ABSTRACT

on the doctoral dissertation of PhD student
of specialty 6D073400 – "Chemical technology of explosives and pyrotechnics"

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"Pyrotechnic compositions for gas generators of destructive impact on concrete structures".

General description of the work. The dissertation is devoted to the development of new gas-generating pyrotechnic compositions based on ammonium nitrate (AN) and ammonium perchlorate (AP) with additives of combustible spent polyethylene, polyethylene terephthalate, with further modification of the obtained pyrotechnic compounds by adding metallic fuel in the form of magnesium MPF-1, and experimental study of their physicochemical properties in order to use energy-intensive systems as a working bodies for the destruction of concrete structures.

The relevance of the thesis topic. Concrete and reinforced concrete are widely used in all countries for the construction of a wide variety of objects. In the near future, these materials will remain the most used in all areas of construction. Quite often there is a need to dismantle reinforced concrete structures. At the moment, the most common method of destruction of reinforced concrete structures is crushing with jackhammers and hydraulic hammers. There are also alternative methods of destruction – this is the detonation of an explosive charge, electric pulse destruction, shock destruction and a number of others. But there are cases when traditional technologies of concrete destruction are inapplicable or too time-consuming. For example, work in the premises of an existing production, in the area of dense buildings, in basements and buried rooms, in the vicinity of cables, water pipes, heating networks and other communications, in connection with these, the development of new, safe and efficient gas generator compositions is an urgent task.

Recently, during the destruction of concrete or the extraction of block stone, gas-generating charges have been used, creating pressure in the cavity of the charging chamber due to the combustion reaction of the composition. Combustion an alternative to the technology of careful blasting (gentle blasting) can be the destruction of concrete structures with the help of gas-generating pyrotechnic compositions that provide a quasi-static nature of loading. Gentle blasting can be carried out by using low-density explosives or pyrotechnic gas-generating compositions that exclude the harmful effects of the explosion, manifested in the form of shock air waves (SAW), seismic explosive waves (SEW) and in the form of the scattering of small fragments. When using low-density gas-generating compositions, the formation of harmful, poisonous gases, the explosive effect of an explosion, expressed in the formation of seismic, shock air waves and the scattering of individual fragments, is completely excluded. In this regard, in this work, gas-generating compositions based on ammonium nitrate and ammonium perchlorate have been developed, operating in combustion mode and excluding the explosive effect of the explosion, manifested in the form of SEW and SAW, as well as in the form of the scattering of small fragments.

Analysis and generalization of the literature data made it possible to evaluate the currently existing gas generator compositions (NH_4NO_3-Al-C, Fe_3O_4-Al-SS, NH_4NO_3-C-nAl), a number of unexplored parameters were identified, such as sensitivity to direct and sliding impact, checking the safety of normalized characteristics for pyrotechnic compounds in the operating temperature range. In this regard, the development of safe compounds operating at low temperatures up to -40 °C, providing minimal operating costs, is an urgent scientific and technical task.

As a result of the performed studies, the obtained gas-generating compositions based on AN, AP can be effectively used as a working fluid in the destruction of artificial concrete objects. The creation of new types of gas generator compositions with low cost and improved characteristics is an urgent direction in the field of pyrotechnics and explosives.

Goal of the work. The purpose of this dissertation work is the development and research of new, effective gas-generating pyrotechnic compositions based on various oxidants operating in critical climatic conditions, which can be used in the destruction of concrete structures with minimizing unit costs and improving labor safety.

Work tasks. In order to achieve this goal, the following tasks were solved:

– thermodynamic modeling of combustion parameters of gas-generating compositions for determination of optimal content of initial components using computer code TDS;

– conducting experimental studies of combustion processes of gas generator compositions based on AN and AP with a subsonic combustion rate;

– study of physical and mechanical characteristics of pyrotechnic systems based on AN, AP;

– approbation of the developed gas generator compositions for efficiency at the test site "ECCEM".

Research methods. When solving the tasks necessary to achieve this goal, the following research methods were used: thermodynamic calculation using the TDS program, thermogravimetric analysis, methods for determining sensitivity to direct and sliding shocks, differential scanning calorimetry, linear method for determining the burning rate, method for determining the ignition delay time, X-ray phase analysis, scanning electron microscopy, method for determining the combustion temperature, landfill studies, chromatographic analysis.

The main provisions for defense:

– energy-intensive composition based on ammonium nitrate (NH_4NO_3) with additives (PE-20%, Mg-10%) with a stoichiometric oxidizer/fuel ratio of 70/30 by weight, identified on the basis of modeling using the TDS program, provides greater destructive effect efficiency due to a high gas yield of 0,129 kg/m^3, combustion temperature and speed (1890 °C, 1,4 mm/s) and a workability of 660 kJ/kg than the compositions described in references;

– a new gas-generating composition based on ammonium perchlorate AP (NH_4ClO_4-85%) and additives (PE-10%, Mg-5%) with a stoichiometric oxidizer/fuel ratio of 85/15 by weight, with a fuel excess coefficient (β=1,004) and oxygen balance (OB =-0,23%), has higher energy characteristics (T, ρ, RT) compared to known

compositions, which is achieved by an exothermic reaction between a strong oxidizer of AP and magnesium powder MPF-1;

– compositions based on AN (NH_4NO_3-70%, PE-20%, Mg-10%) and AP (NH_4ClO_4-85%, PE-10%, Mg-5%), with additives of coarse magnesium (250-400 microns), characterized by significantly lower sensitivity to direct and sliding impact and thermal stability in the temperature range from +40°C to -40°C;

– compositions based on AN (NH_4NO_3-70%, PE-20%, Mg-10%) and AP (NH_4ClO_4-85%, PE-10%, Mg-5%), have a low combustion rate (1,40 mm/s; 1,61 mm/s), which ensures the destruction of concrete structures with minimal violation of the structural array.

The objects of research are pyrotechnic systems consisting of ammonium nitrate, ammonium perchlorate with the use of magnesium, polyethylene, and polyethylene terephthalate as fuels.

The subject of research is the main laws of combustion gas generator compositions based on ammonium nitrate, ammonium perchlorate and their possibility of use for the destruction of artificial objects and block stone.

Novelty and importance of the obtained results. The following results were obtained in the work:

– It is shown for the first time that the creation of effective gas-generating compositions of destructive effects based on AN, AP with the addition of PE and magnesium MPF-1 can be carried out using modeling using the TDS program;

– It is shown that in order to obtain a composition with high energy characteristics based on AP (NH_4ClO_4-85%) and additives (PE-10%, Mg-5%), it is necessary to take into account both the oxygen balance and the possibility of implementing an exothermic reaction between a strong oxidizer of AP and magnesium powder MPF-1;

– It has been established that the addition of magnesium with a dispersion of 250-400 microns (MPF-1) to compositions based on AN and AP, in addition to a significant increase in their energy characteristics, leads to a decrease in sensitivity to direct and sliding impact, which is provided by the inhibitory properties of magnesium MPF-1.

The theoretical significance. The scientific-based criteria determining the choice of technological processes and optimal conditions for the destruction of artificial objects and for the extraction of block stone in conditions with high lability of physico-chemical parameters depending on the composition of the initial components, the stage of metamorphism, storage methods, etc. are presented.

Practical significance.

New formulations of gas-generating compositions based on AN, AP with high energy characteristics, allowing to minimize unit costs and improve labor safety, are proposed.

For the first time, gas-generating compositions were developed, where spent PE and PET were used as fuel, which are binding and gas-forming agents.

For the first time, the safety of the normalized characteristics for pyrotechnic compounds based on AN, AP in the operating temperature range from +40 °C to -40 °C was checked.

The main results of the study obtained in and established in the course of the dissertation work:

1. TV, HP - problems have been solved by the method of the extremum of characteristic functions embedded in the TDS software package to determine the optimal number of initial components of the composition. A new composition based on ammonium nitrate has been developed that destroys concrete blocks of medium strength. Composition No. 1: NH_4NO_3-70%, PE-20%, Mg-10%, characterized by a combustion temperature of 1890°C, a burning rate of 1,40 mm/s, a working capacity of 660 kJ/kg, a gas output of 0,129 m^3/kg;

2. It has been found that with 5% addition of magnesium to composition No. 2: NH_4ClO_4-85%, PE-10%, Mg-5%, characterized by a combustion temperature of 2425°C, burning rate 1,61 mm/s, efficiency 1024 kJ/kg, gas output 0,131 m^3/kg. The TG-DSC method shows that at a temperature of 279.9 °C, 372.3 °C, AN and AP oxidize PE well, which indicates the possibility of their use in a pair;

3. When conducting a physico-mechanical study for compositions based on AN (NH_4NO_3-70%, PE-20%, Mg-10%), AP (NH_4ClO_4-85%, PE-10%, Mg-5%), it was found that with direct and sliding impacts on the test samples, the temperature of their heating does not reach the ignition temperature, the estimated safe impact energy for our systems was at least 9.8 J, which confirms the insufficiency of the impact energy equal to 49 J (initial pulse) to excite the explosive transformation. All samples based on AN, AP after exposure to temperatures from +40 to -40 °C for two hours worked flawlessly;

4. Compositions based on AN, AP have been tested for effectiveness at the ECCEM landfill (Ust-Kamenogorsk). It is proved that these compositions can be used for directional splitting with minimal violation of the structural array of concrete structures of different strength in harsh climatic conditions up to -40 ° C. Theoretically and experimentally, it has been confirmed that toxic gases such as carbon monoxide, nitrogen oxides have concentrations up to 5 mg/m^3, not exceeding the maximum permissible values.

Approbation of work. The materials of the dissertation work were reported and discussed at various international, republican conferences and symposiums:

V International Scientific Conference "Laser, Plasma Research and Technologies – LaPlas 2019" (Moscow, Russia, February 12-15, 2019); IV International Scientific Conference "Chemical Physics and Nanomaterials" (Almaty, Kazakhstan, April 19, 2019); IV International Scientific Conference "Chemical Problems of our time" (Donetsk, Ukraine, May 19-21, 2020); VI International Scientific Conference "Laser, Plasma Research and Technologies – LaPlas 2020" (Moscow, Russia, February 11-14, 2020); VII International Scientific Conference "Laser, Plasma Research and Technologies – LaPlas 2021" (Moscow, Russia, March 23-26, 2021); V International Scientific Conference "Chemical Problems of our Time" (Donetsk, Ukraine, May 18-20, 2021); XIII International Symposium "Chemical Physics, Materials Science, Nanomaterials" (December 20-21, 2022 Almaty, Kazakhstan).

Personal contribution of the doctoral student to the preparation of each publication. The author's personal contribution consists in setting research objectives, conducting theoretical and experimental research, discussing and summarizing the

results obtained, writing abstracts of reports and articles. According to the research results, 10 abstracts of reports at conferences and symposiums, 5 articles in journals recommended by KOKSNVO, 8 articles in journals indexed by Scopus and (or) Web of Science databases have been published. Received 1 copyright certificate No. 17250. Investigation of thermodynamic characteristics of a gas–generating composition based on ammonium perchlorate / Aknazarov S.H., Amir Zh.A., Kudyarova Zh.B., Golovchenko O.Yu., Allan I.K. - Publ. 30.04.2021. In most of the articles, Amir Zh.A. is the first author or corresponding author, thus he made the main contribution in the preparation of all these scientific papers.

Scope and structure of the dissertation. The work consists of an introduction, three sections, a conclusion and a list of references containing 108 titles. The total volume of the dissertation is 107 pages of typewritten text, including 57 figures, 23 tables and 2 appendices.