Investigation of Conditions for the Creation of Hydrophobic Sand

Meruyert Nazhipkyzy, Gulmira Orinbekovna Tureshova, and Zulkhair Aimukhametovich Mansurov

1 Introduction

A surface that exhibits a large wetting angle, more than 150°, called a superhydrophobic surface [1]. Such surfaces have properties of extremal hydrophobicity and less wetting angle hysteresis. These properties occur from having an excessively less area of the solid surface coming into contact with water.

To obtain a superhydrophobic surface, two requirements should be satisfied. First of all, the surface should have roughness. The second is the material should have a low surface energy [2]. If these two conditions are contented, a water droplet on the surface matches to the Cassie law.

Currently, there is a wide range of modern hydrophobic coatings that provide reliable protection against the effects of aggressive environmental components, as well as reduce the water absorption of the surface of materials, but their main disadvantage is the high cost of production. In addition, over time, water leaches hydrophobic compounds and, therefore, with a certain interval, they need to be restored. Considering the expensive cost of these materials, the economic part of this issue plays an important role. Therefore, today there is a need for hydrophobic composite materials, the fabrication of which would be profitable, and their application would be effective [3, 4].

In recent decades, there has been a steady demand in the world for materials with hydrophobic properties. Because such kinds of materials have a number of exceptional functional properties, such as water resistance, resistance to bio corrosion, as well as resistance to pollution of organic and inorganic origin [3]. According to the

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above properties, the advantages of using such materials in everyday life and in technology are obvious. For example, with the penetration of water in building structures, corrosion and deformation can occur. Such destruction for traditional materials is primarily associated with the action of stresses that occur when water gets into defects and splits in the surface layer of the material and its subsequent freezing [4]. However, this problem can be solved using hydrophobic water-repellent materials, which can provide materials such as brick, concrete, plaster, gypsum, and asbestos cement water-repellent properties. The composition of all types of mortars, concrete, and asphalt concrete includes sand. It is also used in the form of a sandy "pillow" in the construction of foundations of buildings, in the road construction industry, and when laying pavers and paving slabs. Sand is also widely used for drainage.

In early studies, conditions were obtained for the formation of hydrophobic sand based on synthesized soot during the combustion of propane-oxygen mixture/waste oils. The results showed that the obtained sand covered with polyurethane glue and soot having hydrophobic properties was not wetted by water and the surface grains of the hydrophobic sand were fully enveloped by a nanoscale layer of superhydrophobic soot [5–7]. The results showed a decrease in water shortages and an increase in water conservation for the irrigation of crops [6–8].

Therefore, an urgent task is to impart hydrophobic properties to the sand. Sand with such properties will find wide application not only in construction but will also be able to solve the problem of acute water shortages in many regions. It is able to reduce water consumption for irrigation, and in desert territories it takes up to 80% of water for irrigation. Hydrophobic sand can be used as a protective barrier between the upper layer of the earth, which is agriculturally viable, and the rest of the soil. A hydrophobic sand layer of 10 cm would not allow water to seep, which would significantly reduce water consumption for irrigation. Such discovery allows for the purification of water from oil and other fatty substances. Hydrophobic sand repels water but allows molecules of oil and oil to react with it and penetrate into the sand. Due to this, oil and oil are absorbed into the sand, and at the outlet there is clean water. This will make it feasible to purify/filter water if it is polluted with oil. Hydrophobic sand is also useful for irrigation. It is able to hold oily substances and prevent groundwater contamination. It can be coated with pipes and cables to prevent humidity and corrosion.

An efficient way to prevent water absorption by a material is to modify its surface – hydrophobization. It is known that the hydrophobicity of materials is characterized by the structure and qualitative specifications of the surface layer [4]. Giving hydrophobic properties to materials is possible through the application of coatings with lower energy. The aim of the present work is to identify the conditions for the creation of a hydrophobic coating on quartz (river) sand using recycled silicon-containing waste.

It is known that firing waste organosilicon polymers can be used to obtain mechanically stable hydrophobic material in the form of a powder [9, 10]. For this purpose, the spent silicone products were placed in a metal container and then burned, where the resulting material was subjected to grinding to the necessary particle size [9].

Research in the field of nanoscale effects shows that the hydrophobic properties of surfaces are based on a regular structure of particles, protrusions or tips of submicron and nanometer size, arranged on the surface in an ordered manner. Such surfaces can be obtained by chemical or ion etching or by the method of growing nanoscale materials from the bottom up. Methods have been developed for growing vacuum "carpet" hydrophobic coatings from ordered carbon fibers. Water on such a coating, having contact only with the tips of protrusions or fibers, is fragmented into droplets by surface tension. A similar effect exists in wildlife. A striking example is the surface of the lotus leaf, dotted with numerous microscopic protrusions, giving the surface of the leaves exceptional superhydrophobic properties.

2 Materials and Methods

This study also revealed that soot obtained under certain conditions of hydrocarbon fuel combustion has a superhydrophobic property and can be used as a filler in the creation of hydrophobic coatings. The main disadvantage of soot is that its interaction with water initiates the mobility of nanostructured carbon components and new structural formations appear which lead to a loss of hydrophobic properties. However, if soot is obtained under certain conditions of fuel combustion, the obtained soot retains hydrophobic properties even after interaction with water, and it can be used to impart waterproofing properties to various materials. The optimal conditions for advancing the hydrophobic properties of carbon nanomaterials (soot, carbon nanotubes, carbon fibers) obtained during combustion and pyrolysis of associated gases from oil fields were determined [5]. Thus, silicone waste was burned. As a result, a gray polydisperse powder was obtained. The method developed for producing nanodispersed powder for the study herein is simple. The method is based on the method of burning silicone waste (supports made of silicone, various forms made of silicone); as a result, a mechanically durable hydrophobic nanodispersed powder is formed, Fig. 1a, b.

The burning method does not require additional energy costs, and the developed method yields a nanodispersed powder with a contact angle of over 155 °. Thus, a method has been developed that allows simple combustion to produce a white-gray colored nanodispersed powder, which does not have an odor and does not have a harmful effect on the skin. Figure 2 shows the resulting powder with droplets of water on its surface.

Figure 3 shows the nanodispersed superhydrophobic powder, obtained during the burning process of waste of silicone materials, with a thin layer rubbed onto the surface of cardboard. The behavior of water droplets on its surface shows the exceptional hydrophobic property of the powder. This test shows that to give the surface a hydrophobic property, a sufficiently small amount of powder is used as a consumable.

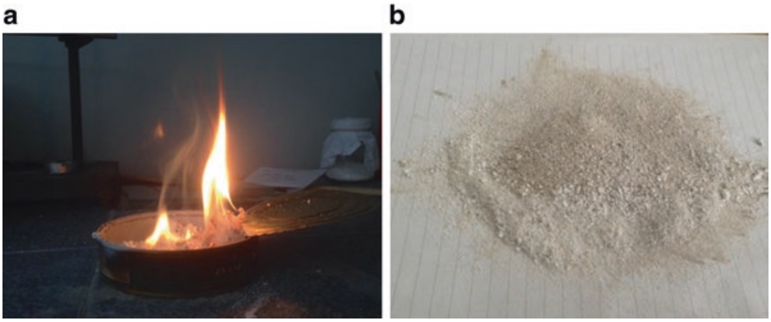

Fig. 1 The burning of waste organosilicon polymer compounds (**a**), the resulting superhydrophobic powder (**b**)

Fig. 2 The contact angle of the powder with the surface

Fig. 3 A droplet of water on the surface of superhydrophobic sand

Microscopic examination showed the presence of particles of various sizes from 10–12 microns to 100–200 microns. The contact angle of the powder surface exceeded 150 degrees, i.e., wetting practically does not occur.

The obtained hydrophobic agent (silicone ash) was used to create a bulk hydrophobic material based on quartz sand, which is 85–90 wt.% silicon dioxide. The sand was previously cleaned and sieved, where a fraction of 0.5–1 mm was selected. Then it was dried at a temperature of 50–70 °C. The prepared sand was intensively mixed with the synthesized hydrophobic agent in a mixer at a speed of 300 rpm for 4–6 min. The role of the hydrophobic powder is to increase the degree of adhesion of the hydrophobic film on the surface of the grains of sand. In order to determine the optimal amount of hydrophobic agent, mixtures of a hydrophobic agent and sand were preliminarily prepared in the following ratios: 0.5:100, 0.75:100, 1:100, 1.25:100, 1.5:100, 1.75:100, and 2:100. As a result of the studies, bulk material was created, characterized by good water-repellent properties and resistance (Fig. 3).

The advantage of this sand based on silicone ash compared to the sand obtained on the basis of soot is that, in this case, it does not require the addition of polyurethane glue in its creation [3, 4].

3 Results and Discussion

To measure the contact angle of the hydrophobicity of the obtained material, a KRUSS tensiometer was used. The initially obtained mixtures of hydrophobic agent and sand were compressed into tablets. Next, a drop of water in a volume of approximately ~2 μl was placed on the tablet surface. A high-speed camera recorded the process of droplet formation on the surface, which allows for the macro images of the surface. Using the mathematical calculation and the advance program, the exact contact angles were calculated using the method of lying drop. Thus, the contact angle for a mixture of hydrophobic agent and sand in various ratios: 1:100, 1.5:100, 2:100, and 3:100, is shown in Fig. 4.

As can be seen from Fig. 4, the contact angle for a mixture of hydrophobic agent and sand in a ratio of 1:100 was 157.8°, respectively, 1.5: 100 was 162.4°, 2:100 was

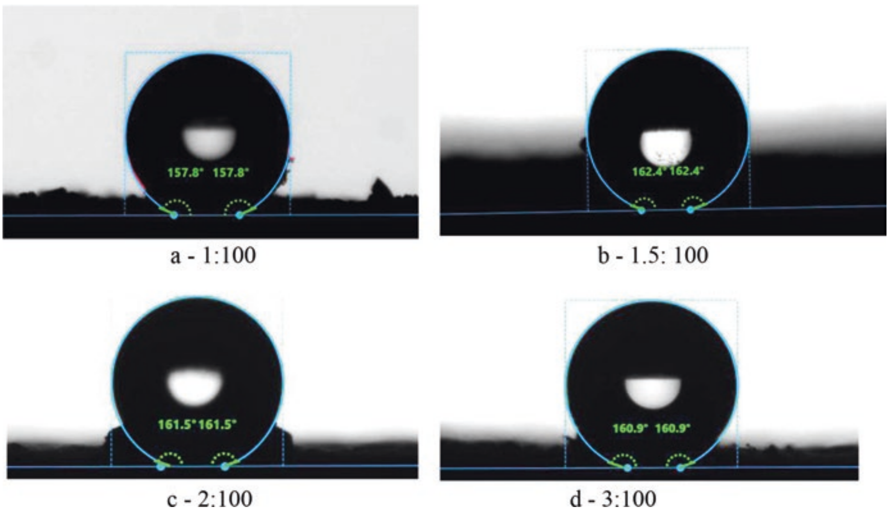

Fig. 4 The contact angle for a mixture of a hydrophobic agent and sand in different ratios

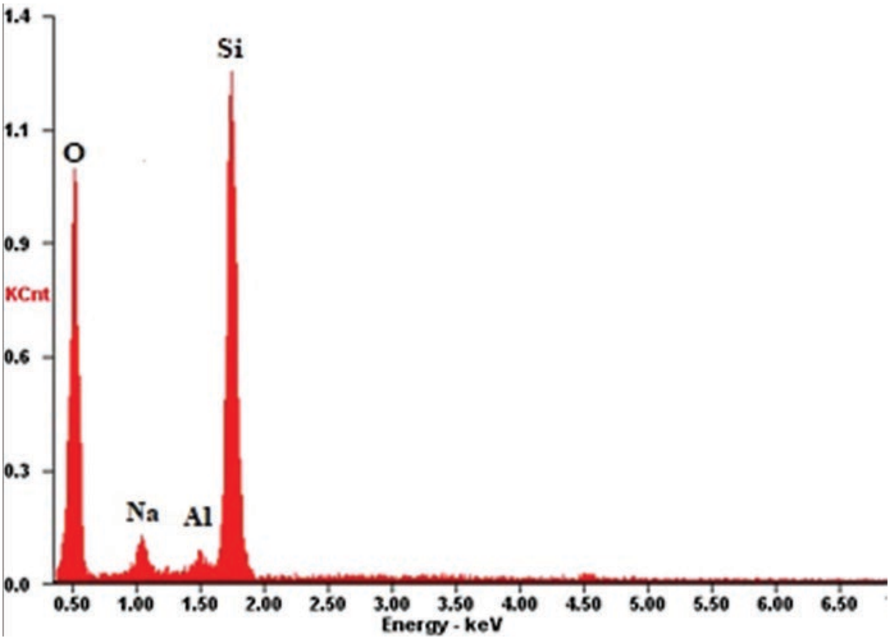

Fig. 5 EDAX analysis of hydrophobic agent

161.5°, and 3:100 was 160.9°. The amount of hydrophobic agent did not affect the hydrophobic properties of the material. This suggests that the sand should contain a sufficient amount of hydrophobic agent and the surface of the sand should be completely covered.

To obtain a quantitative analysis, samples of a hydrophobic agent and sand based on hydrophobic agent were studied by EDAX. The results of the analysis showed the appearance of four peaks, corresponding to oxygen, sodium, aluminum, and silicon, and were observed in the composition of the hydrophobic agent (Fig. 5).

Table 1 shows the elemental composition of the hydrophobic agent obtained by burning silicone waste. The data indicates that the composition of the resulting ash depends on the starting materials that were burned. The silicon content was 29.94%.

EDAX analysis of sand based on hydrophobic agent is shown in Fig. 6.

Three peaks were observed in the X-ray diffraction pattern: O, Al, and Si; the most intense of which were silicon. Table 2 shows the mass ratio of silicon, oxygen, and aluminum.

According to the obtained data, it can be considered that the main component in the composition of quartz sand and hydrophobic agent is silicon dioxide.

The above studies of the elemental composition of the hydrophobic agent and of the sand based on hydrophobic agent were confirmed by X-ray fluorescence analysis. The obtained X-ray diffraction patterns of the materials are shown in Figs. 7 and 8.

One intense peak corresponding to silicon is observed on the X-ray diffraction pattern of the hydrophobic agent.

Table 1 The elemental composition of hydrophobic agent (silicone ash)

Element	Wt., % (by weight)	At, % (atomic mass)
C	20.68	29.73
O	45.39	48.99
Na	2.81	2.11
Al	1.18	0.76
Si	29.94	18.41

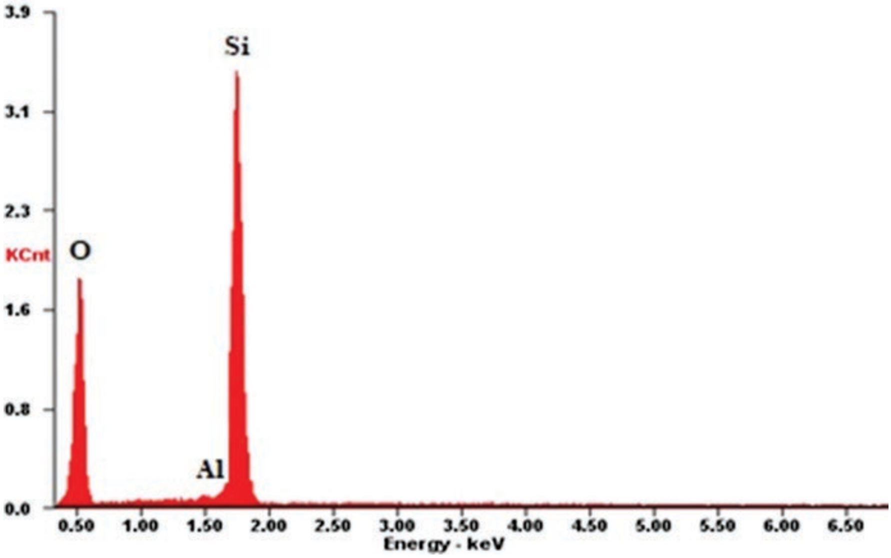

Fig. 6 EDAX analysis of sand based on hydrophobic agent

The created sand contained silicon at 43.77%; aluminum, 26.76%; iron, 15.33%; potassium, 6.03; calcium, 5.66%; and titanium, 1.47%. The remaining elements (manganese, copper, zinc, rubidium, strontium) made up less than 0.5%.

Morphological features of the studied objects were studied by optical and scanning electron microscopy (SEM), as seen in Fig. 9.

Fig. 9 shows that the surface of the hydrophobic agent is inhomogeneous, the size of the microparticles varies over a wide range, and a large number of defects were observed that can reduce the mechanical strength of the sample. An optical image of hydrophobic sand shows how microparticles of silicone ash are located on the surface of sand, but due to the limitations of the method, it cannot give a complete picture. Therefore, to further study the surface structure of the objects, SEM analysis was used.

As can be seen from Fig. 10, the particles of the hydrophobic agent are not evenly distributed, but the surface of the obtained sand is completely covered, the particle size varying from 3 to 6 microns.

Table 2 The elemental composition of sand based on hydrophobic agent

Element	Wt., %	At, %
O	47.77	61.61
Al	0.70	0.53
Si	51.53	37.86

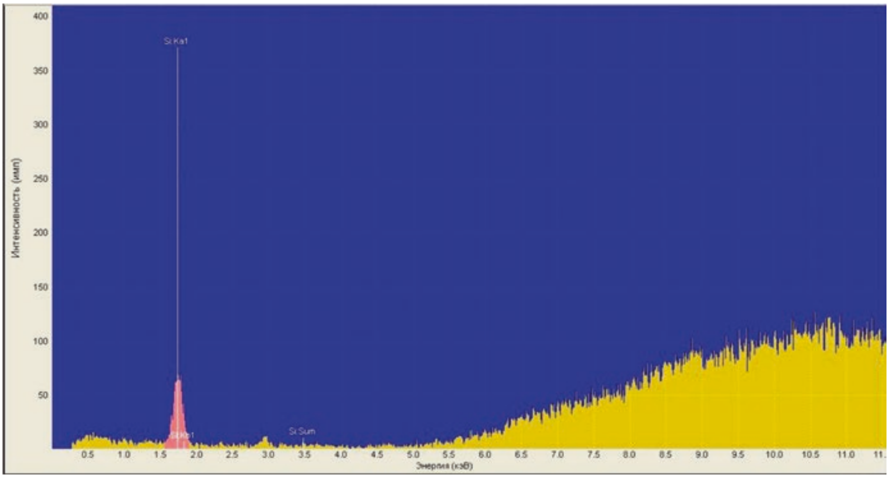

Fig. 7 Radiographs of the hydrophobic agent

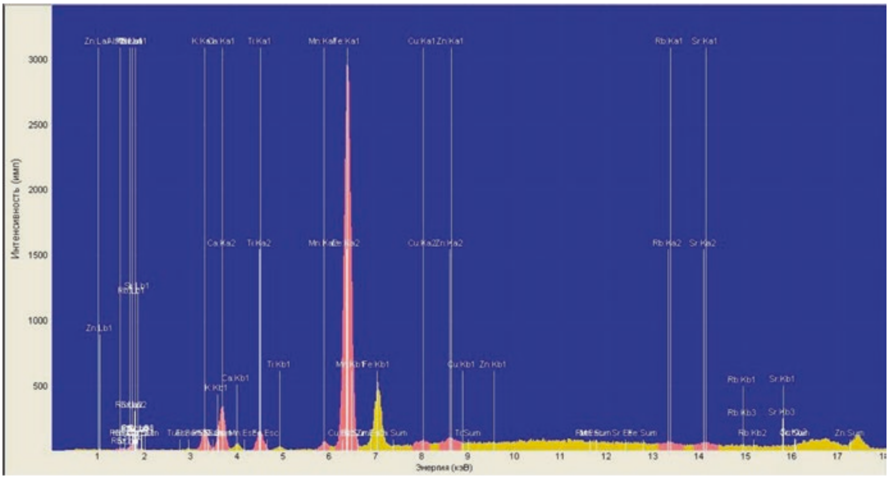

Fig. 8 Radiograph of quartz sand based on hydrophobic agent

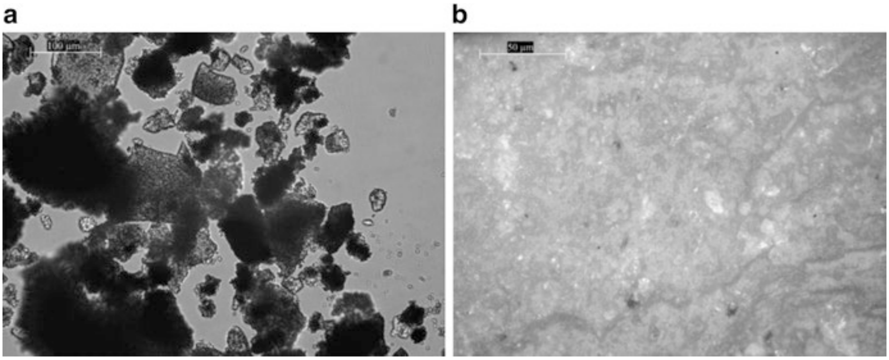

Fig. 9 Photographs (optical images) of the samples: (**a**) hydrophobic agent; (**b**) hydrophobic sand

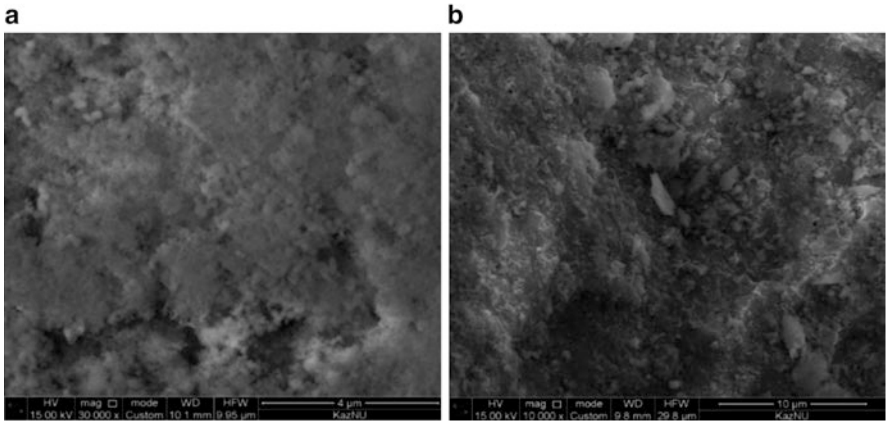

Fig. 10 Electron microscopic images: (**a**) hydrophobic agent obtained by processing waste organosilicon polymers, (**b**) hydrophobic sand

As can be seen from the above studies, the particles of the sample of hydrophobic agent are aggregated from smaller particles, the size of which is about 100–300 nm. According to the color scheme, it can be said that, mainly, silicon (light spots), as well as organic compounds (dark places) are present in the powder. The sample contains particles of two types, the large sizes of which are about 150–200 microns and the small are about 0.1–0.3 microns. At a larger magnification, it can be seen that the particles have asymmetric shapes and small particle sizes, indicating the porosity of the powder's structure.

Electron microscopic studies of the surface of the hydrophobic sand showed that the hydrophobic agent covers the entire surface of the sand. This coating is heterogeneous, and it is characterized by roughness. The average particle size is in the range of 3–6 microns. As it is known from the literature [1], the heterogeneity of the surface is one of the reasons for its hydrophobicity.

Table 3 The results of the analysis of measurement of the specific surface of the studied objects

Substance	Specific surface, m^2/g	Specific pore volume, cm^3/g	The average pore size, nm
Sand	1672	0,001	–
Hydrophobic agent	87,277	0,037	1713
Hydrophobic sand	60,517	0,026	1713

One of the factors determining the contact angle along with the nature of the surface is the specific surface. Research data on the specific characteristics of the hydrophobic agent and hydrophobic sand are represented in Table 3. The specific surface area was determined by the BET method (Brunauer-Emmett-Teller).

According to the BET analysis, the specific surface of hydrophobic sand is the average value between the hydrophobic agent and hydrophobic sand.

To study the stability of the water-repellent properties of the obtained hydrophobic sand, experimental work was carried out in laboratory conditions. Hydrophobic sand made in various proportions of hydrophobic agent was poured into a glass of water. When hydrophobic sand was immersed in water, it did not sink but floated on the surface of water. The tests showed that the obtained hydrophobic sand remained absolutely dry for a long time without losing its hydrophobic properties (30 days). Only a sample with a low content of hydrophobic agent (100: 0.5) on day 29 lost the hydrophobic property.

In the next series of experiments, the stability of the water-repellent properties of the hydrophobic sand was studied under different temperature conditions. To study the effect of low temperature on the hydrophobic properties of sand, it was kept at − 24 °C for 28 days. Then, its wettability with water was checked (Fig. 11).

To study the effect of high temperature on hydrophobic sand, a sample of hydrophobic sand was placed in an oven. The stove was heated at a rate of 10 °C/min. Starting from a temperature of 250 to 300 °C, the appearance of white smoke was observed, which is explained by the decomposition of silicone waste, and the sand loses its hydrophobic properties.

A three-layer structure was created on a Petri dish to check the water permeability of the obtained hydrophobic sand (Fig. 12).

The first layer of the structure was well wetted by water. This layer, consisting of a mixture of sand and clay, was an indicator of water, i.e., when water passes, it gives a certain visible signal.

The second layer was a separator, which is a filter paper. Its main role was to separate the first and third layers, and it does not create obstacles to the movement of water. Third layer consisted of synthesized hydrophobic sand, on the surface of which water was periodically poured, since some of it was lost due to evaporation. The experiment lasted 32 days. It was found that the third layer was waterproof, since the indicator did not detect the presence of water in the first layer.

The obtained sand that had hydrophobic properties is recommended to be used as a filler in construction for external decoration and in agriculture to protect irrigation water from seeping into the lower layers of the soil or its evaporation. Hydrophobic

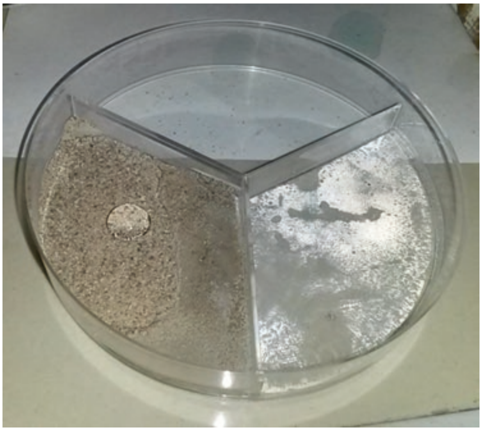

Fig. 11 Photo of the behavior of a drop of water on the surface of hydrophobic sand at temperature − 24 °C

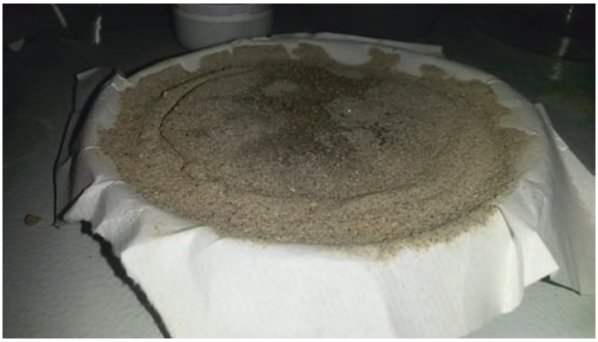

Fig. 12 Three-layer structure for determining the water resistance of synthesized hydrophobic sand

sand can also be used to isolate the soil around plants from salty soil and groundwater, which otherwise can lead to the destruction of the root system of plants.

4 Conclusion

In this work, a method for producing hydrophobic sand using silicone waste was developed. Additionally, the conditions for formation of a water-repellent coating on the sand surface were investigated and the properties of the hydrophobic sand were examined. Hydrophobic sand was created which was based on a hydrophobic agent obtained by the combustion of silicone waste. It was experimentally established that mixtures of the hydrophobic agent and sand with the ratios 1:100, 1.5:100, 2:100, and 3:100 were suitable for the creation of hydrophobic sand. The tests showed that the created sand remains absolutely dry for a long time without losing its hydrophobic properties over a period of months.

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