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ANALYSIS OF WATER-REPELLENT PROPERTIES OF COATINGS BASED ON HYDROPHOBIZED EXPANDED PERLITE UNDER MECHANICAL ABRASION

The object of research in the work is water-repellent surfaces using crushed perlite to form micro-crushing. The existing problem lies in the fact that the level of existing technology of superhydrophobic coatings at the moment is insufficient for wide practical application. The main limiting difficulties are the insufficient resistance of superhydrophobic properties to operational factors, including mechanical wear, the action of vaporous water, as well as the low scalability of classical ways of applying textures to protected substrates.

In this work, it is shown that one of the effective ways to obtain scalable coatings with increased water repellency is to use hollow glassy particles, such as perlite, to create a surface microstructure that allows one to achieve a stable Cassie state for water droplets. In this case, the contact area of the surface with the liquid is minimized, since fragments of hollow particles, the orientation of which is close to normal, are used in the coatings. Of practical interest in the application of such structures is the study of their behavior during mechanical wear, in particular, under the action of particles, which is an important operational factor for outdoor coatings. It is shown that coatings based on crushed perlite during abrasive wear retain and at the initial stage of destruction increase water-repellent properties. Crushed perlite was hydrophobized by treatment with polymethylhydrosiloxane, which provided the values of the wetting angle of the powder material at the level of 145°, and the rolling angle of less than 10°. The surface energy of the acrylic-styrene matrix coatings was determined. It is shown that the surface geometry of such coatings is inhomogeneous. An extreme dependence of the contact angles of the surface on the amount of abrasive was determined. As a result, it is found that under the static action of water, the expected decrease in the contact angle of the surface occurs, but there is no complete loss of the Cassie state.

Keywords: *superhydrophobic coating, water-repellent surfaces, crushed perlite, water contact angle, polymethylhydrosiloxane, water-repellent coating.*

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1. Introduction

The water-repellent properties of surfaces are an important factor in their protection against the action of liquid water. The level of the currently existing technology of superhydrophobic coatings is currently insufficient for wide practical application [1]. The main limiting difficulties in this case are the insufficient resistance of superhydrophobic properties to operational factors, including mechanical wear, the action of vaporous water, as well as the low scalability of classical ways of applying textures to protected substrates. In [2], it was shown that one of the effective ways to obtain scalable coatings with increased water repellency is the use of hollow glassy particles, for example, perlite, to create a surface microstructure that makes it possible to achieve a stable Cassie state for water droplets. In this case, the contact area of the surface with the liquid is minimized, since fragments of hollow particles, the orientation of which is close to normal, are used in the coatings. The efficiency of such a solution follows from the analysis of the equation [3] describing the Cassie state. Namely, considerations of reducing the proportion of the fraction of the perimeter of the drop that is in contact with the protrusions of the surface while increasing the distance between them. Of practical interest in the application of such structures is the study of their behavior during mechanical wear, in particular, under the action of particles, which is an important operational factor for outdoor coatings. As shown in [4], microelements of hierarchical structures, however, are quite resistant to abrasive wear compared to nanosized ones. It should be taken into account that in order to ensure high water-repellent properties, the surface of the fragments of hollow particles must be functionalized with agents that ensure the maximum decrease in its surface energy. Therefore, during abrasion, one should take into account the presence of a balance of competing processes of destruction of the layer itself under the action of abrasive particles, removal of texture elements, etc., which has not yet been considered in other works.

Thus, *the object of research* is water-repellent surfaces using crushed perlite to form micro-crushing. *The aim of research* is to determine the nature of the loss of water-repellent coatings based on fragments of hollow pearlite particles during abrasive wear. To achieve this aim, the paper solves the problems of characterizing the initial material, selecting the mode of its dispersion to obtain microstructures of suitable geometry, creating the microstructure of coatings, reducing their surface energy, structural characteristics, behavior under abrasive wear conditions and under the static action of water. Provided sufficient strength of the functional layer is ensured, the fulfillment of these tasks will be a significant contribution to the creation of bulk superhydrophobic coatings, the expected service life and stability of which are much higher than those of traditional surfaces with flat texturing [5, 6].

2. Research methodology

Expanded perlite with a bulk density of 150 g/l was used in the work. It has been shown [7] that silane compounds are an effective means for hydrophobizing pearlite. Was used polymethylhydrosiloxane (Xiameter MHX-1107) manufactured by Dow, USA.

The process of modification of ground perlite took place in a 1 % solution of a silane modifier in xylene. Perlite and mortar were mixed in a ratio of 1:1 and left for a day. Next, the material was filtered and dried at 50 °C for 48 hours.

To obtain the coatings, a 20 % solution of acrylic/styrene polymer (Neocryl B-880 (DSM NeoResins, Netherlands)) in xylene was prepared, which was mixed with the filler at the required concentration. The coatings were obtained in bulk and dried at 50 °C for 24 h.

Using a digital goniometer and the corresponding software, the sessile drop method was used to characterize the water-repellent properties of the coatings by the contact angles of water wetting. Optical microscopy photographs were obtained using an optical microscope, a digital camera and the corresponding software (ScopeTek View). Electron microscopy photographs were taken with a REM-106 scanning electron microscope (Selmi, Ukraine). The wear resistance of the coatings was evaluated by a sand abrasion test [8]. The technique consists in spilling sand with a particle size of 200–500 μm through a tube 1.5 cm in diameter and 100 cm high, the feed rate was 50 g/min. Every 25 g of sand, the contact angle was measured.

3. Research results and discussion

The expanded perlite used in the work is a solid foam (Fig. 1, *a*) with an average particle size of 31±1.2 μm and a wall thickness of about 2±0.1 μm (Fig. 1, *b*). In this case, there are areas of bubble cleavage, which probably make the greatest contribution to the value of the bulk density of the material, which is 92 kg/m^3. It is known that the main oxide in perlite is silicon dioxide (about 80 %), the material also contains oxides of alkali metals [9]. It should be noted that the configuration of particles after swelling, in addition to the properties of the initial pearlite, is also determined by the parameters of the process of its production: temperature, time of flight of particles through the hot zone, etc. [10].

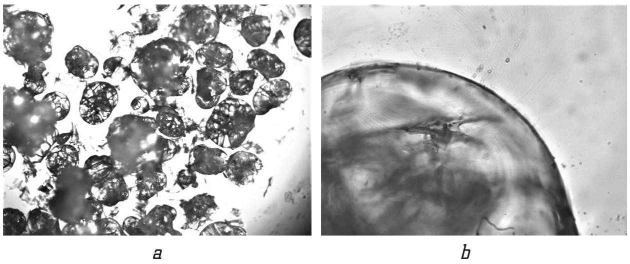

a *b*

Fig. 1. Configuration of hollow particles of expanded perlite: *a* – particles themselves, 48x magnification; *b* – outer wall of the chamber, 480x magnification

The geometry of the particles obtained in the crushing process depends on the duration of processing. So, for example, after being in a ball mill for 2 hours compared to 1 hour, the average particle size decreases from 14±0.6 to 5±0.4 μm, while the shape of the particles remains very close – in the form of curved plates of irregular shape. Cleavage areas are transformed into three-dimensional particles.

Given the rather wide size distribution of the material particles (Fig. 2), after grinding, it was decided to use a 1-hour milled product in order to ensure the presence of relatively large microparticles in the coating.

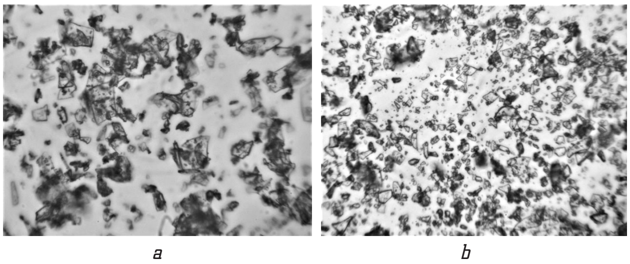

a *b*

Fig. 2. Products of grinding hollow particles of expanded perlite in a ball mill: *a* – 1 hour of processing, 480x magnification; *b* – 2 hours of treatment, 480x magnification

Treatment of the surface of the obtained particles with polymethylhydridesiloxane leads to the formation of a hydrophobic covalently bound layer on its surface, as was shown in [11]. The particle surface contact angle reaches values above 145°, and the roll angle is less than 10°, which is a rather high indicator for a structure created only from microparticles, without the presence of a nanosized fraction.

When creating coating systems based on this dispersed material, a styrene-acrylic polymer was used as a film former. The mass content of hydrophobized ground perlite in the matrix was 85 %. On Fig. 3 is a Zisman plot for this coverage. Its critical surface energy is 27 mN/m, which is higher than the expected values for a completely hydrophobized layer – about 21 mN/m for pure polymethylsiloxane [12].

This could be explained by the fact that perlite particles are covered with a film former in the area of contact with a water drop, however, it is known that the surface energy of polyacrylates is in the range of 37–41 mN/m [13], and that of polystyrene is 34–38 mN/m [14]. A probable explanation for the actual value of the critical surface energy of the coatings can be that the hydrophobized particles are wetted by the matrix polymer only in the lower part of the coating layer, while the upper one, which is in contact with the liquid in the Cassie state, is covered only with a hydrophobizer layer and, therefore, has a reduced energy.

In the course of determining its value by the Zisman method, with a decrease in the surface tension of the test liquid and the transition from the Cassie state to the Wentzel state, both this surface and the film former are wetted, which leads to an overestimated indicator.

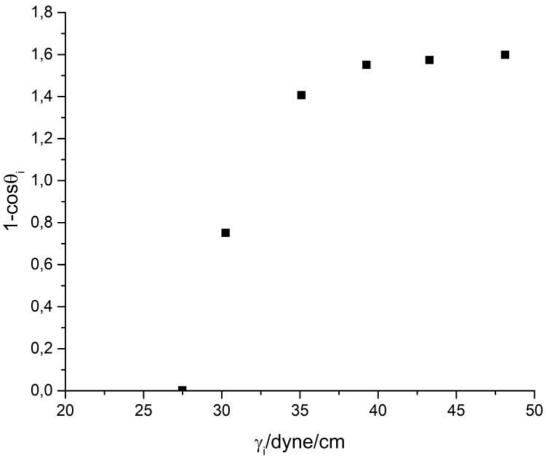


Fig. 3. Determination of the surface energy of coatings based on perlite by the Zisman method

The structure of the surface of such coatings is rather inhomogeneous (Fig. 4): along with particles oriented almost normally to the substrate surface, there are also particles which main plane is parallel to it. However, the conditions for a plane contact of a liquid drop with the surface of the fragments are also absent due to their unevenness.

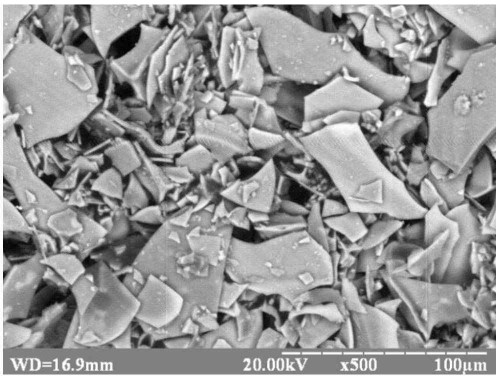
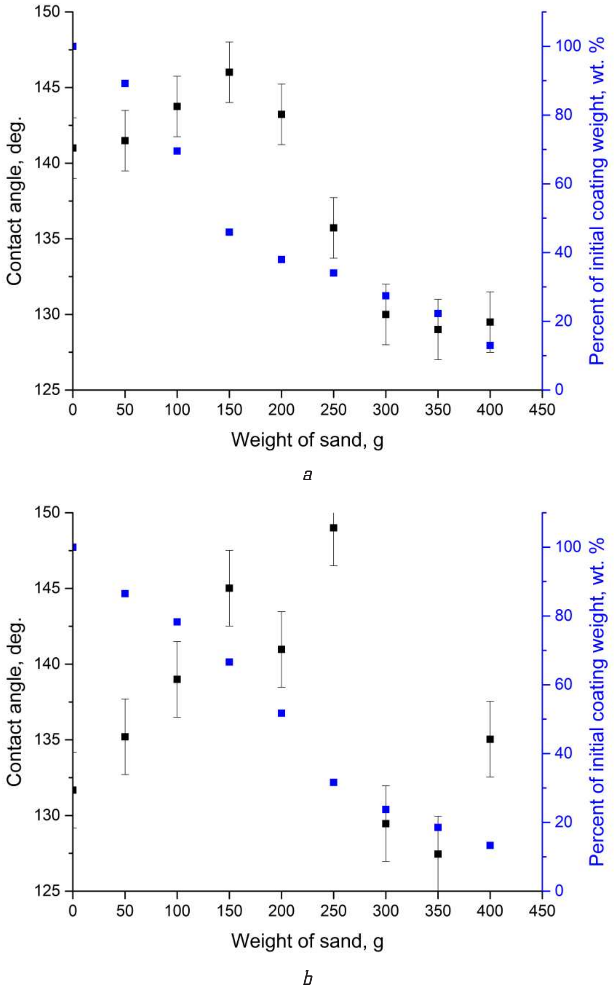


Fig. 4. The surface structure of the coating based on crushed perlite (75 wt. %) and acrylic polymer (25 wt. %)

It is noteworthy that the surface of large particles is dotted with small ones, which form a fairly stable contact, which, as can be assumed, is provided by the presence of an adhesive layer of polymer, which increases the surface heterogeneity.

During the wear test, as shown in Fig. 5, the value of the contact angle of the coatings increases to a certain limit (175 g of abrasive for a system containing 15 wt. % polymer (Fig. 5, *a*) and 275 g in the case of a content of 35 wt. % polymer (Fig. 5, *b*)), after which begins to decrease to the initial values and below. The increase in the contact angle to the extremum point can be explained both by surface contamination of the microtextured coating with fragments or whole pearlite particles, and by the removal of a part of the acrylic film former. A decrease in this indicator after the extremum point, in turn, can be explained in a gradual removal of pearlite microparticles that form the structure of the coating this assumption is partially confirmed by the correlation of the contact angle curves and the mass loss of the coating.



a

b

Fig. 5. Resistance of coatings to mechanical abrasion depending on the content of perlite filler: *a* – 85 wt. %; *b* – 65 wt. %

Long-term resistance to the action of liquid water, in fact, also includes the resistance of the Cassie state provided by the surface microstructure to the action of saturated water vapor. As is known [15], this is one of the serious operational problems of superhydrophobic coatings, which violates their long-term stability. Coatings containing 25 wt. % when exposed to liquid water reduce the contact angle from 138 to 125 degrees in 10 hours (Fig. 6). After this time, the contact angle remains relatively stable.

It should also be noted that this stabilized angle is higher than the expected angle in the Wentzel state, which indicates the fact that the Cassie state is partially preserved for some surface fragments. This is an expected consequence of having such a heterogeneous surface structure in terms of possible wetting states, as shown in Fig. 4.

The dependences obtained, especially regarding abrasion, suggest the presence of a more effective coating structure in terms of water repellency, as well as a promising configuration of interparticle voids, which ensures the preservation of the Cassie state during long-term exposure to water. An additional resource for improving coatings is the choice of a binder whose surface energy is initially lower than that of the polymers used. Contact with the surface of the particles in this case can be ensured by using limited amounts of wetting agents.

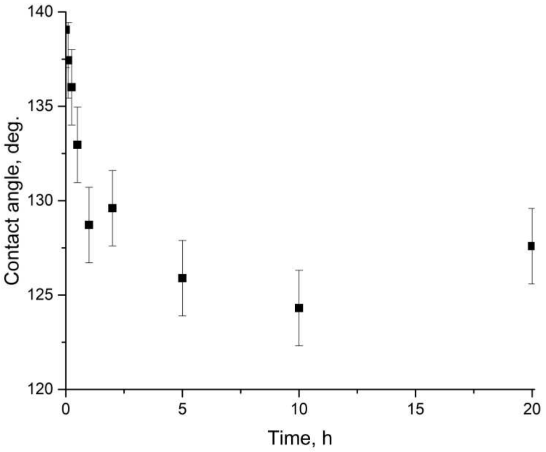


Fig. 6. Changes in the wettability of coatings under the action of static water

The limitations of this study are the quartz sand abrasion method itself, which leads to errors, and it is not well understood how the composition of the coating affects abrasion resistance. In this work, two variants of the binder concentration were used, and the relationship between the amount of binder, abrasion resistance, and the wetting angle with water is not visible.

A promising direction of this research can be considered the search for and change in the granulometry of perlite to increase efficiency, the selection of a binder with a lower surface energy, and the addition of a nanolevel structure strongly associated with microparticles.

4. Conclusions

The paper shows that coatings based on crushed perlite retain their water-repellent properties during abrasive wear and, at the initial stage of destruction, increase. The maximum value of the wetting angle obtained during destruction is 152° (with the initial 136°), and the resistance of the coating to abrasion increases with an increase in the amount of binder.

When using expanded perlite with an average particle size of 31 µm as a starting material, products with an average particle size of 5 to 14 µm were obtained by grinding in a ball mill. The latter was hydrophobized by treatment with polymethylhydrosiloxane, which ensured the values of the wetting angle of the powder material at the level of 145°, and the rolling angle of less than 10°. Surface energy of coatings containing 85 wt. % of this acrylic-styrene matrix material was 27 mN/m.

It is shown that the surface geometry of such coatings is rather inhomogeneous; however, most of the fine fraction of lamellar particles is oriented in the direction normal to the substrate. An extreme dependence of the wetting angles of the surface with water on the amount of abrasive is observed, the position of the extremum point is determined by the content of the binder in the system.

It has been established that under the static action of water, the expected decrease in the contact angle of the surface (from 138 to 125°) occurs, but there is no complete loss of the Cassie state.

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