the line. However, compound 20 is closer to stoichiometry than all of the others and one may propose that, in this specific case, the flame temperature and the corresponding velocity of the reaction at this temperature really satisfies the usual $u_m(T_f)$ relation.

All of the solid AN-based substances with no catalyst or with minor content (Am, AmZ, Am + WF, Am + CB) are positioned much lower than the line in Fig. 6. This demonstrates that the leading reactions in the condensed and the gas phases proceed much slower than those in the burning of regular nitrocompounds. Probably this results from the large ammonia concentration in the mixture. That NH_3 retards the burning of explosives was postulated by Glaskova.[21] This effect was considered to result from the reverse reaction of the type of equilibrium (7). The real influence of ammonia is probably a much more complicated problem, and may be stipulated preeminently by the reactions

$$NH_3 + H \rightarrow NH_2 + H_2$$

$$NH_3 + OH \rightarrow NH_2 + H_2O$$

$$NH_2 + H \rightarrow NH + H_2$$

Here, active hydrogen and hydroxyl radicals are eliminated in flame and replaced by the relatively passive species NH_2 and NH.

Conclusions

Ammonium nitrate, AN, is a widely used oxidizer yielding no environmentally harmful constituents when burned under conditions of thermodynamic equilibrium in mixtures with the usual organic fuels. The relatively low enthalpy of formation of this oxidizer is expiated by the very low cost of the commercial-grade product, which provides correspondingly inexpensive specific impulse. Another essential advantage of AN-based compositions is the comparatively low sensitivity to mechanical stimuli.

Two main categories of AN-based model propellants were preferably studied: 1) mixtures of AN catalyzed by AD with magnesium; and 2) water-filled or water-impregnated, liquid or gelled compounds, or the reverse, i.e., propellants specifically simulated as water-in-oil emulsions. Experimental data on burning of the AN mixtures with catalysts and compositions based on the AN–TNT 80/20 compound also are reviewed briefly.

It is shown that combustion of almost all of the substances studied is characterized by a very low level of burning stability: The PDL value, the critical Peclet number, and the $u_m d_{cr}$ product in the majority of cases are much higher than the corresponding values observed for the usual double-base and composite propellants as well as for the variety of nitrocompounds investigated earlier.

The explanation proposed for this peculiarity takes into consideration the experimental observation that condensed phase reactions determine the burning rate in the moderate pressure region. This behavior is related to the PDL, Peclet number, and $u_m d_{cr}$ values and results from a liquid layer that comprises a mixture of melted AN, water, nitric acid, nitrogen oxides, and some other less-pronounced constituents. Reactions in this layer go on slowly and release correspondingly low quantities of heat at relatively low characteristic temperatures. Reactions in the secondary flame are separated from the liquid–solid interface by a layer of the rather inert fluid and do not participate significantly in formation of the burning process as a whole.

In the presence of carbonaceous additives, primarily CB, the burning stability of AN-based formulations is enhanced drastically. The PDL is decreased practically to atmospheric pressure, and the Peclet and $u_m d_{cr}$ numbers take their usual values for the rocket and gun propellants. The secondary flame also begins to play an essential role during burning of AN-based compositions.

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