Combustion Mechanism of AN-based Propellants

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Abstract

This paper discusses results obtained in studying a row of progressively complicated AN-based systems: AN/catalyst, AN/catalyst/binder, AN/catalyst/binder/AP, and AN/catalyst/binder/AP/Al. Successive addition of AP and Al to the binary mixture of catalyzed AN/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 AN as well as AN-based propellants is controlled by the dissociation reaction of the salt occurring at the surface. Analysis of obtained results allows suggesting a combustion mechanism of AN-based propellants which is based on the leading role of heat release in the condensed phase.

1. 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,[1,2,3] since 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 present time the first two problems have been overcome by using different additives.[3] Increasing the burning rate of the propellants can be achieved either by 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 deterioration of "clean-burning" characteristics of the propellant, which may be considered as a necessary toll to reach the wanted burning velocity and completeness.

Notwithstanding the long history of AN combustion studies since the fifties,[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 combustion of AN-based compositions proceeded mostly in the condensed phase up to pressures of the order of hundreds of atmospheres.

In contrast to that in work,[17] a model for ammonium nitrate composite propellant combustion was developed based on 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/HTPB propellant contained coarse (600 μm) AN prills showed[18] the apparent absence of a distinct monopropellant flame. Based on thermocouple measurements authors of work[18] made the conclusion that the combustion of AN/HTPB propellant was driven by an exothermic, partially premixed gas flame. However, they as well as authors of work[19] suggested that surface temperature remained constant and equal to 300°C over a wide pressure range. The combustion mechanism of AN with the additives of various nature is considered in work.[20] It was shown that this was not the case, 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 300°C at as early as 0.1 MPa that cast some doubt 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.

2. Experimental

Ingredients and sample preparation. Phase-stabilized AN (PSAN), containing additives of $Mg(NO_3)_2$ and $K_2Cr_2O_7$, was used in the burn rate experiments. According to work[21] this PSAN has no modification transition in the temperature range of -50÷90°C. For stabilization 1% $Mg(NO_3)_2$ was added. Before preparing the samples, the mixture of AN/$Mg(NO_3)_2$ has been thoroughly comminuted to obtain grain sizes of the order of 10-40 µm.

Potassium dichromate ($K_2Cr_2O_7$, red-orange regular shaped crystals) has been added mechanically after its crushing in a ceramic mortar. Microscope analysis of these particles revealed a non-uniform distribution of the sizes from 30 µm to 150 µm. 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). Ammonium perchlorate (AP) of commercial type with about 8 µm particle size and aluminum, named ACD-4, in the form of fine monomodal 6-8 µm powder were used. Instead of binder an oligomer of hydroxy-terminated polybutadiene named SKDN was used.

Cylindrical specimens, 7 mm in diameter and 10-15 mm long, with density of 1.68 g/cm^3, were obtained by compression of PSAN1 and PSAN2 in transparent acrylic tubes. Non-cured 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 close oxidizer/fuel ratio of about 0.45-0.46.

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

Burn Rate Measurements. Burn 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.

Temperature Measurements. Temperature profiles in the combustion wave were measured using Π-shaped thermocouples. The thermocouples were welded from 25 or 50 µm diameter tungsten—5% rhenium and tungsten—20% rhenium wires and rolled in bands to obtain 7 or 20 µm bead size.

3. Results

3.1 Combustion behavior

Combustion of PSAN with catalyst. As well known,[4,5] neat ammonium nitrate did not burn in 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 catalyst of

AN combustion.[4-10] Combustion of mechanical mixture of PSAN with 4% $K_2Cr_2O_7$ (PSAN1) proceeds in practically flameless regime with formation of a copious white smoke. Combustion front is substantially non-planar and measured burning rates have a large scatter (Figure 1). So it is necessary to consider the burning rate law of this mixture given in Figure 1 and Table 2 as estimated one.

Combustion of mixtures of PSAN with catalyst and binder. Addition of liquid oligomer of HTPB to the PSAN1 results in a propellant which burns with quite regular burning surface and is able to burn at atmospheric pressure. Combustion of PSAN1/HTPB is accompanied by formation a white dense smoke and after combustion a big amount of condensed products has been collected (10-15% of the initial weight).

The mixture PSAN1/HTPB burns ~1.5 times faster than catalyzed PSAN1 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 cured propellant PSAN/HTPB (80/20),[22] containing 5% catalyst (2% of ammonium dichromate and 3% of potassium dichromate) (Figure 2). Reduction of the amount of catalyst up to 2% (mixture PSAN2/HTPB) results in small increase of the burning law exponent and reduction of burning rate in 1.2 times (Figure 2), though 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. AN/HTPB (78.6/21.4) propellant studied in work[18] contains 3.6% of ammonium dichromate and its composition is close to PSAN1/HTPB and PSAN2/HTPB propellants. But 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 close pressure exponent (0.59) (Figure 2). The authors[18] remark that composition of propellant includes 67.8 % coarse (600 μm) AN prills, implying that flame temperature varies with space and time in the range 1000 to 1600°C. Thus, 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 is however revealed for very large degree of heterogeneity of propellants.

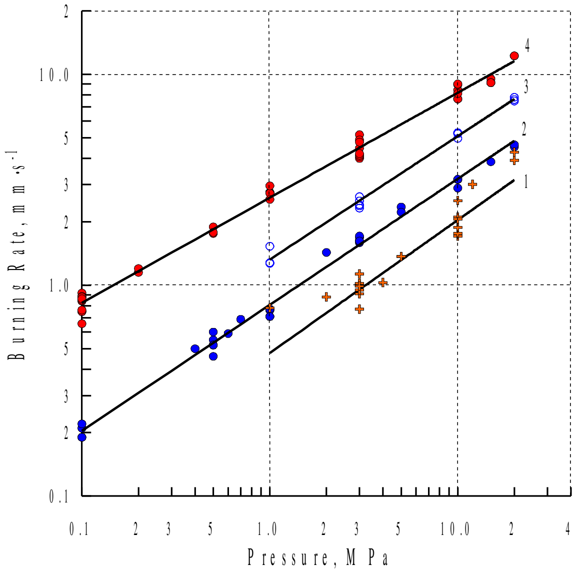

Figure 1: Pressure dependence of the burning rate for PSAN with addition of 4% $K_2Cr_2O_7$ (1), PSAN1/HTPB (2), PSAN1/AP/HTPB (3) and PSAN1/AP/Al/HTPB (4).

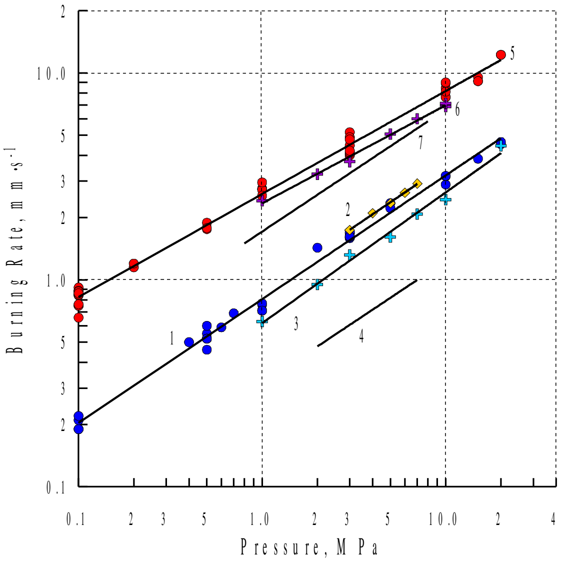

Figure 2: Pressure dependence of the burning rate for PSAN1/HTPB (1), data of work[22] (2), PSAN2/HTPB (3), data of work[18] (4), PSAN1/AP/Al/HTPB (5), PSAN2/AP/Al/HTPB (6) and data of work[11] (7).

Combustion of mixture of PSAN with catalyst, binder and AP. The replacement of part of PSAN1 with fine AP results in a further increase of the burning rate of the composition (Table 2), at the same time the pressure exponent in the burning rate law varies very weakly. Since the compositions have close oxidizer/fuel ratio, the adiabatic flame temperature changes insignificantly. Strange enough, but introducing a more reactive oxidizer results in increasing the PDL to 1 MPa. Also, in this case condensed products have been found in percentages from 10% to 15%.

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, ºC**
PSAN1	1-20	0.477	0.63	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

Combustion of mixtures of PSAN with catalysts, binder, AP and Al. The introduction of fine aluminum in dual-oxidizer propellant PSAN1/AP/HTPB results in a further increase in the burning rate up to 8.2 mm/sec at 10 MPa, at the same time combustion temperature grows very considerably (Table 2). The Al addition reduces the pressure exponent in the burning rate law from 0.6 to 0.5. Literature data[11] on combustion of a cured PSAN1/AP/Al/HTPB propellant with the same composition are presented in Figure 2 also. The differences in the slope and in the values of burning rate are probably due to the generally larger particles of Al (50 µm) and AP (bimodal 140-160 µm/70-80 µm) used in the last case.

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

3.2. Temperature measurements

Temperature distributions in the combustion wave of PSAN with catalyst. As mentioned above in work[19] based on thermocouple studies it was proposed 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). In work[20] combustion of AN with additives of KCl and charcoal have been studied and it was shown 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. In the present work, temperature profiles in the combustion wave of PSAN1 mixture contained 4% of $K_2Cr_2O_7$ were measured with the help of thin thermocouples.

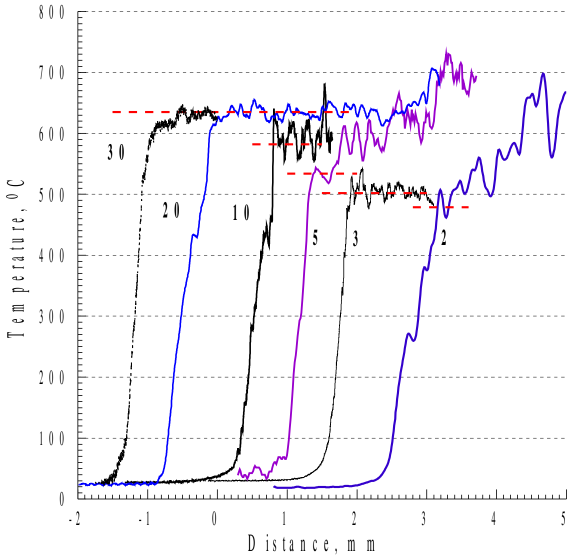

Figure 3: Typical temperature profiles for PSAN1 at pressures 3, 10, 20, 30 MPa and AN mixtures with 5% KCl at pressure of 2 and 5 MPa. Dotted lines are the

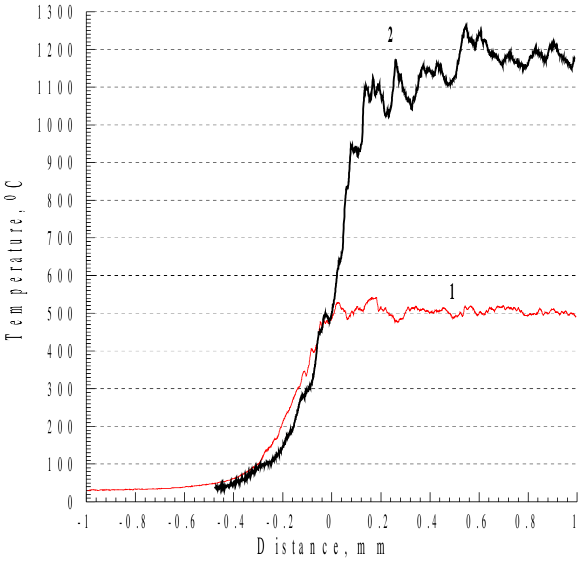

Figure 4: Comparison of temperature profiles for PSAN1 mixture (1) and PSAN1/HTPB propellant (2)

dissociation temperatures of AN at corresponding pressures.

at pressure of 3 MPa.

Typical temperature profiles of PSAN1 combustion at 3, 10, 20 and 30 MPa are shown in Figure 3. Typical temperature profiles at 2 and 5 MPa obtained in[20] for the combustion of AN with 5% KCl are also presented. As seen from Figure 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 in that the profiles of PSAN1 have an extended portions above the surface with a constant temperature, the growth of temperature up to 700-1000°C begins after these portions, while on profiles of AN doped with KCl, a weak temperature gradient is observedin the gas phase above the AN surface, though the maximum temperature (~1000° C) is also achieved at a significant distance (3-4 mm) above the burning surface.

In Figure 3, the dotted lines indicate the AN dissociation temperatures at pressures of 2, 3, 5, 10, and 20 MPa. Despite temperature fluctuations, it is well visible that in the pressure interval 2 to 20 MPa the AN dissociation temperatures practically coincide with the surface temperatures. An exception is the surface temperature at 30 MPa, which revealed 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 breaks at 20-25 MPa, with a strong pressure influence on the burning rate before the break (the pressure exponent, $n = 0.85\text{-}0.95$), and a weaker dependence after it ($n = 0.5\text{-}0.6$). In work,[20] that at these pressures the AN dissociation temperature attains its critical value and does no longer grow. Most likely in this work, we succeeded in obtaining the experimental proofs of achievement of critical temperature at burning. It is necessary to emphasize that the absence of temperature growth with pressure is connected to achievement of temperature critical value rather than with energy reasons, since the maximum temperature of burning achievable in the experiments is much higher (~1000°C).

Temperature distributions in the combustion wave of PSAN1 with binder. Burning of PSAN1 mixed with liquid HTPB oligomer is accompanied by appearance of a gas-phase flame (1100-1230°C), at as little as ~0.2 mm from the surface. Measured maximum temperature of burning appeared to be noticeably higher (~300 K) than calculated adiabatic temperature (See Table 2 and Table 3). It means that the nonequilibrium products, for example soot, are formed during combustion. As mentioned above 10-15% of the condensed combustion products was 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 on the assumption of formation of 9% of soot gives a value close to the experimental one. It was also shown in[21] that 6-7.5% of condensed combustion products were found at burning of AN/AP/HTPB propellants with close oxidizer/fuel ratio (0.43) and AN content (30-40%). In the case of AP/HTPB propellant, chemical analysis showed that condensed combustion products mainly consisted of soot and ammonium chloride.

To obtain the surface temperature of PSAN1/HTPB mixture is more difficult than that of PSAN1 alone, but it is possible to affirm that fuel addition to PSAN1 did not change the surface temperature (Figure 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 combustion of AN-based propellants: surface temperature (T_s), flame temperature (T_f) and temperature gradient above surface (φ).

Parameter	**Pressure, MPa**					
	0.1	0.5	1	3	10	20
	PSAN1					
T_s, °C				490±10	592±10	628±10
T_f, °C				900±90	885±30	1000±100
$\varphi \cdot 10^{-4}$, K/cm				~0	~0	~0
	PSAN1/HTPB					
T_s, °C	325±5	406±11	440±19	480±25	550±35	639±40
T_f, °C	1156±50	1100±20	1125±17	1190±10	1230±15	1185±10

$\varphi\cdot 10^{-4}$, K/cm	1.14±0.33	2.9±1.4	3.3±1.1	6.9±2.5	7.3±1.5	NA
	PSAN1/AP/HTPB					
T_s, °C			430±5	508±28	574±15	563±22
T_f, °C			1150±42	1298±10	1380±20	1365±10
$\varphi\cdot 10^{-4}$, K/cm			7.2±2.4	11.5±2.3	15.3±2.5	22.6±2.0
	PSAN1/AP/Al/HTPB					
T_s, °C			415	500±30	550±30	
T_f, °C			2000	1950±50	2170±70	
$\varphi\cdot 10^{-4}$, K/cm			22.0	28.0±2.5	24.3±3.0	

Temperature distributions in the combustion wave of PSAN1 with binder and AP. Replacement of a part of AN for AP practically does not change the situation: experimental combustion temperature exceeds calculated adiabatic one, there is a formation of condensed nonequilibrium products. As well as in the case with PSAN1/HTPB the definition of surface temperature is complicated, but comparison of profiles shows that breaks on profiles are observed in the same temperature intervals as in the previous cases. The temperature gradient above the surface is appreciably higher in comparison with PSAN1/HTPB mixture and also grows with pressure (Table 3).

Temperature distributions in the combustion wave of PSAN1 with binder, AP, and Al. Addition of aluminum results in a sharp increase of 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). Temperature gradient in the gas phase grows considerably as well (Table 3). The surface temperature of these compositions, while difficult to determine, can be still considered as governed by the dissociation reaction of ammonium nitrate at the surface (Table 3).

4. Discussion

4.1 Surface temperature of AN-based compositions

The surface temperatures measured for PSAN1 are shown in Figure 5. Here is presented the vapor pressure above the AN condensed phase given in work[23] and work.[24] As can be seen from Figure 5, the surface temperatures obtained for PSAN1 fall on the straight line of vapor pressure above liquid AN. 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. In work,[20] it was suggested that in the area of about 20 MPa, the AN dissociation temperature attained its critical value and did not grow longer. Indeed, at 20 MPa the experimental surface temperature is 630 ±10°C. An estimation of the critical temperature, T_{cr}, using Guldberg's equation, gives a quite close value, 616-630°C.

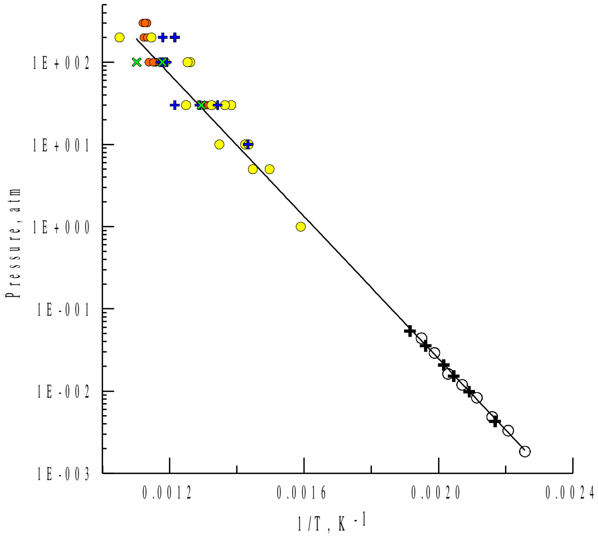

Figure 5: Relationship between vapor pressure and dissociation temperature of ammonium nitrate.[23] Points relate to: vapor pressure of AN (crosses[23] and empty circles[24]), surface temperatures of PSAN1 (filled circles) PSAN1/HTPB (yellow circles), PSAN1/AP/HTPB (blue crosses), and PSAN1/AP/Al/HTPB propellants (green crosses).

All the surface temperatures measured for PSAN1 and AN-based propellants studied in this work are shown in Figure 5. The data obtained allow considering the surface temperature in burning of AN and AN-based systems as determined by reaction of the AN dissociation.

4.2 Combustion mechanism of AN-based compositions

Condensed-phase model of combustion. Negligible values of heat flux from the gas to the condensed phase at combustion allow considering the condensed-phase chemistry as determining the combustion rate of a substance. In this model, according to Zeldovich expression,[25] the mass burning rate (*m*) is defined by kinetics of the leading reaction in the condensed-phase ($A \cdot e^{-E/RT_s}$) at the surface temperature (T_s):

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

The formula contains also the average specific heat, c_p, density of strand, ρ, and thermal conductivity of the condensed phase, λ. The expression in brackets in the denominator represents the heat needed for warming-up of substance to the surface temperature with regard to phase transitions, for example, the heat of melting, L_m. This necessary heat, Q_{need}, generally is not equal to the heat of reaction, Q. Some possible cases of combustion with the dominant reaction in the condensed-phase may be considered: 1). The heat flux from the gas phase is absent ($Q_g \sim 0$); 2). Q_g is less or comparable with the heat necessary for evaporation of unreacted in the condensed phase substance, $(1-\eta)L_v$; 3). $Q_g > (1-\eta)L_v$ and heat feedback from the gas is spent not only for evaporation, but warming-up the condensed phase also, thus influencing the burning rate.

Combustion of PSAN with catalyst. Combustion of AN with $K_2Cr_2O_7$ (PSAN1) obeys the condensed-phase mechanism with the leading reaction in the condensed phase without any heat flow from the gas phase. According to the condensed-phase model, no less than $\eta = 100 \cdot (Q_{need} / Q)$ percent of substance is decomposed in the condensed phase during combustion. The heat effect of decomposition of AN+$K_2Cr_2O_7$ mixture amounts to about 480 cal/g.[24] Taking into account experimental surface temperatures, 49-69% of AN may be considered as decomposed in the melt for the pressure interval of 1-30 MPa. The other part of AN is dispersed from the surface as small drops, in which the decomposition/evaporation continues.

Combustion of PSAN1 with binder. Adding fuel to PSAN1 results in occurrence of the gas flame and temperature gradient above the surface (Table 3). The heat effect of combustion was has been be accepted as 530 cal/g. Using experimental data on the surface temperature and taking into account the binder requires about 535 cal/g for pyrolysis, Q_{need} and degree of AN decomposition in the melt have been calculated. In the interval 0.1-10 MPa, the amount of AN decomposed at the surface is 42-58%. For evaporation of remaining AN, the heat from 178 to 98 cal/g is required, which is very close to the heat coming from the gas phase as calculated from thermocouple measurements. Thus, the combustion of 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). Using the condensed-phase combustion model, it is possible to derive kinetic parameters of heat release in the melt, knowing 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 temperature, which describes decomposition PSAN1/HTPB in the liquid phase.

Combustion of propellant PSAN1/AP with binder. A partial substitution of AN by AP results in increasing both burning rates (Figure 2) and temperature gradient above the surface (Table 3). As stated above, 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[23] that at these temperatures solid AP does not have time to be decomposed at the burning surface. When liquid, AP can decompose faster than in the solid state,[26] however, still one order of magnitude slower than AN. 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 solution the melt. These reactions would increase the heat effect in the condensed phase. A part of AP involved in the reactions with $K_2Cr_2O_7$ is unknown, however may be considered as moderate. Since 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.

A good agreement can be found if one assumes decomposition of AN and partial decomposition of AP (400 cal/g) via modified kinetics. To match experimental and calculated results, the heat release in the condensed phase should be increased 2-3 times only ($k = 2.5 \cdot 10^9 \cdot exp(-13090/T_s)$). Based on this heat effect and 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. To evaporate the rest of AN 92-35 cal/g of heat is needed that is less than the heat feed back from the gas. Thus, combustion of PSAN/AP/HTPB mixtures can be described by a condensed-phase model, with the heat feedback from the gas being used for not only evaporation but also burning rate increase (case 3).

Combustion of propellant PSAN1/AP with binder and Al. A partial substitution of the binder by Al results in a further increase in the burning rate and temperature gradient above the surface (Table 3). 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 was shown by DSC studies to undergo an intensive oxidation in the air at temperatures above 790°C only; 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, and taking into account the decrease of total oxidizer content in the PSAN1/AP/Al/HTPB composition, one can estimate the total exothermic heat effect in the molten surface layer as ~ 400 cal/g. The main heat from the oxidation of Al is produced, according to work,[27] above the surface in the carcass which 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 which can be recorded by the used thermocouples. The experimental data on Q_g of PSAN1/AP/Al/HTPB, therefore, should only be considered as estimation. Because of the high burning temperature, some radiant heat flux to the condensed phase should be also 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. Combustion of this composition, therefore, can be described by the condensed-phase model with a big contribution of heat feedback from the gas which is consumed to not only evaporation but also increasing the burning rate (case 3). This speculation needs additional evidence since heat generated in the condensed phase and heat feedback from the gas at 1 MPa are comparable.

5. Conclusions

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

A weak influence of 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. Heat flux from the gas phase can be used for evaporation of undecomposed AN (as in the case of AN/HTPB mixtures), in which case effect of the gas phase on the burning rate is fully absent. If heat flux from the gas phase exceeds 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 which takes into account heat feedback from the gas.

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