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# Combustion Mechanism of Ammonium-Nitrate-Based Propellants

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**This paper discusses results obtained by studying a row of progressively complicated ammonium-nitrate-based systems: ammonium nitrate/catalyst, ammonium nitrate/catalyst/hydroxy terminated polybutadiene, ammonium nitrate/catalyst/hydroxy terminated polybutadiene/ammonium perchlorate, and ammonium nitrate/catalyst/hydroxy terminated polybutadiene/ammonium perchlorate/Al. The successive addition of ammonium perchlorate and Al to the binary mixture of a catalyzed ammonium nitrate/binder yields a regular increase in the burning rate, accompanied by a small change in the pressure exponent. On the basis of flame-structure investigation by fine tungsten-rhenium thermocouples, it has been determined that the surface temperature of catalyzed ammonium nitrate as well as ammonium-nitrate-based propellants is controlled by the dissociation reaction of the salt occurring at the surface. An analysis of the results obtained suggests a combustion mechanism of ammonium-nitrate-based propellants, which is based on the leading role of heat release in the condensed phase.**

## Nomenclature

$c_p$ = average specific heat of the condensed phase
$E$ = activation energy
$k$ = rate constant, $A \cdot e^{-E/RT_S}$
$L_m$ = heat of melting
$m$ = mass burning rate/ mass evaporation rate
$n$ = pressure exponent
$p$ = pressure
$Q$ = heat of reaction
$Q_g$ = heat feedback from the gas phase
$Q_g'$ = difference between the heat feedback from the gas phase and the heat needed for the evaporation of the undecomposed substance
$Q_{\mathrm{ev}}$ = heat of evaporation
$Q_{\mathrm{need}}$ = heat needed for heating the substance to the surface temperature with regard to phase transitions
$Q_r$ = heat, incoming in the condensed phase at the expense of radiation
$Q_s$ = heat effect in the condensed phase
$r_b$ = burning rate
$T_b$ = boiling temperature
$T_{\mathrm{cr}}$ = critical temperature
$T_f$ = flame temperature
$T_o$ = initial temperature
$T_s$ = surface temperature
$t$ = time
$\eta$ = fraction of the substance reacting in the condensed phase
$\lambda$ = thermal conductivity of the condensed phase
$\rho$ = density
$\sigma_p$ = burning-rate temperature sensitivity
$\varphi$ = temperature gradient above the surface

## I. Introduction

AMMONIUM nitrate (AN) finds an application not only as a fertilizer and component of industrial explosives, but also as an oxidizer in gas generators and solid rocket propellant compositions [1–3], because it is very cheap and generates environmentally friendly combustion products. However, AN-based systems are not free from drawbacks. The main problems associated with AN, in its use as an oxidizer in propellants, are several crystalline-phase transitions at temperatures within the range of normal usage, hygroscopicity, a limited range of burning rates, and the inability to burn aluminum efficiently. At the present time, the first two problems have been overcome by using different additives [3]. An increase in the burning rate of the propellants can be achieved by either using catalysts of AN combustion [4–10] or introducing some ammonium perchlorate (AP) in the propellant composition [11–13]. The latter additive usually solves the problem of inefficient combustion of aluminum as well. However, the use of AP, even in minor quantities, leads to the deterioration of the "clean-burning" characteristics of the propellant, which may be considered a necessary toll to reach the wanted burning velocity and completeness.

Notwithstanding the long history of AN combustion studies since the 1950s [1,2,6,7], the scientific understanding of the combustion mechanism of AN-based propellants is far from satisfactory. In early works, it was assumed that gas-phase reactions of the second order controlled the combustion of AN composite propellants and mixtures [1,2,5]. In recent publications [14–16], it was postulated that the leading reaction in the combustion of AN-based compositions proceeded mostly in the condensed phase up to pressures of the order of hundreds of atmospheres.

In contrast to this, in [17], a model for ammonium-nitrate-composite propellant combustion was developed, based on the idea that the primary diffusion flame by analogy with AP composite propellants was the dominant zone in determining the burning rate of the propellant. However, thermocouple measurements of AN/hydroxy terminated polybutadiene (HTPB) propellant containing coarse (600 $\mu$m) AN prills showed [18] the apparent absence of a distinct monopropellant flame as well as a strong diffusion flame. Based on thermocouple measurements, the authors of [18] reached the conclusion that the combustion of the AN/HTPB propellant was driven by an exothermic, partially premixed gas flame. However, in

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Table 1 Content and some properties of propellants tested

| Mixture | PSAN | AP | HTPB | Aluminum | Density of strand, g/cm$^3$ | Oxidizer/fuel ratio |
|---|---|---|---|---|---|---|
| PSAN1/HTPB | 78 | —— | 22 | —— | 1.40 | 0.453 |
| PSAN2/HTPB | 78 | —— | 22 | —— | 1.40 | 0.455 |
| PSAN1/AP/HTPB | 45 | 32 | 23 | —— | 1.47 | 0.457 |
| PSAN1/AP/Al/HTPB | 40 | 28 | 16 | 16 | 1.53 | 0.456 |
| PSAN2/AP/Al/HTPB | 40 | 28 | 16 | 16 | 1.53 | 0.457 |

[19], the authors also suggested that the surface temperature remained constant and equal to 300°C over a wide pressure range. The combustion mechanism of AN with the additives of various natures is considered in [20]. It was shown that this was not the case, at least not in the burning of AN with KCl and charcoal additives, and that the surface temperature of AN was controlled by the dissociation reaction of the salt into ammonia and nitric acid occurring at the surface. Measured AN surface temperatures increased with pressure and surpassed the value chosen in [18] at pressures as low as 2.75 MPa; this casts doubts upon the correctness of conclusions made in [18] on the basis of heat-balance calculations.

The goal of the present work is to reveal the combustion mechanism of AN-based propellants by studying a row of progressively complicated systems: AN/catalyst, AN/catalyst/binder, AN/catalyst/binder/AP, and AN/catalyst/binder/AP/Al. Preliminary results were presented earlier at conferences [21–23].

## II. Experimental Part

### A. Ingredients and Sample Preparation

Phase-stabilized AN (PSAN), containing additives of 1%$Mg(NO_3)_2$ and 4%$K_2Cr_2O_7$, was used in the burning-rate experiments. According to [24], this PSAN has no modification transition in the temperature range of $-50\text{–}+90\,°C$. For stabilization, 1% $Mg(NO_3)_2$ was added to the saturated water solution of ammonium nitrate. The solution was heated to boiling (120–130°C) and then water was fast evaporated off by vacuum. Subsequently, the mixture was removed from the retort and stored in a vacuum drier at 80°C for an hour. Before preparing the samples, the mixture has been thoroughly comminuted to obtain grain sizes of the order of 10–40 $\mu$m.

In spite of the fact that potassium dichromate ($K_2Cr_2O_7$, red-orange regular-shaped crystals) has a high solubility in a water solution of AN, attempts to cocrystallize AN, magnesium nitrate, and potassium dichromate together have failed. Therefore, $K_2Cr_2O_7$ has been added mechanically after being crushed in a ceramic mortar. Microscope analysis of these particles revealed a nonuniform distribution of the sizes from 30 to 150 $\mu$m. Several mixtures were used: $95\%AN + 1\%Mg(NO_3)_2 + 4\%K_2Cr_2O_7$(PSAN1) and $97\%AN + 1\%Mg(NO_3)_2 + 2\%K_2Cr_2O_7$(PSAN2).

Commercial-type AP with about an 8 $\mu$m particle size and aluminum, named ACD-4, in the form of fine monomodal (6–8 $\mu$m) powder were used. An oligomer of hydroxy-terminated polybutadiene, named SKDN, was used as a binder.

Cylindrical specimens, 7 mm in diameter and 10–15 mm long and with a density of 1.68 g/cm$^3$, were obtained by the compression of PSAN1 and PSAN2 in transparent acrylic tubes. Noncured propellants (Table 1) have been prepared by mixing the components with binder in a Teflon mortar warmed to 80°C. Samples to test were prepared by compact filling the mass into transparent acrylic tubes. All compositions had an oxidizer/fuel ratio of about 0.45–0.46. The density of the filled propellants were calculated to be around 0.93–0.98 of TMD.

### B. Burning-Rate Measurements

Burning-rate measurements were carried out in a constant-pressure window bomb with a volume of 1.5 liters. The pressure range studied was 0.1–36 MPa. A video camera was used to determine the character of the combustion process as well as the burning rates.

### C. Temperature Measurements

Temperature profiles in the combustion wave were measured using Π-shaped thermocouples. The thermocouples were welded from 25- or 50-$\mu$m-diam 95%W + 5%Re and 80%W + 20%Re wires and rolled in bands to obtain a 7 or 20 $\mu$m bead size. The thermocouples were embedded in samples pressed into acrylic tubes. A Pico ACD-216 digital oscilloscope was used to record the thermocouple signal. In all cases, the burning rate and temperature profiles were measured simultaneously.

## III. Results

### A. Combustion Behavior

#### 1. *Combustion of Phase-Stabilized Ammonium Nitrate with Catalyst*

As is well known [4,5], neat ammonium nitrate does not burn in a pressed state, even at 100 MPa. The addition of small amounts of some mineral substances to AN increases its ability to burn strongly. Potassium dichromate is one of the most effective catalysts of AN combustion [4–10]. The combustion of a mechanical mixture of PSAN with 4% $K_2Cr_2O_7$ (PSAN1) proceeds in a practically flameless regime with the formation of a copious white smoke. The combustion front is substantially nonplanar. The combustion propagates by isolated areas (spot mode), and some centers go deep very strongly into a charge, leaving most of the charge unmelted. The problem of the nonflat front was partially solved by the addition of 1% superfine $SiO_2$; however, measured burning rates still had a large scatter (Fig. 1). In this regard, the burning-rate law of this mixture illustrated in Fig. 1 and Table 2 should only be considered as estimates. Note that both the burning rates and law differ considerably from burning parameters of a similar mixture studied in [4].

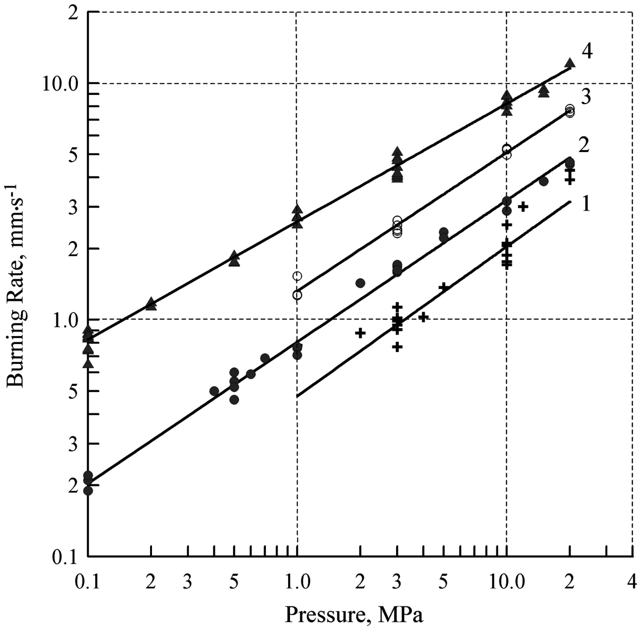

**Fig. 1 Pressure dependence of the burning rate for PSAN with addition of 4% $K_2Cr_2O_7$ (1), PSAN1/HTPB (2), PSAN1/AP/HTPB (3), and PSAN1/AP/Al/HTPB (4).**

**Table 2 Burning-rate laws $r_b = bp^n$ and adiabatic flame temperatures of propellants tested**

| Mixture | Pressure interval, MPa | $b$ | $n$ | Burning rate at 10 MPa, mm/s | Adiabatic flame temperature at 10 MPa, °C |
|---|---|---|---|---|---|
| PSAN1 | 1–20 | 0.477 | 0.630 | 2.04 | 922 |
| PSAN1/HTPB | 0.1–20 | 0.807 | 0.598 | 3.20 | 1027 |
| PSAN2/HTPB | 1–20 | 0.619 | 0.631 | 2.65 | 1032 |
| PSAN1/AP/HTPB | 1–20 | 1.323 | 0.585 | 5.09 | 1177 |
| PSAN1/AP/Al/HTPB | 0.1–20 | 2.600 | 0.498 | 8.18 | 2437 |
| PSAN2/AP/Al/HTPB | 1–20 | 2.344 | 0.474 | 6.98 | 2452 |

Extinguished samples had a hardened, melted layer of brown color on the surface, topped by a tablet of bright yellow color containing products of the catalyst transformation.

### 2. *Combustion of Mixtures of Phase-Stabilized Ammonium Nitrate with Catalyst and Binder*

The addition of a liquid oligomer of HTPB to the PSAN1 results in a propellant, which burns with quite a regular burning surface and is able to burn at atmospheric pressure. The combustion of PSAN1/HTPB is accompanied by the formation of a white dense smoke and, after combustion, a large amount of condensed products are collected (10–15% of the initial weight). At low pressures, ignition clearly takes place after the formation of a thick liquid layer on the surface, whereas, at higher pressures (over 5 MPa), ignition becomes easier.

The mixture PSAN1/HTPB burns ~1.5 times faster than catalyzed PSAN1 even though the addition of fuel has insignificantly increased the adiabatic combustion temperature (Table 2). The burning rates of PSAN1/HTPB are close to those of the cured propellant PSAN/HTPB (80/20), containing a 5% catalyst (2% ammonium dichromate and 3% potassium dichromate) [25] (Fig. 2). A reduction of the amount of catalyst up to 2% (mixture PSAN2/HTPB) results in a small increase in the burning law exponent and a reduction of the burning rate by a factor of 1.2 (Fig. 2), even though the combustion temperature practically does not change (Table 2). It is important to note that reducing the catalyst amount increases the low-pressure deflagration limit (PDL) to 1 MPa as well.

The AN/binder (78.6/21.4) propellant studied in [18] contains 3.6% of ammonium dichromate, and its composition is close to the PSAN1/HTPB and PSAN2/HTPB propellants. However, it has a much lower burning rate (1 mm/s at 0.7 MPa in comparison with 2.6 and 2.1 mm/s) with a similar pressure exponent (0.59) (Fig. 2). It is improbable that this is connected with a smaller catalytic activity of ammonium dichromate in comparison with potassium dichromate. The authors of [18] indicate that the composition of the propellant included 67.8% coarse (600 μm) AN prills and that the flame temperature varied with space and time in the range of 1000–1600°C. Perhaps, in spite of the fact that AN-based propellants have a melted layer on the surface leveling the influence of the oxidizer particle size, this influence appears with a very large degree of heterogeneity.

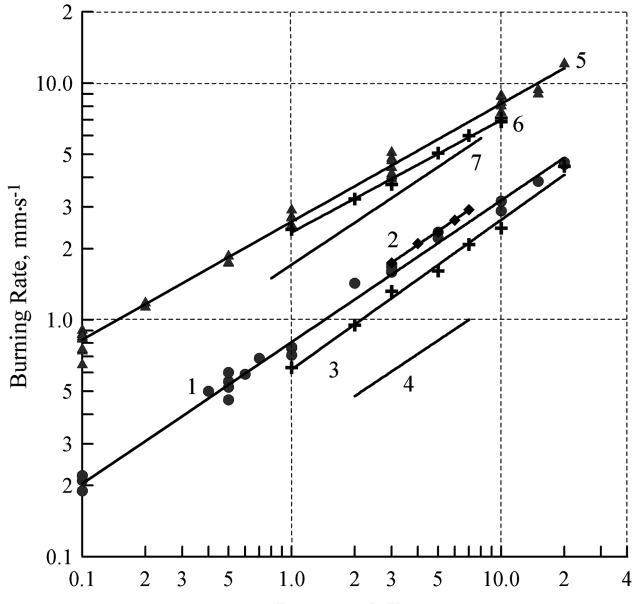

**Fig. 2 Pressure dependence of the burning rate for PSAN1/HTPB (1), data from [25] (2), PSAN2/HTPB (3), data from [18] (4), PSAN1/AP/Al/HTPB (5), PSAN2/AP/Al/HTPB (6), and data from [11] (7).**

### 3. *Combustion of Mixtures of Phase-Stabilized Ammonium Nitrate with Catalyst, Binder, and Ammonium Perchlorate*

The replacement of part of PSAN1 with fine AP results in a further increase in the burning rate of the composition (Table 2); at the same time, the pressure exponent in the burning-rate law varies very weakly. Because the compositions have a close oxidizer/fuel ratio, the adiabatic flame temperature changes insignificantly. Strangely enough, the introduction of a more reactive oxidizer results in an increase in the PDL to 1 MPa. Also, in this case, condensed products have been found in percentages from 10% to 15%. In general, the combustion of this propellant is characterized by oscillations of the flame above the surface, even at higher pressures.

### 4. *Combustion of Mixtures of Phase-Stabilized Ammonium Nitrate with Catalysts, Binder, Ammonium Perchlorate, and Al*

The introduction of fine aluminum to the dual-oxidizer propellant PSAN1/AP/HTPB results in a further increase in the burning rate up to 8.2 mm/s at 10 MPa; at the same time, the combustion temperature grows considerably (Table 2). The Al addition reduces the pressure exponent in the burning-rate law from 0.6 to 0.5.

It is surprising that PSAN1/AP/Al/HTPB and PSAN2/AP/Al/HTPB compositions demonstrate very similar effects of the catalyst content variation from 4 to 2% on the close burning rate as observed in the burning of the PSAN1 and PSAN2 mixtures with fuel, for which the contribution of the gas phase is much less (Fig. 2).

Literature data [11] on the combustion of a cured PSAN1/AP/Al/HTPB propellant with the same composition are also presented in Fig. 2. The differences in the slope and values of the burning rate are probably due to the generally larger particles of Al (50 μm) and AP (bimodal 140–160/70–80 μm) used in the last case.

To gain a detailed understanding of the combustion mechanism of AN-based compositions and to identify leading reactions and leading combustion zones, it was necessary to study the temperature distribution in the combustion wave of AN mixtures.

## B. Temperature Measurements

### 1. *Temperature Distributions in the Combustion Wave of Phase-Stabilized Ammonium Nitrate with Catalyst*

As mentioned, in [19], it was proposed based on thermocouple studies that the surface temperature of catalyzed ammonium nitrate (2.5% $CrO_3$) remains constant and equal to 303 ± 12°C over a wide pressure range (from 7 to 30 MPa). Note that the AN burning surface is not planar but rather consists of protrusions and depressions that very strongly complicate the interpretation of temperature profiles. In [20], studies on the combustion of AN with additives of KCl and charcoal showed that the surface temperature of AN increases with pressure and is controlled by the dissociation reaction of the salt into ammonia and nitric acid occurring at the surface.

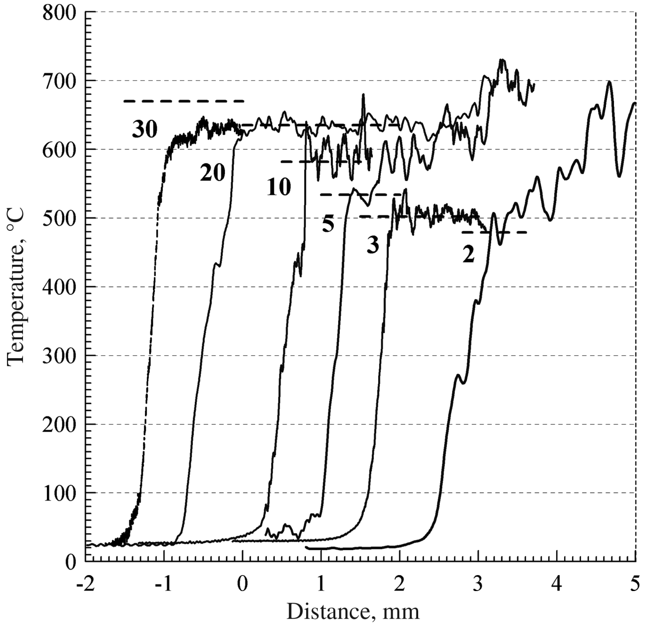

**Fig. 3 Typical temperature profiles for PSAN1 at pressures of 3, 10, 20, and 30 MPa and AN mixtures with 5% KCl at pressures of 2 and 5 MPa. Dotted lines are the dissociation temperatures of AN at corresponding pressures.**

In the present work, the temperature profiles in the combustion wave of the PSAN1 mixture containing 4% of $K_2Cr_2O_7$ were measured with the help of thin thermocouples.

The typical temperature profiles of PSAN1 combustion at 3, 10, 20, and 30 MPa are shown in Fig. 3. The typical temperature profiles at 2 and 5 MPa obtained in [20] for the combustion of AN with 5% KCl are also presented. As can be seen in Fig. 3, the surface temperatures of PSAN1 as well as AN doped with KCl, despite fluctuations, are clearly visible even at 30 MPa as an inflection point of the profile. Differences between the two mixtures consist of the fact that the profiles of PSAN1 have extended portions above the surface with a constant temperature and the growth of temperature up to 700–1000°C begins after these portions, whereas in profiles of AN doped with KCl, a weak temperature gradient is observed in the gas phase above the AN surface, though the maximum temperature ($\sim$1000°C) is also achieved at a significant distance (3–4 mm) above the burning surface.

In Fig. 3 the dotted lines indicate the AN dissociation temperatures at pressures of 2, 3, 5, 10, and 20 MPa. Despite temperature fluctuations, it is very obvious that, in the pressure interval of 2–20 MPa, the AN dissociation temperatures practically coincide with the surface temperatures. An exception is the surface temperature at 30 MPa, which is shown to be close to the surface temperature at 20 MPa. It is well known [5] that, generally, the curves $r_b(p)$ of AN with additives have a break at 20–25 MPa, with a strong pressure influence on the burning rate before the break (pressure exponent $n = 0.85$–$0.95$) and a weaker dependence after it ($n = 0.5$–$0.6$). It was suggested in [20] that, at these pressures, the AN dissociation temperature attains its critical value and no longer grows. In this work, we most likely succeeded in obtaining the experimental proofs of achievement of the critical temperature at burning. It is necessary to underline that the absence of temperature growth with pressure is connected to the achievement of the temperature critical value rather than with energy reasons, because the maximum combustion temperature achievable in the experiments is much higher ($\sim$1000°C).

### 2. *Temperature Distributions in the Combustion Wave of Phase-Stabilized Ammonium Nitrate 1 with Binder*

The burning of the PSAN1 mixed with a liquid HTPB oligomer is accompanied by the appearance of a gas-phase flame (1100–1230°C) at as little as $\sim$0.2 mm from the surface. Significant fluctuations of temperature are observed in the gas-phase flame. The measured maximum temperature of burning appeared to be noticeably higher ($\sim$300 K) than the calculated adiabatic temperature (see Tables 2 and 3). It means that the nonequilibrium products, for example, soot, are formed during combustion. As mentioned, 10–15% of the condensed combustion products were found after burning. If one considers that the catalyst and modifier could give 3–4%, the amount of soot would be 7–11%. A calculation of the combustion temperature, assuming a formation of 9% of soot, gives a value close to the experimental one. It was also shown in [24] that 6–7.5% of condensed combustion products were found at the burning of AN/AP/HTPB propellants with a close oxidizer/fuel ratio (0.43) and an AN content (30–40%). In the case of the AP/HTPB propellant, chemical analysis showed that condensed combustion products mainly consisted of soot and ammonium chloride.

Obtaining the surface temperature of the PSAN1/HTPB mixture is more difficult than that of the PSAN1 alone, but it is possible to affirm that the fuel addition to PSAN1 did not change the surface temperature (Fig. 4). An analysis of the profiles obtained shows that the temperature gradient above the surface grows with pressure (Table 3).

**Table 3 Thermophysical parameters of the combustion of AN-based propellants: the surface temperature ($T_s$), the flame temperature ($T_f$), and the temperature gradient above the surface ($\varphi$)**

| Parameter | Pressure, MPa | | | | | |
|---|---|---|---|---|---|---|
| | 0.1 | 0.5 | 1 | 3 | 10 | 20 |
| | | | | PSANI | | |
| $T_s$, °C | —— | —— | —— | $490 \pm 10$ | $592 \pm 10$ | $628 \pm 10$ |
| $T_f$, °C | —— | —— | —— | $900 \pm 90$ | $885 \pm 30$ | $1000 \pm 100$ |
| $\varphi \cdot 10^{-4}$, K/cm | —— | —— | —— | $\sim$0 | $\sim$0 | $\sim$0 |
| | | | | PSAN1/HTPB | | |
| $T_s$, °C | $325 \pm 5$ | $406 \pm 11$ | $440 \pm 19$ | $480 \pm 25$ | $550 \pm 35$ | $639 \pm 40$ |
| $T_f$, °C | $1156 \pm 50$ | $1100 \pm 20$ | $1125 \pm 17$ | $1190 \pm 10$ | $1230 \pm 15$ | $1185 \pm 10$ |
| $\varphi \cdot 10^{-4}$, K/cm | $1.14 \pm 0.33$ | $2.9 \pm 1.4$ | $3.3 \pm 1.1$ | $6.9 \pm 2.5$ | $7.3 \pm 1.5$ | NA |
| | | | | PSAN1/AP/HTPB | | |
| $T_s$, °C | —— | —— | $430 \pm 5$ | $508 \pm 28$ | $574 \pm 15$ | $563 \pm 22$ |
| $T_f$, °C | —— | —— | $1150 \pm 42$ | $1298 \pm 10$ | $1380 \pm 20$ | $1365 \pm 10$ |
| $\varphi \cdot 10^{-4}$, K/cm | —— | —— | $7.2 \pm 2.4$ | $11.5 \pm 2.3$ | $15.3 \pm 2.5$ | $22.6 \pm 2.0$ |
| | | | | PSAN1/AP/A1/HTPB | | |
| $T_s$, °C | —— | —— | 415 | $500 \pm 30$ | $550 \pm 30$ | —— |
| $T_f$, °C | —— | —— | 2000 | $1950 \pm 50$ | $2170 \pm 70$ | —— |
| $\varphi \cdot 10^{-4}$, K/cm | —— | —— | 22.0 | $28.0 \pm 2.5$ | $24.3 \pm 3.0$ | —— |

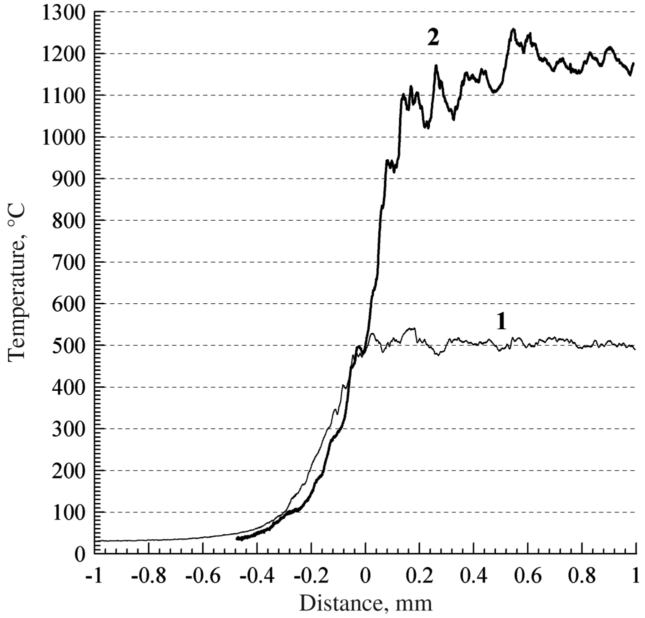

**Fig. 4 Comparison of temperature profiles for the PSAN1 mixture (1) and the PSAN1/HTPB propellant (2) at a pressure of 3 MPa.**

### 3. *Temperature Distributions in the Combustion Wave of Phase-Stabilized Ammonium Nitrate 1 with Binder and Ammonium Perchlorate*

The replacement of part of the AN by AP practically does not modify the situation: experimental combustion temperature exceeds the calculated adiabatic one, and there is a formation of condensed nonequilibrium products. As in the case of the PSAN1/HTPB, the definition of the surface temperature is complicated, but, as clearly pointed out by Fig. 5, breaks in profiles are observed in the same temperature intervals as in the previous cases. The temperature gradient above the surface has appreciably increased in comparison with the PSAN1/HTPB mixture and also grows with pressure (Table 3).

### 4. *Temperature Distributions in the Combustion Wave of Phase-Stabilized Ammonium Nitrate 1 with Binder, Ammonium Perchlorate, and Al*

The addition of aluminum results in a sharp increase in the combustion temperature up to 2000–2170°C (Table 3), which is in a good agreement with the theoretical adiabatic value (2437°C at 10 MPa) if radiation heat losses are taken into account (~2500°C). The temperature gradient in the gas phase grows considerably as well (Table 3). The surface temperature of these compositions, though difficult to determine, can be still considered as governed by the dissociation reaction of ammonium nitrate at the surface (Fig. 5 and Table 3).

## C. Effect of Initial Temperature

The influence of the initial temperature on the combustion was investigated at atmospheric pressure for the PSAN1/AP/Al/HTPB propellant only. The burning-rate data obtained for the temperature range of −25– + 140 °C are presented in Fig. 6.

# IV. Discussion

## A. Mechanism of Thermal Decomposition of Ammonium Nitrate with $K_2Cr_2O_7$

The decomposition kinetics of liquid AN, comprising secondary reactions between AN decomposition products as well as the primary radical-type decomposition of nitric acid, are described by a first-order equation of autocatalysis [26]. It was suggested in [20] that the constant of the initial rate, $k_1$, describes the radical decomposition pathway with activation energy corresponding to the HO–$NO_2$ bond rupture; the constant of the autocatalysis, $k_2$, describes the low-temperature ionic pathway of decomposition. The action of catalysts is connected with the influence of catalysts on these processes primarily by the speed of the secondary autocatalytic reactions. The derivatives of hexavalent chromium are the most effective catalysts.

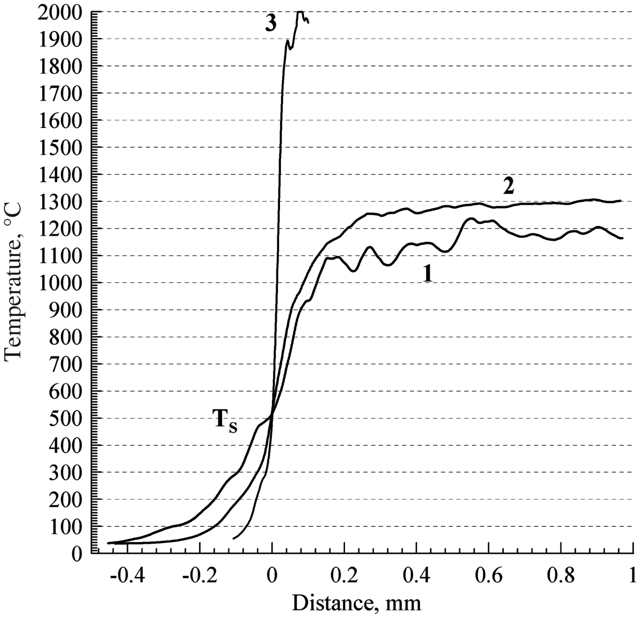

**Fig. 5 Comparison of temperature profiles for the PSAN1/HTPB (1), PSAN1/AP/HTPB (2), and PSAN1/AP/Al/HTPB (3) propellants at a pressure of 3 MPa.**

Shidlovskii [8], studying the combustion of the AN with $K_2Cr_2O_7$ at atmospheric pressure, showed that catalysis proceeds in the melt and, apparently, consists of the following reactions:

$$Cr_2O_7^{2-} + 2NH_4^+ = N_2 + 4H_2O + Cr_2O_3 \qquad (1)$$

$$Cr_2O_3 + 2NO_3^- = 2NO + Cr_2O_7^{2-} \qquad (2)$$

It is quite evident that the reaction written of $Cr_2O_3$ oxidation is not the only one, because, along with nitrate ion, there are oxidizers such as $HNO_3$, $NO_2$, $NO_2^+NO_3^-$, $NO^+NO_3^-$, $N_2O$, and NO in the AN melt. Furthermore, the analysis of the reaction products after combustion shows the absence of nitrogen oxides and the presence of water, nitrogen, oxygen, and nitric acid, with the heat release experimentally measured as 480–500 kcal/mole [8]. Formation of the $Cr_2O_7^{2-}$ ion from $Cr_2O_3$ was proved experimentally by the fusing of the $Cr_2O_3$ green modification with the AN. Besides, 60–70% of the initial hexavalent chromium was revealed in the solid slag after combustion.

Thus, it is possible to consider that the brown color of the AN melt with the additive of the chromium catalyst is caused by the presence of green trivalent chromium and yellow hexavalent chromium. Because AN contains an excess of oxidizing elements, chromium completely passes in the initial hexavalent state at the end of burning.

It is obvious that the rate of reactions (1) and (2) considerably exceeds the rate of decomposition of neat AN. According to [26], the increase in the initial decomposition speed of the AN is proportional to the concentration of metal ions: $d\eta/dt = k_{add}C_{add} + k_1$. At a concentration of 4% $K_2Cr_2O_7$, the rate of AN decomposition at 180°C through the reactions (1) and (2) and comparable ones is 2000 times more than the initial rate of decomposition [26]. Basically, the kinetic parameters of AN decomposition are defined by reactions (1) and (2). It is important to note that, in contrast to other metals of variable valency, chromium additives to AN increase not only the initial rate of decomposition, but also the rate of autocatalysis.

## B. Surface Temperature of Ammonium-Nitrate-Based Compositions

Evaporation of ammonium nitrate as other onium salts proceeds as result of the dissociation reaction of a salt, that is, the splitting of the

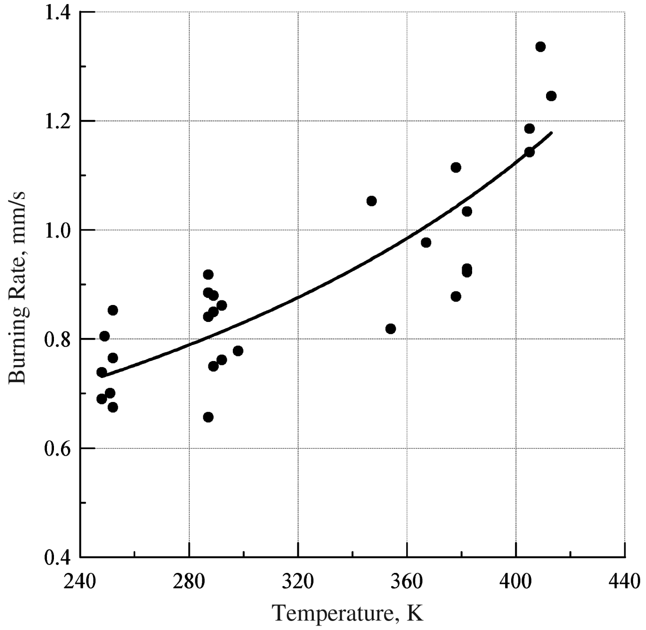

**Fig. 6 Effect of initial temperature, $T_0$, on the burning rate of the PSAN1/AP/Al/HTPB propellant at atmospheric pressure.**

donor–acceptor bonds between the base and acid followed by volatilization into the gas phase. The dissociation process is similar to the boiling of molecular substances, that is, from the standpoint of the thermodynamics, the phase transition is of the first kind, with an abrupt enthalpy change.

The dissociation is characterized by the enthalpy of dissociation, which, in a sense, is equal to the enthalpy of evaporation for molecular substances.

The vapor pressure above the liquid AN is given in [27,28]. The experimental points and the fitting equations reported in these works agree very well. The enthalpies of dissociation given in [27] (166.9 kJ/mole or 39.9 kcal/mole) and [28] (166.5 kJ/mole or 39.8 kcal/mole) are in good agreement with a value calculated from the standard enthalpies of formation of the components (163.2 kJ/mole or 39.0 kcal/mole).

The surface temperatures measured for the PSAN1 are shown in Fig. 7; the vapor pressure above the AN liquid phase given in [27,28] is presented. As can be seen in Fig. 7, the surface temperatures obtained for the PSAN1 fall on the straight line of vapor pressure above liquid AN [28]: $\ell n\ p = \frac{-9960.85}{T} + 16.22$. As with other onium salts, experimental AN surface temperatures increase with pressure. The surface temperature at 30 MPa is an exception; it appears to be close to the surface temperature at 20 MPa. It was suggested in [20] that, at about 20 MPa, the AN dissociation temperature attained its critical value and did not grow greater. Indeed, at 20 MPa, the experimental surface temperature is 630 ± 10 °C. An estimation of the critical temperature, $T_{\mathrm{cr}}$, using Guldberg's equation [29], $T_{\mathrm{cr}} = \frac{3T_b}{2}$, gives a very close value, 616–630°C.

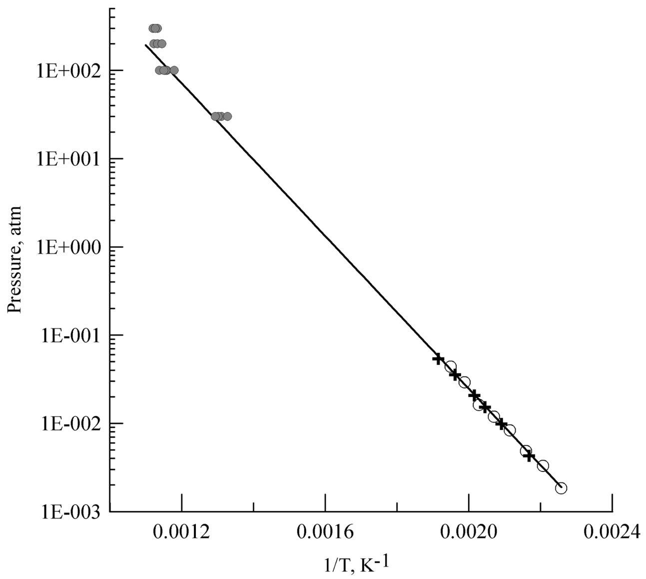

**Fig. 7 Relationship between the vapor pressure and dissociation temperature of ammonium nitrate. The vapor pressure of the AN is represented by crosses [27] and empty circles [28], whereas the surface temperatures of PSAN1 are represented by filled circles.**

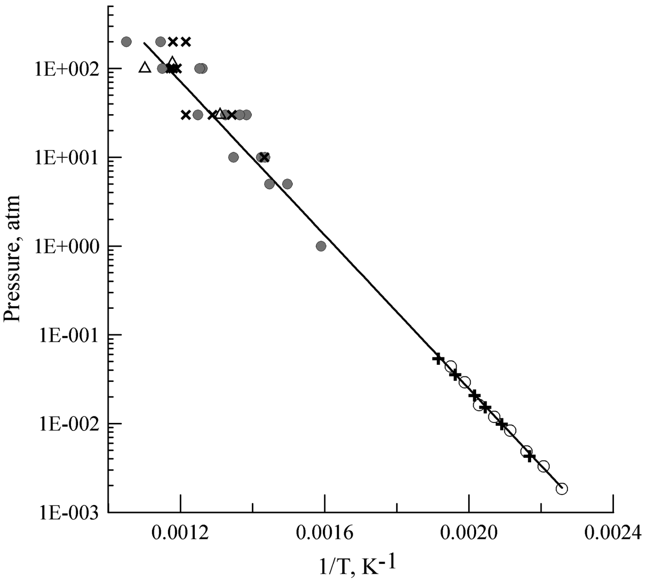

**Fig. 8 Relationship between the vapor pressure and dissociation temperature of ammonium nitrate. The vapor pressure of the AN is represented by crosses [27] and empty circles [28], whereas the surface temperatures of the PSAN1/HTPB, PSAN1/AP/HTPB, and PSAN1/AP/Al/HTPB propellants are represented by filled circles, crosses, and triangles, respectively.**

As mentioned, finding the surface temperatures for AN-based propellants is more difficult than for pure AN, and that results in a scatter of the data. All the surface temperatures measured for the AN-based propellants studied in this work are shown in Fig. 8; the vapor pressure above the AN liquid phase is presented. The data obtained allow consideration of the surface temperature in the burning of AN-based systems as well as for AN as determined by the reaction of the AN dissociation.

## C. Combustion Mechanism of Ammonium-Nitrate-Based Compositions

### *1. Condensed-Phase Model of Combustion*

Negligible values of heat flux from the gas to the condensed phase during the combustion allow the consideration of the condensed-phase chemistry as the determinant of the combustion rate of a substance. In this model, according to the Zeldovich expression [30], the mass-burning rate ($m$) is defined by the kinetics of the leading reaction in the condensed phase ($A \cdot e^{-E/RT_s}$) at the surface temperature ($T_s$):

$$m = \sqrt{\frac{2\rho\lambda Q}{c_p^2(T_s - T_0 + L_m/c_p)^2}\left(\frac{RT_s^2}{E}\right) \cdot A \cdot e^{-E/RT_s}} \qquad (3)$$

The formula also contains the average specific heat, $c_p$; the density of strand, $\rho$; and the thermal conductivity of the condensed phase, $\lambda$. The expression in brackets in the denominator represents the heat needed for heating the substance to the surface temperature with regard to the phase transitions, for example, the heat of melting, $L_m$. This necessary heat, $Q_{\mathrm{need}}$, is generally not equal to the heat of the reaction, $Q$.

Some possible cases of combustion with the dominant reaction in the condensed phase may be considered:

1) When the heat feedback from the gas phase is absent ($Q_g \sim 0$), there is a partial evaporation of the substance at the expense of the heat released in the condensed phase (overheating). But the main part of the unreacted substance is removed from the condensed phase by means of dispersion. The heat effect in the condensed phase is accepted as follows:

$$Q_s \sim \eta Q \sim c_p(T_s - T_0) + L_m \tag{4}$$

where $\eta$ is the fraction of the substance reacting in the condensed phase.

2) If $Q_g$ is less than or comparable to the heat necessary for the evaporation of the unreacted-in-the-condensed-phase substance, $(1 - \eta)Q_{\mathrm{ev}}$, evaporation proceeds at the expense of this heat; the rest of substance is moved away from the condensed phase by dispersion. The heat effect of the condensed phase is still defined by expression (4), and the reactions in the gas phase do not influence the burning rate, which is determined by expression (3). The evaporation of aerosol takes place above the surface and undoubtedly influences the shape of the temperature profiles. Theoretically, the temperature gradient gets smaller when approaching the burning surface from the gas phase, becoming negligible at the surface. However, accurate measurements of the temperature gradient immediately above the surface are hardly feasible for such propellants because of a very narrow aerosol zone. In most publications, including this work, the authors operate on temperature gradients in the gas phase measured at 20–100 $\mu$m off the surface.

3) A contribution of the gas phase to the combustion of systems with the dominant role of condensed-phase chemistry can be imagined as follows. In this case $Q_g > (1 - \eta)Q_{\mathrm{ev}}$ and the heat feedback from the gas is spent not only for evaporation, but also for heating the condensed phase, thus influencing the burning rate. As the difference $Q'_g = Q_g - (1 - \eta)Q_{\mathrm{ev}}$ grows, the fraction of the substance reacting in the condensed phase decreases. Eventually, the leading role passes to the gas phase. The heat effect of the condensed phase can be written as

$$Q_s \sim \eta Q \sim c_p(T_s - T_0) + L_m - Q'_g \tag{5}$$

The burning rate is determined by the modified expression (6), in which the heat necessary for heating is reduced by $Q'_g$:

$$m = \sqrt{\frac{2\rho\lambda Q}{c_p^2(T_s - T_0 + L_m/c_p - Q'_g/c_p)^2}\left(\frac{RT_s^2}{E}\right) \cdot A \cdot e^{-E/RT_s}} \tag{6}$$

The occurrence of a high-temperature flame brings about the radiation heat flux to the condensed phase. In this case, the heat, incoming at the expense of radiation, $Q_r$, should be included in $Q'_g$.

### 2. *Combustion of Phase-Stabilized Ammonium Nitrate 1 with Catalyst*

As shown in [20], the combustion of AN with a KCl additive obeys the condensed-phase mechanism with the leading reaction in the condensed phase without any heat flow from the gas phase. A mixture of AN with $K_2Cr_2O_7$ (PSAN1), investigated in this work, burns in a similar manner. The surface temperature of PSAN1 is determined by the reaction of the AN dissociation (Figs. 3 and 7).

According to the condensed-phase model, no less than $\eta = 100 \cdot (Q_{\mathrm{need}}/Q)\%$ of the substance is decomposed in the condensed phase during combustion. According to [8], the heat effect of the decomposition of the AN + 10%$K_2Cr_2O_7$ mixture amounts to about 480–528 cal/g. It is possible to consider, based on these data, that the heat effect of PSAN1 decomposition makes ~330 cal/g (if the $H_20$ is gas). Taking into account the experimental surface temperature, 71–100% of the AN may be considered as decomposed in the melt for the pressure interval of 1–30 MPa. The heat released during the decomposition of this part of the AN is enough for heating the mixture to the surface temperature, followed by the evaporation of an insignificant part of the AN. The remaining part of the AN is dispersed from the surface as small drops in which the decomposition/evaporation continues.

### 3. *Combustion of Phase-Stabilized Ammonium Nitrate 1 with Binder*

Adding fuel to PSAN1 results in the occurrence of the gas flame and temperature gradient above the surface (Table 3). The maximum flame temperature of the PSAN1/HTPB mixture has been measured to be about 1230°C; that allows estimating the heat effect of combustion as 605 cal/g, given an average specific heat of 0.5 cal/gK. However, $N_2O$ and NO formed in the AN decomposition mostly do not react in the condensed phase, thus reducing the heat effect in the condensed phase. The amount of these gases is unknown, but a value of about 530 cal/g was accepted, because PSAN1 exhibits an experimental decomposition heat of 480 cal/g and a calculated combustion temperature of only 100° less than that of the PSAN1/HTPB mixture. Using experimental data on the surface temperature and taking into account that the binder requires about 535 cal/g for pyrolysis, the $Q_{\mathrm{need}}$ and degree of AN decomposition in the melt have been calculated. In the interval of 0.1–10 MPa, the amount of AN decomposed at the surface changes from 42 to 58%. For the evaporation of the remaining AN, the heat from 178 to 98 cal/g is required, which is very close to the heat feedback from the gas phase as calculated from thermocouple measurements (Table 4, Fig. 9). Thus, the combustion of the PSAN/HTPB mixtures can be described by a usual condensed-phase model of combustion, with the heat flux from the gas phase being spent only for evaporation from the surface without influence on the burning rate (case 2).

An increase in the burning rate after an addition of fuel to PSAN1 is believed to take place at the expense of both changing the kinetics of decomposition in the melt and increasing heat effect. Using the condensed-phase combustion model, it is possible to derive the kinetic parameters of heat release in the melt, given the burning rates and surface temperatures. The obtained rate constant of heat release, $k = 3 \cdot 10^8 \cdot \exp(-11970/T_s)$, has an extraordinary low dependence on the temperature ($E = 24$ kcal/mol) (Fig. 10), which is characteristic of extremely unstable substances. It is necessary to note, however, that these constants describe the PSAN1/HTPB decomposition in the liquid phase. Obviously, in the solid phase, the PSAN1/HTPB mixture possesses a more acceptable thermal stability. Quite a high ignition temperature (230°C) supports this statement. Using the obtained kinetics, a fraction of the AN decomposed in the condensed phase can be calculated using the following formula:

$$\eta = \frac{2\lambda\rho RT_s^2 A e^{-E/RT_s}}{c_p m^2 E(T_s - T_0 + L_m/c_p)} \tag{7}$$

The results are close to the fraction of AN, whose decomposition can provide the heat necessary for heating the mixture to the surface temperature.

### 4. *Combustion of Propellant Phase-Stabilized Ammonium Nitrate 1/Ammonium Perchlorate with Binder*

A partial substitution of AN with AP results in increasing both burning rates (Fig. 2) and the temperature gradient above the surface (Table 3). Because the oxygen balance of the mixture remains practically the same, a small increase in the combustion temperature (see Table 3) is caused by an improved enthalpy of formation of AP as compared with AN. As stated, the surface temperature of the burning mixture is determined by the AN dissociation temperature. It follows from the kinetic data on low- and high-temperature stages of AP decomposition [26] that, at these temperatures, solid AP does not have time to decompose at the burning surface (Fig. 10). When liquid, AP can decompose faster than in the solid state [31]; however, it is still 1 order of magnitude slower than AN (Fig. 10). AP particles appear to be ejected from the surface and to evaporate/decompose in the high-temperature gas phase. However, molten PSAN1 contains $K_2Cr_2O_7$, which should be considered as a possible catalytic reagent in reactions with both solid AP particles at the surface and AP

**Table 4 Terms of the heat balance at the burning surface of AN-based propellants: the heat feedback from the gas phase ($Q_g$), the heat needed for the evaporation of the undecomposed substance ($Q_{ev}$), the heat needed for heating the substance to the surface temperature with regard to phase transitions ($Q_{need}$), and the AN decomposition depth in propellant ($\eta$ AN)**

| Parameter | Pressure, Mpa | | | | | |
|---|---|---|---|---|---|---|
| | 0.1 | 0.5 | 1 | 3 | 10 | 20 |
| | | | PSAN1/HTPB | | | |
| $\varphi \cdot 10^{-4}$, K/cm | 1.14 ± 0.33 | 2.9 ± 1.4 | 3.3 ± 1.1 | 6.9 ± 2.5 | 7.3 ± 1.5 | —— |
| $Q_g$, cal/g | 140 ± 40 | 167 ± 81 | 126 ± 42 | 149 ± 50 | 74 ± 15 | —— |
| $Q_{ev}$, cal/g | 178 | 156 | 145 | 125 | 98 | —— |
| $Q_{need}$, cal/g | 288 | 318 | 333 | 361 | 397 | —— |
| $\eta$ AN, % | 42 | 47 | 49 | 53 | 58 | —— |
| | | | PSAN1/AP/HTPB | | | |
| $\varphi \cdot 10^{-4}$, K/cm | —— | —— | 7.2 ± 2.4 | 11.5 ± 2.3 | 15.3 ± 2.5 | 22.6 ± 2.0 |
| $Q_g$, cal/g | —— | —— | 171 ± 57 | 143 ± 29 | 94 ± 15 | 93 ± 8 |
| $Q_{ev}$, cal/g | —— | —— | 92 | 73 | 43 | 35 |
| $Q_{need}$, cal/g | —— | —— | 315 | 340 | 373 | 396 |
| $\eta$ AN, % | —— | —— | 26 | 30 | 36 | 39 |
| | | | PSAN1/AP/A1/HTPB | | | |
| $\varphi \cdot 10^{-4}$, K/cm | —— | —— | 22.0 | 28.0 ± 2.5 | 24.3 ± 3.0 | —— |
| $Q_g$, cal/g | —— | —— | 290 | 232 ± 30 | 162 ± 20 | —— |
| $Q_{ev}$, cal/g | —— | —— | 137 | 121 | 98 | —— |
| $Q_{need}$, cal/g | —— | —— | 266 | 290 | 321 | —— |
| $\eta$ AN, % | —— | —— | 13 | 16 | 20 | —— |

solution in the melt. These reactions would increase the heat effect in the condensed phase. The fraction of AP involved in the reactions with $K_2Cr_2O_7$ is unknown; however, it may be considered as moderate. Because the perchlorates are known to be stronger oxidizers than the nitrates, one may expect a slight increase in the rate of heat release in the condensed phase.

Figure 11 compares the heat feedback from the gas obtained from temperature profiles and the heat needed for the evaporation of the remaining AN, undecomposed at the surface of the PSAN1/AP/HTPB mixture. It is evident that the heat feedback from the gas phase exceeds the heat required for AN evaporation. In Fig. 11, the lines represent the heat feedback calculated by a modified Eq. (6), which considers the heat required for the evaporation of undecomposed AN in the condensed phase. Neither the assumption of only AN decomposition in the melt (310 cal/g) nor the decomposition of both the AN and AP oxidizers (595–605 cal/g) via AN kinetics can be seen to fit the experimental data by the value or pattern. A good agreement can be found if one assumes the decomposition of AN and partial decomposition of AP (400 cal/g) via modified kinetics. To match the experimental and calculated results, the heat release in the condensed phase should only be increased 2–3 times ($k = 2.5 \cdot 10^9 \cdot \exp(-13090/T_s)$) (Fig. 10). Based on this heat effect and the experimental surface temperatures, and considering heat feedback from the gas, one can calculate the degree to which AN decomposes in the melt as 26–39% in the 1–20 MPa pressure interval (Table 4). A calculation by Eq. (7) gives a part of the AN decomposed in the condensed phase, which is close to that needed for heating the propellant to the surface temperature.

To evaporate the rest of the AN in this pressure interval, 92–35 cal/g of heat is needed, which is less than the heat feedback from the gas. Thus, the combustion of the PSAN/AP/HTPB mixtures

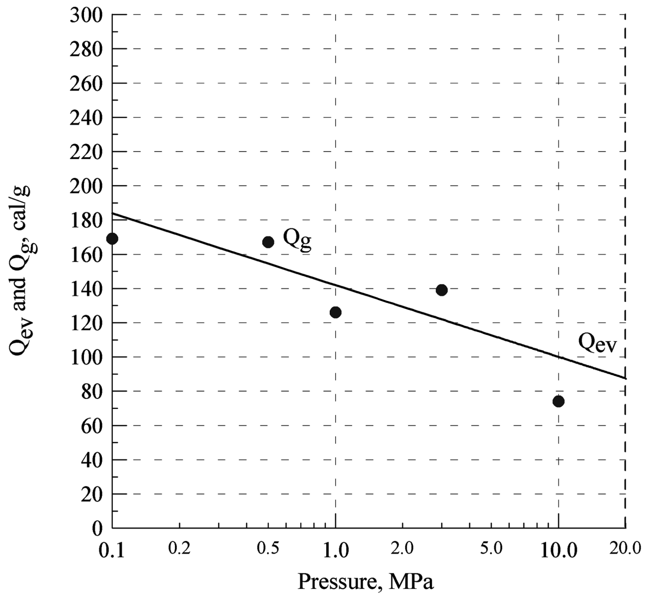

**Fig. 9 Pressure dependence of the heat feedback from the gas ($Q_g$, points) and heat needed for the evaporation of unreacted AN from the burning surface of PSAN1/HTPB ($Q_{ev}$, line).**

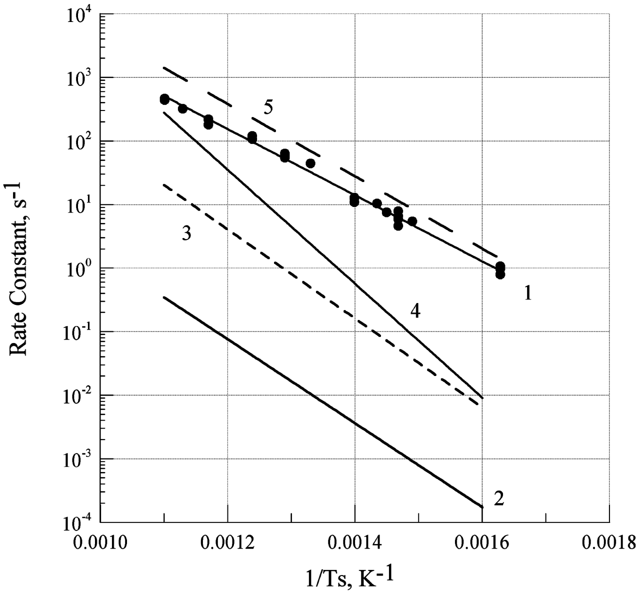

**Fig. 10 A comparison of the heat-release rate constants of PSAN1/HTPB (1) with the rate constants of the AP high-temperature stage decomposition (2), the AP low-temperature stage decomposition (3), and the decomposition of AP in the liquid phase (4). Line (5) represents the decomposition kinetics of PSAN1 promoted by the partial decomposition of AP, calculated from the model with the experimental heat flux from the gas phase taken into account.**

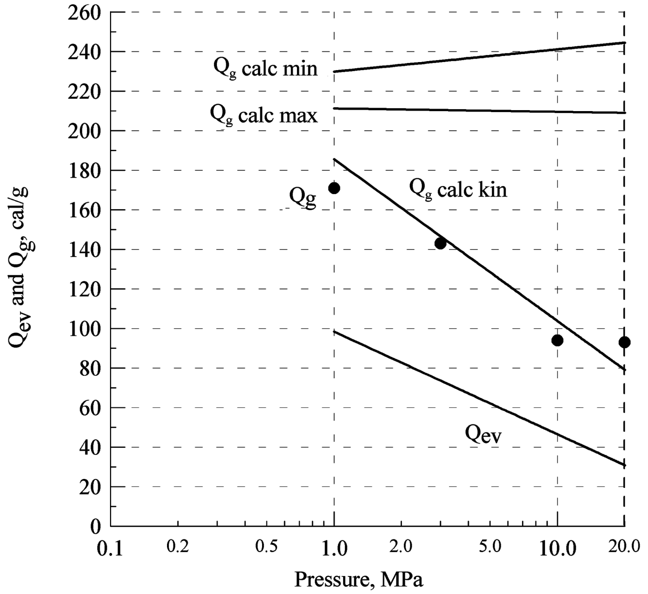

**Fig. 11 Pressure dependence of the heat feedback from the gas ($Q_g$, points) and heat needed for the evaporation of unreacted AN from the burning surface of PSAN1/AP/HTPB ($Q_{\mathrm{ev}}$, line). Lines represent heat feedback calculations made under the assumption of AN decomposition only ($Q_{\mathrm{calc\ min}}$), AN and AP decomposition via the kinetics of AN ($Q_{\mathrm{calc\ max}}$), and partial AP decomposition via modified kinetics ($Q_{\mathrm{calc\ kin}}$).**

can be described by a condensed-phase model, the heat feedback from the gas being used for not only evaporation but also the burning-rate increase (case 3).

### *5. Combustion of Propellant Phase-Stabilized Ammonium Nitrate 1/ Ammonium Perchlorate with Binder and Al*

A partial substitution of the binder with Al results in a further increase in the burning rate and temperature gradient above the surface (Table 3). Because the oxygen balance remains almost the same, a noticeable increase in the flame temperature is caused by the calorific value of Al, which is higher than that of hydrocarbon fuel. As mentioned, the surface temperature of the propellant composition is controlled by the AN dissociation reaction. This temperature turns out to be lower than the melting point of Al, suggesting only heterogeneous oxidation of the metal at the burning surface. The Al powder (ASD-4 type) was shown by differential scanning calorimetry studies to undergo an intensive oxidation in air only at temperatures above 790°C; at temperatures below 630°C (the maximum AN surface temperature), the degree of oxidation was less than 6%.

Knowing the heat effect of Al oxidation is 3928 cal/g, one can estimate the heat contribution of the Al oxidation reaction in the molten layer to be less than 40 cal/g. The total oxidizer content in the PSAN1/AP/Al/HTPB composition is less than in the previous one (68 and 77%, respectively), which results in a corresponding decrease in the heat effect of the oxidizer decomposition to a value of $\sim$400 cal/g $(0.68/0.77) = 350$ cal/g. Therefore, the total exothermic heat effect in the molten surface layer is practically the same for both compositions, equal to $\sim$400 cal/g. The main heat from the oxidation of Al is produced, according to [32], above the surface in the carcass that is formed in pyrolysis of the binder.

The temperature gradient above the surface increases significantly by adding Al to the composition, approaching the maximum value that can be recorded by the used thermocouples. Furthermore, it is difficult to consider the effects of metal and metal oxide on the thermal conductivity of the mixture. The experimental data on $Q_g$ of PSAN1/AP/Al/HTPB in Table 4, therefore, should only be considered as an estimate. As seen from Table 4, $Q_g$ approaches the heat required for heating the condensed phase and evaporation.

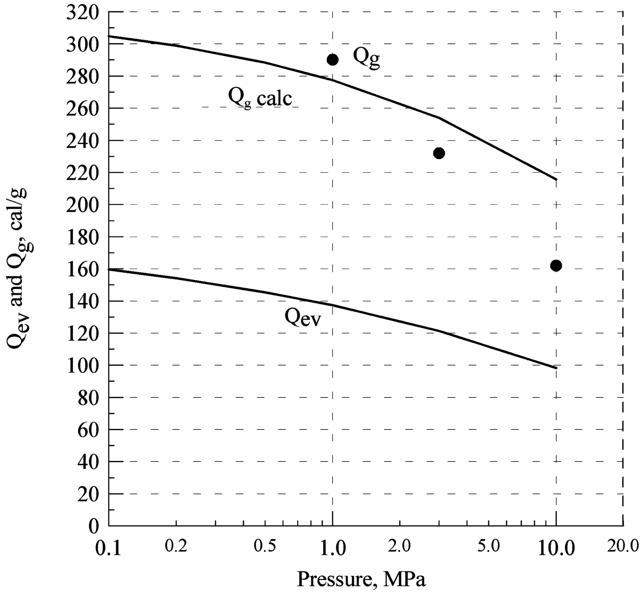

**Fig. 12 Pressure dependence of the heat feedback from the gas ($Q_g$, points) and heat needed for the evaporation of unreacted AN from the burning surface of PSAN1/AP/Al/HTPB ($Q_{\mathrm{ev}}$, line). Line $Q_{g\,\mathrm{calc}}$ represents the calculated heat feedback from the gas.**

Because of the high burning temperature, some radiant heat flux to the condensed phase should also be expected. However, a possible assumption of the leading role of the gas phase in the burning of this composition contradicts the experimentally observed effect of the catalyst content on the burning rate.

$Q_{g\,\mathrm{calc}}$ values calculated from the modified model (6) assuming AN decomposition in the melt and a heat effect of 400 cal/g, are comparable with the experimental ones (Fig. 12). The combustion of this composition, therefore, can be described by the condensed-phase model with a big contribution of heat feedback from the gas that is consumed not only to assist evaporation, but also to increase the burning rate (case 3). This speculation needs additional evidence because heat generated in the condensed phase and heat feedback from the gas are comparable for the PSAN1/AP/Al/HTPB composition at 1 MPa, for example (Fig. 13).

A confirmation of the proposed mechanism is the character of the temperature dependence of the burning-rate temperature sensitivity,

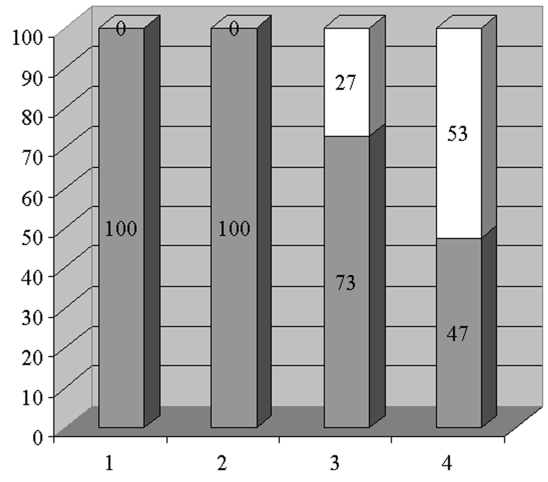

**Fig. 13 Comparison of heats required for heating the condensed phase to the surface temperature for the studied compositions PSAN1 (1), PSAN1/HTPB (2), PSAN1/AP/HTPB (3), and PSAN1/AP/Al/HTPB (4) at 1 MPa; the heat generated in the condensed phase is represented by the dark areas and the heat feedback from the gas is represented by the light areas.**

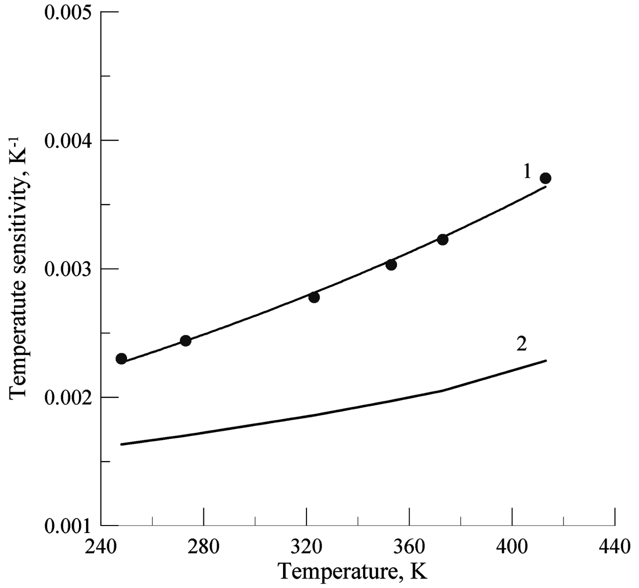

**Fig. 14 Effect of the initial temperature on the temperature sensitivity of the burning rate for PSAN1/AP/HTPB/Al at atmospheric pressure: experiment (1), calculation without the heat feedback from the gas taken into account (2).**

which is theoretically different for the gas-phase and condensed-phase combustion models.

### D. Effect of Initial Temperature

According to the condensed-phase combustion model, the burning-rate temperature sensitivity $\sigma_p = \frac{d \ell n\, m}{dT_o}$ depends only on the surface temperature (i.e., the AN dissociation temperature) and grows with pressure:

$$\sigma_p = 1/(T_s - T_o + L_m/c_p) \tag{8}$$

To take into account the melting of the condensed phase, $L_m/c_p$ is added to the expression, where $c_p$ is the average specific heat of the condensed phase and $L_m$ is the heat of melting.

In contrast to the condensed-phase model, a gas-phase concept offers the burning-rate temperature sensitivity as $\sigma_p = E/2RT_f^2$, that is, decreasing with the initial (or flame) temperature. The dependence of $\sigma_p$ of PSAN1/AP/Al/HTPB composition on the initial temperature at atmospheric pressure is shown in Fig. 14. The dependence demonstrates a behavior typical of the condensed-phase model; the experimental points lie well above the theoretical line calculated by Eq. (8) without taking the heat feedback into consideration. The heat feedback from the gas is likely to exert an effect on the burning rate similar to increasing the initial temperature. Therefore, at equal initial temperatures, $\sigma_p$ derived from the modified model turns to be higher than $\sigma_p$ calculated without considering the heat feedback from the gas.

## V. Conclusions

The combustion study of AN-based propellant compositions has shown that successive additions of AP and Al to the catalyzed AN/binder binary mixture results in a regular increase in the burning rate (from 3 to 5 and 8 mm/s at 10 MPa, respectively), accompanied by a small decrease in the pressure exponent (from 0.6 to 0.5). Adding HTPB, then AP, and, finally, Al results in the appearance of a bright flame above the surface, with the temperature gradient regularly increased in changing from the binary mixture to the multi-component compositions. The burning rate of the final AN/AP/HTPN/Al composition, having a high flame temperature, is practically as sensitive to the content variation of the AN decomposition catalyst as the simple binary AN/HTPB composition.

It has been determined on the basis of flame-structure investigation by fine tungsten-rhenium thermocouples that the surface temperature of the catalyzed AN as well as the AN-based propellants is controlled by the dissociation reaction of the AN occurring at the surface. At pressures higher than 20 MPa, the growth of temperature with pressure is no longer observed, which may be evidence of the surface temperature reaching its critical value.

The weak influence of the AP and Al addition on the pressure exponent as well as very similar effects of the catalyst content variation on the burning rate of both the high-temperature AN/AP/HTPN/Al propellant and the low-temperature AN/HTPB mixture suggests the same combustion mechanism for all the compositions. This mechanism is based on the leading role of heat release in the condensed phase at the expense of the decomposition of AN. Thermally more stable and less volatile AP, as well as Al, reacts mainly in the aerosol zone above the burning surface. The heat flux from the gas phase can be used for the evaporation of undecomposed AN (as in the case of the AN/HTPB mixtures); then the effect of the gas phase on the burning rate is fully absent. If the heat flux from the gas phase exceeds the heat required for evaporation (as in the case of compositions with AP and Al), the gas phase begins to influence the burning rate significantly. However, the process, as before, is described by a condensed-phase model that takes into account the heat feedback from the gas.

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