

# Catalytic mechanism in combustion of propellant with ammonium nitrate

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Received: November 12, 2014 Accepted: March 26, 2015

## Abstract

To clarify the catalytic mechanism in combustion of propellant with high ammonium nitrate (AN) contents the temperature distribution in combustion waves of catalyzed propellant with 70% AN at 1.2 and 2.1 MPa pressures was studied by the aid of tungsten-rhenium alloy micro-thermocouples (thickness  $\sim 5 \mu\text{m}$ ). In addition, the structure and composition of combustion surface of quenched samples at 2 MPa pressure were also analyzed by the aid of electron microscope and x-ray microprobe analyzer (XMA). It was shown that by the aid of combined catalyst, consisting of 3% nickel salicylate, 3% potassium dichromate and 1.5% soot, combustion rate of base propellant with 70% AN can be raised up to 7 times at low pressure region with desirable decrease in pressure exponent  $\nu$  (from 0.88 to 0.43). It was established that a carbonaceous skeleton layer with large accumulation of metallic catalyst agglomerates is formed on combustion surface of catalyzed propellant with AN, resulting the significant increase in conductive heat flow ( $q_a$ ) from gas phase to condense phase. According to the result of heat balance of condense phase,  $q_a$  plays the leading role in propagation of combustion process at 2.1 MPa pressure. It was also established that the decomposition rate constant of catalyzed AN in condense phase is  $\sim 16$  times higher than that of pure AN.

**Keywords** : ammonium nitrate, catalyst, thermocouple, electron microscope, x-ray microprobe analyzer

## 1. Introduction

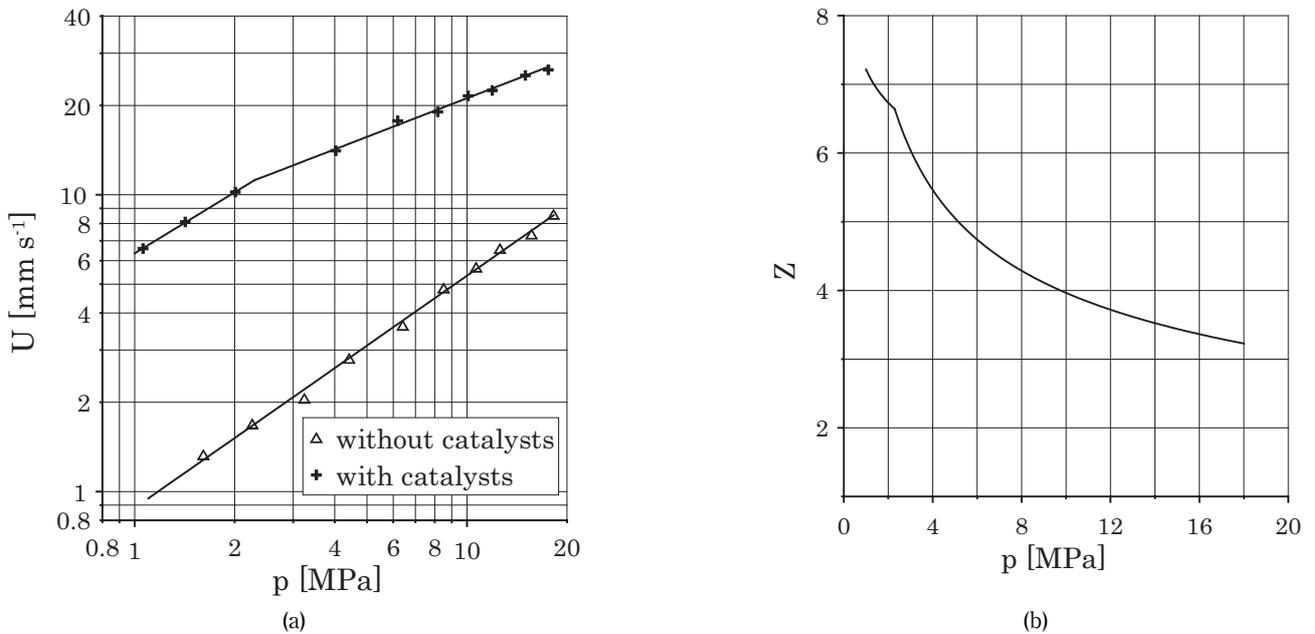
It is well-known that propellants are widely used in civil purposes, such as in anti-hail rockets, geophysical rockets, aerosol fire-extinguishing instruments, various kinds of gas generators and so on. Propellants for such purposes are to be safe to handle, cheap, capable of steady combustion at relatively low pressure and must have the minimal amount of solid residues and lack of hazardous and explosive gases (CO, NO<sub>x</sub>, HCl, etc.) in combustion products. In this regard it is of great interest formulating propellants containing large amount of ammonium nitrate (AN), which is being produced mainly as fertilizer and as a constituent in industrial explosives<sup>1</sup>.

However, compositions based on AN have several drawbacks, particularly, due to the presence of phase-transitions within the production and operation temperature range, low combustion rate with its high dependence on pressure, and relatively low energetic

property. Improving combustion rate and making it less dependent on pressure change of propellants with high AN contents were emphasized in the current work.

Some combustion regularities of double-base propellants with AN were studied in the previous work<sup>2</sup>. The possibilities to obtain actual compositions with up to  $\sim 70\%$  AN, possessing sufficiently high energetic properties, controllable combustion rate at wide pressure range and acceptable mechanical, technological and other properties were also shown later<sup>3</sup>.

However, catalytic mechanism in combustion process of AN is somewhat different from that of double-base propellants. A.P. Glazkova<sup>4</sup> studied the combustion of mechanical mixtures of AN with various additives and established that many organic and inorganic substances to some extents enhance the ability of AN to burn (pure AN is not capable of independent combustion up to 10 MPa pressure), in which, it was noted that catalysts reduce the



**Figure 1** Effect of combined catalyst on combustion rate of propellant with 70% AN (a) and pressure dependence of catalytic efficiency (b).

thermal stability of AN in condense phase (molten AN layer).

Combustion regularities of various calorific propellants with many kinds of catalysts ( $\text{PbO}_2$ ,  $\text{PbO}_2 + \text{CuO}$ , Cu-Pb phthalate,  $\text{SnO}_2$ ,  $\text{NiCO}_3$  and  $\text{Fe}_2\text{O}_3$ ) were studied by A.P. Denisjuk, L.A. Demidova and co-authors<sup>5-10</sup> and it was established that significant catalytic effect is observed only when a specific zone is formed on the combustion surface, that is, carbonaceous skeleton layer, in which a large amount of catalyst particles are accumulated. The high contents of metallic particles improve the conductive heat transfer from gas phase to condense phase.

Therefore to clarify the catalytic mechanism in combustion of propellants with high AN contents the following studies were made in the current work: temperature distribution in combustion waves of catalyzed propellant with 70% AN by the aid of tungsten-rhenium alloy micro-thermocouples (thickness  $\sim 5 \mu\text{m}$ ); structure and composition of combustion surface of quenched samples with the aid of electron microscope and x-ray microprobe analyzer (XMA).

## 2. Experimental

The test sample is composed of 30% low-energetic model propellant (composition: 40.9% nitrocellulose (NC), 45.1% diethyleneglycol dinitrate (DEGDN), 12% dibutyl phthalate, 1% centralite II and 1% industrial oil) and 70% AN. Combined catalyst, consisting of 3% nickel salicylate and 3% potassium dichromate (both with particle size  $< 10 \mu\text{m}$ ) in combination with 1.5% soot (specific surface area =  $250 \text{ m}^2 \text{ g}^{-1}$ ), was chosen. Cylindrical samples of  $\sim 7$  mm diameter were prepared in laboratory according to the production process of double-base propellants, i.e., mixing of ballistic components in water suspension, rolling and extrusion (batch pressing). Solid particles (AN and catalysts) were added during the rolling process. To improve the mechanical and technological characteristics

of samples with high filler contents, 1.5% of complex modifier PTFE (F-4) was also added. The income particle size of AN was  $\leq 100 \mu\text{m}$ , which substantially reduced to 20-40  $\mu\text{m}$  during the rolling process (clearance between the two rollers 0.1-0.2 mm).

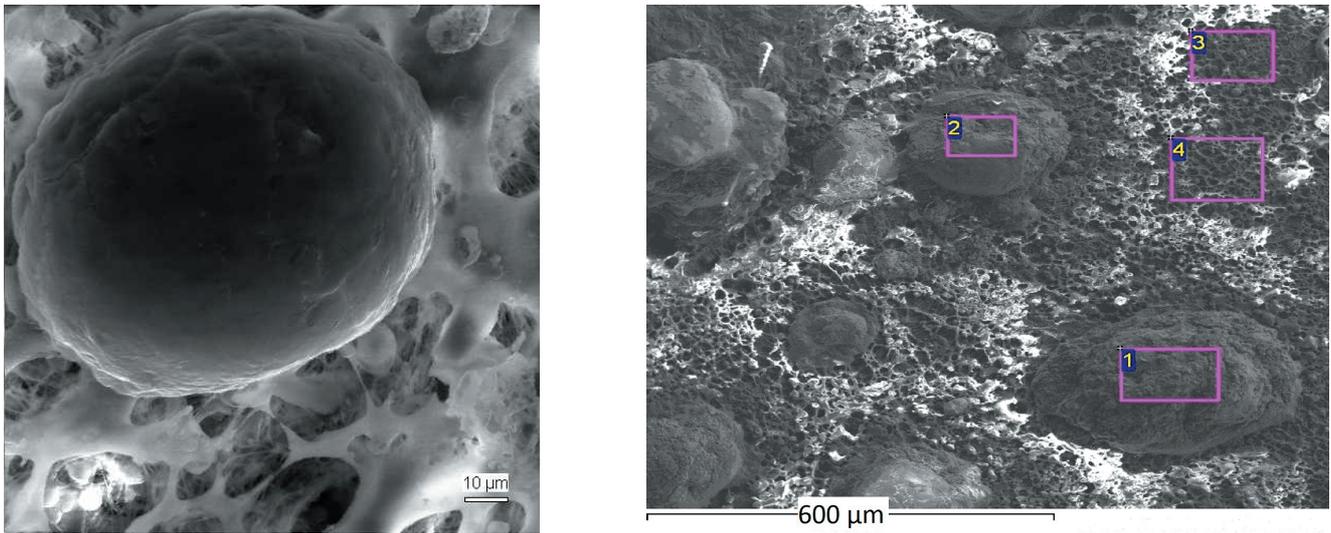
Combustion rate and temperature distribution measurements, as well as the quenching of propellant samples were carried out in constant pressure bomb (also known as Crawford bomb) of internal volume  $\sim 2.5$  liters. The required pressure was achieved by delivering nitrogen gas into the bomb.

## 3. Results and discussion

The applied combined catalyst significantly raised the combustion rate of base propellant with 70% AN (Figure 1). Catalytic efficiency was determined by the index  $Z$  ( $U_c/U_0$ , where  $U_c$  and  $U_0$  - combustion rates of samples with and without catalyst, respectively). It can be seen that maximum catalytic efficiency is observed at low pressure range ( $Z = 6.7$  at 2 MPa pressure) and it decreases with increasing pressure ( $Z = 3.2$  at 18 MPa pressure), which leads to the decrease in pressure exponent  $\nu$  of combustion rate equation  $U = B \cdot p^\nu$  from 0.88 to 0.43 ( $p > 2.3$  MPa).

Therefore temperature distribution measurements in combustion waves of catalyzed propellant samples with AN were carried out at 1.2 and 2.1 MPa pressures, at which high catalytic efficiencies were observed. The structure and composition of combustion surface were studied in samples with and without catalysts, quenched at 2 MPa pressure. The temperature distribution in combustion waves of the sample without catalyst was studied at pressure range 2-10 MPa.

The combustion surface of quenched sample with AN (without catalysts) is in multi-layer structure with polymer partitions, meshed with fine filaments of F-4. The top layer of polymer partitions is in the melted form.



**Figure 2** Combustion surface structure of propellant sample without catalyst, quenched at 2 MPa pressure (a) and XMA sites (b).

**Table 1** Elemental compositions in various sites of combustion surface of propellant with 70% AN at 2 MPa pressure.

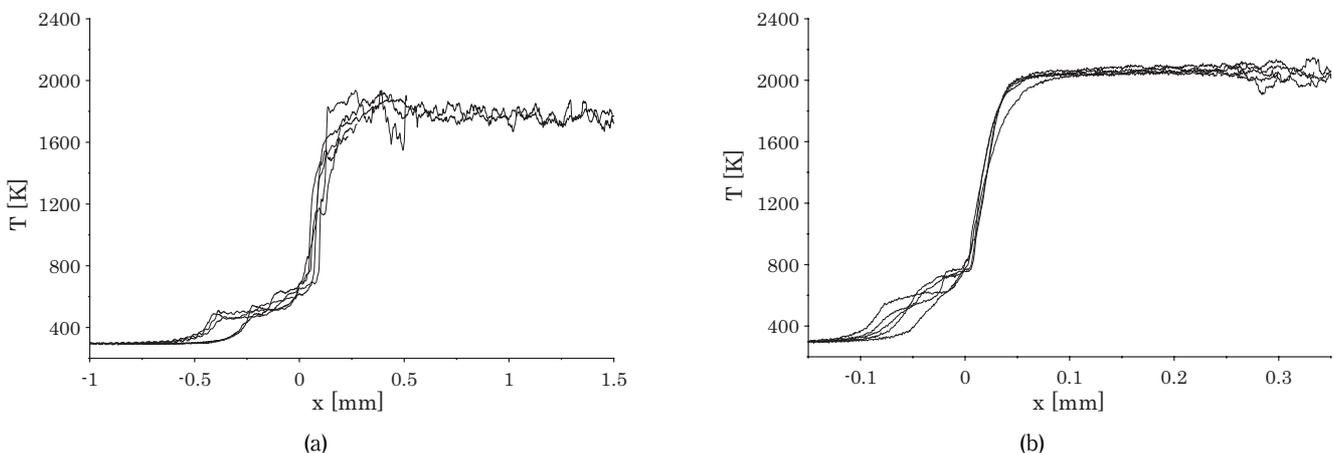
Number of XMA sector	Composition [mass %]			
	C	N	O	F
1	3.96	45.35	50.69	–
2	10.51	38.85	45.68	4.97
Average value	7.24	42.1	48.19	2.49
3	17.21	4.55	5.51	72.73
4	17.04	4.9	5.23	72.83
Average value	17.13	4.73	5.37	72.78

Between the partitions are round AN particles of various sizes (Figure 2a). The XMA results of compositions, taken from the various parts of combustion surface, confirmed the distribution of the components stated above (Figure 2 b, Table 1).

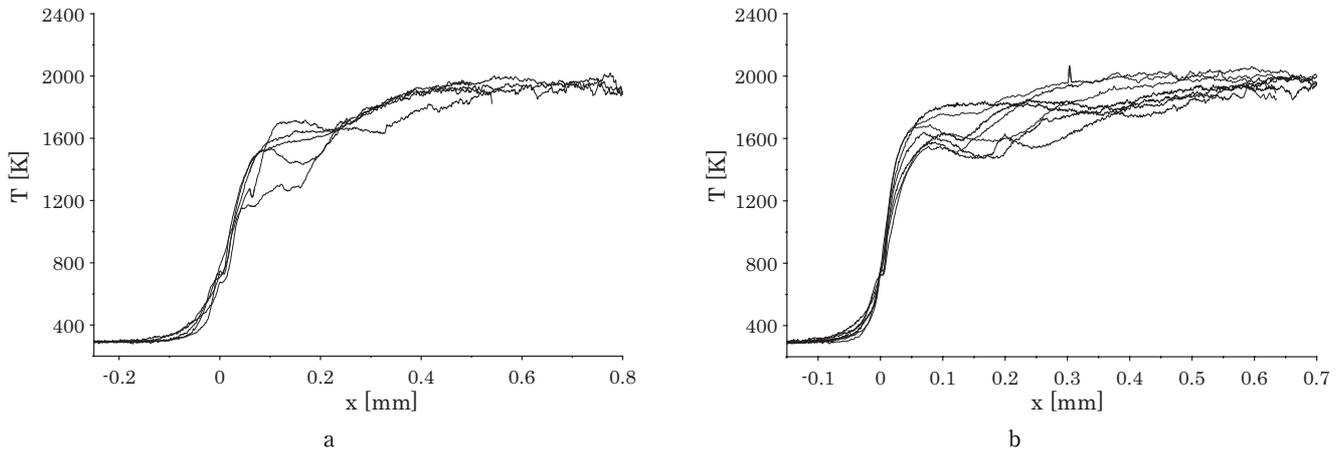
In sites 1 and 2 high contents of nitrogen and oxygen (85-96%) were observed, which indicate the presence of AN in these areas. In sites 3 and 4 carbon and fluorine

dominate up to 90% of total composition, which indicate the presence of thermally stable F-4. Undoubtedly, the less thermally stable components of base propellant (NC and DEGDN) decompose almost completely under this condition and provide heat in condense phase. It is believed that the mesh of F-4 filaments hinder the dispersion of AN particles from combustion surface to gas zone, resulting in the rise in rate of interaction of intermediate decomposition products of AN, NC and DEGDN in condense phase.

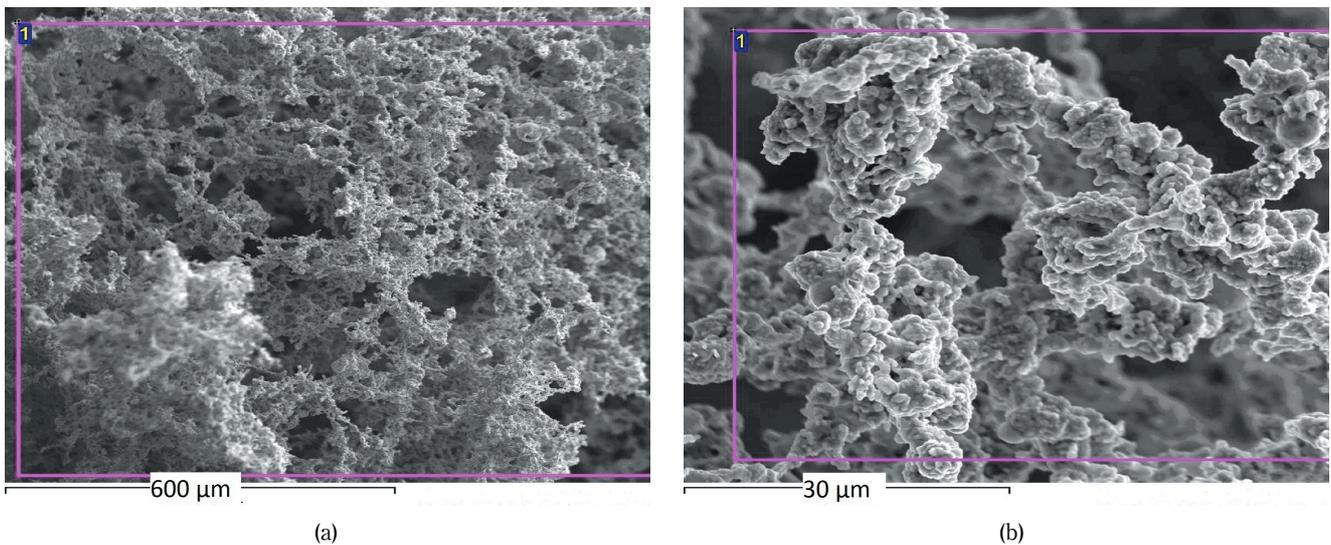
Very large AN formations of sizes up to 300-400 μm were frequently observed on quenched combustion surface, which were formed as a result of freezing of molten AN during the quenching process. According to the temperature distribution measurements average thickness of molten AN layer at 2.2 MPa pressure is 358 μm, which decreases to 46 μm at 10.3 MPa pressure (Figure 3). The average combustion surface temperature ( $T_s$ ) at 2.2 MPa pressure is 679 K (ranging from 667 to 683 K for 6 parallel experiments), which increases to 799 K (ranging from 771 to 819 K for 7 parallel experiments) at 10.3 MPa pressure. The temperature gradient ( $\varphi$ ) on the combustion surface increases from  $4.9 \cdot 10^5$  to  $20.8 \cdot 10^5$  K



**Figure 3** Temperature distributions in combustion waves of propellant with 70% AN (without catalysts): a -  $p = 2.2$  MPa,  $U = 1.66$  mm s<sup>-1</sup>,  $T_s = 679$  K; b -  $p = 10.3$  MPa,  $U = 5.44$  mm s<sup>-1</sup>,  $T_s = 799$  K.



**Figure 4** Temperature distributions in combustion waves of catalyzed propellant with 70% AN: a -  $p = 1.2$  MPa,  $U = 7.3$  mm  $s^{-1}$ ,  $Z = 7.1$ ,  $T_s = 709$  K; b -  $p = 2.1$  MPa,  $U = 10.6$  mm  $s^{-1}$ ,  $Z = 6.7$ ,  $T_s = 743$  K.



**Figure 5** Combustion surface structure and XMA sites of catalyzed propellant with 70% AN.

$mm^{-1}$  during this pressure range. The experimental maximum flame temperature at 2.2 MPa pressure is  $\sim 670$  K lower than the adiabatic flame temperature ( $\sim 2460$  K) due to the radiative heat-loss of thermocouple to surroundings, as well as due to the incompleteness of oxidation reactions, involving NO. The reaction completion is achieved at 4.5 MPa pressure and experimental flame temperature remains almost the same upon further increase in pressure ( $\sim 2050$  K).

The average  $T_s$  values of catalyzed samples are almost the same as the dissociation temperatures ( $T_{diss}$ ) of AN ( $T_{dissAN} = 712$  and  $752$  K<sup>11</sup>) at 1 and 2 MPa pressures, respectively), which are  $\sim 90$  K higher than average  $T_s$  values of samples without catalysts. The thickness of molten layer sharply decreases upon introduction of catalysts (Figure 4) ( $4 \mu m$  at 2.1 MPa pressure). The temperature gradient of catalyzed sample at the combustion surface is 3.8 and 4.2 times higher than that of sample without catalysts, which results in 27-28 times higher heating rate ( $K s^{-1}$ ) in this zone. Experimental flame temperature of catalyzed sample at 2.12 MPa pressure is  $\sim 210$  K higher than that of sample without catalyst, which indicates the higher reaction completeness in gaseous zone (at a distance of  $\sim 0.6$  mm from combustion

surface for both samples).

Electron microscope investigations showed that the combustion surface of catalyzed sample with AN at 2 MPa pressure is fully covered by the thick and well-branched skeleton structures (Figure 5).

A large number of agglomerates of various shapes were observed on these structures. As shown by XMA analysis, catalyst particles were accumulated on them (Table 2).

It can be seen that chromium and nickel are the main constituents of this skeleton zone (64-70%). Based on the experimental results of catalytic mechanism in combustion of propellant N, A.P. Denisyuk and co-authors<sup>5</sup>) established that the thermal conductivity of carbonaceous layer ( $\lambda_c$ ), holding a large number of agglomerates, comprising metallic catalyst particles (Cu, Pb), can be 1.5-15 times higher than that of propellant gases ( $\lambda_g$ ). This leads to an increase in portion of conductive heat transfer ( $q_i = (\lambda/\rho U) \cdot \varphi$ ) from gas phase to condense phase in heat balance of condense phase, in which  $q_i$  becomes predominant if  $Z \geq 1.5$ .

Based on the results of temperature distribution measurements, heat balance of condense phase was made for catalyzed propellant with AN:

**Table 2** Elemental compositions of combustion surface of catalyzed propellant with 70% AN at 2 MPa pressure.

XMA sector	Composition [mass %]						
	C	N	O	F	K	Cr	Ni
a	2.26	0.81	23.94	5.77	3.6	39.38	24.25
b	1.5	2.34	23.57	2.4	0.46	50.81	18.93
Avg. value	1.88	1.58	23.76	4.08	2.03	45.09	21.59

$$0.3 \cdot [c_p (T_s - T_0)]_p + 0.7 \cdot [c_p (T_s - T_0)]_{AN} + 0.7 \cdot \Delta H_{pc+mAN} + 0.7 \cdot \Delta H_{evAN} (1 - \eta_{sAN}) = Q_c + q_\lambda \quad (1)$$

where  $c_p$  - average heat capacity,  $J g^{-1} K^{-1}$  (1.46 for base propellant and 2.05 for AN);  $\Delta H_{pc+mAN}$  - enthalpy of phase changes and melting of AN ( $143.9 J g^{-1}$ );  $\Delta H_{evAN}$  - enthalpy of evaporation of AN ( $2173 J g^{-1}$ );  $\eta_{sAN}$  - degree of decomposition of catalyzed AN in condense phase (unknown value). Similar to the previous work<sup>5)</sup> the value  $\lambda_c$  was taken as the value  $\lambda_g$ , raised by 15 times.

The contribution of heat, generated in condense phase ( $Q_c$ ) comprises from two components: heat effect of base propellant ( $Q_{c,p}$ ) and heat effect of AN ( $Q_{c,AN}$ ) -

$$Q_c = Q_{c,p} + Q_{c,AN} = Q_{c,p} + 0.7 \cdot Q_{NO,AN} \cdot \text{eats}_{s,AN} \quad (2)$$

where  $Q_{NO,AN}$  - maximum heat effect of AN in condense phase ( $1900 J g^{-1}$ ). The value  $Q_{c,p}$  at 1.2 and 2.1 MPa is estimated to be 353 and 264  $J g^{-1}$ , respectively. From Equation 1 and 2 the value  $\eta_{s,AN}$  can be obtained as follow:

$$\eta_{s,AN} = \frac{1+2+3+0.7 \cdot \Delta H_{ev,AN} - q_\lambda - Q_{c,p}}{0.7(\Delta H_{ev,AN} + Q_{NO,AN})} \quad (3)$$

where

$$1+2+3 = 0.3 \cdot [c_p (T_s - T_0)]_p + 0.7 \cdot [c_p (T_s - T_0)]_{AN} + 0.7 \cdot \Delta H_{ps+mAN}$$

Degree of decomposition of AN in condense phase is equal to 42 and 29% at studied pressures, which corresponds to the ~16 times higher rate constants of decomposition of catalyzed AN than that of pure AN. In the work of A.P. Glazkova<sup>4)</sup> it was established, that the rate constant of AN mixture with 10% potassium dichromate at 503 K is 419 times higher than that of pure AN. Therefore the resulting rate constants in current

work for catalyzed AN in propellant sample are quite reasonable. Heat contribution of AN in condense phase accounts 61-60% of  $Q_c$ . It can be seen that  $q_\lambda$  at pressure 1.2 and 2.1 MPa accounts 48 and 68% of the total amount of heat required for propagation of combustion process.

## 4. Conclusion

During the combustion process of catalyzed propellant with 70% AN conductive heat flow from carbonaceous layer with high contents of metal agglomerates to condense phase plays a significant role in condense phase heat balance equation and becomes the major source of heat for the entire combustion process at 2.1 MPa pressure. However, the combined effect of catalysts on thermal decomposition and combustion of AN in condense phase is also necessary to achieve up to 7 times higher combustion rate.

## Acknowledgement

The present work was carried out by the financial support of the Ministry of Education and Science of the Russian Federation within the framework of its basic state tasks.

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**Table 3** Heat balance parameters for condense phase of catalyzed propellant with AN at 1.2 and 2.1 MPa pressure.

$p$ [MPa]	$T_s$ [K]	1+2+3 [ $J g^{-1}$ ]	$q_\lambda$ [ $J g^{-1}$ ]	$Q_{c,p}$ [ $J g^{-1}$ ]	$\eta_{s,AN}$	$Q_{c,AN}$ [ $J g^{-1}$ ]	$Q_c$ [ $J g^{-1}$ ]	$Q_{c,AN}/Q_c$	$\varepsilon^*$ [%]
1.2	709	893	859	353	0.42	561	913	0.61	48
2.1	743	956	1379	264	0.29	389	653	0.6	68

$$\varepsilon^* = q_\lambda / (Q_c + q_\lambda)$$