REVIEW

of official reviewer, Cand. of Chem. Sc., Vongai Igor Mikhailovich for the PhD thesis of Yelemessova Zhanerke Komekovna on the topic: «New nano metal-organic framework energetic materials for pyrotechnics», submitted for the degree of Doctor of Philosophy (PhD) in specialty 6D073400 – «Chemical technology of explosives and pyrotechnics»

1. The relevance of the research topic and its connection with general scientific and national programs.

Energy-intensive materials are widely used in modern industry and technology. They are individual substances and mixtures capable of reacting in the mode of combustion and detonation. While combustion and detonation processes were studied sufficiently for individual energy-intensive materials, then for mixed systems it is of particular interest to study the effect on the combustion macrokinetics of the pyrotechnic compositions of additives, including catalytic ones. Typically, pyrotechnic compositions, especially those based on magnesium, aluminum or alloy powders, have a certain reaction energy and a relatively small range of regulation of macrokinetic parameters with a significant change in the ratio of fuel and oxidizing agent. The introduction of ballasting components leads to a decrease in the stability of combustion parameters and a change in energy indicators, which reduces the prospects of such compositions for use in obtaining one or another pyrotechnic effect.

An important aspect of this work is the study of promising carbon raw materials in pyrotechnic compositions. Usually, for these purposes, for example, in the manufacture of smoke powder, soft wood species-based charcoal is used: alder, buckthorn, etc. Domestic bio resources do not have an industrial base of these plant species, and due to climatic features, replenishment of such raw materials during industrial production will be impossible. Thus, the use of plant waste for the manufacture of the carbon component of pyrotechnic compositions, especially containing an immobilized component that regulates combustion processes, solves a number of environmental and economic problems of the pyrotechnic industry.

Porous carbon materials that have a high porous crystalline structure, high specific surface area and the ability to control physicochemical properties by incorporating various metal centers into their structure are promising technological additives that improve the combustion process of fuels. However, manufacturing methods for such materials are still an expensive and complex multi-stage process. In this aspect, the dissertation work includes the current topic - research to development a metal-organic structures with the use of rice husk, which is a waste of renewable vegetable raw materials. The final result of the thesis is the developed method for creating metal-organic structures with inclusions of various nanoparticles of metal oxides and their application to improve the important characteristics of the combustion process of pyrotechnic compositions, which also emphasizes the importance of the research in the applied aspect.

2. Scientific results and their relevance.

The following results in the frame of the thesis were obtained:

1. New metal-organic framework composites based on rice husk (renewable raw material) were obtained;
2. It was revealed that the addition of activated carbons into reaction mixture effectively initiates the thermal decomposition of ammonium nitrate and reduces the initial temperature of substance decomposition;
3. The influence of the activated carbon concentration on linear burning rate of ammonium nitrate at various values of initial pressure (1 to 3.5 MPa) was found;
4. The possibilities of initiating the combustion process of a pyrotechnic composition by laser ignition with the addition of a metal-organic frame structure (MOF) were investigated;
5. The influence of the metal-organic framework structure (MOF) on the activation energy of the pyrotechnic composition AN/Mg/NC was determined.

3. Degree of validity and reliability of each scientific result (scientific statement) and conclusions of the applicant formulated in the thesis.

The research results and conclusion are clearly described to achieve the main goal of the thesis. The reliability of obtained results is beyond any doubt due to competent choice of modern methods.

The research results were presented in 12 publications. 2 articles in the Scopus journals and 1 article in the Thomson Reuters journal. 4 papers were published in journals recommended by Committee for the Control of Education and Science of Ministry of Education and Science of the Republic of Kazakhstan. 4 abstracts in the Proceedings of International Conferences. 1 utility model patent № 2019/0488.2 «Carbon-containing metal-oxide fuel» was received.

4. The degree of novelty of each scientific result (scientific idea), conclusion of author that were obtained in this thesis.

Result 1 is new, on the basis of rice husk and transition metal oxides, a hybrid combustion catalyst for pyrotechnic compositions, which is a metal-organic framework composite, was obtained.

Result 2 is new, it was found that under the influence of a metal-organic framework structure (CRH-CuO), the decomposition of the AN/Mg/NC mixture passes from a III-stage to a II-stage one, which leads to an increase in heat dissipation from 1.2 to 7.2 mW and lowering the initial decomposition temperature from 276 to 209°C.

Result 3 is new, conditions for increasing the linear burning rate of the AN/Mg/NC pyrotechnic composition using CRH and CRH-CuO additives were found. At an initial overpressure in the system of 3.5 MPa, the burning rate of the pyrotechnic composition in the presence of pure CRH increased to r_b=17.53 mm/s^{-1} and CRH-CuO to r_b = 20.46 mm/s^{-1}.

Result 4 is new, it was established that the metal-organic framework structure (CRH-CuO) can significantly reduce the limit for laser ignition of the AN/Mg/NC pyrotechnic composition ignition. The pyrotechnic AN/Mg/NC/CRH-CuO composition stably ignites at a low laser energy ≥ 4.35 J, with an ignition delay of 506 ms.

5. Practical and theoretical significance of scientific results.

Practical significance lies in the development of compositions with a high specific surface area and a developed topographic structure based on plant waste with addition of nanosized transition metal oxides, which are promising materials for use in practice as catalytic additives in energy materials.

The theoretical significance of the work is to establish the basic laws of the influence of transition metal oxides and activated carbon on the characteristics of thermal decomposition and combustion of ammonium nitrate. The results can be used both in basic and in applied research related to the development of energy materials.

6. Comments, suggestions on the thesis.

1. Studies of the influence of the developed metal-organic framework structures on the combustion characteristics were carried out using only one pyrotechnic composition. The use of other combinations of pyrotechnic compositions would make it possible to carry out comparative characteristics and expand the field of scientific results.

2. There are minor stylistic errors in the work that do not change the scientific data and the integrity of the work presented.

The results of this work can be the basis for a deeper (especially in the postdoctoral level) research of the effect of MOF components on the macrokinetic characteristics of the combustion processes of complex pyrotechnic systems, but this is beyond the scope of the present work.

However, the above-mentioned shortcomings are not fundamental and do not reduce the scientific and practical significance of the dissertation results.

7. Compliance with the content of the thesis within the requirements of Rules for awarding academic degrees.

The dissertation work on the topic: **«New nano metal-organic framework energetic materials for pyrotechnics»** was performed at the appropriate scientific and technical level. In accordance with the relevance of the tasks to be solved, the novelty of the obtained results and their practical significance corresponds to the requirements of the «Rules for the awarding of degrees» of Committee for the Control of Education and Science of Ministry of Education and Science of the Republic of Kazakhstan (CCES MES of RK). The presented work for the PhD degree in the content of the dissertation fully meets the requirements of CCES MES of RK, and its author, **Yelemessova Zhanerke Komekovna**, deserves the PhD degree in the specialty 6D073400 – «Chemical technology of explosives and pyrotechnics».

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