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Potassium perchlorate – the component of the low-speed explosive composition

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Abstract
The results of the researches on the potassium perchlorate (PP) use as the component of the low-speed industrial explosive (IE) are presented. To improve the operability of IE the influence of catalysts on the thermal decomposition of potassium perchlorate using the method of the differential and thermal analysis and thermogravitation measurements has been investigated. It is established that the metal oxides reduce the decomposition temperature of PP on 80-100 ^{0}C. By the means of Freeman and Carroll's method based on the processing of decomposition thermograms, the activation energy and the speed constant of catalytic decomposition of PP were calculated. It's shown that the manganese oxide, which is the catalyst of decomposition of PP, reduces its activation energy by 2.5 times. It allowed improving the work reliability of IE on the basis of PP from the regular means of initiation.
Keywords: INDUSTRIAL LOW-SPEED EXPLOSIVES, POTASSIUM PERCHLORATE, THERMAL DECOMPOSITION, CATALYSIS, ACTIVATION ENERGY

The industrial explosives (IE) should have low sensitivity to external influences, be safe in handling, transportation and storage and have a relatively low cost. They shouldn't adversely affect the person, both at production, and in the course of application. However, IE must have the sufficient power and high velocity of detonation, reliably detonate from the modern means of initiation, ensure the stable detonation throughout the mass, maintain their properties for a long time in the charging capacities [1, 2].

To perform some explosive works the IE with low sizes of detonation speeds, for example, for the soft blasting of decorative block stone are necessary. Pyrotechnic explosive compositions on the basis of potassium perchlorate (PP) conform to such requirements. PP is one of the strongest oxidants and in mixture with combustible components such as diesel fuel or mineral oils may form the low-speed explosive pyrotechnic compositions. Such structures have the low detonation speed with the critical detonation

diameter no more than 20 mm, low warmth of explosion and the small volume of explosion gaseous products [3]. Potassium perchlorate has a number of advantages, such as low hygroscopicity, sealing and resistance to mechanical influences. However, the potassium perchlorate decomposes with extremely low heat generation, and therefore there occurs explosive decomposition in mixtures with $KClO_4$ and spreads with great difficulty [4, 5]. Therefore for the reliable operability of pyrotechnic compositions on the basis of PP the research of various additives action on the decrease of the decomposition temperature of this oxidizer is actual.

It is known that as catalysts of thermal decomposition of PP various oxides of metals, such as MnO_2, MgO, Cr_2O_3, CuO, Fe_2O_3, NiO, TiO_2 etc., and also their mixtures [6] may be applied. In result of analysis of influence of these oxide additives on the process of thermal decomposition, the studied catalysts according to the influence on decrease of decomposition temperature PP were placed towards its decrease as follows CuO, MnO_2, MgO, NiO, Cr_2O_3, Fe_2O_3, TiO_2. Thus, the best of the considered catalysts accelerating potassium perchlorate decomposition are CuO and MnO_2 [7].

In this case, the catalysis becomes the main tool for the implementation of chemical reactions, control their speed and direction. Researching of the most effective catalysts for improvement of this process is one of the leading factors of technical progress in area of pyrotechnic compositions use to perform the industrial explosive works. Also it is important to determine the catalyst percentage required for the reaction of thermal decomposition, which will promote the best operational characteristics.

The optimum structure of the catalyst in explosive mixture, which represents the chemical, which is accelerates the reaction, but not being a part of reaction products and providing decrease of the potassium perchlorate decomposition temperature was defined, studying the thermal decomposition of mixes on the basis of PP using the methods of the differential and thermal analysis (DTA) and thermogravitation measurements (TG) on the device "Thermoscan-2". For detailed studying of the catalysts influence on the decomposition temperature decrease and activation energy of $KClO_4$, and also definition of the speed constant of the catalytic decomposition, the manganese oxide MnO_2 as rather effective PP decomposition catalyst was chosen. The selection of the catalyst optimum amount was carried out empirically.

Various samples of catalysts not necessarily have identical relative activity under various conditions of carrying out the thermal decomposition process. This can be explained by the fact that in different conditions not always the same parts of the surface show high catalytic activity. Therefore, to eliminate the factors of the results distortion, the following parameters of carrying out of all experiences were established: hinge plate – 0,2 g, heating speed – 10 degree/min., the temperature research interval of the samples makes from 20 to 700 ^{0}C. The sample of aluminum (III) oxide Al_2O_3 was applied as a standard.

Research results of thermal decomposition of all explosive mixture samples with changing percentage of components are introduced in the tables 1 and 2.

Table 1. The composition of PP samples during thermal decomposition study

No.	Name of the components	The content of the components in the sample, %				
		1	2	3	4	5
1	Potassium perchlorate	100	99.5	99.0	98.0	97.0
2	Manganese oxide	0	0.5	1.0	2.0	3.0

Table 2. Data of thermal decomposition of PP with the decomposition catalyst MnO_2

Periods of	Name of	Values of parameters according to the samples

decomposition process	parameters	1	2	3	4	5
Polymorphic transition	Temperature, ^{0}C	303.5	303.9	304.9	303.8	300.1
	Warmth, J	0.938	2.375	2.039	1.648	0.725
Melting	Temperature, ^{0}C	603.2	533.8	529.9	523.7	516.3
	Warmth, J	1.236	1.056	1.356	0.908	0.691
Decomposition	Temperature, ^{0}C	646.2	549.9	561.4	551.3	541.2
	Warmth, J	7.01	10.05	12.2	9.34	4.97

The results of the thermal decomposition process study in graphical form for potassium perchlorate without catalyst, and the mixture of PP with the addition of 0.5 % manganese oxide is provided in the form of thermograms in figures 1 and 2, respectively.

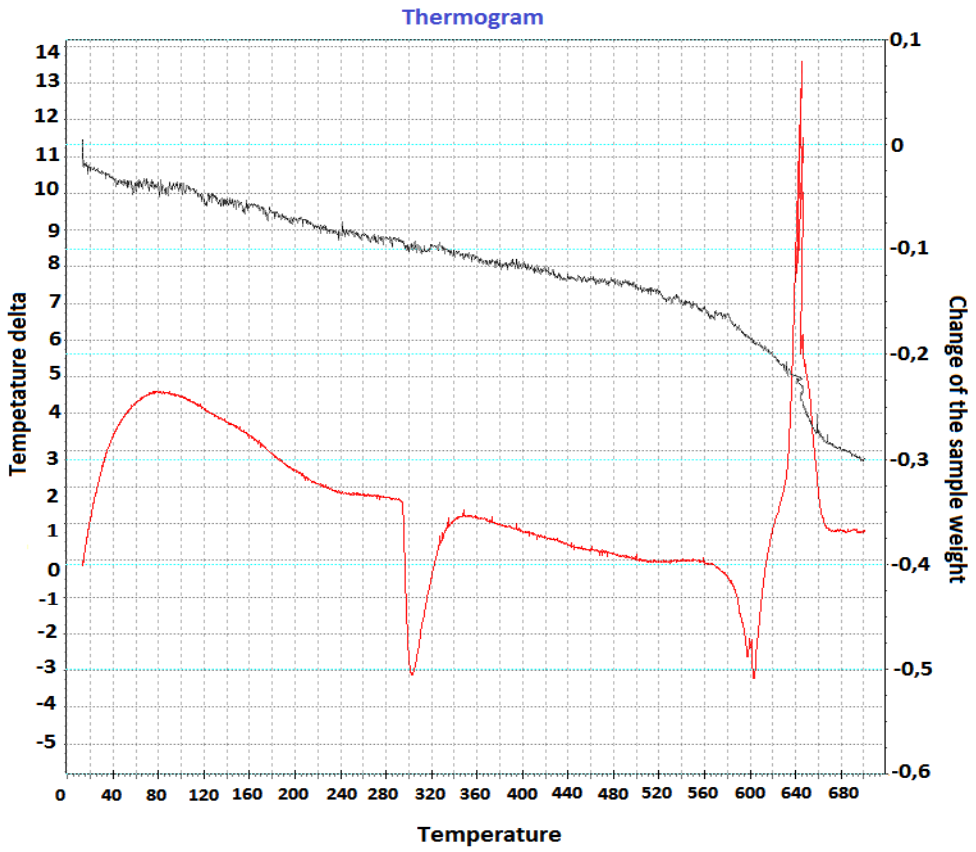

Figure 1. The thermogram of potassium perchlorate decomposition without catalysts

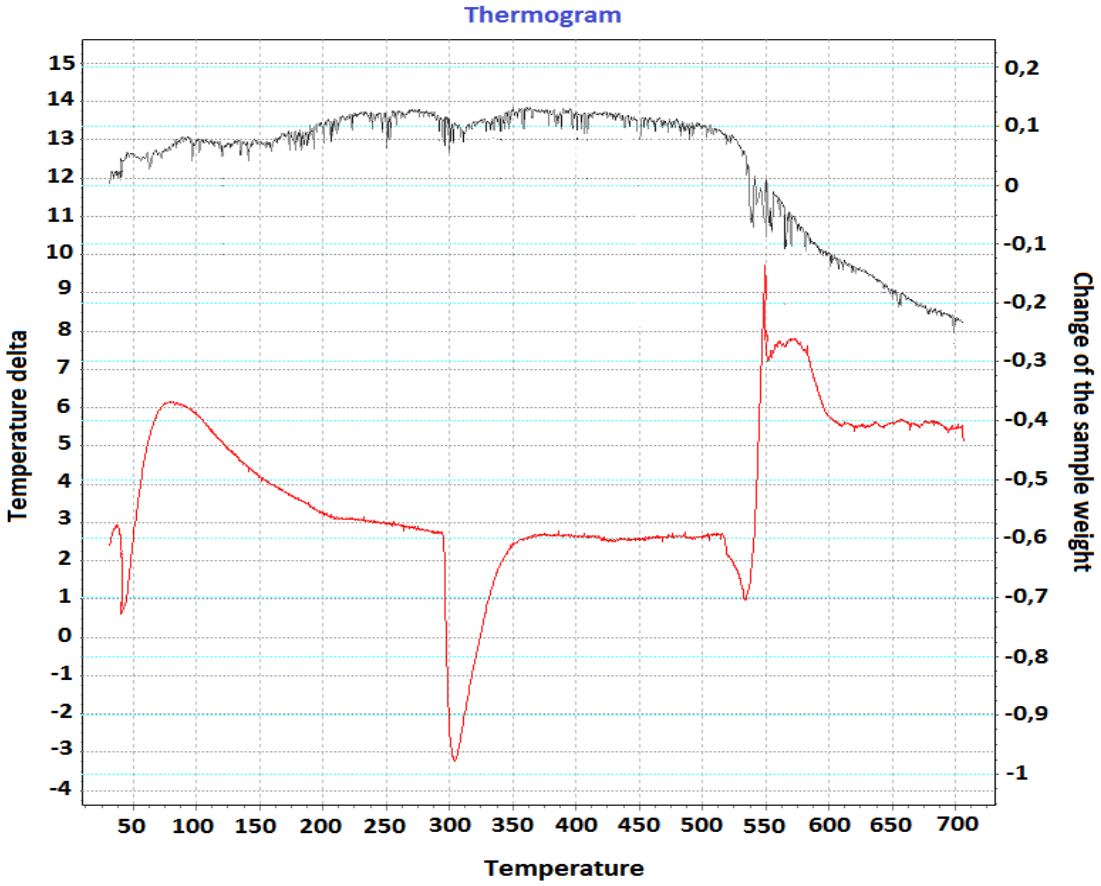

Figure 2. The thermogram of the decomposition of potassium perchlorate mixture with catalyst manganese oxide

From the results of PP thermal decomposition it follows that the introduction of the decomposition catalyst manganese oxide leads to reduction of decomposition temperature of the mixture up to 80-100°C. It is enough to enter 0.5% of the decomposition catalyst MnO_2 to achieve the minimum PP decomposition temperature. Thus it is necessary to use rather high-disperse catalyst and to pay attention to thorough agitation of the mixture.

The kinetic researches of the mixes based on PP decomposition are conducted. Earlier received thermograms of the mixes based on potassium perchlorate decomposition [7] were used for kinetic researches of decomposition and determination of activation energy at non-isothermal heating.

For the simplest single-stage reaction of decomposition of the substance Q which can be presented with the equation Q=B+C (where B – condensed substance, C – gas) the following dependence of transformation speed $P_\tau=dW/d\tau$ from the concentration W is true:

$$P_T = \frac{dW}{dT} = K * W^n, \quad (1)$$

where K – transformation speed constant.

It is supposed that the transformation speed constant K submits to Arrhenius's equation which can be presented in the following form:

$$K = Z * e^{-\frac{Ea}{RT}}, \quad (2)$$

where Z – pre-exponential multiplier;

E_a – activation energy;

R – universal gas constant;

T – absolute temperature.

As the thermal decomposition process of potassium perchlorate and compositions based on it is the difficult process which represents a number of consecutive and parallel reactions, Arrhenius's equation can't be applied to determinate the kinetic parameters with sufficient accuracy.

Among the proposed methods for determination of kinetic parameters of the compounds thermal decomposition, based on the

mathematical treatment of TG curves, the greatest application has found a method of Freeman and Carroll [8]. The advantage of this method is that continuous kinetics studying in the wide interval of temperatures requires a few data. The main disadvantage of the method is that the finding of the decomposition speed is performed by holding the tangent to the curve of the sample weight change during the decomposition process.

According to this method for the current decomposition speed P_T of the condensed substance Q, at the temperature T at the given time the expression is true:

$$P_T = \frac{dW}{dT} = \frac{Z}{q} * e^{-\frac{Ea}{RT}} * W^n, \quad (3)$$

where P_T – temperature speed of decomposition, mg/^{0}C;

q – heating speed, ^{0}C/min;

The activation energy of PP decomposition process and mixes on its basis was calculated for the area of substance mass changing (TG) until the establishing of sample constant mass, that is the end of decomposition process. For this purpose on this part of the curve four points were noted and the temperature corresponding to each of them, the inverse value of this temperature, and also temperature speed of decomposition in each of them were determined.

Data on determination of the activation energy of potassium perchlorate are provided in the table 3.

Table 3. Values of the parameters used for determination of the activation energy of PP decomposition process without catalyst

No.	t_i, ^{0}C	$1/t_i$, $^0C^{-1}$	α_i, ^{0}	P_{T_i}	$P\tau_i$	$lgP\tau_i$
1	538	0.00186	60	1.73	17.3	1.24
2	568	0.00176	78	4.70	47	1.67
3	574	0.00174	83	8.14	81.4	1.91
4	578	0.00170	85	11.43	114.3	2.06

The following formulas were applied to calculations:

$$P_{T_i} = tg\ \alpha_i, \quad (4)$$

where P_{T_i} – temperature speed of decomposition, mg/^{0}C;

α_i – angle of arrival to the thermogram area in the point with value of temperature t_i.

$$P\tau_i = P_{T_i} * q, \quad (5)$$

where $P\tau_i$ – speed of transformation, mg/min.;

q – heating speed at the thermogram removal, ^{0}C/min, q=10 ^{0}C.

Then according to the graphic dependence lgP=f (1/T), namely according to curve tilt angle β we may find the size of the speed constant K, then we may find the activation energy by calculation. This graphic dependence is displayed in figure 3.

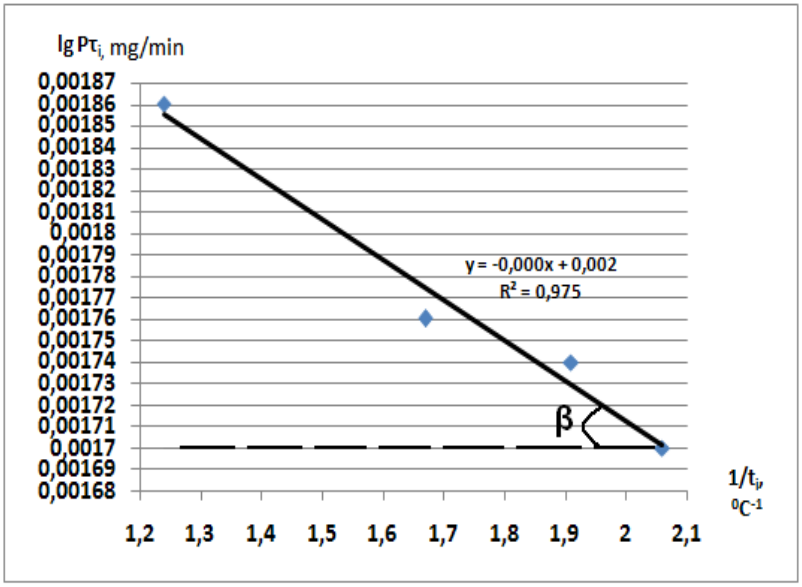

Figure 3. Semi-logarithmic dependence of the change of PP decomposition speed on the inverse temperature

The values β = 49^0 were determined according to the graphic dependence, therefore:

$K=tg\beta=tg\ 49^0=1.15.$

$K=E_a/(2,303*R)$

$E_a=22.01*10^{-3}$ kJ/mol

At the following stage the speed constant and value of the activation energy of decomposition process of explosive mixture, which consists from potassium perchlorate – 99.5% and manganese oxide– 0.5% were defined. The received values of the parameters required for further calculations in four points are displayed in the table 4.

Table 4. Values of the parameters used for determination of the activation energy of PP decomposition process with the catalyst MnO_2

No.	t_i, ^0C	$1/t_i$, $^0C^{-1}$	α_i, ^{0}	$P\tau_i$	$P\tau_i$	$lgP\tau_i$
1	515	0.00194	38	0.78	17.3	0.89
2	528	0.00189	59	1.66	47	1.22
3	539	0.00186	79	5.14	81.4	1.71
4	550	0.00183	85	11.43	114.3	2.06

Then according to the graphic dependence lgP=f (1/T), namely according to the curve tilt angle β we may find the size of the speed constant K, then we find the activation energy by calculation. This graphic dependence is displayed in figure 4.

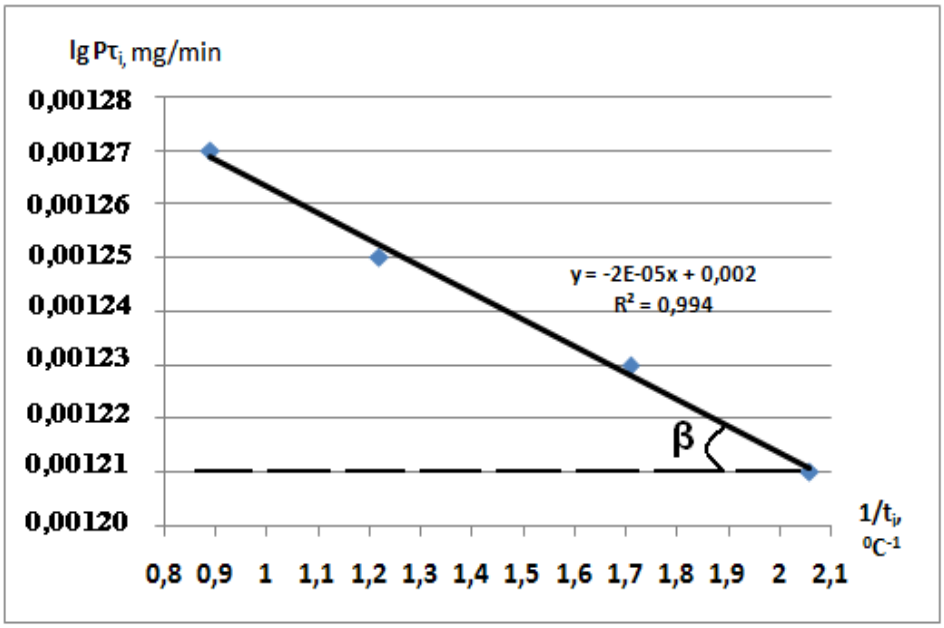

Figure 4. The semi-logarithmic dependence of the change of decomposition speed of the mixture, which consists of PP and manganese oxide from the inverse temperature

The values β = 26^0 were determined according to the graphic dependence, therefore:

$K=tg\beta=tg26^0=0.49.$

$K=E_a/(2,303*R)$

$E_a=9.13*10^{-3}$ kJ/mol

Thus, during research of pure PP the activation energy value makes $22.01*10^{-3}$ kJ/mol, at addition of 0.5% of the manganese oxide the activation energy value decreases to $9.13*10^{-3}$ kJ/mol, herein the values of speed constants are 1.15 and 0.49 respectively. This fact is one more confirmation of catalytic action of the manganese oxide additive on the thermal decomposition of potassium perchlorate.

The activation energy represents the minimum quantity of energy which is required to be reported to the system to obtain the thermal decomposition reaction. The catalyst of thermal

decomposition the manganese oxide reduces the potassium perchlorate activation energy in 2.5 times that improves the reliability of operation of PP from the regular means of initiation. It is established by explosive tests that IE based on PP with the addition of 0.5% MnO_2 - 94% and diesel fuel - 6% reliably works from the regular initiation mean such as electrodetonator ED-8. Thus the detonation speed of the structure depending on the PP dispersion makes from 1.5 to 2.0 km/s, and the detonation critical diameter makes from 6 mm to 15 mm respectively.

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