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FORMATION PROCESSES OF THE CATALYTIC SURFACES STRUCTURES

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ABSTRACT

The structure formation processes of primary (metallic) and secondary (ceramic and glass-crystalline) catalyst carriers used for the conversion of exhaust gases of internal combustion engines are considered. X-ray diffraction analysis, scanning electron microscopy and atomic-force microscopy are used for the study of the formation of a new catalyst carrier surface, the physicochemical features and morphology of that are critical for the final efficiency of catalytic coatings in waste gas purification processes. The features of surface formation of secondary identify the variation in their qualitative and quantitative composition determine the change in their physico-chemical properties and as a consequence the structure and catalytic activity.

Key words: catalyst, exhaust gases cleaning, coating, catalyst carrier, surface, carrier structure.

INTRODUCTION

Internal combustion engines, waste processing facilities and heat power plants exert considerable environmental pressure on the environment [1]. A well-known and well-proven method for the purification of exhaust gases from carbon monoxide, nitrogen oxides and products of incomplete combustion of hydrocarbons is catalytic purification [2]. Thermomechanical operational characteristics of catalysts along with their catalytic activity are important indicators that determine not only the efficiency, but also the life of the catalyst [3, 4]. The present work is devoted to the morphological features of primary and secondary catalyst carriers that arise during their thermochemical formation and have a key effect on the resulting catalytic activity, mechanical strength and thermochemical stable catalytic coating both on metals and ceramics.

MATERIALS AND METHODS

The primary metallic carrier, the morphology of its surface.

The primary metallic carrier is a nichrome foil of the NiCr80/20 alloy whose atomic-force microscopy of the surface is shown in Fig. 1.

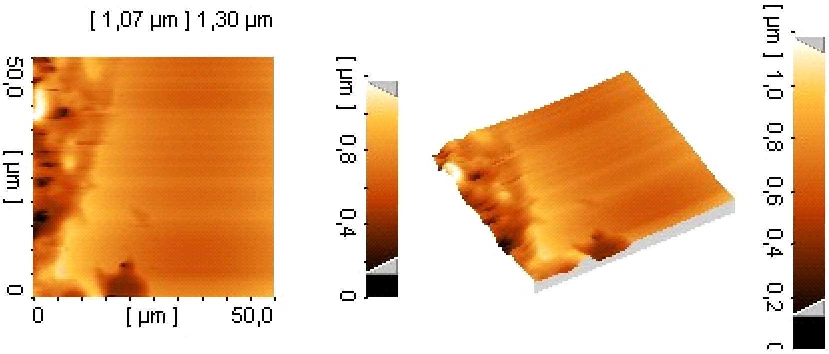


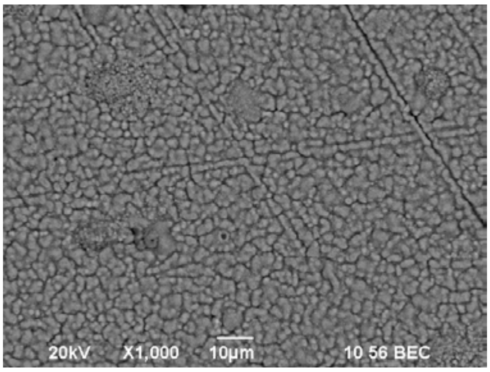
Fig. 1. Microrelief of the primary carrier surface, atomic force microscopy.

The surface of the foil of NiCr80/20 alloy is characterized by deformation traces in the form of uniform bands left by irregularities of the working surfaces of the devices forming the foil. However, in this case there are places with abnormal defects on the surface, which have their development in the thickness of the foil.

RESULTS AND DISCUSSION

Secondary glass crystalline carrier, morphology of its surface. The primary metal carrier acts as a carrier for the secondary coating that is a glass-crystalline or ceramic layer. In accordance with the methods proposed by us [5, 6] a layer of the secondary carrier is formed on the surface of the primary pre-prepared and unprepared carrier. In the process of preliminary preparation that is chemical etching in acid solutions followed by thermal oxidation of the surface, the chemical composition and surface structure of the primary carrier undergo significant changes (Fig. 2).

The primary metal carrier acts as a carrier for the secondary coating that is a glass-crystalline or ceramic layer. In accordance with the methods proposed by us [5, 6] a layer of the secondary carrier is formed on the surface of the primary pre-prepared and unprepared carrier. In the process of preliminary preparation, which is chemical etching in acid solutions followed by thermal oxidation of the surface, the chemical composition and surface structure of the primary carrier undergo significant changes (Fig. 2).



a) b)

Fig. 2. Thermo-oxidized surface of nichrome foil: a) increase 500 times, b) increase 1000 times. Scanning electron microscopy.

As can seen from Fig. 2 the primary carrier acquires an additional surface in the process of pretreatment due to a change in its chemical composition (the surface is a system of chromium and nickel oxides whose molar volume exceeds the molar volume of the parent metals). Nevertheless the dimensions of newly formed structures are not large enough and the features of the microrelief of the initial metal surface are clearly traced on their background.

Further on a layer of a secondary glass crystalline carrier [5, 6] is formed on the previously prepared and untreated surfaces, which is based on a system of silicon, boron and aluminum oxides as basic, as well as potassium, calcium, magnesium, barium, cobalt, nickel, manganese and copper as auxiliary.

The results of a study of the morphology of the layers of synthesized secondary carriers are shown in Fig. 3.

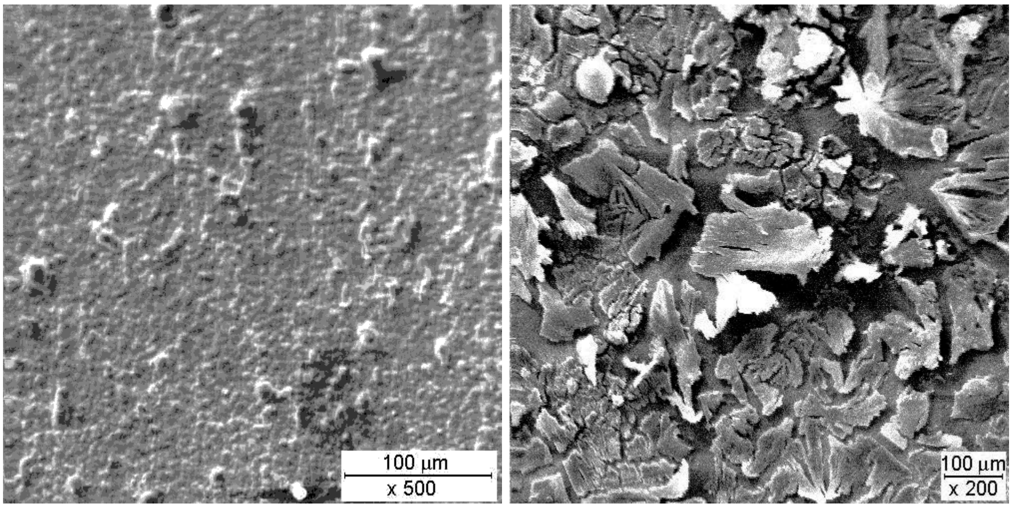


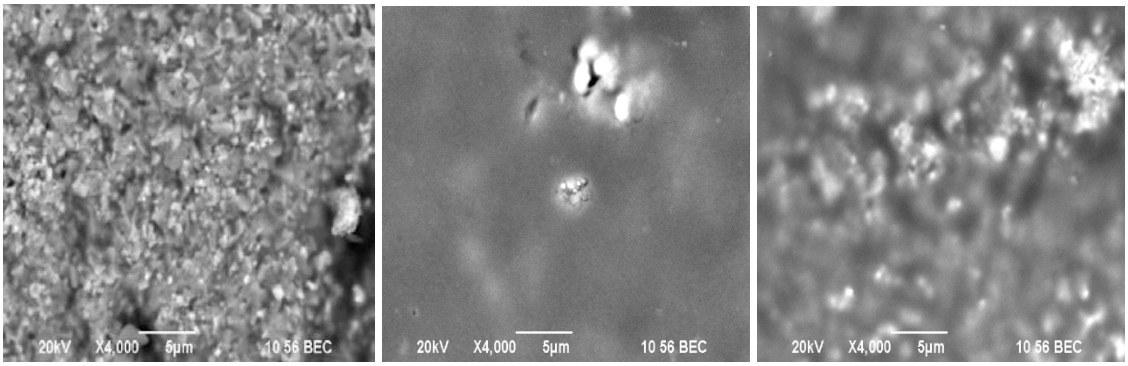
Fig. 3. The morphology of the secondary carrier surface on the prepared surface (a) and unprepared (b) surface. Scanning electron microscopy.

The application of secondary carriers in a film form to an unprepared pre-metallic surface leads to their peeling (Fig. 3b) due to the different chemical nature of the secondary carrier and substrate. The film coatings obtained in this case are characterized by a considerable number of defects and detachments from the primary carrier. Such coatings cannot be used to manufacture catalytic converters of internal combustion engines, since such coatings are easily separated from the carrier even under the influence of weak gas flows.

In the case of the use of the preliminary treatment of the surface of the primary carrier for the purpose of its thermal oxidation, the layer of the secondary carrier is a mechanically strong, resistant to reusable film (Fig. 3a).

Control of secondary glass silicon crystalline carriers' structure

In accordance with the method we propose borocrystalline coatings doped with nickel (Fig. 4a), cobalt (Fig. 4b), and manganese (Fig. 4c) have been synthesized.



a) b) c)

Fig. 4. Borocrystalline coatings containing nickel (a), cobalt (b) and manganese (c). Scanning electron microscopy.

It can be seen from Fig. 4b that the Co-containing coating has a continuous structure and completely covers the carrier of the NiCrA alloy foil. A characteristic feature of the coating in Fig. 4b is the absence of granulation of the surface substance, which presupposes the presence of a significant amount of the vitreous component in its composition and the practically complete absence of the crystalline component. But in accordance with the results of X-ray diffraction analysis, Co-containing borocrystalline coating has in its composition a significant amount of the crystalline phase represented by various cobalt oxides. The resulting contradiction can be explained by the formation of nanoscale particles of these oxides and their high wettability around the glassy component.

The Ni-containing coating (Fig. 4a) is characterized by the absence of large-scale morphological formations, such as canals, caverns and elevations. The predominant surface structure of this coating is a fine-grained component that covers the entire surface of the carrier. The morphology of the Ni-containing coating allows us to assume a significant amount of the crystalline phase in its composition, which is confirmed by the results of X-ray diffraction analysis, indicating a significant amount of nickel oxide.

The Mn-containing coating (Fig. 4c) occupies an intermediate position between Ni- and Co-containing in its morphology. On the one hand, the Mn-containing coating exhibits continuity and the absence of a fine-grained structure, like a cobalt coating. On the other hand, the Mn-containing coating has a “protogranularity” - the presence of half-soluble microstructures, the surface and edges of which are well moistened with the surrounding vitreous phase, but having an explicit morphological expression with respect to the surrounding vitreous phase. The structures described are represented by light formations in Fig. 4c. X-ray diffraction analysis of the Mn-containing coating indicates the presence of a crystalline phase in its composition.

CONCLUSION

The received data on surfaces structure change of primary and secondary carriers of catalytic coatings under the influence of physical and chemical agents allow revealing the mechanism of formation and developing principles of management of the specified surfaces morphology. The results of the study allow to conclude an importance of the metal carrier pretreatment in order to increase its adhesion properties with respect to the secondary carrier. Secondary carriers in this case show the greatest mechanical strength and thermal stability. The qualitative and quantitative composition of the secondary carrier determines its structure, the ratio of the vitreous and crystalline phases in it that are a necessary condition for the high activity of the catalytic coatings formed on them.

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IRSTI 669

STUDYING THE OPTIMIZATION OF ENVIRONMENTALLY SAFE METALLURGICAL WASTE UTILIZATION TECHNOLOGY

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ABSTRACT

The article presents data on the impact of the residual content of the heavy and non-ferrous metals containing in waste metallurgical slag on the environment and human health. Methods of physicochemical analysis allowed us to determine thermal effects during heating of waste slags, as well as features of their mineralogical structure and elemental composition. To reduce the number of experiments, the rotatable experiment planning design was used. The process' temperature and duration were chosen as independent factors. The processing of experimental data for the parameters of mathematical planning was performed using a special computer program based on the MsExcel system used in the MsWindowsXP system environment. The analysis of three-dimensional dependences of the nickel extraction degree – slag and calcium chloride content showed that the maximum extraction degree (above 94%) can be achieved with 90% of slag and up to 10% of calcium chloride. The results of mathematical planning made it possible to reduce the number of experiments and determine the technological parameters of the process of extracting associated non-ferrous and refractory metals.

Key words: waste slag, chlorination, sublimation, utilization, optimization, mathematical planning, safe technology, refractory clay.

INTRODUCTION

The city of Shymkent is a territory of powerful technogenic impact. Soils around the city, which are contaminated with lead, zinc, arsenic and chromium at the concentrations up to 10 times more than the respective maximum allowable concentrations, are of primary concern. This phenomenon affects large areas and, in particular, areas intended for the cultivation of vegetable crops [1].

Any waste products can be considered as secondary material resource, since they can be used for production purposes, either partially (i.e. as an additive), or completely replacing traditional types of raw materials. In terms of their physical and chemical properties, slags are very close to igneous rocks, which are used for the production of building materials. At modern metallurgical plants, blast-furnace slag is practically not stored, but it is immediately processed into semi-finished products for their further processing. At the same time, slags are not placed in landfills, but are immediately used in construction. Thus, the harmful effect of slag on the ecology of adjacent territories is completely excluded [2].

The residual content of metals in slags has the ability to be transferred through food chains, accumulating in the tissues of plants, animals and humans. Lead dust settles on the soil surface, is adsorbed with organic substances, moves along the profile with soil solutions, but it is removed from the soil profile in small amounts. Due to the processes of migration in acidic conditions, technogenic lead anomalies are formed in soils with a length of 100 m. Lead from the soils enters plants and accumulates in them. Lead content in wheat and barley grains is 5-8 times higher than the background content, in the tops of potatoes – more than 20 times, in potato tubers – more than 26 times.

It should be noted that the toxicity of heavy metals increases with their combined effect on living organisms in the soil. The combined zinc and cadmium effect has several times stronger inhibitory effect on microorganisms than the same concentration of each element separately. The penetration of heavy metals into the food chain is an important public health problem [3].

In terms of natural resource conservation, environmental protection and human health safety, slag recycling has attracted the attention of scientists, environmentalists and politicians in recent years. Increasing the use of slags in various industries such as agriculture is a must for sustainable development.

Lead pollution of the environment is a global problem, as evidenced by the rising lead concentration in the blood of people living in polluted areas.

Lead is one of the most common heavy metals, and its toxicity adversely affect the environment and human health. Depending on its persistence in the contaminated areas and the complexity of the mechanism of biological toxicity, lead is particularly dangerous for children.

An analysis of literary sources showed that the solution of environmental problems in the Turkestan region is closely related to the disposal and processing of lead slags that have a negative impact on the environment. This is especially noticeable on the soils around the range and wetlands of the Badam River. At present, technologies for the processing of lead-containing slag, associated producing valuable components and extraction of useful material from the waste rocks have not been introduced into production [4].

Solid waste contains precious metals and their compounds, which can be used as secondary raw materials. When recycling waste, an economically viable raw material can be obtained [5].

MATERIALS AND METHODS

The following methods of analysis and instruments were used to study the chemical and physicochemical characteristics of waste slags and products of their processing. Chemical compositions of the initial waste metallurgical slag, calcium chloride and refractory clay were determined using complexometric and atomic absorption analysis techniques.

The effect of heat treatment was studied using a Q-1500D derivatograph. The differential thermal analysis is a study of mass loss in the temperature range from 20 to 1500 °C, as well as the interaction mechanisms, phase transformations, melting temperatures in various systems.

The elemental composition and microstructure of the starting materials and the obtained products were analyzed using a JSM-6490LV (JOEL, Japan) scanning electron microscope. The use of an electron microscope makes it possible to study the microstructure and sizes of individual crystals, as well as the elemental and weight composition.

To perform an environmental assessment study on the impact of non-ferrous and heavy metals on the environment, slag samples were taken from a storage of waste slags from lead production at several points. Sample No. 1 was taken from the main mountain at a height of 1-1.5 m. Sample No. 2 was taken from the base of the mountain. Sample No. 3 was taken at a distance of 10 m from the base of the slag mountain near the entrance to the storage.

RESULTS AND DISCUSSION

The results of the differential thermal analysis of the initial waste slag sample are shown in Fig. 1.

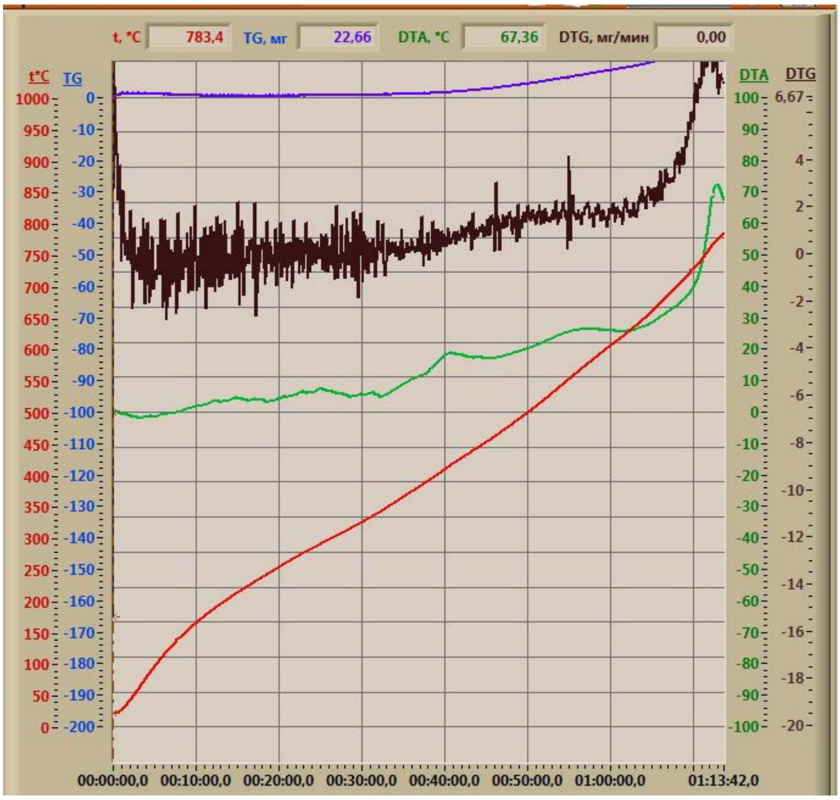
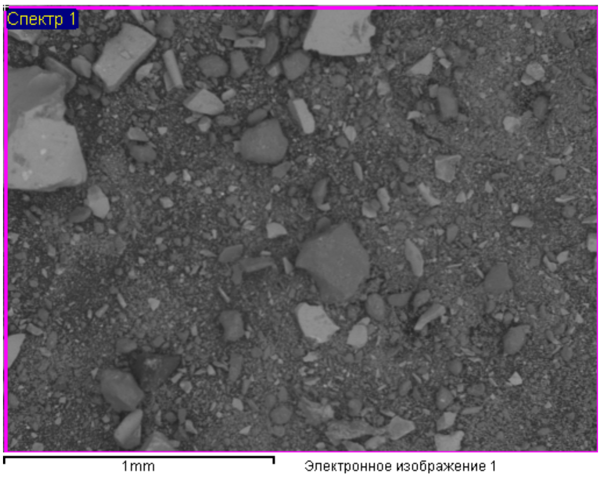


Fig. 1. The results of differential thermal analysis of the test sample

The curve of the slag sample’s differential thermal analysis does not have pronounced endoeffects in the studied temperature range. Week exothermal effects are observed in the region of 300, 400 and 500 ºC, and an intense exothermal effect is observed at 750-780 ºC.

These exo-effects, apparently, are a consequence of the combustion of volatile impurities and sulfur-containing iron compounds.

The analysis showed that the microstructure of the average sample (Figure 2) is characterized by the predominance of iron-bearing minerals. The content of fayalite and calcium ferrite crystals is about 55-60%.



Element	Mass %
O	46.74
Na	0.96
Mg	1.77
Al	5.26
Si	17.51
S	0.41
Pb	1.62
Ca	10.15
Ni	0.45
Fe	12.83
Cu	1.07
Zn	1.24
Total	100.00

Fig. 2. The microstructure of the waste slag sample

The general structure of the test sample includes also aluminosilicate components in the form of light gray irregular-shape lamellar crystals. These aluminosilicate crystals are surrounded by fine rounded crystals of calcium monosilicates and ferrites.

A laboratory studying the process of chlorinating roasting of the waste slag mixed with refractory clay and calcium chloride was carried out on an installation including a horizontal electric furnace.

To reduce the number of experiments, we used a rotatable experiment planning design. To build rotatable central compositional plans, the so-called “star distance” was used. For two factors, the value of the star distance φ is 1.414 (on the coded scale). The process temperature and duration were chosen as independent factors.

Mathematical processing of the experimental results made it possible to determine the coefficients *b* in the regression equation:

$$\alpha_R = b_0 + b_1 \cdot X_1 + b_2 \cdot X_2 + b_{11} \cdot X_1^2 + b_{22} \cdot X_2^2 + b_{12} \cdot X_1 \cdot X_2, \tag{1}$$

where α_R – the calculated value of the output.

The assessment of the regression equation coefficients’ significance was carried out using the Student's criterion. The adequacy of the regression equation was checked using the Fisher’s criterion [6].

As the target output variables, the following were chosen: the Zn and Pb chloride sublimation degrees and the cinder’s physical properties. The independent parameters were the slag, calcium chloride and clay contents. The ranges of the factors are shown in Table 1.

To automate the processing of the results, a special program for a personal computer was developed based on the MsExcel system and used in the MsWindowsXP environment. This program allowed us to perform all the necessary calculations almost instantaneously during the results’ processing and to determine the optimal modes of the process.

Table 1 – Initial data for planning the experiments

Levels and intervals of variation of variables	Coded kind			Natural kind		
	x_1	x_2	x_3	Slag, mass part	Calcium chloride, m.p.	Clay, m.p.
Basic level	0	0	0	85	6	9
Interval of variation	Δ	Δ	Δ	2	2	4
Upper level	+1	+1	+1	86	8	5
Lower level	-1	-1	-1	80	4	9
Upper star distance	+1,682	+1,682	+1,682	83,318	8,182	9
Lower star distance	-1,682	-1,682	-1,682	,318	6,318	3,318

The significance of the equation coefficients was checked using the Student's criterion. The use of the Fisher’s criterion confirmed the adequacy of the resulting equation.

In the coded form, the regression equation looks like:

$$a_{Pb.} = 85,06 + 2,45 \cdot X_1 + 0 \cdot X_2 + 2,55 \cdot X_3 + 1,87 \cdot X_1^2 + 1,81 \cdot X_2^2 + 0 \cdot X_3^2 + 0 \cdot X_1 \cdot X_2 + 0 \cdot X_1 \cdot X_3 + 2,94 \cdot X_2 \cdot X_3 \quad (2)$$

After screening out the independent coefficients according to the Student's criterion, the equation takes the form:

$$\alpha_{Pb.} = 85,06 + 2,45 \cdot X_1 + 2,55 \cdot X_3 + 1,87 \cdot X_1^2 + 1,81 \cdot X_2^2 + 2,94 \cdot X_2 \cdot X_3, \quad (3)$$

For carrying out the chlorinating roasting, a mixture of a certain composition was prepared. The roasting of the dried granules was carried out at 1000 ºC for 60 min.

The results of mathematical modeling of the nickel chloride sublimation degree – the charge composition dependence is shown in Figures 3 and 4.

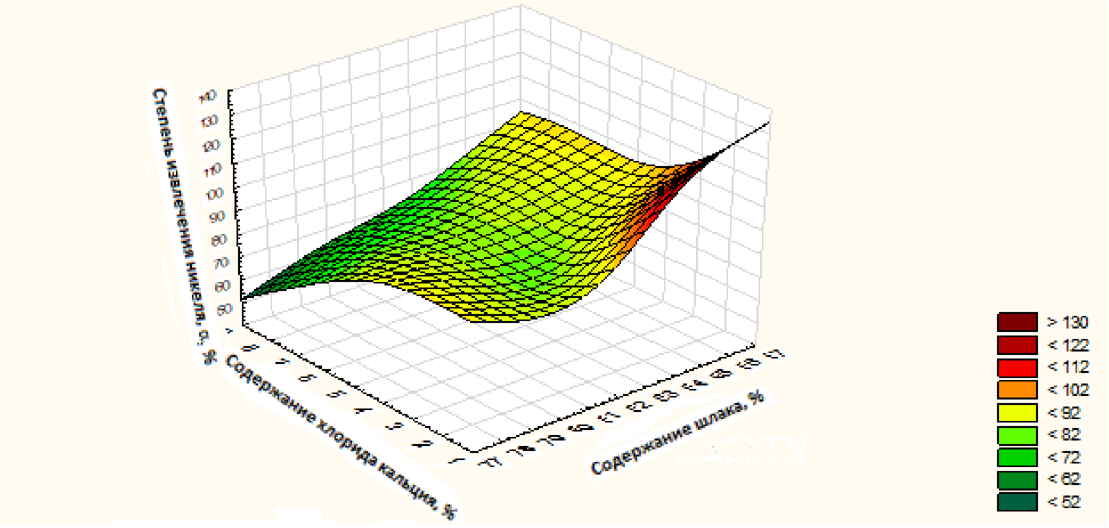


Fig. 3 – Three-dimensional nickel extraction degree – slag and calcium chloride content graph

An analysis of the three-dimensional dependences of the nickel extraction degree on the slag and calcium chloride content in the charge showed that the maximum nickel extraction degree – above 94% – was achieved in a case of 90% of slag and up to 10% of calcium chloride.

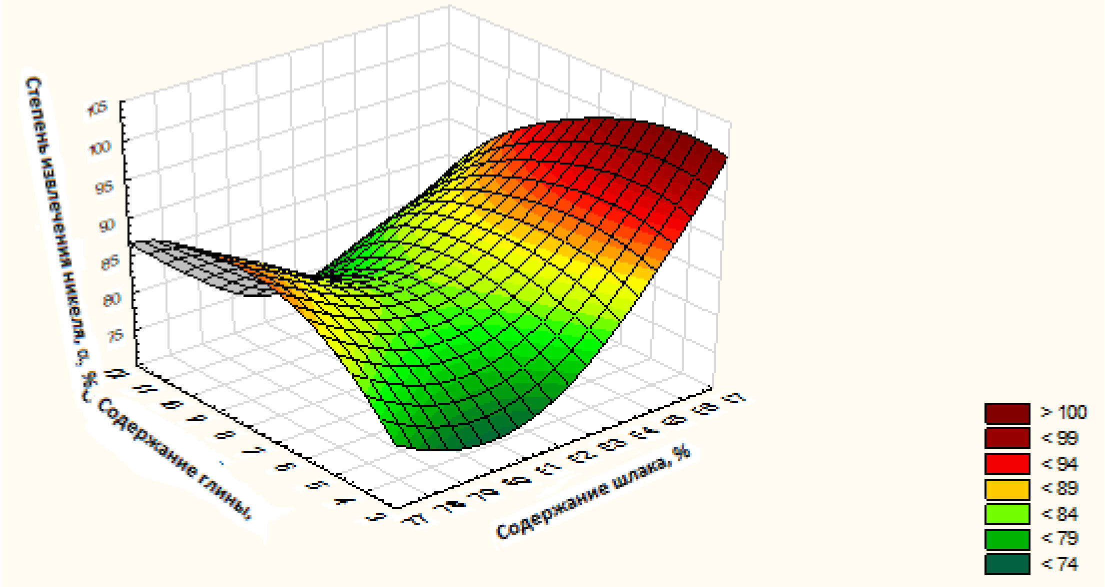


Fig. 4. Three-dimensional nickel extraction degree – slag and clay content graph

The dependence of the nickel extraction degree on the amount of the clay component added to the mixture was determined by the same way. The maximum extraction degree – above 95% – was achieved for the charge containing 87% of slag and up to 12% of clay.

Thus, the obtained results make it possible to reduce the number of experiments and determine the technological parameters of the extracting associated non-ferrous and refractory metals from the waste metallurgical slag.

CONCLUSION

The physicochemical analysis of the initial waste slag showed that its composition is characterized by the predominance of the iron-containing phase: fayalite and calcium monosilicates. The curve of the differential thermal analysis of the slag sample is characterized by insignificant exothermic effects in the temperature range of 400-470 ºC and 870 ºC, which corresponds to the burnout of volatile and sulfur-containing components of the slag.

Mathematical optimization of the chlorination of the nickel contained in the slag along with lead, zinc and copper, checking the significance of the coefficients of the regression equation using the Student's criterion and the adequacy of the resulting equation using the Fisher’s criterion made it possible to establish that the maximum nickel extraction degree (94%) can be achieved if the charge contains 90% of the slag and 10% of calcium chloride.

The experimental and theoretical values of the metals’ extraction degrees, obtained by comparing the values of the Student's coefficient and Fisher's criteria, allowed us to determine the ratios of the components that ensure the maximum extraction of metals into their chlorides.

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DURABILITY PREDICTION OF MACHINE PARTS WITH A HARDENED SURFACE LAYER

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ABSTRACT

The article deals with the issues of improving the methods of surface hardening of machine parts and predicting their durability. During operation, parts are exposed to many different factors. These are external mechanical loads, internal residual stresses, the impact of the environment and the atmosphere. Under these conditions, there is a gradual accumulation of damage in the form of fatigue failure of the surface layer of parts, and sometimes their complete destruction. Sometimes a violation of operating conditions, for example, leading to dry or semi-dry friction in the absence of lubrication, is the cause of increased wear. Thus, the development of methods for increasing the durability of parts, taking into account their operation, is an important area of research. The paper presents the results of applying the methods of chemical-thermal hardening of the surface of steel parts to increase their durability. A technique for evaluating and predicting the durability of parts with coatings based on the principle of damage accumulation has also been developed. Criteria and equations for damage accumulation have been developed for various stages of the life cycle of engineering products.

Keywords: machine parts, surface hardness, wear resistance, durability, damage.

INTRODUCTION

Modern machines consist of many mechanisms and components, the parts of which work in various conditions and experience various loads. Parts that are most susceptible to failure are those operating under conditions of simultaneous exposure to several factors leading to the phenomenon of fatigue. The action of external cyclic loads is simultaneously complicated by friction in mating movable joints. Violation of the surface layer of parts due to wear of rubbing surfaces leads to the formation of microdefects. These defects can manifest themselves as uniform surface wear that exceeds the allowable size. However, more dangerous is the formation of microdefects in the form of pitting and microcracks, leading to a change in the stress-strain state in the surface layer of the part. The concentration of local stresses in these zones, which significantly exceed the rated stresses, leads to the fatigue nature of the destruction of parts. In the study of fatigue, a number of researchers have established the important role of the surface layer of parts, especially its processing quality, hardness and tribological properties. It has been established that damages are mainly formed on the surface of parts, leading to subsequent destruction [1-3]. Therefore, in the process of designing and engineering analysis of new designs of machine parts, it is necessary to have tools, or methods for assessing and predicting the durability of parts, taking into account the features of the technological process of manufacturing parts and their operational features. This technique should also allow one to determine the effectiveness of applying various types of surface hardening and refine their technological regimes (temperature, holding time, composition of the hardened layer and its structure). The improvement of surface hardening technologies makes it possible to harden the surface of parts, to obtain high wear resistance, corrosion resistance and cyclic durability.

Thus, studies aimed at ensuring the specified durability of machine parts, taking into account the above factors, are very relevant. As such studies, the results of the work carried out on the development of methods for predicting the durability of machine parts after chemical-thermal treatment are proposed.

MATERIALS AND METHODS

PURPOSE AND OBJECTIVES OF RESEARCH

The purpose of the study is to develop methods for predicting the durability of machine parts based on the criterion of material damage. The stages of the life cycle of products are considered. At the stage of the manufacturing process, during the application of surface hardening methods, qualitative and quantitative criteria are determined, such as roughness, hardness, toughness, wear resistance and residual stresses. Technological parameters that affect the properties of the base metal of the part, its core, surface layer and their quantitative characteristics are investigated.

For the operation stage, damage accumulation equations are applied, taking into account the characteristics of the hardened layer and external mechanical loading by cyclic stresses. A technique for predicting the durability of products during operation is being developed.

DURABILITY IMPROVEMENT METHODS

As noted in previous articles [4,5-7], surface hardening is achieved using various methods, such as ultrasonic hardening, cementation, cyanidation, carbonitration (carbonitriding), and other methods. The advantage of carbonitriding is an increase in the hardness and wear resistance of the surface layers at relatively low temperatures of the order of 550-6500C, which significantly affects the energy consumption of the process. This is a chemical-thermal treatment for the purpose of diffusion saturation of the surface of steel and cast iron parts with nitrogen and carbon in molten salts with the formation of iron nitrides and alloying elements, as well as carbonitrides having a hexagonal structure with a hardness of 10-12 GPa.

At the same time, nitrogen and carbon have a positive effect on martensitic transformations, which leads to an increase in wear resistance and hardness of the surface layer. A distinctive feature of the process is the ability to provide the original shape of the part, roughness and dimensional accuracy of the product. The positive aspects can also be attributed to the reduction of residual stresses resulting from the mechanical processing of the product. There is also no need for post-finishing. As established in [4–6], surface hardening also leads to an increase in corrosion and fatigue strength by 30–80% [7–11]. Wear resistance increases by 2-8 or more times [7]. It was shown in [8–12] that an increase in the hardness of the surface layer to 2–4.5 GPa significantly reduces the amount of abrasive wear. Carbonitriding has a number of advantages, such as the ability to harden a wide range of steels, cast irons, and other alloys. This method is widely used in serial or mass production of medium-sized products.

Moreover, the physicochemical processes occurring during this type of hardening have been studied in sufficient detail. However, the question of the behavior of hardened parts under operating conditions remains unclear. Classic structural strength calculations ensure the strength and reliability of the base material of the parts. The resistance of materials to various external forces is mainly determined by the properties of the surface layer and the forces of adhesion of this layer to the base metal. The mating parts of friction pairs must have high durability and wear resistance characteristics.

Therefore, technologists strive to obtain the greatest hardness and wear resistance of the surface layer. In this case, the surface layer and the base metal of the core of the part can have different plasticity indices. Under fatigue loading, the initiation of damage to parts mainly occurs in the surface layer. It is known that harder coatings tend to have less ductility. Therefore, the main task becomes the need to provide high hardness of the surface layer while obtaining high ductility to ensure resistance to fatigue loading.

The hardening of industrial batches of parts, such as crankshafts, camshafts, plungers, bushings and mechanism guides, is carried out by carbonitriding. To reduce the cost of electrical energy, the hardening process during carbonitriding occurs at a temperature of 550-6500C. By varying the composition of the pasty carburetor, the temperature and holding time in the carburetor, it is possible to obtain coatings up to 0.01-0.5 mm thick, sometimes up to 1 mm.

To determine the effectiveness of chemical-thermal treatment, the method of measuring hardness is used, as the most accessible and fastest way. In the study of the surface layer of parts made of steels of the 40X type, we used a hardness tester model HBRVU - 187.5, which allows us to measure the hardness according to Brinell, Rockwell and Vickers. For more subtle studies, microhardness testers are used with the ability to determine the hardness of various materials. In this case, the microhardness of carbonitrated layers can be obtained within 6 GPa. According to the results of hardness measurement, the mechanical properties of the surface layer are predicted

RESULTS AND DISCUSSION

Modern methods for calculating the durability of parts make it possible to ensure their performance at the entire stage of the life cycle even at the stage of designing engineering products. For this purpose, it is necessary to consider the details from the standpoint of its behavior in operational conditions. This takes into account the design features of parts, as well as the properties of materials for these parts, such as wear resistance, hardness of the surface layer, resistance to aggressive media, and many others. Fundamentally, the prediction of the durability of machine parts, taking into account their operating conditions, occurs on the basis of already existing methods of engineering calculations. Recently, they often resort to using the "Damage" parameter. Damage or damage is used as a result of the interaction of parts with the surrounding atmosphere, environment, or with another part. Damage to the surface layer occurs due to mechanical wear due to friction forces, due to the impact of a corrosive environment, due to mechanical loading with variable stresses, and many other factors. In order to develop methods for taking into account operating conditions in the calculations of the durability of parts, the following modeling types of the damage accumulation to materials are proposed. In the general case, the model should allow taking into account changes in the mechanical characteristics of the material during the manufacturing process and during the operation of the part.

And the parameter "Damage" can be represented as a quantitative measure of the relative damage to the part. This parameter is denoted by the symbol $\varPi$ and takes values in the range from 0 at the initial moment of time to 1 at the moment of reaching the critical state. Such a phenomenological approach allows us to consider step by step the contribution to the damage of the part of various processes occurring simultaneously. The parts in question are subjected to joint loading by contact friction stresses and external loads during operation. External forces can be both static and cyclic. Under cyclic loads, approaches describing the fatigue process of materials are known. For the general case, you can apply the theory of damage to the material of the part. Then the damage equation in general form can be represented as:

$$\varPi = \varPi_W + \varPi_S + \varPi_C \tag{1}$$

where Π is the total damage, $\varPi_W$ - damage to the part due to wear of the hardened layer, $\varPi_S$ - damage accumulated in the part from the action of static stresses, $\varPi_C$ - damage from the action of cyclic stresses leading to fatigue of the part material. It is quite difficult to unambiguously establish the mutual influence of simultaneously occurring processes. As a first approximation, we accept the hypothesis of linear summation of damages. Within the framework of the article under consideration, the effect of static stresses will not be considered in detail, since during the design calculation of parts for static strength, sufficiently large safety margin coefficients are laid. In this case, the case is considered when the change in the cross-section of the part practically does not occur. The abrasion of the surface layer with a thickness of about fractions of a millimeter practically does not affect the stressed state of the part.

The main attention will be paid to the consideration of the joint process of fatigue and surface wear. The process of accumulation of fatigue damage occurs in the volume of the part, but is most often localized in the surface layer. At the same time, the wear mechanism is realized in the surface layer due to friction forces and contact stresses. To reduce the intensity of wear, we harden the surface, in our case, we carry out carbonitriding. At the same time, the hardness and wear resistance of the surface layer increases. The amount of uniform wear that causes failure or replacement of parts reaches up to 1 mm, but wear of 0.15...0.30 mm is mainly the cause of failure [6]. Durability prediction is made in this case according to the data of the wear rate and the specified resource. However, during the operation of parts, local damage is also observed that does not cover a significant part of the surface.

In general, the rate of damage accumulation is a function of several parameters, then the damage equation takes the form:

$$\frac{d\varPi}{dt} = F[\varPi, \sigma_a, HB(t), N(t),], \tag{2}$$

where t is time, σ_a - is the amplitude of cyclic stresses, $\sigma_{0,2}$ - is the yield strength of the surface layer material as a function of wear values, HB(t) - is the hardness of the surface layer, N(t) - is the number of cycles of alternating stress with amplitude σ_a. The rate of damage accumulation can be represented as the total effect of stationary loading and damage accumulation due to a decrease in hardness as the hardened layer wears out, according to the equation:

$$\frac{d\Pi}{d\tau} = f(\sigma) + \psi(\tau), \tag{3}$$

Let us separately imagine the effect of reducing the yield strength of the hardened layer over time and the accumulation of damage during cyclic loading with amplitude σ_a . After transformations and integration according to [14] in time, we obtain the equation for damage at a given time τ :

$$\Pi = \frac{\sigma_{0.2}(\tau)}{\sigma_{0.2S}} + \int_0^{\tau} \frac{1 - \dfrac{\sigma_{0.2}(\tau)}{\sigma_{0.2S}}}{t[\sigma_a(\tau)]} d\tau , \tag{4}$$

where $\sigma_{0.2}(\tau)$ - is the current value of the yield strength on the surface when worn to a depth Δh, $\sigma_{0.2S}$ - is the yield strength on the surface of an unworn surface layer at the initial time. $t[\sigma_a(\tau)]$ - is a theoretical equation of the fatigue curve for the main material of the part at a given stress amplitude σ_a.

Resistance to the action of friction forces and contact stresses is represented as a dependence on the yield strength. In this calculation, we use experimental data obtained in [4] to calculate the yield strength of the hardened layer of parts.

Moreover, as the analysis of experimental data showed, the hardness and yield strength of the surface layer synchronously decrease in depth of the hardened layer, that $\sigma_{0,2}$ is, it will also be a function of time. As the surface layer wears down to a depth Δh over a period of time Δt , that is:

$$\sigma_{0,2} = f[(\sigma_{0.2S}), t]. \tag{5}$$

The dependence of the yield strength on the depth of the surface layer during its wear during time t is obtained by approximating the experimental data by the equation:

$$\sigma_{0.2} = A\sigma_{0.2S}^{n}, \tag{6}$$

where A and n are the empirical coefficients of the equation describing the stress distribution over the depth of the surface layer.

After the formation of microdefects to the entire depth of the hardened layer, further calculations can be carried out on the basis of the principles of fracture mechanics. If we take the initial crack length l_0 equal to the depth *h* of the hardened layer, then we can calculate the period of operation of the part with the crack.

The condition of destruction will be written in the form:

$$l \geq l_{cr} . \tag{7}$$

We can assume the initial crack length equal to the thickness of the hardened layer $l_0 = h$.

The critical stress intensity coefficient is determined by the known dependence:

$$K_{1C} = \sigma\sqrt{\pi l_{cr}} \quad , \tag{8}$$

where K_{1C} - is the critical stress intensity coefficient, σ - is the level of acting stresses, l_{cr} - is the critical crack length corresponding to the transition to spontaneous crack growth or destruction.

The value K_{1C} can be determined by calculation in the presence of data on the impact strength and hardness of the hardened layer of the part. As it was shown in [4], it can be determined by the equation:

$$K_{1C}^2 = \alpha(KCV) - \beta(HRC)^2 + C , \tag{9}$$

where KCV - is the impact strength determined by the impact method on the Sharpie samples, HRC - is the Rockwell hardness, α , β , C - the coefficients, depend on the type of hardening and the properties of the material and are determined experimentally.

In the case of the prevailing action of cyclic stresses, a similar condition for cyclic crack resistance is used – the Paris - Erdogan equation:

$$\frac{da}{dN} = C\left(\Delta K\right)^m \ , \tag{10}$$

where ΔK - is the magnitude of the stress intensity coefficient, C and m are empirical coefficients for the material, $\frac{da}{dN}$ - is the crack growth rate of length a.

However, the overwhelming number of parts of general mechanical engineering for crack resistance are practically not calculated. Moreover, it should be noted that the wear rate for a long time at the first stage of operation is of the least importance. Therefore, our task was to study the possibility of predicting the durability of parts at the stage of wear of the surface layer. Note that the proposed approach to summation of damage to the surface layer of a part is practically feasible. For calculations, it is necessary to experimentally determine several characteristics and set operating conditions and wear rate. The advantage is the availability of determination of hardness and toughness of the main material of the part and the hardened layer by express analysis methods.

CONCLUSION

A general method for predicting the durability of machine parts is presented, taking into account the stages of the life cycle of products. Machining technology, surface hardening and operating conditions are taken into account. Damage accumulation equations based on the concept of nonlinear damage summation are proposed. The equations make it possible to predict the durability of parts based on the technology of machining and surface hardening. Surface characteristics of manufactured parts are used as variables that affect the durability of parts in service. The equations make it possible to predict the durability of machine parts under given operating loads and conditions. The inverse problem can also be solved. In this case, according to the given durability and operating conditions, the required mechanical characteristics of the parts after machining and surface hardening are determined.

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UDC 665

APPLICATION OF NEW ANTI-CORROSION PUTTY COMPOUNDS BASED ON WASTE FAT AND OIL INDUSTRY REGIONS OF KAZAKHSTAN

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ABSTRACT

The development of anti-corrosion materials using non-deficient fillers while maintaining the necessary protective and physical-mechanical properties is very relevant.

In this regard, the use of local waste as fillers not only improves the properties of anti-corrosion materials, but also contributes to the improvement, to some extent, of the environmental situation in industrial areas.

Spackling a car is a rather laborious process, which is carried out by experienced craftsmen during body repairs. Both the appearance of the part and its service life will depend on material application quality. A special automotive putty is used for work, which allows to align the damaged part of the body and restore the original surface shape.

The aim of our work is the development of new anti-corrosion coatings based on waste from the regions of the Republic of Kazakhstan as a putty compound, intended for leveling metal and non-metal surfaces, rough bumps and car bodies, using local fillers.

Automobile spackling is used for the most part in the field of auto repair.

The purposes of its application are: to prevent moisture from penetrating into the microcracks of car bodies; prevents corroding of the body by chemical reagents, oils; enhances the anti-corrosion properties of the metal, etc. The quality of putties is assessed according to the following indicators: ease of application; nature of filling of surface defects; duration and drying temperature; shrinkage value; grinding ability; adhesion strength with contacting layers; crack resistance.

Keywords: putty composition, paint and varnish material, coatings, protective properties, corrosion, aggressive environment

INTRODUCTION

The use of paint and varnish coatings and their efficiency is explained by the possibility of manufacturing paint and varnish materials of various formulations that provide the required properties in the coating.

The film-forming part is the obligatory component in Paints and varnishes in most cases which are multicomponents. The film-forming substance must be able to create a film on the surface to be painted with certain properties. Paints and varnishes can be obtained on the basis of organic (oils, polymers, rubbers) or inorganic (liquid glass, cements) film-forming substances

Paint coatings are widely used to cover vehicles, performing two functions - protective and decorative, i.e. technical and aesthetic. With the development of all branches of mechanical engineering, the requirements for the quality of applied paintwork materials and coatings from them are correspondingly increasing. Paint coatings have significant advantages over other types of coatings, as they are easier to apply to the surface, which reduces the cost of painting work.

Paint coatings have great durability; they can be applied to metal, plastics and other materials.

Recently, more and more often there is a need to conduct research related to the assessment of the quality of vehicle paintwork, especially cars. The objects of the study are the paint coatings of both new and restored cars of domestic and foreign production after road accidents. However, the examination of the car paintwork is not carried out as often as other types of inspections, but in some situations, it is simply necessary.

The study of paint and varnish coatings of technical means refers to automotive - technical types of diagnostics. The study of the paintwork helps to assess the condition of the car's paintwork and, if there are flaws, to identify the true causes of the appearance

The main properties of the coating are characterized by its adhesion to the protected surface, permeability, resistance to operational influences, appearance, etc. To do this, an analysis of the hardness, thickness and adhesion of the coating of the car body and other equipment is carried out in accordance with GOST. Complete diagnostics of the car paintwork reveals flaws and damage to the surface of the body or parts [1]

MATERIALS AND METHODS

Various methods were used to study the protective properties of the developed putty composition based on waste from the hydrolysis and oil and fat industry in accordance with GOST, namely [2]:

- GOST - 9.409 - 88 Unified system of protection against corrosion and aging Paint and varnish coatings. Methods for accelerated resistance testing;
- GOST 22233 - 2001 Measurement of the hardness of paints and varnishes;
- GOST 6589-91: Determination of the degree of grinding of the coating
- GOST 11736-91: Determination of water absorption of a free film
- GOST 9.403-90: Testing of coating systems in aggressive environments
- GOST - 9.407 - 2015 Unified system of protection against corrosion and aging Paint and varnish coatings. Appearance evaluation method

GOST - 21.402-83 SPDS. Anti-corrosion protection and others

RESULTS AND DISCUSSION

Paints and varnishes (coatings) are complex chemical multicomponent systems. When applied to a surface, they form a special coating or film that has certain protective and other properties. The main function of paints and varnishes is to protect the surface from damage (corrosion, decay, etc.), giving the product a decorative look (meeting aesthetic requirements). Any paint and varnish coatings consist of film-forming substances and vary in chemical composition; sometimes substances are added that affect individual chemical or technological properties

The purpose of paint and varnish coatings is to protect metals from corrosion, wood and fabrics from decay and swelling. When protecting vehicles against corrosion, the role of paint and varnish coatings is reduced to isolating the metal from an aggressive environment. Due to the appropriate paint coating (especially for cars and buses), it is possible to increase the service life of cars and beautiful appearance, high adhesion to the surfaces to be protected, heat resistance, chemical resistance, be inexpensive, durable, etc. Among the numerous consumers of paints and varnishes, mechanical engineering and road transport occupies a prominent place. [3].

The main stages of the examination of the paintwork of the car body are: visual inspection of all elements of the car body; measurement of the thickness of the complex paintwork; photographic fixation of all defects on the surface of the coating, etc.

Examination of the paintwork in most cases is aimed at studying the physical and mechanical properties of the paintwork. The closest for protection against corrosion of cars and for leveling metal and non-metal surfaces of car bodies are putty compositions. Putty is a paste or powder material used for leveling metal and non-metal surfaces. Putties are compounds used to level surfaces that are to be painted. Epoxy-based putty is considered the most reliable and high-quality material, with which you can putty various surfaces without much difficulty. The main requirements for putty compositions are high adhesion to the substrate, gas impermeability and water resistance, mechanical strength, wear resistance and resistance to operating conditions (weather resistance, chemical resistance, etc.).

For this purpose, we have developed a putty composition based on industrial waste from the regions of Kazakhstan. The objective of our study is to increase the physical and mechanical properties of the putty composition, reduce the drying time, reduce the thickness of the defective layer while maintaining viability, increase the plasticity of the putty composition and reduce its cost [4-5].

Tables 1, 2 and 3 show the physicochemical properties of EKS-22 epoxysilitane resin and gossypol resin, their purpose in the developed composition of the putty composition

Table 1 - Physical and chemical properties of EKS-22 epoxyxylitane resin

The name of indicators	EKS-22
Appearance	Yellow-brown to brown viscous liquid
Dynamic viscosity according to Hepyler at 250C, cPs	160000
Content, %	
epoxy groups,	18-20
hydroxyl groups,	5,4-6,2
total chlorine,	9,5-10,7
chloride ions	0,005
Volatile content, (at 1200C for1 hour)	0,34-0,5
Brinell hardness, MPa	210-240
Impact strength, kJ/m2	10-21
Breaking stress, Pa in compression	135,6

An easily accessible industrial waste - gossypol resin - an oligomer was chosen as the main raw material to develop new generations of anti-corrosion coatings with low cost and high efficiency, the quality indicators of which are given in table 2.

Table 2 - Physical and chemical characteristics of gossypol resin

gossypol resin	properties
appearance	viscous-fluid mass
Color	dark brown to black
acid number, mg KOH	50-100
ash content, mass %	1,0 – 1,25
moisture content and volatile substances, %	to 46
specific gravity, g/cm^3	0,98 -0,998
saponification number, mg, KOH	80 - 130

The putty composition is prepared as follows: the composition components (EKS-22 epoxyxylitane resin, dibutyl phthalate, polyethylenepolyamine, vermiculite and polyethylenepolyamine) were weighed with an accuracy of 0.01 g.

After 30 minutes, the thickened putty is thoroughly mixed, and it is suitable for use.

Table 3 - Formulation of putty composition based on epoxyxylitane resin

№	Name of Components	Components' purpose
1	Epoxysilitane Resin (EX-22)	used as a complexing agent to improve the quality of the protective film
2	Gossypol Resin (waste oil and fat industry)	to give the protective film elastic properties
3	dibutyl phthalate	plasticizer
4	white soot	filler
5	polyethylenepolyamine	hardener

Putty is applied with a spatula to the product's surface to be leveled. The composition has thixotropic properties, non-toxic and non-hazardous. Putty properties are determined by standard methods.

The physical and mechanical properties of the putty composition based on epoxyxylitane resin and the known are shown in table 4 [6].

Table 4 - Physical and mechanical properties of putty composition based on epoxyxylitane and gossypol resin

Properties of putty composition	Putty composition	
	known	developed
hardness according to M-3, conditional units after drying at a temperature, ^{0}C, not less than 18-20^{0}C	0.78	0.98
drying time, hour	16	5
coating bending, mm, no more	2	1-2
gel fraction, %	76	99.8
plasticity, %	9	18
portability	good	good
grindability	satisfying	good
adhesion according to the method of lattice cuts before testing, score	3	1
impact strength, kgf/cm	24.5	50,0
water absorption for 24 days, %	0.8	0.5
duration of preservation of viscoplastic properties on the surface, min	30 – 40	30 – 40
drying time at 18-20 ^{0}C, hour.	8-12	6-8
surface condition after drying	self, flat, smooth	self, flat, smooth

CONCLUSION

1. The optimal composition of the putty composition based on the wastes of the hydrolysis and oil and fat industry was developed, in particular, based on gossypol and

epoxyxylitane resin, in a mixture of solvents, filler and amine-type hardener, suitable for obtaining putty composition of cold curing mode

2. The process of curing putty composition at room temperature in the presence of an amine-type hardener was studied. It is shown that an effective hardener of the developed putty composition based on epoxyxylitane and gossypol resin is polyethylenepolyamine (PEPA), introduced in an amount of 5% by weight of the dry residue.

3. One of the main technological properties of the putty composition is adhesion, workability and their protective ability.

4. A comparative study of the physical and mechanical properties of the known and proposed putty composition indicates that the proposed putty composition reduces the drying time, reduces the thickness of the defective layer while maintaining viability, increasing the plasticity of the putty composition and reducing its cost

5. The physical, mechanical and protective properties of the developed putty composition based on production waste are not inferior to those of industrial putty compositions, and to some extent surpass them.

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UDC 667

CONDUCTIVE PAINTING COATINGS BASED ON EPOXY NOVOLAC BLOCKPOLYMER XILITANE

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ABSTRACT

Polymeric materials are widely used in modern technology, which have a number of advantages over traditional structural materials - metals. One of scientific and technological progress areas in the field of paints and varnishes production and use is the expansion and replenishment of the range of paints and varnishes with new types and brands with fundamentally new properties.

Scientific and research work in the field of creating conductive polymeric materials is developing in the development of composite materials consisting of a polymer binder and a conductive filler. A special place among conductive polymeric materials is occupied by conductive paints and coatings based on them. The selection of specific elements in the formulation of conductive paint and varnish depends on the overall set of criteria regarding the electrical, physical, mechanical, and protective characteristics of the coating. In certain situations, the key requirements can be summarized as follows: the ability to apply the conductive material onto product surfaces without extensive preparation, ensuring strong adhesion of the coating; simplicity in the application process; curing of the coatings at low temperatures (18-20°C); and the attainment of superior physical and mechanical properties in the coatings. These requirements are met by paints and varnishes based on epoxy xylitane resins, which are characterized by high adhesion to various materials, water and chemical resistance and mechanical strength. Among paints and varnishes based on epoxy resins, epoxy-phenolic varnishes have become widely known, combining high adhesion with weather and chemical resistance, increased heat resistance and good mechanical properties. For this purpose, we have studied the physico-mechanical properties of the developed conductive paint coating based on epoxy-novolac block copolymer xylitan ($ENBC_X$), which is obtained through the chemical interaction of epoxy xylitan resins with novolac phenol-formaldehyde resins.

Key words: paint and varnish coatings, environment, physical-mechanical and protective properties, hardener.

INTRODUCTION

Technological progress and the expansion of human activities present science with new challenges and increasingly higher demands on materials. Paint coatings are a unique composite material, where a small amount, in relation to the entire product, is capable of preserving the properties of the item and, in some cases, even imparting new properties, which, in turn, depend on the characteristics of the paint coating. It is possible to meet the requirements for paint and varnish coatings and expand the possible functions of their application through the use and study of new approaches to obtaining paint and varnish coatings [1]. Paint coatings are widely used to protect industrial products, metal structures and equipment, where there is an intense impact of aggressive environments on structural materials. Polymer coatings are one of the effective ways to protect metal structures and equipment. By preserving all the qualities of polymer paints and varnishes - high film strength and elasticity, good adhesion and anticorrosive properties, physical-chemical and mechanical performance - another important property of metal is its ability to conduct electric current. Conductive paint coatings, like pigmented paint systems, are a suspension of a filler in a binder. Often, the electrical conductivity of a paint coating depends on the type of conductive filler, on the concentration of the filler, the chemical nature of the binder, the coating technology, its curing mode and operating conditions. Polymeric materials are dielectrics, therefore, the basis for the creation of conductive polymeric materials was the formation of a conductive structure in polymers when various conductive fillers are introduced into them. Under certain conditions, the filler (binder) particles form conductive structures, which are a three-dimensional network structure consisting of filler chains. The electrical conductivity of the paint system depends on the dispersion of the conductive filler and the size of its particles.

RESULTS AND DISCUSSION

Various methods were used to study the protective properties of the developed conductive paint coating based on xylitane epoxy-novolac block copolymer ($ENBC_X$) in accordance with GOST, namely [2]:

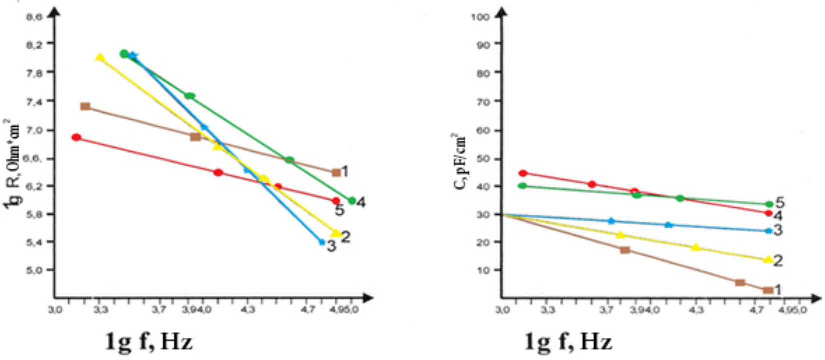
- GOST - 9.409 - 88 Unified system of protection against corrosion and aging. Paint coatings. Methods for accelerated resistance testing;
- GOST 22233 - 2001 Measurement of the hardness of paints and varnishes;
- GOST 11736-91: Determination of water absorption of a free film
- GOST 9.403-90: Testing of coating systems in aggressive environments
- GOST - 9.407 - 2015 Unified system of protection against corrosion and aging. Paint coatings. Appearance evaluation method
- GOST - 21.402-83 SPDS. Anti-corrosion protection and others

The chemical nature of the binder not only determines the anti-corrosion, physico-chemical properties of coatings, but also has a significant effect on their electrical conductivity. The dispersion medium, which forms the basis of a conductive paintwork material, is a mixture of various organic solvents. Good wetting ability of the film-forming agent is a necessary condition for obtaining high-quality electrically conductive paints. During the study of the influence of binder's chemical nature on the soot distribution in resins, as well as on the structural, mechanical and electrical properties of uncured carbon black-filled compositions based on xylitan epoxy-novolac block copolymer ($ENBC_X$), it was found that soot particles are more firmly bonded to the resin. The binder's chemical nature determines the behavior of the conductive polymer coating. To obtain conductive paintwork materials, binders based on both thermoplastic polymers and thermosetting resins are used. The electrical and physico-mechanical properties of conductive coatings based on the xylitan epoxy novolac block copolymer ($ENBC_X$) are presented in table 1 [4].

Table 1 - Electrical and physical-mechanical properties of conductive coatings based on xylitan epoxy-novolac block copolymer ($ENBC_X$)

N	indicators	$ENBC_X$
1	Specific volume electrical resistance, ohm*mm^2/m	$1*10^4 – 5*10^4$
2	Bending strength of the film according to the Schlegel hardness scale, mm, not more than	10
3	Film impact strength U-1, kg*sm, not less than	50
4	coating adhesion according to the lattice cut method in points	1
5	coating hardness according to pendulum type M-3	0.89-0.92
6	coating thickness, µm	100
7	water absorption in 24 hours at 20^{0}C, %	0.06
8	shrinkage, %	0.2-0.6
9	ultimate strength, MPa under compression when bending	 120-140 80-110
10	Vicat softening temperature, ^{0}C	120-130

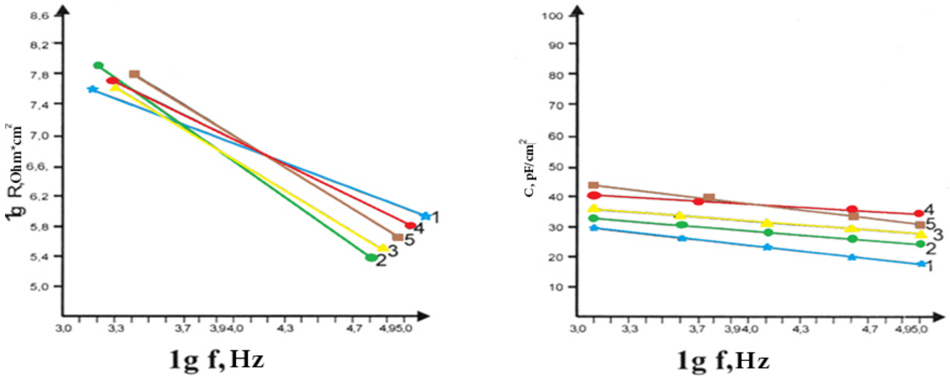
Particular attention is paid to research on the development of conductive coatings, epoxyxylitane resins are used in which as a binder, which have a complex of valuable properties. Films based on xylitane block copolymers have good adhesion, elasticity, ability to cure without detecting volatile substances, low shrinkage during curing, high mechanical strength, good chemical and atmospheric resistance. $ENBC_X$ is the most versatile. Their main properties can be regulated by the choice of hardener and filler. To obtain conductive coatings based on epoxy resins, compositions of xylitan epoxy-novolac block copolymer ($ENBC_X$) are used, cured in a cold curing mode (18-20^{0}C), containing various conductive additives as fillers - carbon black of grade PM-15. The capacitive-ohmic method has become increasingly important for coatings' anticorrosion properties evaluation. The protective properties of coatings are characterized by the frequency dependence and resistance of protected samples and the change in their values over time. In the absence of defects, the values of the frequency dependence (R) are small and the resistance of protected samples and the change in their values over time (C) are practically independent of frequency. The presence of defects in the film and discontinuity lead to an increase in (C) and an increase in its dependence on frequency. Therefore, this method makes it possible to detect defects before their visual manifestation. Aggressive media were used as electrolytes: 3% NaCI and 10% $HN0_3$ (Figure 1, 2)



1 - 1 day; 2-15 days; 3-45 days; 4- 150 days; 5- 240 days

Fig. 1. The relationship between the protective properties of coatings and the $ENBC_X$ and carbon black grade PM-15 in the cold curing mode can be analyzed through the frequency dependence and resistance of protective samples, as well as their changes over time in a corrosive environment with 3% NaCl.

Experimental results indicate that immediately upon immersion of the coatings in the aggressive environment, a significant frequency-dependent resistance is observed, while the capacitance remains constant. Measurements were conducted at intervals of 15, 45, 150, and 240 days. The obtained curves maintain their original characteristics even after prolonged exposure to the corrosive environment, suggesting that the developed coatings effectively prevent the penetration of corrosive substances onto the metal surface over an extended period. As a result, these coatings can be employed as protective measures for metal structures, equipment, and machinery [5].



1 - 1 day; 2-15 days; 3-45 days; 4-150 days; 5- 240 days

Fig. 2. Dependence of the protective properties of coatings on $ENBC_X$ and carbon black grade PM-15 of the cold curing mode according to the frequency dependence and resistance of protective samples and the change in their values over time in an aggressive environment of 10% HNO_3.

CONCLUSION

1. An epoxy-novolac conductive material based on xylitan epoxy-novolac block copolymer ($ENBC_X$) was developed, suitable for producing cold-curing conductive coatings.

2. The process of curing conductive coatings of cold curing mode in the presence of an amine hardener polyethylenepolyamine (PEPA) was studied.

3. It is shown that PM-15 grade carbon black is suitable as a carbon filler for conductive compositions based on $ENBC_X$, which has good dispersion in the binder and provides coatings with a specific volumetric electrical resistance of 1*104 - 5*104 ohm*mm^2/m

4. It was determined that coatings based on the developed composition of the cold curing regime have high adhesion to the surface of various materials.

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UDC 66-9

PECULIARITIES OF NATURAL PHOSPHATES CALCINATIONS AT MECHANOCHEMICAL ACTIVATION

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ABSTRACT

The research considers the problem of producing fodder calcined phosphates according to environmentally safe technology. The fluorine removal out of phosphorites is the basic operation of this technology. In order to intensify it, it is suggested to treat phosphorite to preliminary mechanical activation with the addition of 0.005-0.03% surfactant К-9. The macromolecules of surfactant cause the disjoining pressure, which leads to structural changes and partial destruction of the crystal lattice of fluorine carbonate-apatite. The reactivity of phosphorite increases due to defects accumulation, but not because of specific surface growth.

Keywords: bodder calcined phosphate, mechanochemical activation, surfactant, low-waste technology.

INTRODUCTION

The deterioration of rock phosphate quality of Karatau requires a search for innovative technological solutions that allow their deep and complex processing without polluting the environment [1].

Fodder calcined phosphate (tricalcium phosphate) is one of the products, produced from Karatau phosphorites. Unlike fertilizers the content of harmful admixtures (fluorine, arsenium, heavy metals) in fodder phosphates is strictly regulated. Because of the high concentration of toxic fluorine in phosphorites its removal is one of the main operations in the technology of fodder phosphates [2, 3].

The peculiarity of the crystal structure of fluorine carbonate – apatite, which is the main mineral of Karatau phosphorites, is the presence of two significantly different from each other sophisticated coordination positions of calcium cations [4, 5]. To remove the fluorine it is necessary to destroy the crystal lattice of fluorinecarbonateapatite [6].

At present in Kazakhstan for obtaining fodder calcined phosphates a melting cyclone furnace with WHB is employed. The efficiency of such a energy technological unit [7] has been proved at operation in other branches of industry. Intensive turbulent mode and high-speed burning of fuel significantly improved technical and economic indexes of the process compared with phosphorite melting in rotating furnaces.

At the same time the suggested method has also disadvantages linked with the necessity to use more rich raw material (26-28 % P_2O_5). The complexity of instrumentation design of this method does not allow to achieve high results. In addition, at such a scheme a significant amount of diluted exhaust gases, wastewaters and solid wastes, containing toxic compounds of fluorine and phosphorus is being formed. Their purification and utilization also require additional expenses [8].

To intensify the processing of phosphorites into fodder phosphates of particular interest is the method of mechanochemical activation. In our case such a phosphorite preliminary treatment with the following roasting is supposed. Thus the main task of destroying the structure of the crystal lattice of phosphorite at mechanicochemical activation is the maximum removal of fluorine, temperature reduction of the subsequent thermal decomposition, reduction of the roasting time. The need for high energy-intensive medium is a tough requirement for the technical realization of mechanicochemical activation in the grinding apparatus [9, 10].

In the course of mechanical activation under the influence of external forces, volumetric - stress state and with the growth of its intensity in hard particles defects appear, which then lead to the destruction of the particles [11, 12]. The development of defects occurs in the field of elastic and plastic deformations. The developing defects, gradually turning into the category of dangerous ones, define the sharply reduced real strength of hard particles in comparison with their theoretical strength. In this case the surface defects, sensitive to adsorptive influence of various additives, acquire particular importance [13-16].

To intensify the mechanochemical calcination of phosphorites the use of rich experience of adsorption reduction of solids' strength is rather interesting [17, 18]. Therefore research has been conducted to obtain fodder calcined phosphates with preliminary mechanochemical activation of phosphorite. In this case the triturating in a liquid medium is implemented with the addition of surfactant K-9 [19-22].

The phenomenon of adsorption reduction of solids’ strength, discovered by academician P.A. Rebinder and having received the name of the Rebinder effect, at present is widely enough used to solve various practical issues [23, 24].

It is known from practice that achieving high dispersiveness in the absence of surface active medium is practically impossible. Due to management of surface properties of the material in such a medium the grinding process is continuous and is not restricted by aggregating [25].

MATERIALS AND METHODS

With the use of mill -activator the influence of adding surfactant K-9 on the kinetics of dispergating of phosphorite in liquid medium has been studied. In this case the phosphorite sample was at first treated by 0.03% solution of acrylic polyelectrolyte surfactant K-9. After a short exposition suspension in the ratio of S: L = 1:5 was prepared from this sample, then the suspension was loaded into the vibromill. The useful volume of vibromill body was 10 litres, the working number of vibrations was - 3000 per minute.

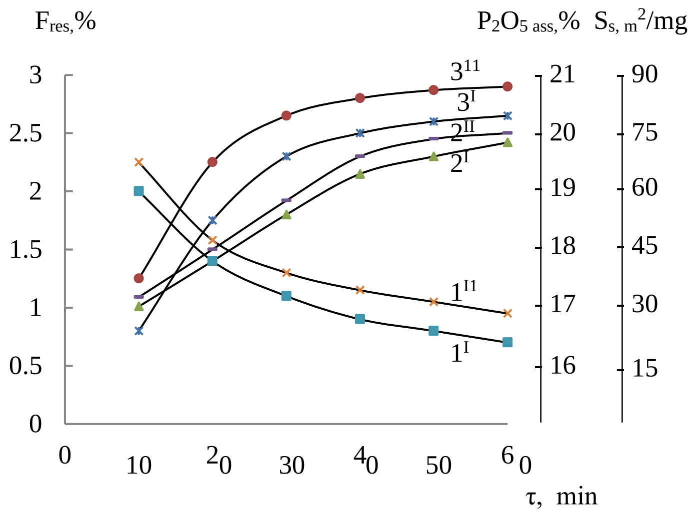
From works [26,27] it is known that the character of mechanical activation of phosphorite considerably depends on the size of the balls and the volume, being filled with balls. Preliminary research found out that in our case the most optimal diameter of balls is - 30 mm, and the volume, being filled with balls, is 50%. Therefore, the volume of vibromill was filled with steel balls with 30 mm diameter approximately by 50%. After finishing the experiments the value of specific surface and fluorine content have been defined separately for each sample. The content of assimilable P_2O_5 was assessed by the product solubility in 0.4% chlorohydric acid [28].

RESULTS AND DISCUSSION

Studies have shown that the mechanical activation of phosphorites significantly increases the value of specific surface of phosphorite particles. The sample grinded with addition of 0.03% surfactant K-9 has the largest value of specific surface, indirectly characterizing the efficiency of mechanical activation of phosphorites. With the addition of the surfactant K-9 the specific surface of phosphorite increases from 76 up to 88 m^2/mg.

Studies have shown, that at the addition of surfactant in small concentrations, the calcination and accompanying to it processes proceed more intensively (Figure 1).

When adding 0.03% of surfactant K-9 the residual fluorine content in the phosphorite after the mechanical activation reduces from 3 to 0.7% while at mechanical activation without adding surfactant K-9 this index was equal to 1.2%. The content of assimilable P_2O_5 (soluble in 0.4% hydrochloric acid) at mechanochemical activation in presence of surfactant K-9 increases by 20% (at the duration of grinding 52-55 minutes).



Diameter of the balls -30 mm, number of balls – volumetric 50%, 1^I, 2^I, 3^I, - without additives; 1^{II}, 2^{II}, 3^{II} - with additives of 0,03% surfactant K-9.

Fig. 1. Influence of duration of treatment and concentration of surfactant K-9 on the residual content of fluorine (1), content of the assimilable P_2O_5 (2) and specific surface (3)

Study of the influence of the mechanical activation duration in the presence of surfactant K-9 on the residual content of fluorine, the content of assimilable P_2O_5 and specific surface value have shown, that the calcination of fluorine at small concentrations of surfactant K-9 proceeds more intensively. Thus at the addition of 0.03% surfactant K-9 after mechanochemical activation the residual content of fluorine in phosphorite reduces from 3% to 0.7%, whereas in medium without additives it was 1.2%.

In these processes the phenomenon the destruction of fluorinecarbonatapatite under the influence of surfactant K-9 plays a significant role. This facilitates the development of microcracks. Research revealed that at concentrations 0.005-0.03% individual macromolecules of surfactant easily travel to capillaries and adsorb on active centres, appearing at deformations. As a result of this the macromolecules of surfactant cause disjoining pressure, which leads to structural changes and the destruction of the crystal lattice of fluorinecarbonatapatite. The high reaction capacity of activated natural phosphates is stipulated by accumulation of defects rather than by increase of its specific surface [29].

Presence of surfactant К-9 in the carrying phase facilitates the deformations, which are the initial stage of phosphorite particles destruction. Two-dimensional pressure, tending to push apart the crack further, in its value is proportional to the reduction of free energy of a unit of the phases separation surface [30]. In this case the critical width of the gap in the wedgelike crack plays the role of a barrier. It is approximately equal to the doubled diameter of macromolecules of surfactant K-9 that are being absorbed.

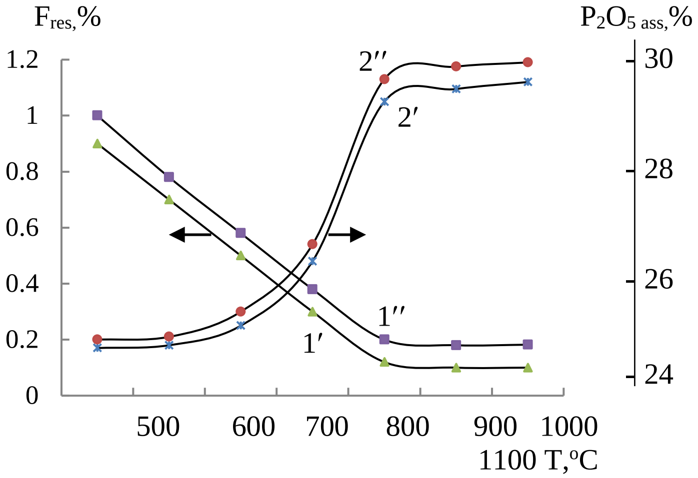
It should be noted that the adsorption effects of surfactant K-9 influence on the destruction of hard particles of phosphorite have a kinetic character. That is why in a considerable degree they depend on kinetics of deformations in the particles, also on time of working bodies impact on it. Significant adsorption effects occur both at the time of new surfaces formation at deformations, preliminary to the destruction of phosphorite crystal lattice, and at the time of the destruction process.

Figure 2 shows the results of research of the influence of roasting temperature and the concentration of surfactant additives on the residual content of fluorine in phosphorite, content of assimiable P_2O_5.

After the liquid-phase triturating in vibromill the roasting temperature can be reduced to 900^{0}C, which in static conditions was of the order 1350-1400^{0}C. At this, the transition point of β-modification of tricalcium phosphate into α-modification can be reduced to 820-850 ^{0}C. This is explained by the fact that at liquid-phase triturating of phosphorite in places of hitting of grinding bodies the temperature increases to 1400-1500 ^{0}C, after which abrupt cooling till the temperature of surrounding liquid phase (40-60^{0}C) occurs. Due to this effect of instant heating and quick cooling it is possible to detect α- modification of the being formed tricalciumphosphate.

Thus the liquid-phase triturating allows to combine the phosphorite melting at temperature of 1400-1500 ^{0}C and saving α- modification of tricalciumphosphate due to its hardening at its `quick heating and no less quick cooling.

The destruction of fluorinecarbonatapatite crystal lattice, occurring at its triturating, is accompanied by fluorine removal. Fluorine, remaining in the solid phase after the mechanical activation is already not bound in the phosphorite crystal lattice and so it can be removed by roasting at the temperature of approximately 900 ^{0} C.



Correlation S:L = 1:5, time of roasting – 50 minute. 1′, 2′ – without additives; 1″, 2″ – 0,03 % - K-9 with additives

Fig. 2. Influence of the temperature of roasting and of the concentration of additives of K-9 mixture on the residual content of fluorine in phosphorite (1), content of assimilable P_2O_5 (2)

From practice it is known that phosphorite decomposition is accompanied by decarbonization (at 850-950^{0}C) and defluorination (at 1300-1550 ^{0}C) [2]. When the temperature is 2000 ^{0}C the solid phase passes into melt. The change of composition of soluble forms of phosphates in its structure depends on this cooling rate of the melt. At this the composition of α- and β- modifications of tricalcium- phosphate changes qualitatively.

Knowledge of dependence of the amount of assimilable and non-assimilable P_2O_5 on the cooling rate gives the possibility to define optimal conditions of obtaining fodder calcined phosphate.

Considerable and sufficiently complex increase of deficiency of fluorinecarbonatapatite structure, including into it water and macromolecules of polyelectrolyte, that significantly change the composition and properties of phosphorite, in direction of its reaction capacity. At triturating of phosphorite because of the change of distances between ions of its crystal lattice and their transition into other positions, initially "stress" chemical bonds appear, the majority of which later break. As a result of such polymorphic transformations phosphorite calcination starts already at the stage of mechanical activation.

The results of experiments and infrared spectroscopy showed that at triturating of phosphorite suspension the phosphorite calcination, growth of its reaction capacity and transition of tricalciumphosphate from β-modification into assimilable α-modification is the result of more of the growth of the deficiency fluorinecarbonate apatite crystals rather than of the specific surface growth. The change of symmetry of phosphate- ion, due to the increase of deficiency, is considered as the main process, facilitating the subsequent thermal decomposition of phosphorite and determining the assimilability of the calcined tricalcium phosphate. To reveal the role of liquid phase mechanical activation of phosphorites in accumulating defects, that facilitate the removal of fluorine and increase of specific surface ,analyses have been carried out with the help of infrared spectroscopy. On the basis of their results one can assume that defects, being formed in the structure of fluorinecarbonate apatite, primarily localize in coordination complexes, binding calcium ions with the surrounding it oxygens of the tetrahedron PO_4^{3-} and ion F.

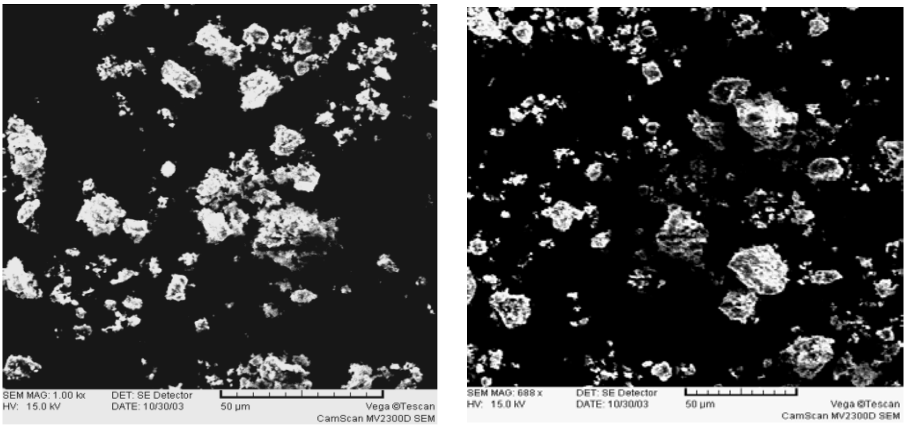
At mechanical activation of phosphorite in liquid-phase in surface active medium (with addition of surfactant K-9 and correlation S: L = 1:5), considerably higher dispersiveness has been achieved than in the samples, obtained in the medium without additives. This is the proof of a rather complex character of the process of defects accumulation at mechanical activation. One can not exclude the existence of mechanism of fixation of the being formed defects at adsorption of macromolecules of surfactant K-9. In this case the macromolecules of surfactant K-9 through two-dimensional travel on again being formed surfaces decreases their surface energy. As a result of this the development of microcracks – the surface defects is facilitated and this hinders their back closing under the influence of adhesion powers after external influence remaval.

At different stages in the course of mechanical activation the main minerals, accompanying fluorine carbonateapatite, play a positive role in building –up the reaction capacity of phosphorite. At the same time, except the reasons, connected with physical properties of minerals, the mechanochemical interactions with the participation of minerals of this complex multi-phase system play a considerable role.

For example, quarts, being the hardest mineral, plays the role of internal abrasive, contributing to dispergating and activation, also its mechanochemical interactions with phosphate substance and other minerals are not excluded.

Dolomite and calcite undergo profound structural deformations as evidenced by the disappearance of the final samples of dolomite and calcite lines on the X- rayograms.

Opinion about the changes, that occur during mechanical activation, is based on the results of studying the surface of mechanically activated phosphorites with the help of scanning electron microscope Cam Scan MV2300D SEM (Figures 3a and 3b).



a (before roasting) b(after roasting)

Fig. 3. Microstructure of the phosphorite surface that has undergone mechanochemical activation with adding surfactant K-9

The samples of mechanically activated phosphorite in the process of roasting do no change their sizes, the forms of particles remain close to spherical. The surface of the initial sample has a "loose" celled structure with numerous microcracks.

Heat- treated at 900 ^{0}C phosphorite particles have a smoother surface. A relatively small number of sufficiently large pores, having roundish shapes, is being observed.

The received data prove the firming of the structure of activated phosphorites in the process of roasting. Microcracks are usually formed in weak points of the crystal lattice. However, the formation of microcracks doesn't yet mean the destruction of crystal lattice, because at load removal if complete destruction has not been achieved, microcracks close and sometimes even disappear. The task of adsorption decrease of a solid body strength is exactly in complete opening of all these defects.

The comparison of the received X-rayograms with the benchmark ones (Figure 5,6) allows to say that in the submitted samples most likely is the presence of the following compounds: carbonatapatite $Ca_{10}(PO_4)_6CO_3$ (№ according to the database ASTM 35-180), fluoirinecarbonat hydroxidapatite $Ca_{10}(PO_4)_5CO_3F_{1,5}(OH)_{0,5}$ (ASTM 31-267), carbonathydroxiapatite $Ca_{10}(PO_4)_5CO_3OH$ (ASTM 21-145), quartz SiO_2 (12-708).

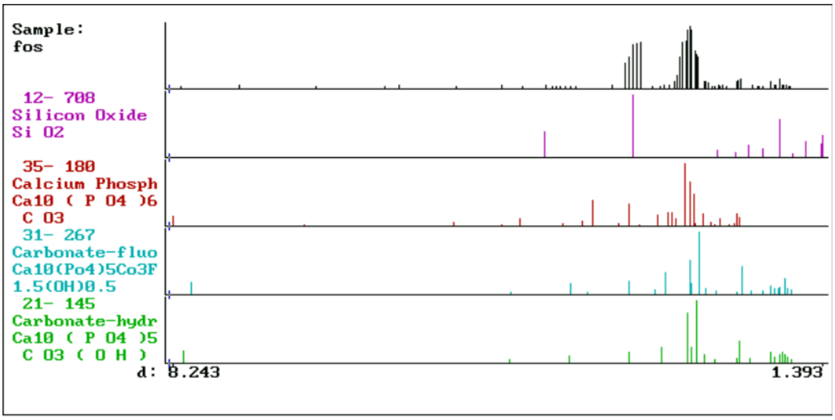


Fig. 4. Comparison of X-rayogram of sample of phosphorite with benchmark X- rayograms according to ASTM data

The phase composition of phosphorite before and after roasting does not differ considerably. Out of all studied samples phosphorites mechanically activated in the presence of added surfactant K-9 are notable. For them the intensity of reflexes peaks, corresponding to $Ca_{10}(PO_4)_6CO_3$ and $Ca_{10}(PO_4)_5CO_3F_{1,5}(OH)_{0,5}$, is considerably lower compared with other samples, that may be the consequence of more intensive removal of fluorine and CO_2 in the process of mechanical activation at using surfactant K-9.

One can judge about the changes in the chemical composition of phosphorite in the course of mechanical activation and the following roasting also on the basis of microprobe analysis. The data on the elemental composition of the being researched samples are presented in figure 3, figure 4 presents data about the chemical composition of phosphorite in conversion on oxydes. Imbalance on oxygen is distributed between carbonic acid, which is a part of natural carbonates and by water, which is part of hydroxilapatites and hydrated aluminum silicates. Possibilities of the method do not allow to record the presence of the series of light elements, including hydrogen and carbon.

Results of microprobe analysis showed that the chemical composition of phosphorites is rather nonuniform. Ratio of CaO/P_2O_5 for various samples varies widely: from 0.82 to 1.74.

Comparison of pairs of samples before and after roasting shows that during the process of roasting the content of fluorine regularly decreases. Imbalance decrease on oxygen indicates the considerable removal of carbon acid and bound water at heat-treatment.

Attention is drawn to increased content of oxygen and decreased content of calcium. A number of parallel analyses of various samples of these phosphorites gives similar results.

In the process of roasting of initial samples at temperature 900 ^{0}C, a regular decrease of specific surface of ground phosphate by 3-4 times is being observed; this can be explained by grading of substance structure as a result of defects and microcracks rebonding, closing micropores as a result of melting of free-melting admixtures. At this more notable firming of the structure in the process of heat treatment is being observed on phosphorite sample, obtained through activation with adding surfactant K-9.

The obtained results allow to judge that increase of calcinations’s degree of transition of tricalcium phosphate from unassimilable β— modification into assimilable α- modification, also the growth of solubility of tricalcium phosphate in weak chlorohydric acid,first of all are linked with the destruction of crystal structure of tricalcium phosphate and increase of deficiency of fluorine –carbonatapatite crystals rather than with the increase of material dispersiveness.

Changing of the symmetry of phosphate -ion, occurring as a result of deficiency increase, is considered as the main process, facilitating the subsequent thermal decomposition of phosphorite and defining the assimilability of calcined tricalcium phosphate.

Kinetics of transition of α- modification into β- one or vice versa, apparently occurs only in the melted state of phosphorite. The secondary phosphorites before and after the mechanochemical activation are the most soluble ones. This is due to the natural feature of phosphate substance (the lowest crystallinity and considerable content of quartz clay aluminosilicates) [31].

It can be assumed that the destruction of the structure of tricalcium phosphate under the influence of macromolecules of polyelectrolyte is accompanied by the change of its coordination complexes. Apparently, this is the reason of changing the symmetry of phosphate –ion, determining factor of solubility of tricalcium phosphate. Such changes as transition of carbonates, sulphides, fluorides into a relatively easily decomposed form are possible in the crystal lattice of fluorinecarbonatatapatite. The results of lumped laboratory tests confirmed the possibility and efficiency of using the developed way of producing feed calcined phosphates and the statement that surfactant K-9 considerably increased the efficiency of the mechanochemical activation.

The obtained results of research have become the basis of new environmentally safe technological scheme to manufacture calcined fodder phosphates [32].

CONCLUSION

The carried out research has shown that the process of mechanochemical activation of phosphorite allows not only to obtain a product meeting the requirements of the GOST (State Obligatory Standard), but also to reduce significantly the quantity of wastes and emissions.

The research resulted in establishing a considerable intensification of solid-phase reactions due to preliminary mechanical activation of phosphorite. If at usual heating at first low temperature stages are realized and then high temperature ones, the high temperature processes mainly take place at impulsive heating and abrupt cooling.

Liquid phase triturating of phosphorite in the presence of surfactant K-9 considerably increases the degree of calcination and content of assimilable form of P_2O_5 in the product. The main minerals of phosphoric ores, accompanying apatites, play a positive role at building –up the reaction capacity of phosphate substance in the course of mechanical activation at its different stages.

The results of the chemical composition analysis of the obtained product indicate phosphorite calcinations, decrease of water and carbon dioxide. The product fully meets the requirements of GOST 23 999-80E (State Obligatory Standard) for fodder calcium phosphate, and after grinding it is a finely dispersed powder of grey colour (with admixtures of sinter because of the increased content of iron oxide); the water solution of which has an alkalescent reaction, does not cake, is not hygroscopical and diffuses well.

The advantages of the developed method, compared with the known one, is in carrying out this process at considerably lower temperatures (900^0C instead of 1400-1450^0C) with, considerable economy of fuel and raw materials. The quantity of waste waters, gas-dust emissions significantly reduces, the concentration of fluorine compounds in them increases, which in its turn, facilities their purification and gives a real possibility to obtain tradeable calcium as a product of water –gas purification.

The economy according to this scheme is achieved also due to decreasing the maintenance cost because of simplifying the technological cycle. In particular, replacement of energy-and material intensive constructions: cyclone chamber, WHB, air heater and granulating unit of melted phosphorite to the mill and roasting drum, takes place.

Results obtained during the pilot tests fully confirm the conclusions made on the basis of laboratory research. The changes of pH suspension and fluorine content in liquid phase during the test indicate at acid neutralization, being formed as the result of sulubilizing fluorine by salts, passing into the solution in the process of triturating.

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DEVELOPING MUTUALLY AGREED GENERALIZED SEMI-EMPIRICAL MODELS OF TEMPERATURE DEPENDENCE OF THE DYNAMIC AND KINEMATIC VISCOSITY AND DENSITY OF MELTS

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ABSTRACT

The article suggested the form of uniform temperature dependence of the dynamic, kinematic viscosity and density of melts based on the concept of chaotical particles. To their mutual agreement showed the combination of the two expressions for the temperature dependence of the third, preferably for the kinematic viscosity through dynamic and density. All calculations are illustrated for the first time on liquid potassium.

Keywords: dynamic viscosity, kinematic viscosity, density, melt, chaotical particles

INTRODUCTION

The fundamental relationship dynamic (η, Pa·s), kinematic (ν, m^2/s) viscosity and density of the liquid (ρ, kg/m^3) at any temperature is given by

$$\eta = \rho\nu \qquad (1)$$

As for the temperature dependence of the specific expression for each variable, they are not separated by physical models and fairly strictly expressed only in approximating the equations of non-comparable accuracy and the possibility of extrapolation to higher temperatures [1].

For example, calculated the equation for dynamic viscosity and density of one of the most studied of alkali metals – potassium [1]:

$$\ln\eta = -4{,}1735 - 0{,}4313\ln T + 479{,}578/T, \qquad (2)$$

$$\rho=0{,}94516 - 0{,}49188(T/1000) + 0{,}6445(T/1000)^2 - 0{,}75076(T/1000)^3 + 0{,}4197(T/1000)^4 - 0{,}09205(T/1000)^5, \qquad (3)$$

where the viscosity is expressed in g/(cm·s) (in Poise), the density - in g/cm^3. It is obvious that these two are different depending on the form of even purely mathematical approximation, not to mention the unity of a physical model that underlies these relationships. Moreover, mathematical analysis (2) and (3) by differentiating and equating to zero the first derivative inevitably leads to such equations which are solved on a few roots, which requires the expression of the corresponding number of extremes in the dependences of the base (2) and (3), although this in principle contradicts the physical meaning of dynamic viscosity and density. As for the kinematic viscosity, its temperature dependence is calculated using (2) and (3) by formula (1) and approximated by a study on their own.

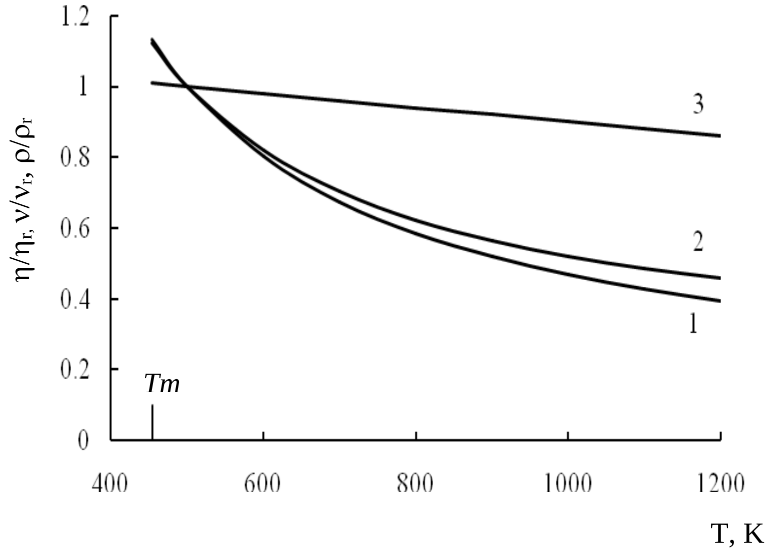
In general, fragmentation of research and discussion of approximation in three variables generates a significant lack of harmonization so that it leads to large errors when trying to express one of the three characteristics of the two others, followed by a comparison with the first experimental determination, as is easily seen by reference data, such as [2]. This also contributes and to the different strength temperature dependences of each of the three characteristics melt.

It is known [1] that the viscosity in the range of the liquid state of matter is changed 3-4 times [1], whereas the density – only a few percent. To directly compare the two types of viscosity and density due to their different units of measurement appropriate to transfer these units to dimensionless form, for example, referring to the same fixed point: η/η_r, ν/ν_r, ρ/ρ_r. Show this using the data for lithium [1] at the fixed point 500 K (Table 1, Fig. 1).

Table 1. Normalized reference values of the dynamic, η/η_r, kinematic, ν/ν_r, viscosity and density, ρ/ρ_r, for liquid lithium [1]. T_m – temperature of melting

T, K	$\eta\cdot10^4$, Pa·s	η/η_r	$\nu\cdot10^7$, m^2/s	ν/ν_r	ρ, kg/m^3	ρ/ρ_r
T_m=453,7	5,99	1,134	11,561	1,124	518,37	1,01
500	5,28	1,000	10,285	1,000	513,64	1,00
600	4,23	0,801	8,408	0,818	503,43	0,98
700	3,56	0,673	7,218	0,702	493,22	0,96
800	3,09	0,584	6,387	0,621	483,01	0,94
900	2,74	0,518	5,789	0,563	472,80	0,92
1000	2,47	0,467	5,335	0,519	462,59	0,90
1100	2,25	0,427	4,985	0,485	452,38	0,88
1200	2,08	0,394	4,704	0,457	442,17	0,86

As can be seen from Fig. 1, all three of decreasing dependency is that for the dynamic viscosity (1), is the strongest. Somewhat weaker than it is for the dependence of kinematic viscosity (2), and quite sharp different from the first two – the dependence of the density (3), and this is due to the proximity of the two temperature dependences of viscosity. This is dictated by the expediency of matching three interrelated characteristics of a viscous liquid state by a single original in the physical sense and the analytic form of expression of the strongest and weakest relationships – for the dynamic viscosity and density – with the subsequent calculation of the intermediate according to the kinematic viscosity, although in principle possible, and any other combination considered in the order formalizing dependencies.



η/η_r (1), kinematic, ν/ν_r (2), viscosity and density, ρ/ρ_r (3), for liquid lithium [1] T_m – temperature of melting

Fig. 1. Normalized reference values of the dynamic

Direct comparability and clarity of the normalized data makes this approach preferable to the approval of interrelated variables. In this regard, certain advantages of the concept of chaotical particles, based on a fundamental and universal Boltzmann’s distribution, which itself operates on equity, non-dimensional characteristics pertaining to the content of particles with different energies chaotic thermal motion [3-5]. In particular, this concept has been applied successfully to coordinate disparate data on the vapor pressure, temperature and heat of boiling substances [6, 7].

MATERIALS AND METHODS

T_m

The essence of the concept is reduced to determining the share of particles with energies less than the heat of melting, called crystal-mobile, as well as parts of particles with energies between the heats of melting and boiling points, called liquid-mobile, and with energy above the boiling heat, called vapor-mobile. Proportion of these particles, in the amount of accounting unit is uniquely dependent on temperature to overcome or not been overcome their respective thermal barriers according to the Boltzmann’s distribution [16]:

$$P_{crm} = 1 - \exp[-\Delta H_m/(RT)], \tag{4}$$

$$P_{vm} = \exp[-\Delta H_b/(RT)], \tag{5}$$

$$P_{lqm} = \exp[-\Delta H_m/(RT)] - \exp[-\Delta H_b/(RT)], \tag{6}$$

where ΔH_m and ΔH_b – heat of melting and boiling points.

All three types of particles contained in a given ratio in the solid, liquid and gaseous states are defined by their presence and predominant energy specific long, close or zero order of connection, while maintaining its influence in each of the states [8].

Thus, in liquid state the presence crystal-mobile particles leads to the formation of virtual clusters of the solid phase and their associates, defining the viscous state and melt’s flow and temperature dependence of viscosity [9]. This relationship is derived as follows.

In dimensional form the viscosity changes from a first fixed point, located in the crystallization of the melt to the asymptotic limit $\eta \to 0$ as $T \to \infty$, which can be fixed in the form of inequality

$$\eta_1 \geq \eta \geq 0. \tag{7}$$

With the normalization of η_r this inequality takes the form

$$1 \geq \eta/\eta_1 \geq 0. \tag{8}$$

Share of crystal-mobile particles according to (4) is also asymptotically decreases to zero as $T \to \infty$, which will correspond to the inequality

$$\{1-\exp[-\Delta H_m/(RT_1)]\} \geq \{1-\exp[-\Delta H_m/(RT)]\} \geq 0 \tag{9}$$

Pose the problem of lead (8) and (9) for the full like of the limits by identical transformations (9) as the basis for changes in viscosity, as well as share crystal-mobile particles is the thermal motion, obeying the Boltzmann’s distribution.

At first remove the brackets, from all parts of the inequality unit subtracted, and the remnants multiply by minus one, which will change the direction of the inequality:

$$\exp[-\Delta H_m/(RT_1)] \leq \exp[-\Delta H_m/(RT)] \leq 1. \tag{10}$$

Next, the logarithm inequality,

$$-\Delta H_m/(RT_1) \leq -\Delta H_m/(RT) \leq 0, \tag{11}$$

again multiplied by minus one

$$\Delta H_m/(RT_1) \geq \Delta H_m/(RT) \geq 0 \tag{12}$$

and divide on the left-hand side:

$$1 \geq T_1/T \geq 0. \tag{13}$$

As a result, obtain an expression identical to the limits of the inequality for the normalized viscosity (8).

However, the inequality (13) can be expressed without changing the limits, and more generally in the construction of all its parts in some positive degree a [10, 11]:

$$1 \geq (T_1/T)^a \geq 0. \tag{14}$$

The unity of the physical nature of (8) and (14) allows for the identification and internal parts of these inequalities:

$$\frac{\eta}{\eta_1} = \left(\frac{T_1}{T}\right)^a , \tag{15}$$

which yields the desired relation

$$\eta = \eta_1 (T_1/T)^a , \tag{16}$$

which can be defined as a generalized semi-empirical, since, while maintaining involvement in the fundamental Boltzmann’s distribution, it uses fixed value.

When identifying the relationship (16), reference values of viscosity was found that the index *a* is meaningful degree of association clusters equal to their average number of associates in the whole temperature range. This was confirmed by determining the activation energy of viscous flow in the coordinates $\ln\eta$–$1/T$ from the Frenkel’s equation, resulting in the activation energy divided by the degree of association, was in all cases within the energy of van der Waals attraction [12], which corresponds to a similar value of connection between the clusters, obtained by molecular dynamics methods [13]. In turn, the index *a* itself the temperature increases albeit slowly, but naturally falls in line with the decrease in the number of clusters in associates by accelerating their degradation during heating of the melt.

To display this pattern, which follows trends in reducing crystal-mobile particles in the clusters, the temperature dependence of the degree of association expressed as in (16) [14]:

$$a = a_2 (T_2/T)^b . \tag{17}$$

Strengthening the theoretical basis of the generalized equation of viscosity, which has resulted in more detailed form

$$\eta = \eta_1 (T_1/T)^{a_2 (T_2/T)^b} , \tag{18}$$

necessitated the introduction of additional control points. Thus, to determine the values of a_2 in accordance with (18) requires the inclusion of two fixed points η_1, T_1 and η_2, T_2:

$$a_2 = \frac{\ln(\eta_2/\eta_1)}{\ln(T_1/T_2)} , \tag{19}$$

and to identify the second indicator *b*, having a sense measures the degree of reduction association clusters and assumed to be constant for the entire temperature range, requires a third fixed point η_3, T_3 for the initial determination

$$a_3 = \frac{\ln(\eta_3/\eta_1)}{\ln(T_1/T_3)} \tag{20}$$

with subsequent calculation

$$b = \frac{\ln(a_3/a_2)}{\ln(T_2/T_3)} \tag{21}$$

The choice of the second and third fixed points in principle arbitrary, but in addition to using the most reliable experimental data appropriate to focus on their assignment, respectively, to the middle and upper values of the temperature range.

The resulting generalized form of the temperature dependence of dynamic viscosity is characterized by the position of the minimum temperature

$$T_{\eta,\min} = T_1 e^{1/b} \tag{22}$$

This temperature is a result of testing for all simple substances for which data are available in reference books [1, 2, 15], were far above the critical point for these substances, which ensures compliance with the physical meaning of viscosity decrease with deceleration with increasing temperature.

High correlation coefficients close to unity, the model (18) with the reference data indicate the functional nature of this model that makes it advantageous to use its physical nature and the form and to a weaker dependence, which is the density dependence on temperature.

This dependence is also decreasing as the viscosity, and this decrease can be attributed to a decrease of the same the share crystal-mobile particles, but in this case is not at the expense of their smaller size and mobility, and this is due to their decisive influence on the strength of the internal friction of fluids in comparison with single liquid- and vapor-mobile particles, but due to the greater *density* of clusters and associates from crystal-mobile particles, representing a virtual solid phase in the liquid state of matter. Thus the difference of the physical processes of viscous flow and decompression of melts must determine the different effect on force crystal-mobile particles, as well as in the first case they are working on the viscous flow of three factors: the low mobility, large sizes cluster and associates, as well as a large total surface area of a virtual solid phase, and the second – only one thing: change the overall share of the dense virtual entities. It is not excluded that the decompression of the melt may have an additional impact of liquid- and vapor-mobile particles having due to their high mobility, respectively, reduced of the virtual density.

Since the conclusion of the generalized temperature dependence of density on the basis of similarity of the Boltzmann's distribution in the normalized form repeats the steps (7)-(18), this dependence takes the same form

$$\rho = \rho_1 (T_1/T)^a = \rho_1 (T_1/T)^{a_2 (T_2/T)^b} \tag{23}$$

also using the three fixed points ρ_1, T_1; ρ_2, T_2; ρ_3, T_3 and the calculation a_2, a_3 and b like (19)-(21):

$$a_2 = \frac{\ln(\rho_2/\rho_1)}{\ln(T_1/T_2)}, \tag{24}$$

$$a_3 = \frac{\ln(\rho_3/\rho_1)}{\ln(T_1/T_3)}, \tag{25}$$

$$b = \frac{\ln(a_3/a_2)}{\ln(T_2/T_3)} \qquad (26)$$

In this case, obviously, need to clarify the physical meaning of the index *a* based on concrete analysis of the experimental reference data for the temperature dependence of the density.

To illustrate all the features of temperature dependence of the density present comparative data for the melt of potassium, which are presented in sufficient detail and in a wide temperature range in reference [2], as well as the above equation (3) of [1]. In addition, use the estimated value of the critical temperature T_c = (2223) K from the handbook [15] to extrapolate relationships compared to the boundary of the existence of the liquid state as a separate phase.

RESULTS AND DISCUSSION

To identify the proposed density model used reference values [2]: T_1 = 350 K, ρ_1 = 825,3 kg/m^3; T_2 = 1050 K, ρ_2 = 659,5 kg/m^3; T_3 = 1750 K, ρ_3 = 485,9 kg/m^3. As a result, the calculated dependence took the form of

$$\rho = 825{,}3(350/T)^{a=0{,}204135(1050/T)^{-0{,}935209}}, \text{ kg/m}^3 \qquad (27)$$

As shown in Table 2, reference data cover a very wide temperature range, well above the boiling point and almost approaching the critical temperature. In this range, approximating equation (3) is closely describes the reference values (with an accuracy of about 0,5 %) up to 1550 K with a further sharp lower results at 1800 K for 8 %, and when extrapolated to the critical point – to give absurdly low value density of 41,4 kg/m^3 of less than 10 % from the previous reference values.

Moreover, further extrapolation leads to a negative (!) values, than once again emphasizes the highly adjustable nature of the dependences of type (3).

The proposed model (27) high adequacy describes the full range of reference values of density, and extrapolation to the critical point and then followed by a physically reasonable asymptotic decrease in the calculated values from the far limit of $\rho \to 0$ by $T \to \infty$. The nature of the changes compared dependencies shown in Fig. 2.

In fig. 2, as shown in table 2, in addition to the marked regularities observed a sharp loss of monotonic change in the reference data of the viscosity at 950 K. This is probably the wrong decision or a misprint, since this deviation is not commenting. Without this value, the correlation coefficient of model (3) with reference data was R = 0,99617 in its significance t_R = 701 > 2, a model (27) – R = 0,99936 in its significance t_R = 4233 > > 2.

Practical proximity to one correlation coefficient for the proposed model indicates that it is functional, as evidenced for other simple substances. At the same time revealed some regularity, that require explanation.

Table 2. Reference [2] and calculated values of the density of liquid potassium from the equations (3), (27) and index *a*. T_b – boiling point

T, K	ρ[2], kg/m^3	ρ(3), kg/m^3	ρ(27), kg/m^3	a	T, K	ρ[2], kg/m^3	ρ(3), kg/m^3	ρ(27), kg/m^3	a
T_m = 336,66	828.5	829.0	827.6	0.071	1100	647.3	650.9	646.5	0.213

350	825.3	825.6	825.3	0.073	1150	635.1	639.0	633.6	0.222
400	813.7	813.3	816.3	0.083	1200	622.9	626.9	620.7	0.231
450	802.0	801.4	806.4	0.092	1250	610.7	614.8	607.8	0.240

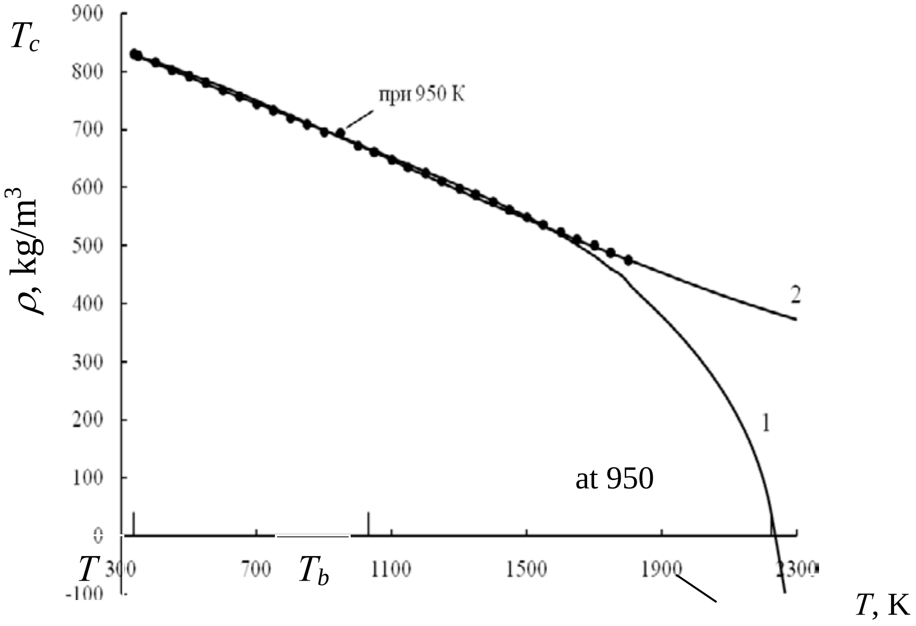
Table 2 continuation

500	790.4	789.9	795.8	0.102	1300	598.4	602.4	595.1	0.249
550	778.7	778.5	784.7	0.112	1350	586.0	589.9	582.4	0.258
600	766.9	767.1	773.2	0.121	1400	573.6	576.9	569.9	0.267
650	755.2	755.8	761.3	0.130	1450	561.2	563.5	557.4	0.276
700	743.3	744.4	749.1	0.140	1500	548.8	549.4	545.1	0.285
750	731.5	733.0	736.7	0.149	1550	536.3	534.4	533.0	0.294
800	719.6	721.5	724.1	0.158	1600	523.7	518.3	521.0	0.303
850	707.6	709.9	711.3	0.168	1650	511.1	500.8	509.1	0.312
900	695.7	698.2	698.4	0.176	1700	498.5	481.5	497.4	0.320
950	693.6?	686.5	685.5	0.185	1750	485.9	460.0	485.9	0.329
1000	671.6	674.7	672.5	0.195	1800	473.2	436.0	474.5	0.338
T_b = 1032	–	667.1	664.2	0.201	T_c = (2223)	–	41.4	385.6	0.413
1050	659.5	662.8	659.5	0.204	3000	–	-3373	256.0	0.545

First of all, this is a index *a* increase with increasing temperature. The meaning of this parameter in the model for the viscosity (16) is the degree of association of clusters, which, according to the thermodynamics of the dissociation process should naturally fall, as observed for the model (16). The opposite change the index *a* in the density model suggests otherwise its physical-chemical sense. Above emphasize different nature of viscous flow and decompression of the melt in the concept of chaotical particles in terms of different kinds of influence on these properties crystal-mobile, liquid-mobile and vapor-mobile particles. In relation to the decompression besides determining influence share crystal-mobile particles arranged in denser clusters and their associates, and the destruction of which leads to a decrease in density, in this case their additional effect on decompression provided the liquid- and vapor-mobile particles, the total proportion of which increases with increasing temperature in accordance with (4)-(6) according to the law

$$P_{lqm+vm} = 1 - P_{crm} = \exp[-\Delta H_m/(RT)] \tag{28}$$

Liquid-mobile and vapor-mobile particles, being high-energy, not able to aggregate and are therefore isolated. Their relationship to each other is provided by the van der Waals attraction, which weakens with increasing temperature, which leads to a corresponding contribution of these particles in the decompression of the melt.



Points – reference data [2], 1 – by (3), 2 – by (27)

Fig. 2. Dependence of density on temperature according to the known (3) and proposed (27) models in comparison with reference data

Mathematically the growth index *a* of the proposed model density (23) is realized by negative values of the secondary index *b*. Related to this is a different sense and extreme position (22), typical of the general form of dependence (18) and (23). When $b < 0$ extreme does not refer to a minimum and the maximum

$$T_{\rho,\max} = T_1 e^{1/b}, \qquad (29)$$

that is, in this case the left side depending on closer to absolute zero, i.e. in the solid state of matter. Thus, for potassium $T_{\rho,\max}$ = 120 K, far below T_m = 336,66 K. In view of this model (23) describes the area of the liquid state only as a monotonically decreasing dependence.

In principle, the negative values of *b* can be avoided by writing the temperature dependence of the exponent *a* in the form of

$$a = a_2 \left(T/T_2\right)^b, \qquad (30)$$

i.e. by applying the fraction in brackets. In this case more directly expressed by increasing the temperature dependence for the exponent *a* and the exponent *b* only a change of sign. In any case, the meaning of the indicator *a* will remain the same – is *the degree of decompression melt*. Given that in some cases, which require separate consideration, the exponent *b* is positive when using the model (23) and thus the degree of decompression melt does not increase, but decreases, it is advisable to maintain a uniform format for the temperature dependence of the viscosity and density.

This is all the more necessary, if in the same form and display the temperature dependence of kinematic viscosity:

$$\nu = \nu_1 (T_1/T)^{a_2 (T_2/T)^b} , \tag{31}$$

since the conclusion of this dependence also repeats the procedure (7)-(18) with the appropriate use of three fixed points. However, the independent calculation of the three interrelated characteristics of the melt – η, ν and ρ – a common format is the only prerequisite for the full harmonization, because each of them experimentally determined by its methods and has unequal accuracy. As noted above, it is appropriate to adequately display the most strongest and most weak dependence, which are for the dynamic viscosity and density, so that through them, then by (1) express an intermediate dependence on force for the kinematic viscosity.

If the first fixed point on the temperature selected for the overall dynamic viscosity and density, the temperature dependence of kinematic viscosity can be expressed as

$$\nu = \eta/\rho = \frac{\eta_1}{\rho_1} \left(\frac{T_1}{T} \right)^{a_\eta - a_\rho} , \tag{32}$$

where a_η and a_ρ revealed through their fixed points:

$$a_\eta = a_2^{/} \left(T_2^{/} / T \right)^{b^{/}} , \tag{33}$$

$$a_\rho = a_2^{//} \left(T_2^{//} / T \right)^{b^{//}} . \tag{34}$$

The need to harmonize η, ν and ρ can be illustrated based on data from reference [2] for the alkali metals. For all five of these metals are tabulated values of these characteristics of the melts in a wide temperature range, and dynamic viscosity data have been overstated in exactly 10 times, which is easily checked by (1) and confirmed by the values of η in reference [15]. This regular error went unnoticed in the first edition of the handbook [2] in 1985, and a third in 2003 ("the revised and updated"). In addition, the calculation of kinematic viscosity through dynamic and density is also accompanied by regular deviations from the reference values even after the increase is 10 times the data of η.

For example, strict matching η, ν and ρ restrict the analysis of data for potassium [2], the more the temperature dependence of the density is obtained.

In Table 3 shows the reference and the calculated values for the new model of the dynamic viscosity of potassium, but the model is identified by fixed points T_1 = 350 K, η_1 = 0,5096 mPa·s; T_2 = 700 K, η_2 = 0,198 mPa·s; T_3 = 1050 K, η_3 = 0,129 mPa·s:

$$\eta = 0{,}5096 (350/T)^{1{,}3639 (700/T)^{0{,}214025}} , \text{ mPa·s}. \tag{35}$$

For comparison, the results of calculations by approximating the model (2).

Table 3. Reference [2] (with increasing order of magnitude) and calculated by model (2) and (35) of the dynamic viscosity of liquid potassium. Indicate the degree of association clusters *a*

T,K	η[2], mPa·s	η(2), mPa·s	η(35), mPa·s	a	T, K	η[2], mPa·s	η(2), mPa·s	η(35), mPa·s	a
T_m = 336,66	0.544	0.520	0.542	1.595	750	0.183	0.168	0.183	1.344
350	0.5096	0.485	0.5096	1.582	800	0.1707	0.157	0.1707	1.325
400	0.413	0.385	0.415	1.537	850	0.160	0.148	0.160	1.308
450	0.347	0.321	0.350	1.499	900	0.1507	0.140	0.1504	1.292
500	0.300	0.275	0.302	1.466	950	0.1425	0.133	0.1423	1.278
550	0.265	0.242	0.266	1.436	1000	0.135	0.126	0.135	1.264
600	0.237	0.217	0.238	1.410	T_b = 1032	–	0.123	0.131	1.256
650	0.216	0.197	0.216	1.386	1050	0.129	0.121	0.129	1.251
700	0.198	0.181	0.198	1.363	1100	0.123	0.116	0.123	1.238

The correlation coefficient of the proposed model (35) with reference dependence was R = 0,9999 at t_R = 44268 >> 2, indicating that the functional nature of the new model of viscosity. At the critical point at T_c = 2223 K η_c = 0,071 mPa·s, and the minimum of (35) according to (22) is attained at $T_{\eta,\min}$ = 37432 K, i.e., at very far distant extrapolation into the area of coexistence mixed of liquid and gaseous phases. Like all metals, potassium is characterized by low average values for each temperature, the degree of association clusters because of the practical absence of covalent bonds in metals, as well as a regular decrease in this parameter with increasing temperature. Approximating the dependence (2) was regularly underestimated against reference [2], which is due to significantly worse correlation coefficient equal to R = 0,9889 at t_R = 174 > 2.

It is possible to direct processing of reference data for the kinematic viscosity of potassium with fixed points at the same temperature:T_1 = 350 K, ν_1 = 6,175·10^{-7} m^2/s; T_2 = 700 K, ν_2 = 2,665·10^{-7} m^2/s; T_3 = 1050 K, ν_3 = 1,956·10^{-7} m^2/s. This yields the calculated dependence

$$\nu = 6{,}175(350/T)^{1{,}2123(700/T)^{0{,}36292}}, \text{ m}^2/\text{s}. \qquad (36)$$

The calculation results are shown in table 4.

Table 4. Reference [2] and calculated values of (36) the kinematic viscosity of liquid potassium

T, K	ν·10^{-7} [2],m^2/s	ν·10^{-7} (36),m^2/s	a	T, K	ν·10^{-7} [2],m^2/s	ν·10^{-7} (36),m^2/s	a
T_m = 336,66	6.570	6.566	1.581	750	2.504	2.508	1.182
350	6.175	6.175	1.559	800	2.372	2.377	1.155
400	5.076	5.064	1.485	850	2.261	2.266	1.130
450	4.233	4.138	1.423	900	2.166	2.171	1.107

500	3.802	3.788	1.370	950	2.085	2.090	1.085
550	3.406	3.396	1.323	1000	2.016	2.019	1.065

Table 4 continuation

600	3.101	3.094	1.282	T_b = 1032	–	1.978	1.056
650	2.859	2.857	1.245	1050	1.956	1.956	1.046
700	2.665	2.665	1.212	1100	1.905	1.901	1.029

The correlation coefficient between the calculated and reference data was R = 0,99988 at t_R = 15869 >> 2, which also indicates the functional dependence (36). Exponent a practically does not differ from that of the dynamic viscosity and can also be interpreted as the average degree of association clusters. At the critical temperature T_c = 2223 K in (36) is obtained with a value $\nu_c = 1{,}415 \cdot 10^{-7}$ m^2/s, it is appropriate delayed decrease in viscosity at a distant extrapolation of temperature, the more that the minimum ν according to (22) is achieved at 5505 K, i.e. far in area inseparable coexistence of liquid and gaseous phases at ultrahigh pressures.

Thus, the kinematic viscosity of the possible comparison with reference data of the three calculated temperature dependences: the first – by dividing the point of reference data on the dynamic viscosity on the point reference data on the density; the second – on the model (36); the third – on the model (32), and third relationship should examine the possibility of extrapolation.

Model (32) in a calculated form in accordance with the inclusion of models (27) and (35) and transfer the last of mPa·s in Pa·s to be expressed as

$$\nu = 6{,}175 \cdot 10^{-7} \left(\frac{350}{T}\right)^{1{,}3639(700/T)^{0{,}214025} - 0{,}204135(1050/T)^{-0{,}935208}} \text{, m}^2\text{/s} \qquad (37)$$

The calculation results are shown in Table 5.

Table 5. Reference [2] and calculated directly from formula (1), as well as models (36) and (37) values of the kinematic viscosity of potassium

T, K	$\nu \cdot 10^{-7}$ [2], m^2/s	$\nu \cdot 10^{-7}$ (1), m^2/s	$\nu \cdot 10^{-7}$ (36), m^2/s	$\nu \cdot 10^{-7}$ (37), m^2/s
T_m = 336.66	6.570	6.566	6.566	6.552
350	6.175	6.175	6.175	6.175
400	5.076	5.076	5.064	5.085
450	4.233	4.327	4.138	4.336
500	3.802	3.796	3.788	3.797
550	3.406	3.403	3.396	3.393
600	3.101	3.090	3.094	3.083
650	2.859	2.860	2.857	2.839
700	2.665	2.664	2.665	2.643
750	2.504	2.502	2.508	2.484
800	2.372	2.372	2.377	2.353
850	2.261	2.261	2.266	2.244
900	2.166	2.166	2.171	2.153
950	2.085	2.055 ?	2.090	2.076

1000	2.016	2.010	2.019	2.011
T_b = 1032	–	–	1.978	1.975

Table 5 continuation

1050	1.956	1.956	1.956	1.956
1100	1.905	1.900	1.901	1.910

The first of the compared relationships, being a point, describes the reference data for the kinematic viscosity with high accuracy, but the inevitable repetition of erroneous determinations in one of two used reports – on the dynamic viscosity or density. Thus, at 950 ^{0}C, as determined by analysis of reference data on the density (Table 2) falsely inflated value of the density results in an equally low value of kinematic viscosity. Without identifying this error correlation with reference data remains high even though (R = 0,99985, t_R = 12611 >>> 2), but with no guarantee of strict mutual agreement η, ν and ρ. In addition, extrapolation of data in the absence of an analytical expression of temperature dependence of kinematic viscosity is impossible here.

The second relation (36) discussed above and has all the advantages of direct correlation with reference data for the kinematic viscosity, but also no guarantee of strict agreement with the dynamic viscosity and density.

Consistency guarantees contained only in the third model (37), combining two smoothed depending on the dynamic viscosity and density. Its correlation coefficient with reference data on the kinematic viscosity was quite high (R = 0,99979, t_R = 9095 >> 2) to hold it close to functional. However, to extrapolate to higher temperatures required for its analysis of the extremity in this area.

Indeed, in its most general form (32) the exponent is, as stated above, the difference decreasing, a_η, and growing, a_ρ, values. Already this is predetermined by the possibility of null values and the difference of the inversion depends on the effect of temperature. Omitting the details of the mathematical analysis of the dependence (32) in the form

$$\nu = \nu_1 (T_1/T)^{a_{\eta,2}(T_{\eta,2}/T)^{b_\eta} - a_{\rho,2}(T_{\rho,2}/T)^{b_\rho}}\text{, m}^2\text{/s} \qquad (38)$$

by its logarithm, differentiating and equating to zero, eventually arrive at the expression

$$\frac{a_{\rho,2} T_{\rho,2}^{b_\rho}}{a_{\eta,2} T_{\eta,2}^{b_\eta}} T^{b_\eta - b_\rho} - \frac{1 + b_\eta \ln(T_1/T)}{1 + b_\rho \ln(T_1/T)} = 0 \qquad (39)$$

with which the numerical solution can determine the temperature of minimum kinematic viscosity. Applied to the model (37) found a similar solution $T_{\nu,\min}$ = 1644 K. This is far above the boiling point of potassium (1032 K), but still below the estimated value of the critical temperature (2223 K). Therefore, extrapolation of the negotiation of dependence (32) in this case should be limited to about half the interval between T_b and $T_{\nu,\min}$. Thus, at 1300 K in (36) obtain the value ν = 1,733·10^{-7} m^2/s, and by (37) – 1,786·10^{-7} m^2/s with honors only 3,1 %. In the general case requires verification of the possibility extrapolation to the condition (39) with the corresponding restriction extrapolation at half the interval between $T_{\nu,\min}$ and the temperature of the last experimental (or reference) point.

CONCLUSION

1. On the basis of the Boltzmann’s distribution, and in accordance with this distribution based on the concept of chaotical particles are designed to form uniform temperature dependence of the dynamic, kinematic viscosity and density of melts.
2. To identify these relationships in a wide temperature range with a possible extrapolation to the area of the critical temperature requires the use of three control points.
3. In order to harmonize the three research characteristics of the melt can be a combination of two temperature dependences for the expression of a third, preferably for the kinematic viscosity through dynamic and density.
4. The accuracy of the proposed semi-empirical models viscosity based on their adequate extrapolation to the critical temperature area and despite the limited number of points used exceeds the known approximate dependencies, requiring for their construction of a much larger number of points, not least among the members of the approximating polynomial.
5. For the first time are consistent temperature dependence of the dynamic, kinematic viscosity and density of liquid potassium in the form of mathematical models, and in tabulated form.

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