Combustion Mechanism and Kinetics of Thermal Decomposition of Ammonium Chlorate and Nitrite

Valery P. SINDITSKII and Viacheslav Yu. EGORSHEV

Mendeleev University of Chemical Technology,
9 Miusskaya Square, Moscow 125047, Russia
E-mail: vps@rctu.ru

Abstract: Combustion data of ammonium chlorate and nitrite have been analyzed. The leading reactions of combustion of both NH_4ClO_3 and NH_4NO_2 at low pressures have been shown to proceed in the condensed phase, with the burning rate defined by the decomposition kinetics at the surface temperature. The kinetics of NH_4ClO_3 and NH_4NO_2 decomposition have been calculated by using a condensed-phase combustion model.

Keywords: ammonium chlorate, ammonium nitrite, combustion mechanism, decomposition, rate constant

Introduction

Ammonium salts of such oxidizing acids as HNO_3, HNO_2, $HClO_4$, and $HClO_3$ are energetic materials capable of exothermic decomposition. These compounds have the identical combustible part in their molecules, but differ in stability, heat of explosive transformation, and reactivity of the oxidizing part. The ability of some ammonium salts to burn was shown by Shidlovskii [1-3]. In works [4, 5], the combustion of these compounds was studied in the form of pressed strands (TMD is 0.85-0.95) in acrylic tubes of inner diameter 4 or 7 mm in a wide pressure interval (0.1-40 MPa). Their burning rates were shown to vary vastly. Authors of works [4, 5] suggested that the difference in the burning rates could be explained by different oxidation properties of acids, which are included in the composition of the salts rather than different thermal stability of the salts. They characterized oxidation properties of acids by the oxidation

potential and showed that the bigger the value of potential the higher the burning rate of corresponding ammonium salt.

This explanation implies that the leading reaction on combustion is a high-temperature oxidation-reduction process in the flame, since the decomposition is known to be the slowest process at moderate temperatures (and, moreover, in the condensed phase) [6]. However, it does not seem to be absolutely correct to assume that decomposition reactions are absent in the condensed phase for such unstable compounds as NH_4NO_2 and NH_4ClO_3. Moreover, it is well known now that burning rates of two other ammonium salts, ammonium perchlorate NH_4ClO_4 [7-11] and nitrate NH_4NO_3 [12-14] are determined by kinetics of their decomposition in the condensed phase.

Recently [15], it has been shown that the decomposition kinetics of an energetic material can be derived from its burning rate data provided its combustion is governed by condensed-phase reactions. In order for kinetic parameters of the rate-controlling reaction could be evaluated from an adequate combustion model, the experimental data on burning rates and surface temperatures must be obtained.

Decomposition kinetics of NH_4ClO_4 and NH_4NO_3 were studied widely [11], at the same time kinetic data on NH_4NO_2 and NH_4ClO_3 decomposition are practically absent in the literature.

In this connection, the purpose of the present work was an analysis of the existing combustion data for ammonium chlorate and nitrite aimed at determination of their combustion mechanism and decomposition kinetics.

Results and Discussion

Ammonium chlorate

Burning rates of ammonium chlorate are presented in Figure 1. Ammonium chlorate in the form of samples pressed into acrylic tubes of 4 mm diameter is capable of sustained combustion at atmospheric pressure [4, 5]. However, burning rates measured at atmospheric pressure are much lower than the general dependence of the burning rate *vs.* pressures (Figure 1) that may be connected with heat loses becoming significant at this pressure and sample diameter influencing the burning rate. In the pressure interval 0.4-40 MPa, the burning rate of NH_4ClO_3 can be described as: $r_b = 12.96 \, P^{0.6}$. For comparison, burning rates of ammonium perchlorate (AP) [16] are also presented in Figure 1. As seen from the figure, ammonium chlorate, having chloric acid as oxidizer with standard oxidizing potential $E_{Cl_2/HClO_3} = 1.47$ V burns much

faster than ammonium perchlorate, containing perchloric acid as oxidizer with $E_{Cl_2/HClO_4} = 1.39$ V [17]. At the same time, ignition point of NH_4ClO_3 (130 °C [18], 70-100 °C [19]) is much less than that of NH_4ClO_4 (350 °C) [20], which is an evidence of lower thermal stability of ammonium chlorate in comparison with ammonium perchlorate. In order to understand which factor has major effect on the burning rate, one needs to decide on the combustion mechanism, since reaction activity of the oxidizer is important for gas-phase combustion model, while kinetics of thermal decomposition is important for combustion governed by condensed-phase reactions.
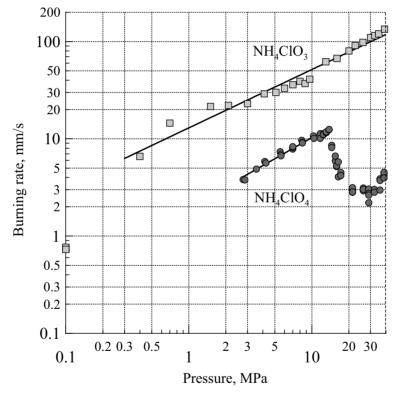

Figure 1. Comparison of combustion behaviors of ammonium chlorate and perchlorate.

The heat effect of decomposition reaction of solid NH_4ClO_3 to oxygen, gaseous water, and HCl (or chlorine) averages 42.5-49 kcal/mole or 419-482 cal/g depending on product composition. Calculated combustion temperature of NH_4ClO_3 is 1660 K at 10 MPa, which gives a heat effect of 452 cal/g taking

an average heat capacity (c_p) as 0.33 cal/g×K. Taking into account heat of condensation (ΔH_{cond}) of water and HCl, the decomposition heat increases to 680-700 cal/g.

Knowing enthalpies of formation of solid NH_4ClO_3 (-65.1 kcal/mole [21]), gaseous NH_3 (-11.0 kcal/mole [22]), and $HClO_3$ (-13 kcal/mole, estimation) and taking into account heat of melting ($\Delta H_m \sim 3$ kcal/mole, estimation), it is possible to calculate easily the thermodynamic enthalpy of NH_4ClO_3 dissociation of in the melt to gaseous NH_3 and $HClO_3$ ($\Delta H_{diss} \sim 38.2$ kcal/mole or 376 kcal/kg).

In work [23], the temperature distribution in the combustion wave of NH_4ClO_3 was measured by thin thermocouples. According to those data, the surface temperature at atmospheric pressure is 584 ±21 K. This temperature is significantly less than the surface temperature of AP (820 K) [24]. Knowing a dissociation temperature at one pressure and the enthalpy of dissociation, it is possible to calculate dissociation temperatures in a wide pressure interval: $\ln P = -9612/T + 16.46$. In turn, assuming that the salt is heated to the maximum possible temperature in the condensed state i.e., dissociation temperature, it is possible to estimate heat expenses for warming-up NH_4ClO_3 to the surface temperature and melting. In the pressure interval 0.1-40 MPa, heat needed for warming-up the condensed phase from initial temperature, T_0, to the surface temperature, T_s, $Q_{need} = C_p(T_s-T_0) + \Delta H_m$ is 136-256 cal/g. It is also needed 0.33(1660 - 584) = 355 cal/g for warming-up the gas phase to the flame temperature at atmospheric pressure. A comparison of enthalpy change in the combustion wave of NH_4ClO_3, assuming warming-up the condensed phase to the surface temperature (T_S), melting, evaporation, and warming-up the dissociation products to the flame temperature (T_f) with heat released in combustion of NH_4ClO_3 is presented in Figure 2. The comparison of calorimetric value of NH_4ClO_3 (~690 cal/g) with heat expenses shows that the remaining heat (690 - 491 = 199 cal/g) is not enough for complete transition of the substance into the gas phase (376 cal/g).

If combustion of a material obeys a gas-phase model, the lacking heat is provided by the ignition system. In the subsequent combustion events, heat of evaporation is transmitted from layer to layer. In the case when an energetic material decomposes in the condensed phase, amount of heat needed for evaporation is decreased. In the case of NH_4ClO_3 if we assume a condensed-phase combustion model, ~30% of the substance should be decomposed in the condensed phase at atmospheric pressure to provide for warming-up the condensed phase to the surface temperature and melting. The remaining part of the substance is thrown out into the gas phase by flowing-off gases (disperse) and decomposes in the condensed state in the aerosol flow above the surface.

Probably, the dispersion results in a significant scatter of the burning rate observed at low pressures (see Figure 1).

The leading role of the condensed phase in combustion of NH_4ClO_3 can be confirmed by an analysis of the temperature sensitivity of the burning rate. According to the condensed-phase model [25], the dependence of the burning rate on initial temperature is described by an expression $r_b = A/(T_S - T_0 + \Delta H_m/c_p)$, while for the gas-phase model this dependence is expressed as $r_b = A \times \exp(-B/(C+T_0))$, where A, B, and C are constants. In coordinates $\ln r_b$ *vs.* T_0, the first dependence looks like a curve with convexity downwards, and the second one has convexity upwards. Hence, the shape of the $\ln r_b(T_0)$ curve can indicate to the leading role of one or the other combustion mechanism.
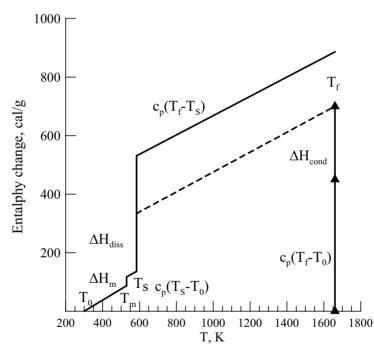

Figure 2.   Comparison of the enthalpy change in the combustion wave of NH_4ClO_3 with heat released in combustion at atmospheric pressure.

In work [23], the temperature sensitivity of the burning rate of NH_4ClO_3 was determined at atmospheric pressure in the interval of initial temperatures of -68-80 °C. The authors described experimental points by a piecewise-linear method and obtained one value of the temperature sensitivity in the interval of -68-60 °C and significantly large value in the very narrow interval of 60-80 °C.

At the same time, experimental points are well described by a function of kind $r_b = A/(B-T_0)$, with scatter of data no more than 10% (Figure 3).
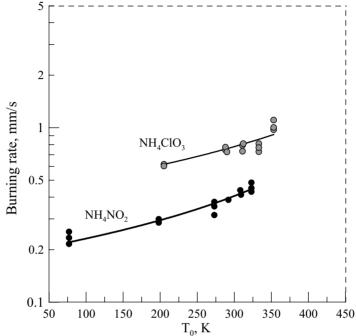

Figure 3. Effect of initial temperature on the burning rate of ammonium nitrite and chlorate at atmospheric pressure.

Differentiation of the received $r_b(T_0)$ dependence allows obtaining the temperature sensitivity of NH_4ClO_3 as a continuously growing function (Figure 4). Besides, in Figure 4 are presented two theoretical dependences of the burning rate temperature sensitivity. One is described by the formula $\sigma = 1/(T_s - T_0 + \Delta H_m / c_p)$ for the condensed-phase combustion model, using experimental surface temperature $T_S = 584$ K, and the other is defined by the formula $\sigma = E / 2RT_f^2$ for the gas-phase model, using experimental flame temperature $T_f = 1378$ K [23]. It is obvious that the gas-phase concept, which shows decreasing temperature sensitivity with initial temperature, contradicts experimental observations.
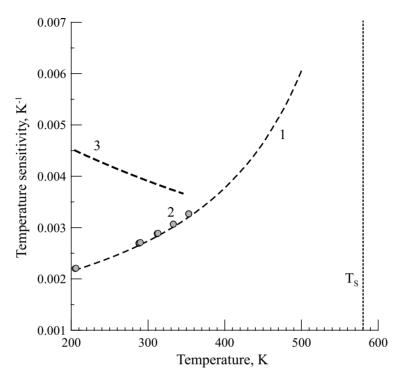
Figure 4. Dependence of temperature sensitivity of ammonium chlorate burning rate on initial temperature: 1 – condensed phase model (theory); 2 – experimental data (description with known T_S); 3 – gas-phase model (theory).

Knowing dependences of the burning rate and surface temperature on pressure it is possible to estimate kinetic parameters of NH_4ClO_3 decomposition by using a condensed phase combustion model [25]:

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

Here c_p, ρ, and λ are specific heat, density, and thermal conductivity of the condensed phase, T_s and Q are the surface temperature and heat of reaction, E and A are activation energy and preexponential factor of the leading reaction in the condensed phase. The expression $T_s - T_0 + \Delta H_m / c_p$ accounts for warming-up of the condensed phase from initial temperature, T_0, to surface temperature, T_s, and melting, where ΔH_m is heat of melting. A comparison of kinetics of the

leading reaction of combustion and decomposition for ammonium chlorate is presented in Figure 5. The following input data were used: $c_p = 0.365$ cal/g×K, $\lambda = 3.85 \cdot 10^{-4}$ cal/cm·K, $Q = 452$ cal/g, and $\Delta H_m = 3$ kcal/mol. Since NH_4ClO_3 decomposition data are not available, rate constants of decomposition have been estimated from the adiabatic thermal explosion model using known ignition temperatures. As seen from Figure 5, the kinetics of the leading reaction of combustion, calculated by the condensed-phase model, is in a good agreement with rate constants of decomposition, estimated by ignition points. The rate constants are described by the equation: $k = 3.3 \times 10^{11} \times exp^{-23700/RT}$. Kinetic data of the leading reaction of ammonium perchlorate combustion [26] and kinetic data of AP decomposition in the liquid state [27] are also presented in Figure 5. A comparison of the constants shows that the decomposition rate of NH_4ClO_3 is almost three orders of magnitude more than that of the leading reaction of AP combustion. This is a reason for ammonium chlorate, having the same combustion mechanism and less surface temperatures than AP, to burn much faster than AP.
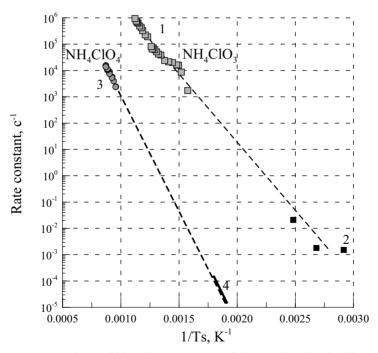

Figure 5.   Comparison of kinetic parameters of the combustion leading reaction (1 and 3) with decomposition kinetics in the liquid states (2 and 4) for ammonium chlorate and perchlorate.

Ammonium nitrite

By analogy with ammonium chlorate and perchlorate, ammonium nitrite burns faster than ammonium nitrate (AN) containing a combustion catalyst (Figure 6). Pressed samples of ammonium nitrite of 7 mm diameter are capable of burning even at pressure 0.55 atm [4, 5], while uncatalyzed ammonium nitrate will not burn at all. Combustion of NH_4NO_2 can be described by a line with two breaks: $r_b = 5.97P^{1.05}$ at pressure 0.1-4 MPa, $r_b = 13.62P^{0.44}$ at 4-20 MPa, and $r_b = 2.57P^{1.01}$ at 20-40 MPa. As in the previous case, the standard oxidizing potential of nitrous acid $E_{N_2/HNO_2} = 1.45$ V is higher than the potential of nitric acid $E_{NO/HNO_3} = 0.85$ V [17], and stability of nitrite is less than that of AN: its ignition point is 89-90 °C [3]. It was noted in paper [28] that a 0.25 g sample of NH_4NO_2 was decomposed completely for 2 minutes at 85-90 °C, and for 9 minutes at 55-60 °C. It was shown in [3] that NH_4NO_2 was decomposed to 10% at room temperature during 6 weeks.
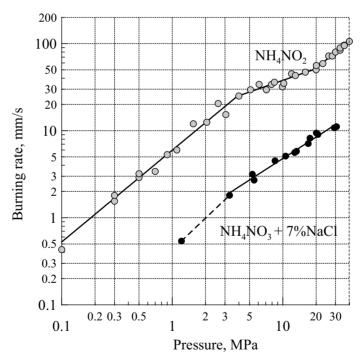

Figure 6. Comparison of combustion behaviors of ammonium nitrite and nitrate.

Experimental points of the burning rate *vs.* initial temperature received in work [23] at atmospheric pressure can be well described by dependence $r_b = A/(B-T_0)$, that testifies to the leading role of the condensed phase reaction (see Figure 2). In work [3], it was revealed that catalysts of NH_4NO_2 decomposition also increased its burning rate, which argues for the condensed-phase mechanism of combustion.

The NH_4NO_2 surface temperature (dissociation temperature) at atmospheric pressure can be estimated from the $r_b(T_0)$ dependence; it is equal to 167 °C (440 K). This temperature is significantly less than the surface temperature of AN (580 K) [14].
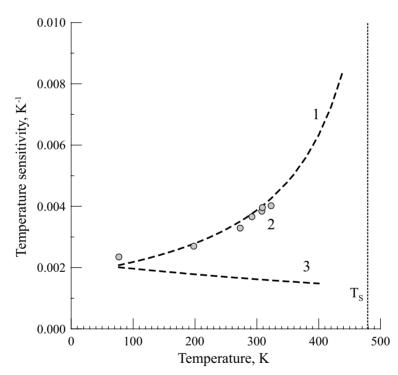

Figure 7. Dependence of the temperature sensitivity of ammonium nitrite burning rate on initial temperature: 1 – condensed phase model (theory); 2 – experimental data; 3 – gas-phase model (theory).

Differentiation of the $r_b(T_0)$ dependence allows obtaining the temperature sensitivity of NH_4NO_2 burning rate at atmospheric pressure (Figure 7). Besides, Figure 7 shows theoretical dependences of the burning rate on initial temperature assuming either gas-phase ($T_f = 2180$ K) or condensed-phase

(T_S = 440 K) mechanisms. As seen from the figure, the temperature sensitivity of NH_4NO_2 burning rate grows with initial temperature that is characteristic for the condensed-phase mechanism of combustion.

A comparison of enthalpy change in the combustion wave of NH_4NO_2, assuming warming-up the condensed phase to the surface temperature, melting, evaporation, and warming-up of the dissociation products to the flame temperature, with heat released in combustion provides us with additional information on combustion mechanism.

The enthalpy of NH_4NO_2 dissociation (27 kcal/mole or 422 cal/g) can be calculated from enthalpy of formation of the solid substance (-58.7 kcal/mole [21]), estimated enthalpy of melting (2.5 kcal/mole), and enthalpies of gaseous dissociation products NH_3 (-11.0 kcal/mole [22]) and HNO_2 (-18.34 kcal/mole [29]). Heat effect of the decomposition reaction $NH_4NO_2 \rightarrow N_2 + 2H_2O$ is equal to 864 cal/g for $H_2O_{(gas)}$ or 1203 cal/g for $H_2O_{(l)}$. Heat effect of 1203 kcal/kg is consumed for warming-up the substance to the surface temperature (including melting) $c_p(T_S-T_0) + \Delta H_m = 111$ kcal/kg, heating gaseous products to the flame temperature (2180 K) $c_p(T_f-T_S) = 887$ kcal/kg, and evaporating a part of the substance. In the case of condensed-phase combustion, the other part decomposes in the liquid state without evaporation. A comparison of heat needed for warming-up the substance to the surface temperature (including melting) with the heat effect of decomposition reaction to gaseous products (864 cal/g) shows that about 13% of NH_4NO_2 must be decomposed at atmospheric pressure to supply the required amount of heat. Hence, as with ammonium chlorate, combustion of NH_4NO_2 is probably characterized by partial decomposition in the condensed phase and formation of the aerosol flow above the surface, which serves as a buffer zone consuming heat flux from the gas phase. Thus, despite a considerable heat effect of decomposition, high flame temperature, and small decomposition depth in the condensed-phase, the low thermal stability of NH_4NO_2 leads to conclusion that its combustion at low pressures is determined by reactions in the condensed phase. The first break on the $r_b(P)$ curve is observed at 4 MPa (see Figure 6). It is possible to assume that in this area the evaporation temperature (in case of salts the dissociation temperature) achieves its critical value and does not grow further. After achieving critical conditions, the enthalpy of dissociation turns to zero. The area of 4-20 MPa is transitive, and at pressure higher than 10 MPa, the leading role in ammonium nitrite combustion is probably passed to the gas phase.

Using experimental burning rates of NH_4NO_2 in the pressure interval of 0.1-4 MPa and calculated dependence of dissociation temperature on pressure $\ln P = -6794/T + 15.44$, taking it as the surface temperature, it is possible to estimate kinetic parameters of the leading reaction of NH_4NO_2 combustion from

the condensed-phase model: $k = 6.7 \times 10^{15} \times \exp^{31700/RT}$ s^{-1} (Figure 8). The following parameters were used in the calculation: $c_p = 0.49$ cal/g×K, $\lambda = 1.42 \cdot 10^{-3}$ cal/cm·K, $Q = 864$ cal/g, and $\Delta H_m = 2.5$ kcal/mol. Kinetics parameters derived from the NH_4NO_2 combustion data appeared to be in a good agreement with rate constants of its decomposition calculated from the ignition temperature and decomposition rate at 25 °C [3]. For comparison, the kinetics of the leading reaction of combustion of AN + 7% NaCl [14] are also presented in Figure 8. As seen from the figure, the decomposition rate of NH_4NO_2 is almost five orders of magnitude higher than the rate of the leading reaction of NH_4NO_3 combustion. This is a main reason explaining the fact that ammonium nitrite having the same combustion mechanism and less surface temperatures than AN, burns much faster than AN.
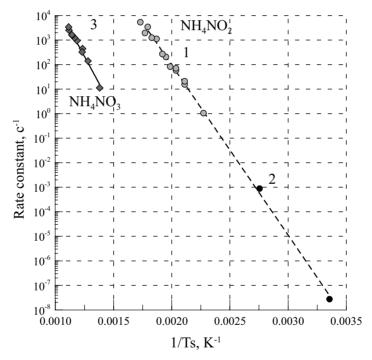

Figure 8.   Comparison of kinetic parameters of the leading reaction on combustion of ammonium nitrite (1) and ammonium nitrate (3) with kinetic parameters of ammonium nitrite decomposition (2).

Conclusion

An analysis of combustion data of ammonium salts of oxygen-containing acids shows that the leading reaction of combustion of NH_4ClO_3 and NH_4NO_2 at low pressures proceeds in the condensed phase as it is the case of NH_4ClO_4 and NH_4NO_3. The burning rate is determined by decomposition kinetics at the surface temperature. Thus, the correlation between standard oxidizing potential of the acid-oxidizer and the burning rate previously offered for these salts seems to be a coincidence. The kinetic parameters of NH_4ClO_3 and NH_4NO_2 decomposition have been calculated from a condensed-phase combustion model.

References

[1] Shidlovskii A.A., Ability to Intramolecular Combustion of Inorganic Salts of Ammonium, *Izvestia Vysshikh uchebnykh zavedenii, Khimia and Khim. Technologia*, **1960**, *3*(3), 405-407.

[2] Shidlovskii A.A., Shmagin L.F., Popovich A.S., Rogozhnikov V.M., On Explosive Properties of Some Unstable Salts – Ammonium Nitrite and Bromate, *Dokl. Akad. Nauk SSSR*, **1968**, *181*, 415-417.

[3] Shidlovskii A.A., Shmagin L.F., Popovich A.S., Rogozhnikov V.M., Study of Properties of Crystal Ammonium Nitrate, *Zhurnal Prikladnoi Khimii*, **1970**, *43(2)*, 434-436.

[4] Fogelzang A.E., Adzhemian V.Ja., Svetlov B.S., On the Role of Oxidizer Group Reactivity at Combustion of Explosives, *Proc. 3rd All-Union Symposium on Combustion and Explosion,* Nauka, Moscow, **1972**, pp. 63-66.

[5] Fogelzang A.E., Adzhemyan V.Ja., Svetlov B.S., Effect of the Nature of Oxidizer Contained in Explosive Compound on Burning Rate, *Dokl. Akad. Nauk SSSR,* **1971**, *190*(6), 1296-1299.

[6] Sinditskii V.P., On the Nature of the Burning Rate-Controlling Reaction of Energetic Materials for the Gas-Phase Model, *Comb. Expl. and Shock Waves,* **2007**, *43*(3), 297-308.

[7] Maksimov E.I., Grigor'ev Yu.M., Merzhanov A.G., Combustion Behaviour and Mechanism of Combustion of Ammonium Perchlorate, *Izv. AN SSSR, ser. khim. (Proc. Acad. Science of USSR, Division of Chemistry Science)*, **1966**, *3*, 422-429.

[8] Winograd J., Shinnar R. Combustion of Ammonium Perchlorate – Some Negative Conclusions, *AIAA J.,* **1968**, *6*(5), 964-966.

[9] Manelis G.B., Strunin V.A., *Proc. XI Intern. Symp. on Space Technology and Science*, Tokyo, **1975**, pp. 97-104.

[10] Manelis G.B., Strunin V.A., The Mechanism of Ammonium Perchlorate Burning, *Comb. and Flame*, **1971**, *17*, 69-77.

[11] Manelis G.B., Nazin G.M., Rubtsov Yu.I., Strunin V.A., *Thermal Decomposition and Combustion of Explosives and Propellants*, Nauka, Moscow, **1996**, 223.

[12] Strunin V.A., Dyakov A.P., Petukhova L.B., Manelis G.B., The Combustion Mechanism of Ammonium Nitrate and Its Mixture, *Proceeding of Zeldovich Memorial*, **1994**, 12-17 Sept., Moscow, Russia, pp. 218-221.

[13] Kondrikov B.N., Annikov V.E., Egorshev V.Yu., DeLuca L., Bronzi C., Combustion of Ammonium Nitrate-Based Compositions, Metal-containing and Water-impregnated Compounds, *J. Propulsion and Power,* **1999**, *15*(6), 763-771.

[14] Sinditskii V.P., Egorshev V.Yu., Levshenkov A.I., Serushkin V.V., Ammonium Nitrate: Combustion Mechanism and the Role of Additives, *Propellants, Explos., Pyrotech.*, **2005**, *30*(4), 269-280.

[15] Sinditskii V.P., Serushkin V.V., Egorshev V.Yu., Levshenkov A.I., Berezin M.V., Filatov S.A., Smirnov S.P., Evaluation of Decomposition Kinetics of Energetic Materials in the Combustion Wave, *Thermochim. Acta*, **2009**, *496*, 1-12.

[16] Atwood A.I., Boggs T.L., Curran P.O., Parr T.P., Hanson-Parr D., Price C.F., Wiknich J., Burning Rate of Solid Propellant Ingredients. Part 1: Pressure and Initial Temperature Effects, *J. Prop. Power*, **1999**, *15*(6), 740-747.

[17] Latimer V.M., *The Oxidation States of Elements and their Potentials in Aqueous Solutions*, **1954**.

[18] Kast H., Uber Explosible Ammonsalze, *Z. Gesamte Schiess- und Spreangstoffwesen*, **1927**, *22*, 6.

[19] Fedoroff B.T., Sheffield O.E., Reese E.F., Clift G.D., *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, Dover, New Jersey, **1962**, vol. 2, p. 641.

[20] Meyer, R., *Explosives*, 3rd Ed., Weinheim; New York, VCH, **1987**, p. 452.

[21] Karapetjants M.Kh., Karapetjants M.L., *Principal Thermodynamic Constants of Inorganic and Organic Substances*, Khimiya, Moscow, **1968**.

[22] Lide D.R., *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., 75th Edition, 1994-1995.

[23] Fogelzang A.E., Adzhemyan V.Ja., Kolyasov C.M., Svetlov B.S., Effect of Initial Temperature on Burning Rate of Explosives, *Proc. IV All-union Symposium on Combustion and Explosion*, Chernogolovka, **1974**, 210-214.

[24] Langelle G., Duterque J., Trubert J.F., Physico-Chemical Mechanism of Solid Propellant Combustion, in Combustion of Energetic Materials, (K.K. Kuo, L.T. DeLuca, Eds.), Begell House Inc., New York **2002**, pp. 287-333.

[25] Zeldovich Y.B., Theory of Combustion of Propellants and Explosives, *Zh. Eksperimentalnoy i Teoreticheskoi Fiziki (Russ. J. Exper. and Theor. Physics)*, **1942**, *12*(11-12), 498-524.

[26] Sinditskii V.P., Egorshev V.Yu., Serushkin V.V., Levshenkov A.I., Chemical Peculiarities of Combustion of Solid Propellant Oxidizers, *Edited book of Proc.*

8th Inter. Workshop on Rocket Propulsion: Present and Future, Pozzuoli, Na, Italy, 16-20 June, **2002**, paper 34, pp. 1-20.

[27] Rubtzov Yu.I., Ranevskii A.I., Manelis G.B., Kinetics of Thermal Decomposition of Ammonium and Guanidinium Perchlorate Mixture, *Zh. Fiz. Khimii (Russ. J. Phys. Chem.)*, **1970**, *44*(1), 47-51.

[28] Sorensen S.P.L., *Z. Anorg. Chem.*, **1894**, *7*, 40.

[29] Chase, M.W., Jr., NIST-JANAF Thermochemical Tables, Fourth Edition, *J. Phys. Chem.*, Ref. Data, Monograph 9, **1998**, p. 1951.