DEVELOPMENT AND INVESTIGATION OF PYROTECHNIC GAS GENERATING BURNING COMPOSITIONS

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ABSTRACT

The basic laws and features of combustion of pyrotechnic gas generating compositions were studied. The components and their ratios for preparation gas generating compositions on the base of ammonium nitrate (an oxidizer) and coal arenes (the fuel-binder) and melamine and polyvinyl alcohol (the gasification supplements) were found. The thermodynamics calculations of the characteristics (adiabatic temperature of burning and equilibrium composition of products) of pyrotechnic compositions with the use of complex of the programs "Thermo" based on the method of minimization of thermodynamics potential of energy of Gibbs were carried out. Two formulations were created and investigated. It was shown that the compressive strength of compositions of pyrotechnic products was provided by cementators (coal arenes).

Keywords: pyrotechnic, burning, explosives, ammonium nitrate.

INTRODUCTION

The increasing prospects for the use of high-energy explosives in various sectors of the national economy: mining, construction, metalworking, and building materials industry-required increased security measures (including environmental) in the use of these compositions. There is a need to develop a methodology for calculating the values of the charges of these compositions, taking into account the specific properties of the environment being destroyed [1 - 3]. The use of pyrotechnic gas-generating mixtures with ammonium nitrate is one of the promising ways to ensure the improvement of the ecology of the environment from harmful effects of explosive gases and protection of natural resources, decreasing the cost of mining and energy intensity of mining operations and increasing the safety of their management [4 - 6]. Its mass application is explained by the availability of simplicity and safety of the technology for the production and processing of ammonium nitrate in the production of explosives. Ammonium nitrate in pure form is explosive with a heat of explosion about 3 times less than heat of explosion of a trotyl, with the explosive fragmentation in a lead bomb of Trautsl to 165 - 230 cm^3. It is well known that before starting the main explosive work should be carried out the tuning tests to determine of the conditions, especially in the destruction of objects with unknown structure of reinforcement [7 - 10].

The objective of the work is a study of the main regularities and features of combustion of the pyrotechnic gas-generating compositions as well as development and testing of compositions on the base of ammonium nitrate and determination of technological parameters of combustion in the chosen conditions.

EXPERIMENTAL

For research of the processes of combustion of the gas generating charge a construction has been made, which ensures combustion of charge for 1.5 seconds at a pressure within the chamber - not more than 2 MPa (Fig.1). The presence of the channel inside gas-generating charge causes a rapid combustion due to

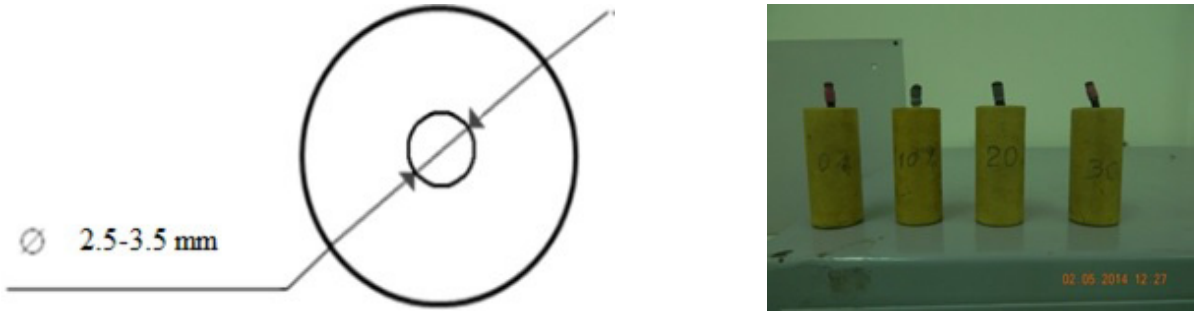

Fig.1. The design of gas-generating charge.

decreasing thickness of the conflagrant vault up to 4.5 mm. The sequence of development of formulations of gas-forming composition consisted in the following: a ratio between the oxidizer and fuel was determined at which the maximum rate of combustion and largest gas capacity of binary mixtures was reached. Then, into the selected mixture was introduced the required amount of gasifying additives for increase of the gas-productivity while preserving the required levels of pressure in chamber and the combustion rate. The experimental part was carried out taking into account the methodology in [11 - 14].

An installation for determining the pressure of the gases released in the combustion of pyrotechnic gas generating compositions is shown on Fig. 2. The combustion was initiated with the help of tungsten spiral. The pressure of the gases released are recorded by means of manometer. The starting components were chosen for

Fig. 2. Installation for determining of gas pressure.

development of compounding of gas-forming compositions: ammonium nitrate - an oxidizer, coal arenes - both fuel and binder, melamine, dicyandiamide, polyvinyl alcohol - gasification supplements. For measurements of combustion temperature a chromel-aluminum thermocouple was used. The burning rate was measured through

Table 1. The composition of combustion gas binary mixture of ammonium nitrate - coal arenes accordingly calculations.

Coal-arenes content, %	Combustion products, %					
	Methane	Carbon oxide	Carbon dioxide	Hydrogen	Nitrogen	Water vapor
30.0	0.58	53.0	0.5	31.7	13.4	0.82
40.0	2.15	45.13	1.26	38.0	11.2	2.26
50.0	4.33	37.87	2.57	41.15	9.27	4.81
60.0	7.44	30.14	3.99	42.92	7.39	8.12
70.0	11.0	23.6	4.87	43.83	5.5	11.2

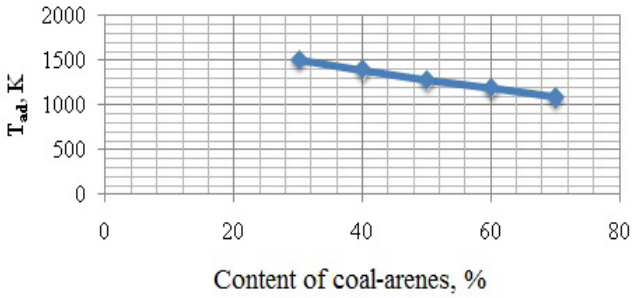

Fig. 3. Influence of the content of coal arenes in a binary mixture of ammonium nitrate - coal arenes on the adiabatic temperature of combustion.

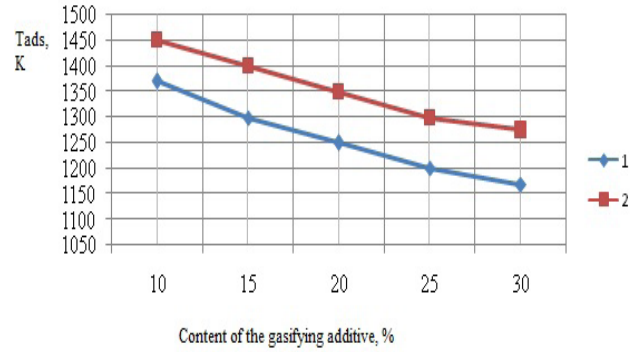

Fig. 4. The dependence of the adiabatic combustion temperature from the content of the gasifying additive in the triple mixture of ammonium nitrate - coal arene - gasifying agent (1 - dicyandiamide, 2 - melamine).

the following operations: the necessary pyrotechnic compositions were placed in a thick-walled pipe with a diameter of 1.5 cm, with a height of 22.7 cm. Combustion was initiated with the upper part of the tube with the initiating composition (50 % Mg + 50 % smokeless powder). The duration of combustion of compositions was fixed by a stop-watch. The burning rate is determined by dividing the height of the compositions of the pipe at the time of combustion compositions. The pressure of released gases was measured on the installation, which was designed and mounted in the laboratory. The first series of thermodynamic calculations was carried out for the base mixture "oxidizer - fuel" for different ratios of the components. The second series of calculations was carried out for the triple mixtures "oxidizer - fuel - gasifying agent" for different ratios of the components. For defining the strength characteristics of the pyrotechnic compositions were taken two systems: 1. KNO_3-Mg-smokeless powder-coal arenes, 2. KNO_3-coal arenes.

RESULTS AND DISCUSSION

Data of thermodynamics calculations of adiabatic temperature of burning of binary mixture of ammonium nitrate - coal arenes show that adiabatic temperature of burning is decreased from 1521K to 1162K with increasing of coal arenes content. These results were used to create the recipes of pyrotechnic gas of generating composition with the low temperature of the generated gas. The data of calculation of the adiabatic temperature of combustion of binary mixture of ammonium nitrate - coal arenes are presented in Fig. 3. Results of calculation of composition of gaseous products of burning of double mixture ammonium nitrate - coal arenes are summarized in Table 1.

On the basis of thermodynamic calculations of equilibrium composition of the combustion products it was shown that in the basis of the products of combustion of binary mixture of ammonium nitrate - coal arenes comprised carbon monoxide and hydrogen. It was revealed that in appreciable quantities nitrogen, methane, carbon dioxide and water vapour are formed and the proportion of the latter is increased with increasing of coal arenes content.

In Fig. 4 the results of calculation of the adiabatic combustion temperature of triple mixtures of ammonium nitrate - coal arenes - gasifying additive are shown.

It was shown on the basis of the thermodynamic calculations that the adiabatic combustion temperature depended on the content of additives in the gasifying of the triply mixtures, the lowest temperature is observed in the triple mixtures with melamine (1170 - 1370K), thus the temperature decrease was observed with increasing of content of melamine in the triple mixture. The basis of products of burning of triple mixtures is constituted by the carbon oxide, hydrogen and nitrogen, thus increase of content of the latter was due to the use of the nitrogen compounds as the gasifying additives (Table 2).

The obtained experimental data of binary mixtures combustion are shown in Figs .5 - 7. The data presented in Figs. 5, 6 indicate that the optimal composition for a large amount of gas evolution and maximum combustion rate is for the composition containing 30.0 % coal arenes and 70.0 % ammonium nitrate. By results of investigations as the basis of a ternary mixture was chosen the double mixture of ammonium nitrate/coal arenes = 70/30, because for this mixture the highest

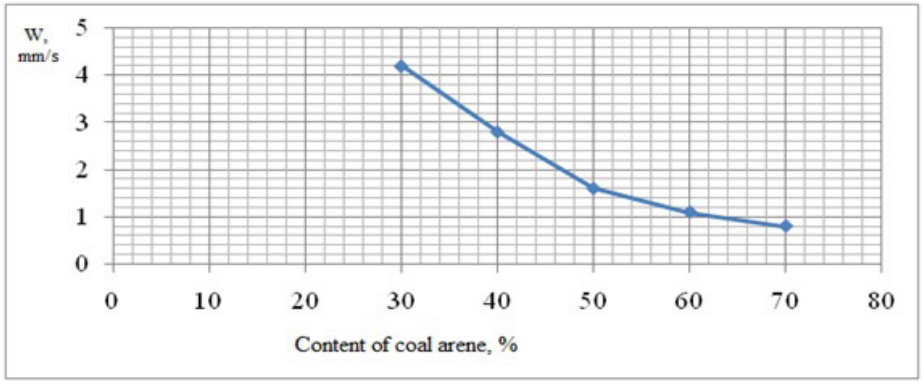

Fig. 5. Influence of the content of coal arenes in the binary mixture of ammonium nitrate - coal arenes on the combustion rate.

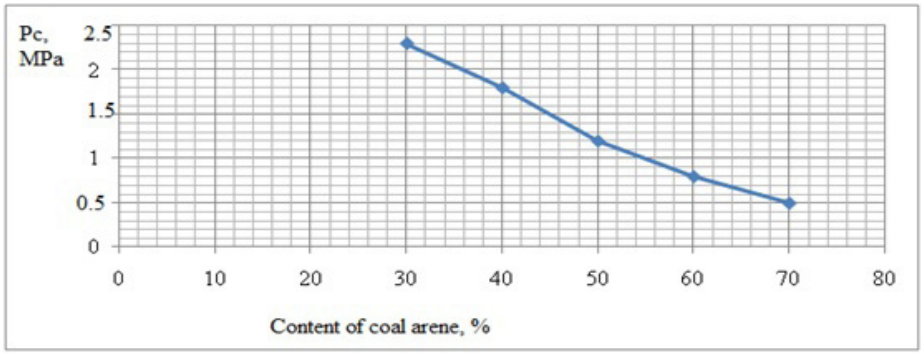

Fig. 6. Influence of the content of coal arenes in the binary mixture of ammonium nitrate - coal arenes on the maximum pressure in the chamber.

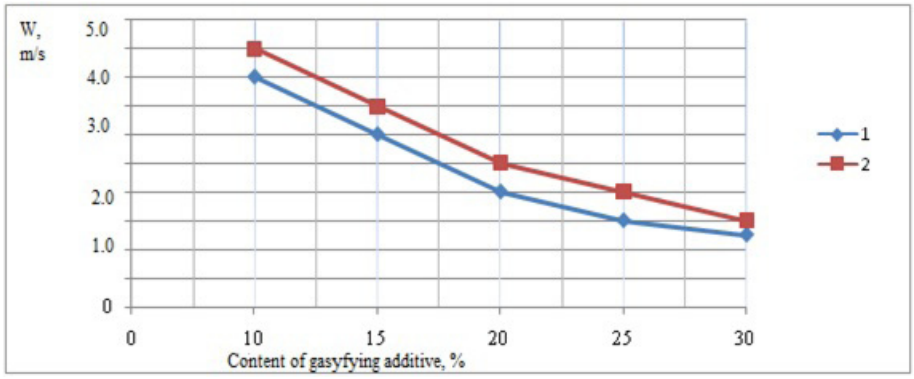

Fig. 7. The dependence of the combustion rate on the content of gasifying additive in the ternary mixture of ammonium nitrate - coal arenes - gasifying additive (1 - polyvinyl alcohol, 2 - melamine).

rate of combustion and very high specific gas capacity of the studied binary mixtures was observed. The experimental results confirmed the choice as a fuel and at the same time the binder coal arenes, which was as a reactor stratum. As a result of the reaction of coal arenes with ammonium nitrate the solid wastes are formed as well as the formation of durable porous framework thus preventing entrainment of condensed reaction products from the combustion zone.

The frame as a block is remained in the chamber before the filter and to the receiver capacity through the filter are entered only the gaseous products of gasification. Therefore, the filter is necessary to cool the already partially cooled pure gas without condensed impurities.

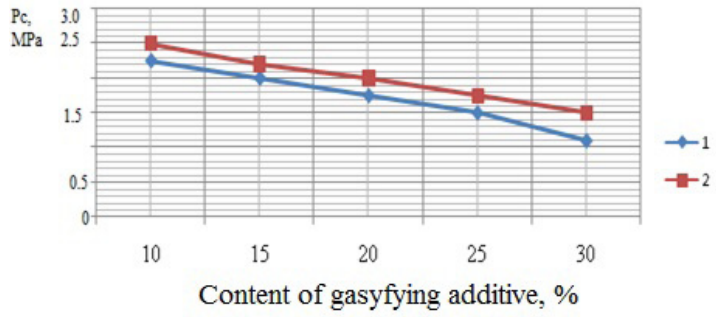

Fig. 8. The dependence of the maximum pressure in the chamber (Pc) on the content of the gasifying additive in the ternary mixture of ammonium nitrate - coal arenes - gasifying additive (1 - polyvinyl alcohol, 2 - melamine).

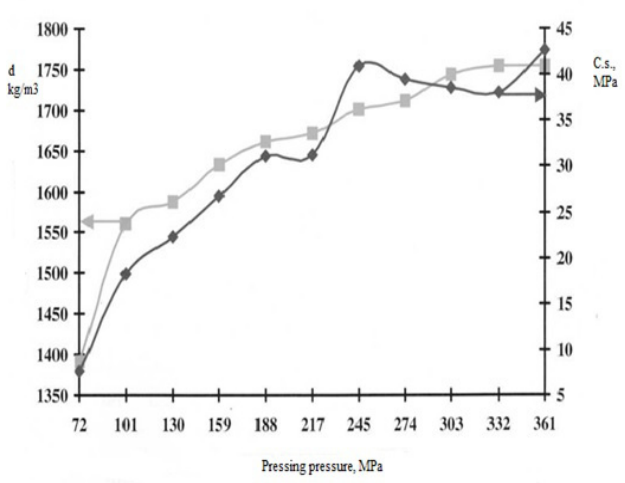

Fig. 9. The dependence of the density (d) and the compressive strength (C.s.) of the pressing pressure in the system KNO_3 - Mg - smokeless powder - coal tar.

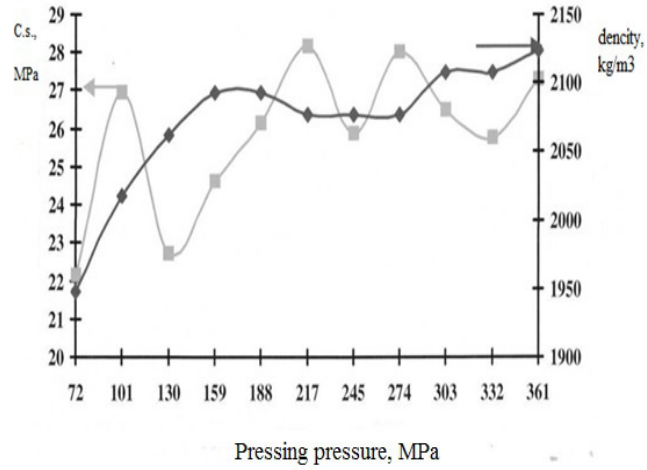

Fig. 10. The dependence of the density and the compressive strength (C.s.) of the pressing pressure in the model system KNO_3 - coal tar.

These results of combustion of triple mixtures are shown in Figs. 7 - 9. The temperatures of burning of triple mixtures are experimentally determined with the content of gasifying additive polyvinyl alcohol and melamine according to which the temperature of combustion mixture is dependent on the content of gasifying additive and its decrease is observed with an increase in the content of additives. The combustion temperature of researching triple mixtures with polyvinyl alcohol was 423 - 723K, and with melamine – 423 - 673K. The data presented in Figs. 7, 8 showed that the optimal composition for a large amount of gas evolution and maximum combustion rate was a composition containing 10 % of the gasifying agent (polyvinyl alcohol), 70 % ammonium nitrate and 20 % coal arene. According to the research as the basis of a ternary mixture was chosen triple mixture of ammonium nitrate/coal arene/polyvinyl alcohol = 70/20/10, the mixture had the highest rate of combustion of the investigated ternary mixtures.

Undertaken researches allowed to develop two formulations of the gas generating composition, which ensure the necessary values for the rate of combustion-chamber pressure and temperature of the generated gas:

Recipe Formulation No1	**Recipe Formulation No2**
Ammonium nitrate 58 (± 4) %	Ammonium nitrate 58 (± 4) %
Coal arenes 25 (± 3) %	Coal arenes 25 (± 3) %
Polyvinylalcohol 17 (± 3) %	Melamine 15 (3) %
Graphite 1% more than 100	Graphite 1% more than 100

As a result of experimental research the dependences of the density and ultimate strength the pressed pyrotechnic compositions from the pressure of compressing have

Table 2. The calculated composition of the gaseous products of combustion of a triple mixture of ammonium nitrate - coal-bearing arenes – melamine.

Acetic acid content, %	Combustion products, %					
	Methane	Carbon oxide	Carbon dioxide	Hydrogen	Nitrogen	Water vapour
10.0	1.38	49.34	1.74	29.39	16.02	2.13
15.0	1.3	46.79	3.11	27.54	17.52	3.31
20.0	2.14	43.18	4.91	26.28	18.77	4.72
25.0	2.59	38.29	7.51	24.41	20.61	6.59
30.0	2.69	35.55	9.29	22.75	22.11	7.61

been received. For determination of the limit of strength on compressing at the platform of the hydraulic press a dynamometer was attached on which the testing sample was set. The press force was applied to the lever and the moment of destruction of the sample visually was fixed. As for the magnitude of the compressive strength it can be judged from the moment of destruction recorded in readings of dynamometer.

To determine the dependence of the strength of finished products from the pressing pressure, that ultimately led to the implementation of a technological process of pressing of pyrotechnic articles and in particular the choice of pressing equipment were measured the specific density and the compressive strength of the pyrotechnic products with application of various polymeric binders.

At first it was tested the system KNO_3 - Mg which was presented a smokeless powder, in that as a binder coal tar is used. In Fig. 9 dependences of density and pressed strength in the given system were presented. Ranging from 70 MPa compaction pressure the density of the sample was sufficiently fast growing and reached a limit of the corresponding to 1730 kg/m^3 at 300 MPa the pressing pressure. The further increase of the pressing pressure to an appreciable increase in the density did not lead. The compressive strength of the sample also increases monotonically to a point in which the compacting pressure of 245 MPa correspondence value after that remains at the same level. In this case, the main component responsible for the strength of the composite article is a resin. Resin obviously at a pressure above 230 - 240 MPa significantly is deformed and wrapped around all of the elements of the composite article. That is, the pressing condition value exceeds a plastic deformation for that substance. Model experiments were carried out with two-component binder system component. The only component that determines the final strength of pyrotechnic products is the coal tar (Fig. 10). Density of the products increases monotonically from 1950 to 2100 kg/m^3 in the interval of pressure on the press from 72 to 361 MPa. It was found that the pressure range 303 - 361 MPa of the cylinder density of the pyrotechnic articles did not change and corresponded to 2100 kg/m^3. The strength of the product increases monotonically to the pressing pressure 245 - 274 MPa and remains unchanged in the interval 245 - 361 MPa, taking into account the experimental error. Thus it is not necessary to increase the pressure of compression above than the value of pressure which is corresponded to the cylinder pressure 245 - 274 MPa because the working characteristics of the products do not change.

For determination of the safety of use and manufacturing of the developed gas-forming compositions the tests on sensitivity to shock and friction were carried out. The tests showed that the developed gas-forming compositions are insensitive to shock (explosion frequency in the instrument 1 is 0 %) and friction at a shock shift (relative frequency of explosions at a pressure of pressing $P_{sn.}$ = 353 MPa (3600 kgf/cm^2) was equal to 0 %). The thermal stability and sensitivity of the developed gas-forming composition to the thermal effects of the method of differential thermal analysis of high resolution were studied. The conducted differential thermal analysis of a high resolution showed the high thermal

stability and low sensitivity to thermal effects of the elaborated gas-forming compositions. The obtained values of the flash temperature (396±10°C), and of the activation energy (309.9 kJ/mmol) of compositions are indirect characteristic for stability of the working descriptions of the gas generating charges on the basis of the developed recipes of the gas-forming compositions in the process of prolonged storage.

CONCLUSIONS

On the basis of thermodynamic calculations of the pyrotechnics gas generating compositions the components and of their correlation for creating of formulations of gas generating compositions: ammonium nitrate - an oxidizer, coal arenes - the fuel-binder, melamine and polyvinyl alcohol - gasification supplements were found. The features of combustion of pyrotechnic gas generating compositions were determined. Two formulations of gas-forming compounds: 1) ammonium nitrate - 58 (± 4) %, coal arenes - 25 (± 3) %, polyvinyl alcohol - 17 (± 3) %, graphite - 1 % excess mass, 2) ammonia nitrate - 65 (± 4) %, coal arenes - 20 (± 3) %, melamine - 15 (3) % graphite – 1 % over 100 were developed and comprehensively studied. The data of the study of dependencies of the compressive strength of the pressing pressure showed that the composite strength of pyrotechnic products was ensured by cementators (coal arenes).

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