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Determination of the activation energy of a gasless pyrotechnic composition
Wyznaczanie energii aktywacji kompozycji pirotechnicznej bezgazowej

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Abstract: *This article presents the determining of some parameters of a gasless pyrotechnic composition. Thermo-analytical studies have been carried out. The activation energy of the gasless pyrotechnic composition was determined experimentally and by calculation. The flashpoint was 100 °C. The value of the activation energy of the pyrotechnic composition was 369.39 kJ/mol, which exceeds the activation energy of standard solid and liquid explosives by 2.4-2.8 times and makes it more stable. The change in the mass of the pyrotechnic composition during heating did not exceed 1%.*

Streszczenie: *Artykuł dotyczy zagadnień wyznaczania niektórych parametrów bezgazowej kompozycji pirotechnicznej. Przeprowadzono badania derywatograficzne. Energię aktywacji bezgazowej kompozycji pirotechnicznej wyznaczono doświadczalnie i obliczeniowo. Temperatura zapłonu wynosiła 100 °C. Wartość energii aktywacji kompozycji pirotechnicznej wyniosła 369,39 kJ/mol, co przewyższa energię aktywacji standardowych materiałów wybuchowych stałych i ciekłych 2,4-2,8 razy i czyni ją bardziej stabilną. Zmiany masy kompozycji pirotechnicznej pod wpływem temperatury nie przekraczają 1%.*

Keywords: *activation energy, gasless, pyrotechnic composition, flashpoint*
Słowa kluczowe: *energia aktywacji, bezgazowa, skład pirotechniczny, temperatura zapłonu*

Abbreviations and symbols

E Activation energy [kJ/mol]
t Temperature [°C]
T Absolute temperature [K]
T_R Reciprocal of temperature [1/K]
Y Double logarithm of weight loss
R Molar gas constant [J/(K·mol)]
Δm Mass loss [%]

1. Introduction

Pyrotechnic compositions of various types are essential in sectors of the national economy [1]. Gasless compositions are of particular importance among the varieties of pyrotechnic compositions. Gasless pyrotechnic compositions are those which generate less than 10 cm^3 of gases after the combustion of 1 g of the mixture [2]. It is necessary to select the components for gasless pyrotechnic compositions which can form metal oxides during combustion.

Compositions of this type must be highly flammable and be able to ignite the secondary link of the fire chain without fail. According to [3], zirconium, niobium, manganese, chromium, silicon powders are used as fuel for gasless compositions. Barium and lead chromates are used as an oxidizer for gasless compositions.

The main problem of such pyrotechnic compositions is their limited use. Gasless pyrotechnic compositions are firmly entrenched in the field of delay compositions. Rarely are they used in given heating products, remote-control tubes and fuses, and auxiliary systems in rocket and space technology [3, 4]. Most of the studies of such compositions are aimed only at studying the properties necessary for pyrotechnic delays with a search for improving these very properties [2, 5]. Such properties are delay time, burning rate, and the nature of the chemical reaction. It is necessary to study all the possible properties of gasless pyrotechnic compositions for their applications in new directions of various industries.

This article presents the determination of some parameters of a gasless pyrotechnic composition.

2. Experimental

2.1. Materials

A pyrotechnic composition in sheet form with the following composition of an unknown percentage was investigated: zirconium powder, barium chromate, dinitrocellulose, polyacrylamide and fibreglass.

2.2. Equipment and methods

The aim was to conduct a derivatographic study of the pyrotechnic composition and determine its activation energy, flash point, and changes in mass of the composition upon ignition. Derivatograph Termoscan-2 (Analitpribor, St. Petersburg). The Termoscan-2 combines two systems in one device: a thermal balance and a differential thermal analyzer (DTA). The control of the temperature conditions, data collection and processing is carried out with the help of a specific program Thermoscan:

- temperature range: 20-1000 °C,
- heating rates: 0.5, 1.0, 2.5, 5.0, 7.5, 10 and 20 °C/min,
- temperature determination error: ±1 °C,
- specific thermal conductivity measurement range: 3.6-1200 J/g,
- accuracy of determining the magnitude of thermal effects: 2.2 J/g,
- accuracy of determination of change in sample weight: 0.02 g.

A thermogravimetric analysis of the samples was carried out using the Termoscan-2 in accordance with the requirements of the Broido method, which is used to determine the activation energy of various combustible and polymer systems [6, 7]. The essence of Broido's method is to determine the activation energy due to the dependence of the double logarithm of mass loss with the reciprocal of temperature. The study took place under the following conditions:

- laboratory room temperature: 21°C,
- relative humidity: 65%,
- sample weight: 200 mg,
- heating rate: 5 °C/min,
- analysis environment: normal (air),
- chart recording time: 96 min.

Heating was carried out from 20 to 500 °C.

3. Results and discussion

The resulting thermogram of the pyrotechnic composition in the form of a sheet product is shown in Figure 1. Analyzing the TG and DTA curves allows the following analytical results to be obtained:

– Since the TG curve is straight (except for two peaks with a change of less than 0.1 mg), it can be concluded that the mass of the sample did not change. This means that only metal oxides and soot were formed during the combustion reaction.
– There is a peak on the DTA curve at a temperature of 100 °C. This peak characterizes a sharp change in the phase of the pyrotechnic composition i.e. a flash. Therefore, the flashpoint of this composition is 100 °C.

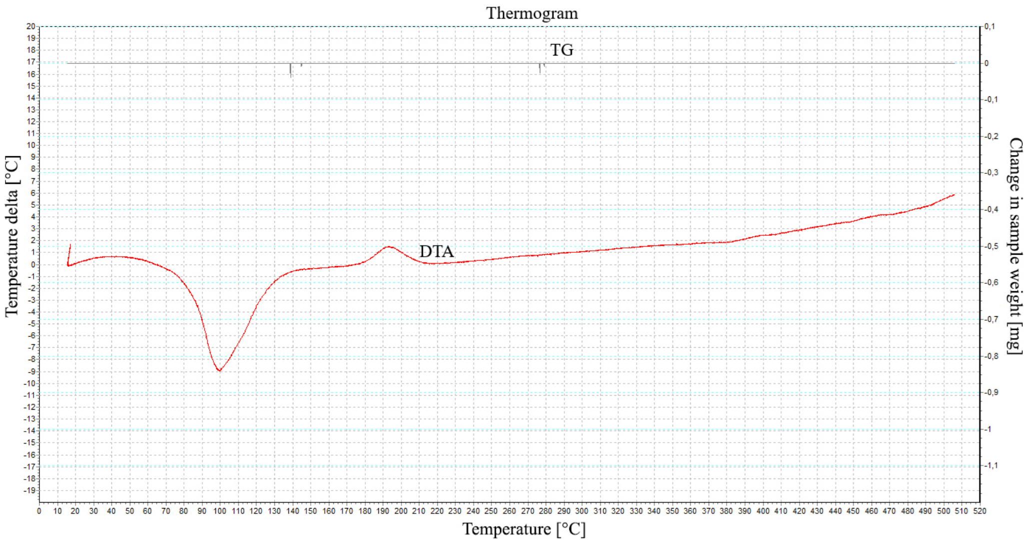

Figure 1. Thermogram of pyrotechnic composition

To obtain an empirical result of the analysis of the TG and DTA curves, the activation energy of the pyrotechnic composition by the Broido method is determined. For this, the value of the double logarithm is calculated, which has the form of Equation 1. The calculated results are listed in Table 1.

$$Y = \ln\left[\ln\frac{100}{100-\Delta m}\right] \tag{1}$$

Based on the data obtained, a graph of the dependence of the double logarithm on the value of the reverse heating temperature of the pyrotechnic composition is drawn. This graph is shown in Figure 2.

Table 1. Calculation of the values of the double logarithm of weight loss according to the obtained thermogram, in a stable area

t [°C]	T [K]	$T_R = 1000/T$ [1/K]	Δm [%]	$100 - \Delta m$	$Y = \ln\left[\ln\frac{100}{100-\Delta m}\right]$
230	503	1.988	0	100	0
240	513	1.949	0	100	0
250	523	1.912	0.05	99.95	–7.6
260	533	1.876	0.05	99.95	–7.6
270	543	1.842	0.1	99.9	–6.9
280	553	1.808	0.1	99.9	–6.9

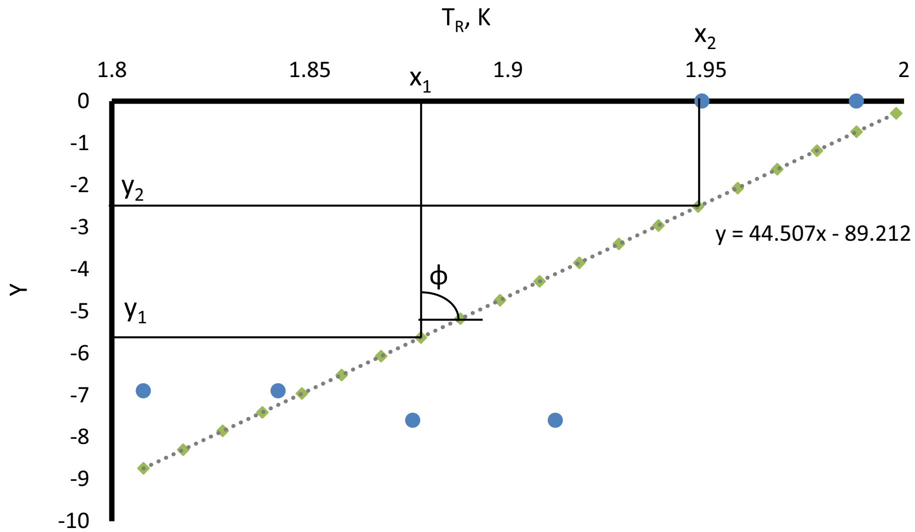

Figure 2. Graph of the dependence of the double logarithm on the reciprocal of temperature of the pyrotechnic composition

For the selected area, tgφ is calculated:

$$tg\,\varphi = \frac{y_2 - y_1}{x_2 - x_1} \tag{2}$$

$$tg\,\varphi = \frac{-2.96-(-6.07)}{1.938-1.868} = 44.43 \tag{2a}$$

The activation energy (E), kJ/mol, was calculated by the formula:

$$E = R \cdot \mathrm{tg}\varphi \tag{3}$$

The value of the activation energy E:

$$E = 8.314 \cdot 44.43 = 369.39 \text{ kJ/mol} \tag{3a}$$

The activation energies of solid and liquid standard explosives at atmospheric pressure (for example, PETN, nitroglycerine, ethyl nitrate, etc.) range from 130 to 154.6 kJ/mol [8]. Thus, the value of the activation energy of the investigated pyrotechnic composition exceeds the activation energy of standard solid and liquid explosives by 2.4-2.8 times. It means that the composition is more stable under normal conditions than these explosives.

4. Conclusions

- Thermo-analytical studies of a gasless pyrotechnic composition have been carried out. The flashpoint has been determined. The activation energy of a gasless pyrotechnic composition has been determined experimentally and by calculation.
- The value of the activation energy of the investigated composition exceeds the activation energy of standard solid and liquid explosives by 2.4-2.8 times. The change in mass of the composition does not exceed 1%, which indicates an insignificant amount of gas being released during combustion.
- The results obtained can help find alternative ways of using gasless pyrotechnic compositions and will serve as a basis for their further detailed study.

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