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Development of Compositions and Technologies for Producing Heterocomposite Materials for Technological Equipment Using Mineral Fillers and Organic Modifiers

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ABSTRACT: The article presents the results of research in the field of the development of compositions and technologies for the production of new materials using mineral fillers as fillers for machine-building composite materials based on thermosetting polymers.

KEYWORDS: Polymeric coatings, casting materials, heterocomposite materials, corrosion, wear-resistant coatings, fillers, kaolin, gassypole resin, modifiers, epoxy resin.

I. INTRODUCTION

Introduction Due to the intensive development of mechanical engineering, construction and other industries, as well as the modernization of technological processes, the problem of corrosion-wear protection of metal products and metal structures becomes even more urgent.

It should be noted that in the industrial – production complex of economic sectors, technological and auxiliary equipment are widely used, operated under the influence of pronounced unfavorable factors, such as corrosive environment, abrasive components, temperature difference, ultraviolet radiation. In some cases, these adverse factors act simultaneously, leading to a reduction in the service life of machines, mechanisms, transport systems, lifting and transport equipment and specialized metal structures, tanks, containers and technological equipment for processing and storing raw materials.

To ensure the safety of the marked objects and increase their durability during operation, the nomenclature of protective coatings and technologies for their formation is continuously expanding, which provides a reasonable choice for specialists in the field of mechanical engineering, oil and gas, mining and chemical industries, the construction industry and other industries.

II. OBJECT AND METHODS OF RESEARCH

Composite coatings based on the ED-20 thermoplastic were introduced by introducing various fillers: graphite, wollastonite, polyethylene including mechanically activated Angrene kaolin of production brands, organic modifiers of gassipole resin (HS) and low molecular weight polyethylene, polyethylene polyamine hardener (PEPA).

Composite materials based on ED-20 have high physic mechanical properties and adhesive strength to the metal bases from which the process equipment and structures are made, high anticorrosion and wear-resistant properties when interacting with various media. In addition, the binding of ED-20 with the structurant PEP allows to obtain coatings in natural conditions under the influence of direct solar radiation without special heat treatment, which is very important for large-sized products and structures.

The physic mechanical properties (strength, hardness, modulus of elasticity) of hetero composite materials were determined by well-known standard methods.

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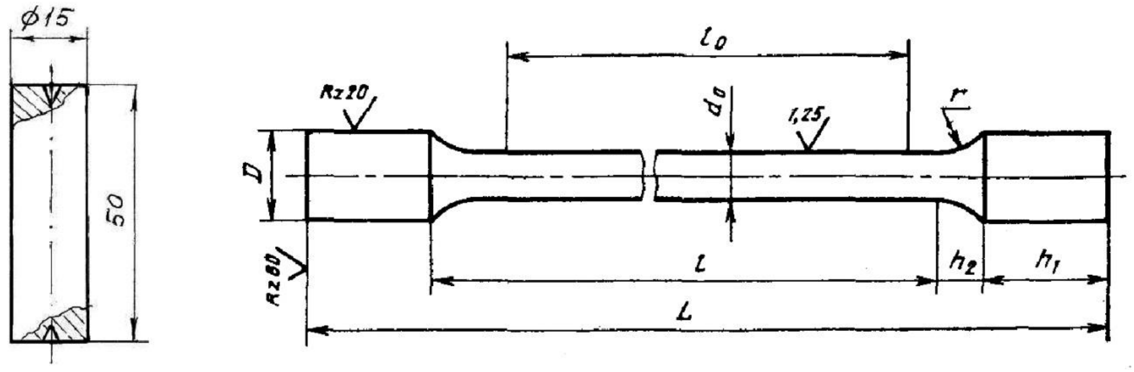
In particular in fig. 1 shows the samples and their geometrical parameters for mechanical testing.
The adhesive strength of hetero composite materials to the steel surface was determined by the fungal method (sample diameter D-25mm) on a tensile machine.
The intensity of linear wear was determined by the formula:

$$I = \frac{1}{L}\sum_n \frac{\Delta l_i}{n} \qquad (1)$$

where L is the friction path;
Δl_i- linear wear of samples (determined by the compass with compasses before and after the wear test, µm),
The rate of wear is controlled by changing the linear size or mass of the experimental samples per unit of time.



a) b)
a - in compression; b - tensile
Figure 1. Drawings of experimental samples according to GOST 1497-73

The wear rate was determined by the formula:

$$I_V = \Delta V/t \qquad (2)$$

Where t is the test time, hour; ΔV - volumetric wear value, mm3
Experimental studies on hydroabrasive wear in the laboratory were carried out according to the method proposed in [1]. The installation diagram is shown in Figure 2.

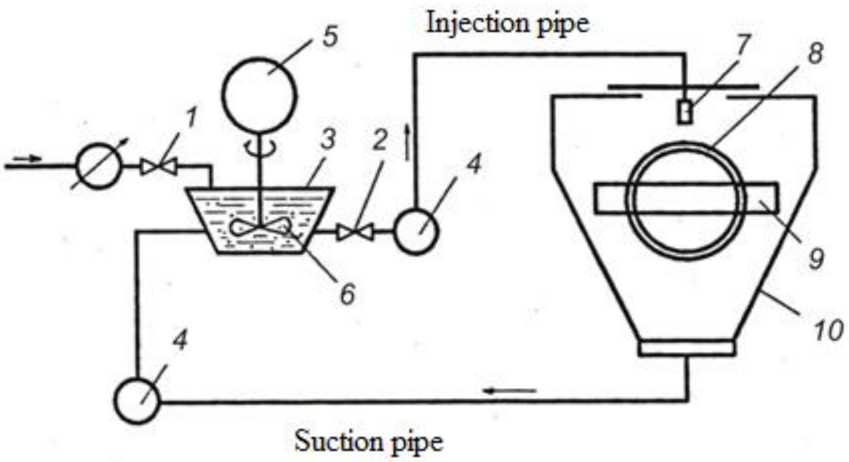


Fig.2. Diagram of the laboratory setup for the study of impact-abrasive wear of surfaces in the fluid flow: 1.2 - valves, 3 - pulp tank, 4-centrifugal pump, 5-electric motor, 6-agitator, 7-replaceable nozzle, 8- holder, 9 sample of the test material, 10 test bunker.

Laboratory installation works as follows: The finished hydro-forming solution from the tank through the valve (1) enters the laboratory tank (3), where with the help of a mechanical stirrer (6) homogenized pulp is formed, which is directed towards the discharge pipe with the help of the valve (2) through the injection pump (4). The pulp with the help of a replaceable nozzle (7) with the necessary pressure and speed acts on the sample (9) mounted on the holder (8). The surface of the sample (9) is coated with heterocomposite materials with a thickness of 0.5-2 cm. The advantage of this installation is that in small rooms the laboratory conditions provide the ability to simulate the operation of pipelines in production conditions.

Samples for hydro abrasive wear in the form of coatings with a thickness of 7-12 mm, on a metal surface of St-3 with a size of 50X100X3мм. subjected to hydro abrasive impact in the test bunker. The amount of mass wear was determined by weighing on an electronic scale with an accuracy of ± 1 mg. As an estimate of the relative wear resistance, we used the intensity of relative mass wear per unit of time.

At the same time, the microhardness of the coatings on the PMT-3 instrument was controlled, and the strength of the polymer film was determined on a P-05 tensile testing machine.

III. RESULTS OF THE RESEARCH

It is known that the greatest technical and economic effect in combating corrosion is achieved by isolating metals with the help of various protective coatings - metallic, inorganic nonmetallic, organic. Regardless of the type of coating material, they must have good adhesion, be non-porous and resistant in the environment in which the product is used. Metallic coatings are divided into cathode (more electropositive than the base metal) and anodic (more electronegative), while the coating protects the base metal electrochemically. They are applied in the hot way, immersing the product in a bath with molten metal, electroplating (electrodeposition), thermal diffusion and mechano-thermal (cladding) methods.

Inorganic nonmetallic coatings — silicate, cement, oxide, phosphate, chromate, and others — are used either alone or in combination with paint and varnish and other coatings, usually as a sublayer. Their main advantage is increased heat resistance.

Organic coatings include all types of polymer coatings, including paintwork and melt extrusion and cladding methods, as well as various lining coatings; coatings, linings with thin-sheet material, rubber gumming. Of organic protective materials, protective lubricants are still widely used - substances that are viscous in consistency, are made on the basis of refined petroleum products, non-drying vegetable oils, organosilicon and other oligomers.

Practice shows that the most important aspects of the effective use of protective coatings are the cost and availability of components, their impact on environmental parameters and safe use in current industrial production, as well as energy costs in the manufacture of semi-finished products and coating formation, especially based on local raw materials, in particular local minerals with industrial output. In this regard, the idea arose that such mineral fillers could be kaolins of the marks AKF – 78, AKS – 30, AKT – 10. The use of Angren kaolin production brands as fillers for machine-building composite materials opens up new opportunities for improving competitiveness in both the domestic and international markets. If effective mechanochemical modification of Angren kaolin is achieved, then it will be possible to use them widely in various economic sectors of the country, but also to determine the ways of export orientation.

One of the effective ways to obtain nano-sized local minerals, in particular, Angrenkaols, is preliminary mechanical activation [2–4].

Mechanical activation was considered as a transformation (change) of the structure of the material through the action of mechanical forces, giving it new physical and chemical properties. According to this physical representation, it can be argued that the range of changes in a substance caused by mechanical activation or the degree of mechanical activation depends both on the structure of the material itself and on the size and type of mechanical forces acting on it, and in the case of periodically acting forces also on amplitude and frequency .

The results of studies of the physicochemical properties of solids treated in vibratory and ball mills, mechanical activation is described as a result of changes in the type and number of defects in the structure of materials [2]. Moreover, in the ongoing process of processing a part of the previously occurring defects disappear. In such cases, mechanical activation can be increased by more intensive processing, not only to achieve the maximum effect of dispersion (grinding) to the nano size of natural minerals, but also to provide additional physical and chemical bonds due to the formation of electro-polarized particles of mineral fillers.

There are also other methods of dispersion, such as ultrasonic dispersion, which is also effective for grinding metal powders. Unlike mechanical dispersants, ultrasonic treatment promotes monochemical transformations of

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substances. At the same time, quite small nano-sized particles of materials from 10–20 nm to 2–1 nm and below are obtained.

The general tasks that determine further technical progress in the production technology of fillers for composite polymeric materials based on physicochemical mechanics can be considered:
- increase the physico-chemical activity of substances at the interface;
- achievement of maximum homogeneity (homogeneity) of processed mixtures, especially when mixing and compaction of multicomponent systems;
-compliance with the principle of minimum energy intensity of all technological processes;
- increasing the intensification of processes in order to drastically reduce their duration (increase in production).

The term "physical and chemical mechanics", or, in other words, "activation-technological mechanics" is a synthesis of three concepts: "activation", "technology" and "mechanics".

Activation means in this case the excitation of molecules, atoms, bringing the latter into a state in which they easily enter into a chemical reaction.

Technology - a set of methods and means of carrying out production processes to obtain the finished material.

At present, the term **"mechanics"** has acquired the meaning of "process theory". Thus, we can formulate the following general definition of the term "activation-technological mechanics" - this is a set of scientific principles underlying technological processes that optimally combine mechanical effects on components of a heterocomposite and methods for their physico-chemical activation (surface, bulk, combined), use which is offered in our research. Heterocomposites are common types of composite materials consisting of dissimilar organic, like polymeric, and inorganic, like mineral, metallic, etc., components that have virtually no chemical interaction with each other at the macrostructural level. Moreover, each component has its own purpose. The traditional three-component technology (pressure, temperature, time) for obtaining a composite material with the required properties today needs further development in a combination of methods of colloid chemistry and physics, in particular, ultra dispersion of particles — nanoparticles.

From the standpoint of the principle of minimum energy and labor-intensiveness of the full cycle of "activation-technological mechanics", mineral fillers possessing not only an inexhaustible source of raw materials, but also the availability of processing, are more profitable.

AKF – 78 kaolin, mainly intended for use as a filler in the paper industry. Among its special distinguishing properties are excellent viscosity and an excellent ratio to the thickness of kaolin particles 30: 1.

Kaolin AKS-30 has a wide range of applications in the manufacture of ceramics. Due to the positive effect on the formation of shards, this brand of kaolin is recommended for use, especially in cases where the process of ceramic molding is carried out by casting.

The physicochemical, granulometric compositions and other properties of local kaolins differ significantly from each other. Production brand AKT-10 is used in limited quantities, and the tail product (AKO) - production waste, which is about 50% of the total volume of processed products is practically not used and its accumulation is fraught with environmental problems of the area.

In recent years, good results have been obtained in the field of application of heterocomposite materials based on thermosetting epoxy resin (ED-20) resin and mechaically active nano particles of angrene kaolin above the marked industrial brands. Heterocomposites consisted of a mixed mass consisting of a binder (epoxy compound, 70-80%) and mechanically activated nanoscale Angren kaolin (20-30%).

The technology of forming casting heterocomposite materials and coatings from them are associated with significant labor and energy costs. In this regard, we used a solar-processing method for the curing of heterocomposite materials and coatings from them.

A number of compositions [4,5] have been developed with optimal use of nano-sized kaolin particles for casting materials and anti-corrosion – wear-resistant coatings with sufficiently high strength properties.

Based on the results of research, we have developed a new technological method of obtaining coatings by an activation-solar technology method on working surfaces of large-sized technological equipment using local material and energy resources, the flow chart of which is shown in Figure 3.

To prepare the compositions for the parts of the working parts of the machines and mechanisms, the initial components (1-4) of the mixture must be metered (6) in the correct ratio. After mechanical activation (7) and before mixing (8), the polymer composition is heated to 50-60 ° C. Mixing is performed on a mechanical stirrer or a ball mill (8).

The concentration of fillers is chosen depending on the types of polymer and filler, based on the desired properties of the products.

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When choosing a compounding of a mixture, one should take into account the effect of individual components of the mixture on the polymer, as well as the interaction of the components with each other. The uniformity of the physical and chemical properties of the finished products largely depends on the correct choice of compounding the mixture.

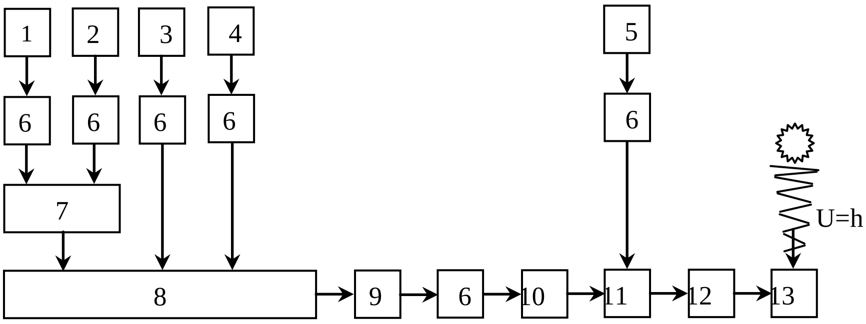

Fig.3. Technological scheme for obtaining heterocomposite epoxy coatings
1-mineral filler (0.0050.5 mm); 2- low molecular weight PE; 3-resin resin; 4- ED-20; 5-PEPA; 6 dispensers; 7 mechanoactivator; 8-ball mill; 9-commodity product (heterogeneous composition for anti-friction coatings); 10 preheating; 11-mechanical stirrer; 12-coating on the working bodies of large-scale technological equipment; 13-helioprocessing coatings.

The polymer composition of (8) as a heterogeneous product composition (9) through a dispenser (6) with preheating (10) enters a mechanical stirrer (11), where it is mixed with a hardener from the tank (5). In the mixer (11) the composition is mixed with the hardener for 3-5 minutes. It should be noted that an increase in the mixing time in the mixer (11) does not lead to good results, because after adding PEPA, the viscosity of the composition associated with the curing process increases and adversely affects the quality of the resulting coating.

The composition is poured by gravity onto the surface of the coated sheet material from which the products are made (12), followed by solar processing (13) for 3-5 hours, depending on the ambient temperature.

Composite polymeric materials for anticorrosion purposes in hydro-abrasive environments are most effective when they are used as two-layer coatings with a thickness of 7-12 mm. At smaller values, it is difficult to ensure single-season durability as a result of wear or peeling of coatings. According to the same technological scheme, you can get potting materials in the required forms.

The optimum amount of Angren kaolin content in potting materials and coatings is 20–30 wt.h. Moreover, from an economic point of view, kaolins with large particles are more beneficial in compositions, which is associated with the consumption of expensive epoxy oligomers [6]. The composition of anticorrosive heterocomposite materials is given in Table 1.

As a result of the conducted research comparing the evaluation of the anticorrosion ability of the compositions investigated by the gravimetric method showed that the best protective properties against corrosion in salt medium are compositions filled with kaolin of the AKT – 10 production grade and in an acidic environment - compositions filled with kaolin of the production brand AKF – 78 (table 2). Such a difference in the properties of coatings filled with kaolin is due to their chemical composition and particle size. Due to the fact that kaolin AKT – 10 compared to AKF – 78 oxides: iron oxide, silicon dioxide is greater, the predominance of aluminum oxide in AKF – 78 gives an advantage to the coating based on it to predominate anticorrosive properties to aggressively acidic media.

Table 1.The composition of anticorrosive heterocomposite materials

The Components of compositions	**Content (parts by weight) and composition of HM**		
	КГПМ-1	**КГПМ-2**	**КГПМ-3**
ЭД–20	100	100	100
Modifier	10	10	10
ДБФ	10	10	10
ПЭПА	10	10	10

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АКF–78	10	–	15
АКС–30	–	10	15
АКТ–10	20	20	–
Graphite	–	5	–

Table 2.The results of the gravimetric determination of the degree of protection anti-corrosion coating

№	Test environment	Indicators	Control sample	КГПМ-1	КГПМ-2	КГПМ-3
1	H_2O	K	0,012	0,000027	0,000018	0,000018
		Z	-	99,8	99,7	99,8
2	NaCl 5%	K	0,0059	0,00056	0,00068	0,00054
		Z	-	98,8	99,8	98,9
3	Na_2CO_3 5%	K	0,0061	0,00060	0,00058	0,00058
		Z	-	94,2	99,1	98,6
4	Na_2SO_4 5%	K	0,0049	0,00055	0,00048	0,00049
		Z	-	98,7	97,8	98,7
5	Na_2S 5%	K	0,0060	0,00066	0,00064	0,00062
		Z	-	94,8	98,7	98,6
6	$NHCO_3$ 5%	K	0,0057	0,00047	0,00047	0,00050
		Z	-	99,8	99,8	99,8
7	$CaCO_3$ 5%	K	0,0029	0,00024	0,00022	0,00029
		Z	-	98,7	99	98,8

K, (kg / m2sut) - corrosion rate; Z%, - degree of protection.

The results of this study allowed us to develop a number of compositions of heterocomposite materials for anti-corrosion and wear-resistant purposes with the optimal structure obtained by activation heliotechnology. In particular, the proposed new compositions of heterocomposite coatings using a small amount of flake graphite. For example (tab. 3), coatings of the type HCPP (anticorrosive heterocomposite coating) can be obtained by adding electrically conductive graphite in the range of 3-5 parts by weight, kaolin 35-37 parts by weight to 130 wt.h. Edk And coating type IGPP (anti-corrosion and wear-resistant heterocomposite coating) - by adding electrically conductive graphite in the range of 3-5 parts by weight, kaolin 15-17 parts by weight, wollastonite-17-19 masses. hours, polyethylene 1-3 wt.h. to 130 wt.h. Edk.

Table 3.Composition and properties of the developed coatings

Types of coatings	The content of components, parts by weight			Properties	
	ЭДК[2]	В: ПЭ[3]	Graphite:Kaolin	$H_м$, MPa	σ_a, MPa
КГПП-1	130	-	3:37	178	32,5
КГПП-2	130	-	5:35	172	34,5
ИГПП-1	130	35:0	5:0	276	38,2
ИГПП-2	130	37:0	3:0	288	39,8

Notes: 1) K-anticorrosive, I-wear-resistant, G-heterocomposite, P-coating; 2)ЭДК: ЭД-20=100 parts by weight, ДБФ=10 parts by weight, ГС=10 parts by weight, ПЭПА=10 parts by weight; 3)В:ПЭ - wollastonite: polyethylene (by numerical ratios in mass parts); 4) sun exposure time (710-750 W/m^2)– 8 h., T_{oc} =42±2 ^{0}C.

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IGKP coatings (wear-resistant heterocomposite coating) can be obtained only on the basis ofwollastonite and graphite. The total number of fillers - 40 wt.h. - due to the limiting values of the viscosity of the compositions, providing manufacturability when applied to the surface of large-sized technological equipment. Structural parameters of the developed coating compositions are given in table 4.

Table 4.Structural parameters of the developed coatings

Types of coatings	Structural parameters: ρ_s, Ω (in numerator); R_z, μ		
	original	ground	run-in
КГПП-1	$1,4\cdot10^8/3,5$	$4,6\cdot10^4/ 2,8$	$0,8\cdot10^3 / 6,2$
КГПП-2	$6,4\cdot10^7/3,9$	$1,2\cdot10^3 / 2,9$	$0,4\cdot10^2 / 6,5$
ИГПП-1	$4,6\cdot10^7/6,2$	$0,6\cdot10^3 / 3,2$	$2,1\cdot10^2 / 5,8$
ИГПП-2	$8,2\cdot10^8/ 6,1$	$3,1\cdot10^4 / 3,6$	$2,8\cdot10^3 / 5,6$

The results of the study allowed us to propose a technology for obtaining coatings by the activation-solar technology method on the working surfaces of technological equipment, with the rational use of local raw materials and energy resources.

IV. CONCLUSION

Summarizing, it can be noted that, as can be seen from the presented materials, composite materials using nano-sized local minerals on the example of Angren kaolin are materials of the future with a great prospect. It should be noted that the existing physical methods of processing composite polymer materials and mechanical activation of fillers in traditional installations, for example, ball mills, disassembrator activators, etc. morally outdated and require further improvement of design and kinematic-dynamic parameters. There is also an acute problem of creating and applying new, more efficient types of chemical modifiers from local raw materials.

Further development of the development of highly efficient heterocomposite polyfunctional materials using local minerals is possible with the effective and targeted integration of scientists, designers, technologists, power engineers and other professionals, entrepreneurs and manufacturers.

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