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PHYSICO-CHEMICAL STUDY OF THE SYSTEMS ON THE BASIS OF SODIUM AND AMMONIUM PERCHLORATE

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Interaction of anhydrous bicomponent systems of $NaClO_4$ $CO(NH_2)_2$, NH_4NO_3; NH_4ClO_4-NH_4NO_3 – ingredients of alternative fuels has been studied by the methods of visual-polythermal analysis and differential-scanning calorimetry.

Nowadays consumption of conventional fuels of oil origin in industrial infrastructure is significant and amounts the order of 80 % of its production. Intensive use of oil hydrocarbons connected with rapid growth of transport and other technology, exhaustion of product stock, opportunities of its resources conservation (for production of lubricants, synthetic materials, aromatic compounds, artificial proteins etc.) poses the urgent problem of replacing fuels of oil origin by renewable sources of alternative energy [1].

Combustion of air-fuel mixture in the cylinder of internal-combustion engine under the condition of high temperature with local or general lack of oxidizing agent results in essential environmental contamination by toxic substances and soot. In large cities and industrial centres nearly 40...60 % of atmosphere contamination falls on transport only. Man-caused CO_2 is one of the factors («green-house» effect) of coming global warming.

Whether sources of hydrocarbons will be used or not depends among other factors on the developments in the branch of alternative engineering, primarily on decrease in «carbonic» proportion of man-caused emissions, i. e. how successful the problem of «environmental friendly» low-toxic fuel on *non-carbonic* base will be solved. Complexity of this problem consists in its contradiction, undesirable correlation between toxicity and efficiency of existing air-heat engines: with increase in efficiency, harmfulness of exhaust gas (EG) by emission of the most toxic substance – nitric oxides grows as a rule (though not always). It is explained by the fact that the highest performance of air internal-combustion engine cycle is achieved in combustion of *lean* mixtures with the excess of air up to 1,5...2,0 – beyond the stoichiometric number (for example, in diesels). Mass part of air in composition of fuel-air mixture amounts more than 90...95 %, but main components of air are nitrogen (77 wt. %) and oxygen (23 wt. %), initial components of oxides NO_x formed at high temperature in combustion chamber.

Besides, natural hydrocarbons contain organic sulphur- and nitrogen containing compounds, at oxidation (combustion) of which oxygen carbon, nitrogen, and sulphur oxides are released in air, being ecologically harmful.

The latest researches have shown that a number of multicomponent physical-chemical systems of «fuel + oxidant» type with the elements of organic and inorganic compounds are capable of exothermic interaction (without air access), liberating significant quantity of chemically inactive gases (working medium) capable of effective expansion work. In the course of searching for the solution of the problem the analysis of promising fuel hydrogen-carriers on the basis of hydrogen-nitrogen-oxygen compounds and so on has been performed. As a common oxidant of monofuels ammonium NH_4NO_3, forming fusible and highly-soluble eutectic molecular-homogenized systems with some fuels of amine origin, with carbamide, in particular, is the most promising fuel [2, 3].

Perchlorates are known to be stronger oxidants than nitrates (saltpetre). They find application in solid propellants as components of gas-generating compositions, chemical sources of oxygen and water-filled explosives. At the same time the disadvantage of perchlorates as fuel oxidants is formation of fixed residue (NaCl) and possible chlorine compounds (HCl). Perchlorate energy-rich systems can be used as pyrotechnic accumulators of high gas pressure in some technological cycles (without compressor), for production of pressure and water-spraying in fire-fighting, blast industry, for creation of oxidizing and reducing gas environment, including that with high temperature, as oxidants in chemical industry and oxidants of solid fuel for hydrojet propulsion of some underwater vehicles.

The most common perchlorates are sodium and ammonium perchlorates. They can be referred to renewable oxidizing agents, since sodium perchlorate $NaClO_4$ is obtained by electric synthesis of common salt solutions NaCl, but in decomposition of sodium perchlorate chlorite NaCl forms again. If electric energy of ecologically-clean sources (wind, waves, sun) or even atomic energy are used in electric synthesis, sodium perchlorate can be considered as a suitable way of storing fuel oxygen (52 % in mass from $NaClO_4$).

Fusible systems of cosoluble fuels and oxidants are of great interest as process fuels, they are also suitable for civil application. Blast-fire risk of oxidant-containing systems sharply decreases in presence of water-solvent. Burning of solution-filled perchlorate system is known to be possible only at rather high pressure (at conventional temperature of charges T~300 °K even in the presence of explosive fuel [4].

In the course of searching for the ways of solution for the problem posed (finding of components and mixtures as ingredients of alternative fuel) the analysis of some potential systems has been carried out, their physical-chemical properties has been studied, heterogeneous equilibriums of some actual two-component systems has been investigated (table 1).

Table 1. *Components characteristics*

Component	Purity	$T_{sq.}$, °C	T, °K	Source of information
NH_4NO_3	Ch.p.	169,6	442,6	[5]
$CO(NH_2)_2$	P.ch.p.	132,7	405,7	[6]
NH_4ClO_4	Ch.p.	240	513	[7]
$NaClO_4$	P.	469	742	[8]

$NaClO_4$-$CO(NH_2)_2$ system is of practical interest as an oxidizing phase of atmosphere-free fuel, in which combustible component is non-deficient carbamide. The data on the system involved are absent in the available literature. In spite of this fact, the system is potential. The experiment has been made by the method of visual-polythermal analysis (VPA) [9], the essence of which consists in determination of melting temperature (crystallization), visual observation of temperature of appearing the first crystals release at slow cooling (heating) and vigorous agitation of alloy before obtaining the reproduced results. Registration of temperature is made by means of thermometer with temperature range from 0 to +500 °C and accuracy to 1 °C.

On the basis of the data obtained the diagram of dependence on system composition has been constructed (fig. 1).

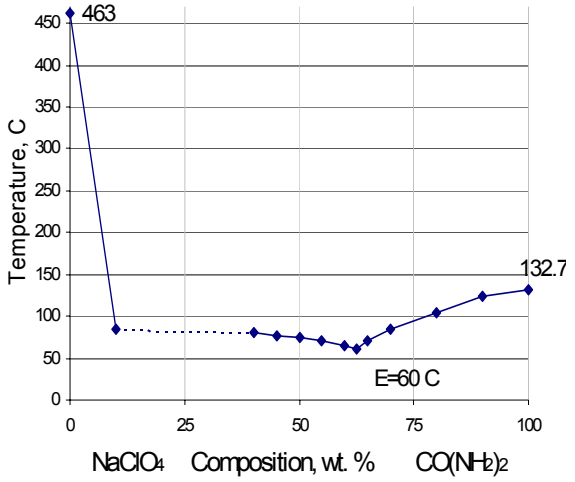

Fig. 1. *Diagram sodium perchlorate-carbamide system state*

In presence of additional oxidants: ammonia nitrates, metals or other perchlorates the melting point of multicomponent eutectic mixture decreases additionally. Depending on the excess of oxidants or fuels, products-gases have oxidation or reduction character.

In products of burning or explosive reaction with combustibles formation of condensation phase of NaCl from sodium perchlorate does not exceed 48 %, according to the decomposition equation of sodium perchlorate:

$$NaClO_4=NaCl+2O_2$$

For the sodium perchlorate-carbamide system the composition and eutectic temperature have been experimentally determined and the eutectic temperature – melting temperature corresponds to 60 °C – composition is 62,5 % of carbamide. The diagram of state is constructed for the first time.

Construction of the diagram of NH_4ClO_4-NH_4NO_3 system state is also of great interest for fusible energy-saturated systems. The data on this system have not been found in the literature available.

In the course of experimental investigation (fig. 2), single experiments were carried out on the DSK-500 device by the VPA method [10, 11]. The average mass of weighted portion was 0,02 g. The rate of heating was 4 °C/min. The curve of system heating in the range of temperatures from 20 to 200 °C of eutectic composition 90 % NH_4NO_3 – 10 % NH_4ClO_4 (wt. %) is presented in fig. 3.

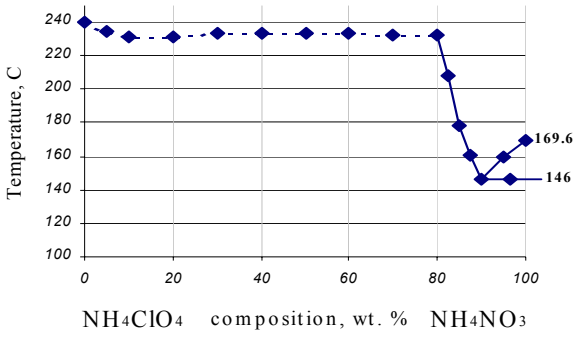

Fig. 2. *Diagram of ammonia perchlorate-ammonia nitrate system state*

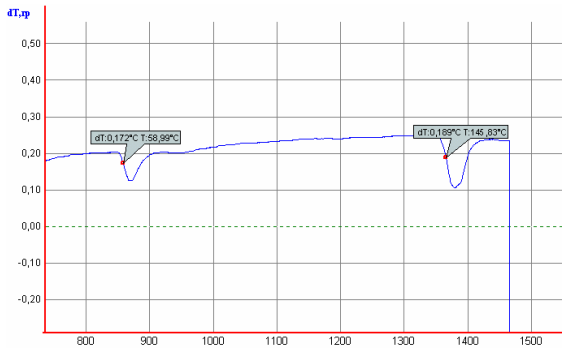

Fig. 3. *Heating curve of NH_4NO_3 – NH_4ClO_4 system of eutectic composition*

The temperature of system eutectics is 146 °C. The heating effect at T=59 °C presented in fig. 3 is, presumably, polymorphous transition of NH_4NO_3.

During the experiment it was stated that at concentration of NH_4ClO_4 in the system beginning from 20 to 90 wt. % foaming is observed. It indicates the redox reaction.

From eutectic mixture of NH_4NO_3/NH_4ClO_4 90/10 in products of burning or explosive reaction with combustibles formation of condensing phase (in contrast to decomposition products of NH_4ClO_4) is absent, but about 3,6 % of hydrogen chloride of the initial eutectics mass is isolated, according to the equation of complete decomposition of ammonium perchlorate:

$$NH_4ClO_4=1/2N_2+3/2H_2O+5/4O_2+HCl$$

The system of ammonium nitrate-ammonium perchlorate has been studied for the first time. The given system is referred to oxidation one. Eutectics is observed at T=146 °C and 10 wt. % of ammonium perchlorate.

NH_4NO_3-$NaClO_4$ system is of interest as a system of rather highly soluble salts forming oxidation gases when

heating, where the main component is common ammonia nitrate. The data on the NH_4NO_3-$NaClO_4$ system have not been found in the literature available.

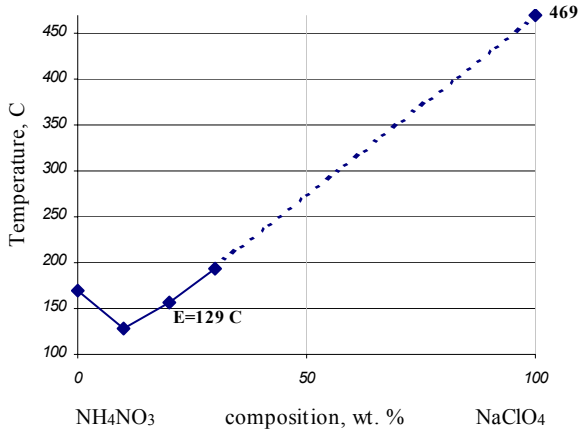

Fig. 4. *Diagram of ammonia nitrate-sodium perchlorate system state*

The experiment was performed by the VPA method. In the course of investigation rich foaming was observed in the range from 30 to 99 wt. % of $NaClO_4$ that indicates the redox reaction. The mixture involved had eutectics of 10 % $NaClO_4$ at melting point 129 °C (fig. 4). The mass of fixed residue (NaCl) did not exceed 5 % of alloy mass of oxidizing salts.

As further investigation show, introduction of fuel-carbamide into the double system of oxidizing salts of NH_4NO_3-$NaClO_4$ to stoichiometric number ~25 % decreases the melting point of triple system lower than 100 °C. However, the alloy formed possesses high hygroscopic property and at usual pressure 1 atm. is not fired even using the catalysts found, the presence of which provides combustion of double alloy of NH_4NO_3/carbamide 80/20.

Thus, the offered different perchlorate compositions can be used as energy-carriers and gas generators in various engineering branches, including solutions of renewable (non-hydrocarbon) power engineering. Physical-chemical research of compositions of large measure (three and more) gives the background for transition in new technological level in development of energy-saturated materials with the complex of specified properties.

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