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METHOD OF RESEARCHING THE FEATURES OF THE INFLUENCE OF EXTERNAL FACTORS ON THE CRITICAL VALUES OF THE COMBUSTION MODES OF PYROTECHNIC MIXTURES BASED ON SODIUM NITRATE, ALUMINUM AND ORGANIC ADDITIVES

The purpose of this work is to study the influence of elevated heating temperatures (T_0, K)and external pressures (P, Pa) on the speed and limits of combustion of compacted mixtures of aluminum powders and sodium nitrate with additives of organic substances for a wide range of changes in technological factors used in pyrotechnics production (coefficient of excess oxidizer α, average particle size of metal combustible powder (d_m, μm), relative mass content of organic substance additives ε and various external pressures (P, Pa), which determine the limiting, stable modes of combustion of mixtures, deviation from which leads to uncontrolled development process of their burning (a sharp increase in the rate of burning or its significant decrease up to the cessation of burning).

The methodology for researching the influence of elevated heating temperatures on the speed and critical values of the combustion regimes of pyrotechnic mixtures based on aluminum and sodium nitrate powders with additives of organic substances for a wide change of technological factors (coefficient of excess oxidizer, average size of metal fuel particles, relative mass content of additives of organic substances) is presented. , which subsequently determines the stable combustion process of the mixture.

Data on changes in the working ranges of technological parameters and external factors, in which the combustion process has a stable character, were obtained. The results of studies of the influence of elevated heating temperatures and external pressures on the rate of development of the combustion process of pyrotechnic mixtures for different values of technological parameters are presented. New maximum and minimum ranges of changes in the concentration limits of combustion of pyrotechnic mixtures based on aluminum and sodium nitrate with additives of organic substances affecting the combustion process have been established.

Keywords*: fire safety, pyrotechnic mixtures, combustion processes, external thermal effects, pyrotechnic products*

Formulation of the problem*. Pyrotechnic products for various purposes (illuminators, tracers, pyrotechnic infrared emitters, firework compositions, etc. [1-4]) based on compacted mixtures of combustible metal powders - aluminum and nitrate-containing oxidizers - sodium nitrate, as the most widely used in practice, are subjected to various kind of thermal effects (in the case of fire in warehouses where pyrotechnic articles equipped with charges of the mixtures in question are stored, in the conditions of transportation with intense convective heating of their surfaces, or in the case of aerodynamic heating of the metal shells of the articles during firing and flight). As a result, under the influence of external heat flows on the metal casings of the products, their overheating occurs, which leads to premature ignition and the development of the combustion process of mixtures under the conditions of increasing temperatures and external pressures. This* *leads to premature activation of products, their destruction with the formation of high-temperature combustion products that fly in different directions at high speeds and are considered fire hazards for surrounding objects.*

Analysis of recent achievements and publications. Nowadays, the research for pyrotechnic mixtures of aluminum powders with sodium nitrate oxidizer is sufficiently fully presented in works [5-8]. Results were obtained regarding the determination of the ignition temperature of metal fuel particles in the decomposition products of oxidants depending on their dispersion, the ratio of components in the mixture, and external pressure [5-11].

Highlighting previously unresolved parts of the general problem, to which the article is devoted. As for pyrotechnic mixtures, the composition of which includes aluminum, sodium nitrate and additives of organic substances, there are currently no systematic studies of the influence of these conditions on the speed and development of critical explosive modes of combustion of mixtures, which prevents the formation of a database on the explosive properties of pyrotechnic mixtures in conditions various thermal influences.

Setting the problem and solving it. Therefore, the purpose of this work is to study the influence of elevated heating temperatures (T_0, K)and external pressures (P, Pa) on the speed and limits of combustion of compacted mixtures of aluminum powders and sodium nitrate with additives of organic substances for a wide range of changes in technological factors used in pyrotechnics production (coefficient of excess oxidizer α, average particle size of metal combustible powder (d_m, μm), relative mass content of organic substance additives ε and various external pressures (P, Pa), which determine the limiting, stable modes of combustion of mixtures, deviation from which leads to uncontrolled development process of their burning (a sharp increase in the rate of burning or its significant decrease up to the cessation of burning).

Presentation of the main material of the study with a full justification of the obtained results. The components of the mixtures were made according to the technology adopted in the pyrotechnic industry [1–6]. Samples of mixtures were obtained by pressing (compaction factor K_c = 0.96...0.98) into metal shells with a diameter of $2\cdot10^{-2}$ m and a thickness of $8\cdot10^{-4}$ m; at the same time, the heights of the pressings were h= 3...$4\cdot10^{-2}$ m. Mixtures were used with an oxidizer excess coefficient α = 0.1...1.5 ($\alpha=\frac{\zeta_{ок}/\zeta_{г}}{(\zeta_{ок}/\zeta_{г})_{ст}}$, where $\zeta_{ок}$, $\zeta_{г}$- are the relative mass fractions of the oxidizer and metallic fuel in this mixture; index "st" denotes the stoichiometric ratio of components; in this case, values α < 1 correspond to the over-enrichment of the mixture with metal fuel, and at α > 1, the mixture contains an oxidizing agent in excess), the relative mass content of the additive of organic matter in the mixture ε = 0.05 ... 0.20 and the dispersion of the components $d_м$ = 50...306 μm and d_N = 100...106 μm. The burning rate u (m/s) of mixture samples was measured by non-contact methods using photo sensors, which make it possible to register the beginning and end of burning of a sample with height$h$ and to find the average value of the burning speed according to the formula $u=\frac{h}{t}$ (t – is the burning time of the sample) . To find the flammable limits (flammable limits according to α): the upper flammable limits α_{UFL} and the lower flammable limits α_{LFL} (α_{UFL} < 1 < α_{LFL}), transition mixtures were used, consisting of the same components as the main ones, but with a smaller excess of aluminum (when determining α_{UFL}) or with its great content (when defined α_{LFL}). In this case, to determine α_{UFL} (similarly α_{LFL}), the following formula was used:

$$y \qquad \zeta_{UFL}=\frac{\zeta_{m1+\zeta_{m2}}}{2}, \qquad (1)$$

where ζ_{m1} – is the relative mass content of aluminum, at which none of the samples taken for the study no longer burns; ζ_{m2} – is the relative mass content of aluminum at which all samples still burn; ζ_{UFL} – is the relative mass content of aluminum in the mixture, which corresponds to α_{UFL}.

For research, standard metrologically certified equipment was used [1-6]. Below is a description of the installation, which allows testing samples of mixtures at elevated heating temperatures (up to 800 K) and external pressures (up to 10^7 Pa).

The installation is designed for simultaneous combustion of three samples. The accuracy of maintaining the working pressure in the installation is ± 5%. The installation consists of a constant pressure device and a heating system, thermal control and temperature recording. The device of constant pressure contains three combustion chambers connected in one block. The combustion chamber block is connected to the liquid filter housing, which is filled with water before testing. Temperature control of the samples is carried out directly in the combustion chambers before burning. During testing, the constant pressure apparatus is filled with an inert gas. All three samples are burned simultaneously. The combustion products, cooled and cleaned of condensed particles in the liquid filter, enter the constant pressure valve controlled by compressed gas. The combustion chamber consists of a housing connected by a branch pipe to a common cover of the chamber block. A removable electric heater is installed on the part of the chamber where the sample is located. The electric heater consists of a nichrome coil enclosed in an insulating ceramic. The heater body is welded, sealed, made of stainless steel. The internal space between the body and the spiral is filled with asbestos packing. An alternating voltage of 100–200 V is supplied to the heating element. The rear cover of the chamber has a thread into which a photo sensor is screwed in order to record the moment when the combustion of the sample ends through a hole in the bottom armor. Opposite the sample, in the section of the chamber that is not subjected to temperature control, there is a socket for installing a pyrogenic igniter mounted on the electrical contact assembly. To control and regulate the thermostating temperature, a thermocouple is embossed in the chamber body, connected to a thermal control system mounted on the basis of an electronic control potentiometer. The electronic control potentiometer is the main unit of the system and is used to sequentially record the temperature in the three chambers of the installation on a chart tape, as well as to issue electrical signals to turn the heating chambers on and off when the set temperatures are reached. Temperature control accuracy is ± 2%. To create a preliminary pressurization before burning the sample, the installation is equipped with an appropriate pneumatic system, consisting of a pneumatic shield, gearboxes, a balloon battery, etc. Simultaneous burning of three samples under the same conditions allows reducing the error in determining the burning rate to 2 ... 3%.

As a result of the studies, it was found that for the considered operating ranges of changes in technological parameters (excess ratio of the oxidizer, content of organic additives and fineness of powders of metal fuel and oxidizer) and external factors (heating temperature, external pressure), the flammable limits of mixtures α_{UFL} and α_{LFL} (α_{UFL} – the upper flammable limit (the maximum allowable content of metallic fuel in the mixture, at which the combustion process is still stable), α_{LFL} - is the lower flammable limit (the maximum content of the oxidizer in the mixture, at which the combustion process has not yet died out)): α_{UFL} = 0, 1...0.20 and α_{LFL} = 1.4...1.5.

In order to study the general behavior of the dependences $u(T_0)$ for mixtures at the considered values of technological parameters and external factors, these dependences were studied in the range of α: $\alpha_{UFL} < \alpha < \alpha_{LFL}$. This was due to the fact that, in practice, mixtures with α values that are close to α_{UFL} or α_{LFL} are not used due to their apparent instability under external thermal conditions.

All the regularities of the behavior of the dependences $u(T_0)$ established below were obtained for the first time and can be used as an integral part of the general database on the formation of fire-hazardous properties of mixtures under conditions of external thermal effects.

Influence of the excess coefficient of the oxidizer, dispersion of the metallic fuel and external pressure on the dependence of the burning rate on the heating temperature. From the data obtained, the main of which are presented in Fig. 1 - 2, it follows that an increase in T_0 from 293 K to 800 K leads to an increase in the burning rate by 1.4 ... 2.6 times; at the same time, with increasing T_0, the dependence $u(T_0)$ increases by 1.2...1.4 times. In addition, an increase in the excess coefficient of the oxidizer leads to a decrease in the burning rate and a noticeable weakening of the dependence $u(T_0)$: an increase in α from 0.15 to 1.5 leads to a decrease in the burning rate by

3.9...4.1 times and weakening dependences $u(T_0)$by 1.5...1.7 times. A decrease in the fineness of the metal fuel powder leads to an increase in the burning rate and an increase in the dependence $u(T_0)$: a decrease in the values of $d_м$ from 306 μm to 56 μm leads to an increase in the burning rate by 2.1 ... 2.4 times and an increase in the dependence $u(T_0)$ in 1.3...1.5 times. An increase in external pressure leads to a significant increase in the burning rate and an increase in the dependence $u(T_0)$ for all studied ranges of α, $d_м$ и d_N: changing the external pressure from 10^5 Pa to 10^7 Pa leads to an increase in the burning rate by 1.9...2, 2 times and strengthening the dependence $u(T_0)$by 1.2...1.4 times. The introduction of organic additives into the mixture in an amount up to ε = 0.20 leads to a decrease in the combustion rate by 1.5 ... 3.6 times and a weakening of the dependence $u(T_0)$by 1.1 ... 1.3 times: for example, an increase in the value of the additive from ε = 0,05 to ε = 0,20 leads to a decrease in the combustion rate by 1.5 ... 1.8 times for the addition of naphthalene and by 2.9 ... 3.3 times for the addition of anthracene, as well as weakening the dependence $u(T_0)$for all additives by 1.15...1.20 times.

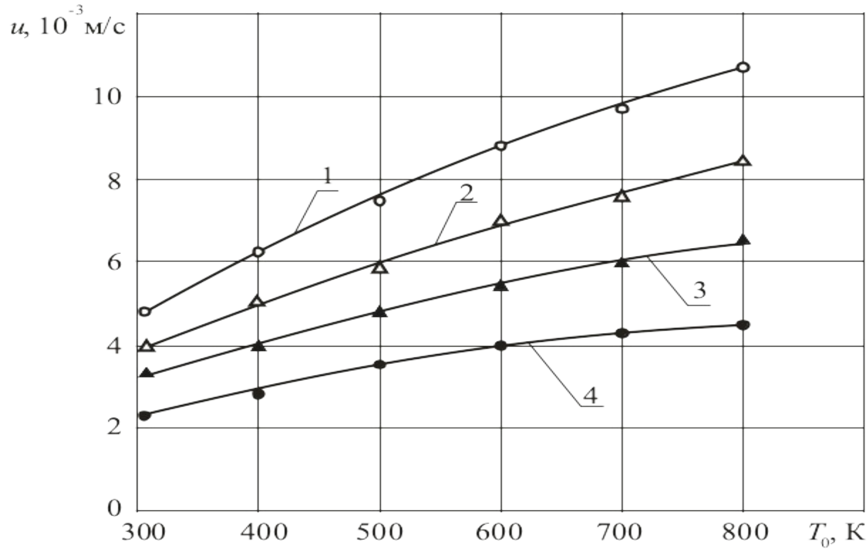

Figure 1 – Influence of dispersion of metal fuel powder on the dependence of the combustion rate of stoichiometric mixtures of aluminum + sodium nitrate on the heating temperature at external pressure $P = 10^5$ Pa ($\alpha = 1.0$, d_N= 106 μm): 1 – $d_м$ = 56 μm; 2 – $d_м$ = 105 μm; 3 – $d_м$= 179 μm; 4 - $d_м$= 306 μm.

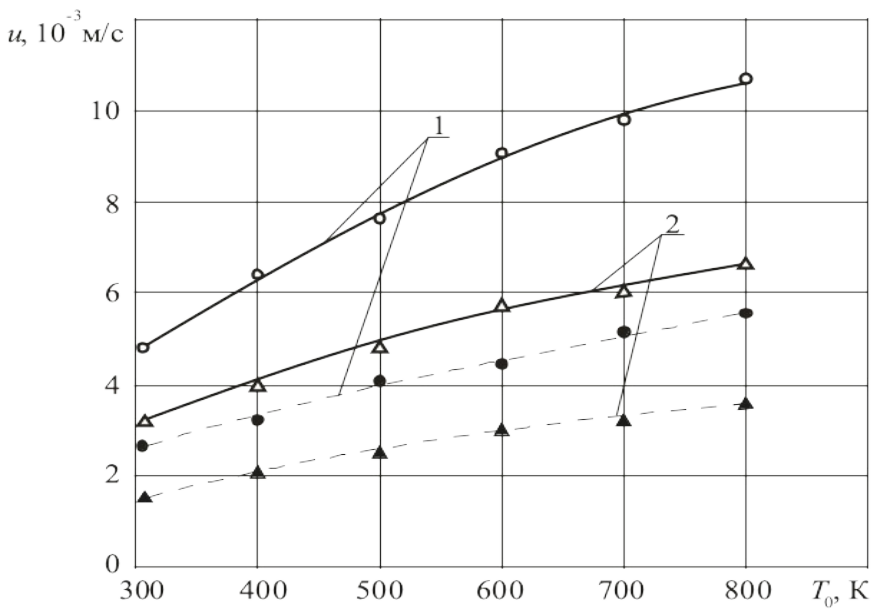

Figure 2 – Influence of additives of organic resins on the dependence of the combustion rate of stoichiometric mixtures of aluminum + sodium nitrate on the heating temperature at $P = 10^5$ Pa (α = 1.0, d_N = 106 μm): 1 – $d_м$ = 56 μm; 2 – $d_м$= 179 μm; ——————— – mixture without additive; – – – – – – ε = 0.20.

Conclusions. As a result of the conducted studies, the following regularities were established:

- the flammable limits α_{UFL} = 0.1...0.2 and α_{LFL} = 1.4...1.5 are determined, within which the combustion process of mixtures is stable and quasi-stationary;
- an increase in T_0 from 293 K to 800 K leads to a significant increase in the burning rate in the range of 1.4...2.6 times and an increase in the dependence $u(T_0)$ by 1.2...1.4 times; at the same time, an increase in the content of the oxidant in the mixture from α_{UFL} to α_{LFL} leads to a decrease in the burning rate by 2.6...2.9 times and a weakening of the $u(T_0)$ dependence by 1.5...1.7 times; an increase in d_m from 56 μm to 306 μm leads to a decrease in the burning rate by 2.1...2.4 times and a weakening of the $u(T_0)$ dependence by 1.3...1.5 times; an increase in external pressure from 10^5 Pa to 10^7 Pa leads to an increase in the burning rate by 1.9...2.2 times and an increase in the dependence $u(T_0)$ by 1.2...1.4 times;
- an increase in the relative content of organic additives in the mixture from 0.05 to 0.2 leads to a decrease in the burning rate by 1.5...1.8 times and a weakening of the $u(T_0)$ dependence by 1.15...1.20 times.

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МЕТОДИКА ДОСЛІДЖЕННЯ ОСОБЛИВОСТЕЙ ВПЛИВУ ЗОВНІШНІХ ЧИННИКІВ НА КРИТИЧНІ ЗНАЧЕННЯ РЕЖИМІВ ГОРІННЯ ПІРОТЕХНІЧНИХ СУМІШЕЙ, ЩО МАЮТЬ В ОСНОВІ НІТРАТ НАТРІЮ ТА АЛЮМІНІЙ

Представлено методику дослідження впливу підвищених температур нагріву на швидкість та критичні значення режимів горіння піротехнічних сумішей на основі порошків алюмінію та нітрату натрію з добавками органічних речовин для широкої зміни технологічних факторів (коефіцієнту надлишку окиснювача, середнього розміру частинок металевого пального, відносного масового вмісту добавок органічних речовин), що в подальшому визначає стабільний процес горіння суміші.

Отримано дані зміни робочих діапазонів технологічних параметрів та зовнішніх чинників, при яких процес горіння має стабільний характер. Наведені результати дослідження впливу підвищених температур нагріву та зовнішніх тисків на швидкість розвитку процесу горіння піротехнічних сумішей для різних значень технологічних параметрів. Встановлено нові максимальні і мінімальні діапазони зміни концентраційних меж горіння піротехнічних сумішей на основі алюмінію та нітрату натрію з добавками органічних речовин, що впливають на сам процес горіння.

Ключові слова: *пожежна безпека, піротехнічні суміші, процеси горіння, зовнішні термічні впливи, піротехнічні вироби*