Hydrophobic Carbon Soot Nanostructure Effect on the Coatings

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1 Introduction

There are many compositions of organic coatings which are utilized to protect against corrosion. Hydrophobic and superhydrophobic coatings were especially shown to provide a good protection due to their improved ability to slow down water. Besides, in the presence of liquid water, the superhydrophobic surfaces equipped with a self-cleaning property can clean the dirt and dust deposited spontaneously, thereby restoring the artistic features simultaneously [1]. When the hydrophobic coating is applied in marine conditions, metal structures have a long service life because these organic coatings can protect these structures against corrosion [2].

Most papers are devoted to the production of hydrophobic and superhydrophobic coatings. In these papers, nano-titanium dioxide, silica nanoparticles, carbon nanotubes, and fluoropolymers are employed to obtain hydrophobic and superhydrophobic coatings. Compounds based on aqueous solutions of nanostructured TiO_2

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fluoropolymer were produced by hydrophobic coatings. These mixtures prevent the destruction of stone buildings [3]. The presence of modified silica nanoparticles in a fluorinated acrylic coating provided fluorine enrichment on the film surface, which resulted in the improvement of surface hydrophobicity [4]. Multiwalled carbon nanotubes can be mixed with bisphenol – a diglycidyl ether (BADGE) which contains an epoxy resin. The multiwalled carbon nanotubes make the preparation of the superhydrophobic nanocomposite surface possible [5]. The other method includes the usage of many fluorinated polymers (e.g., polytetrafluoroethylene (PTFE, Teflon), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF)/fluoroethylene vinyl ether (FEVE)) for the production of hydrophobic coatings [6]. Soot is a material produced in large quantities and mainly utilized to retrofit the mechanical, electrical, and optical properties of building materials in the production of elastomers, dyes, dry power sources, paint and coatings, etc. [7]. During the combustion of hydrocarbon fuels, carbon soot particles were obtained. Fuel burning under specified conditions allows for the production of soot with desirable properties [7, 8]. To disperse carbon soot in the mixture of polyurethane and solvent 646 (the mixture containing 50% of toluene, 15% of ethanol, 10% of butanol, 10% of butyl/amyl acetate, 8% of ethyl cellosolve, 7% of acetone), an ultrasonic wave mixer was used.

Ultrasonic waves were produced in a liquid suspension by placing an ultrasound probe or “horn” into the suspension (when direct ultrasonic was used), and then the container with the suspension was placed into a bath together with a liquid. The ultrasonic waves spread through this container (when indirect ultrasonic was utilized). In a sonication bath (when indirect ultrasound was used), the ultrasonic waves should go through the liquid in the bath and then through the wall of the sample before reaching the suspension. When indirect ultrasonic is utilized, the probe is plunged directly into the suspension, thereby decreasing the physical obstacle to impart the dispersion with force. In the dispersion of dry powders, direct ultrasonic is more effective than indirect ultrasonic. Indirect ultrasonic can be utilized to resuspend ENMs (engineered nanomaterials) which are preliminary processed by direct sonication. It can be also employed for ENMs that may undergo change or damage (e.g., breakage of single-walled carbon nanotubes) when direct ultrasonic waves are used. Sonication is an extremely system-specific dispersion method that includes a variety of concomitant complex physicochemical effects and the reaction caused by cluster separation or further agglomeration, as well as other influences involving chemical reactions. For a specified system, the best sonication conditions should be determined by the influence of various sonication parameters on the dispersion conditions of the suspension in limited related conditions. In addition, the total significant acoustic energy is effective when disconnecting powder clusters are influenced by a system-specific parameter [9].

When sonication power and the experiment duration characterize the amount of energy transmitted to the suspension, the samples of different volumes and particle sizes can change the quantity of the energy delivered. At a fixed volume, the larger particle concentrations resulted in the growth of particle collision frequency. The growth of frequency can increase particle collisions. So, if enough local activation and sintering energies are obtained, increased collision frequencies lead to agglomeration in particle collision and coalescence. Therefore, both the energy transmission to the suspension and the physiochemical properties of the suspension influence the concentration [9].

In this paper, a one-component polyurethane air-drying system was stirred with solvent 646 at 20 ˚C using a pulsed ultrasonic mixer. Then the dispersed hydrophobic carbon soot contained in the resulting mixture led to the formation of a hydrophobic coating, which possessed thixotropic properties, normal dispersion, and adhesion ability for different surfaces such as paper, metal, wood, and tile.

2 Experimental

2.1 Materials

Polyurethane lacquer ("Elakor-PU," TU 2312-009-18891264-2009 produced in the Russian Federation in compliance with ISO 51102-97) was applied to protect floors, walls, ceilings, building materials, etc., from the mechanical and chemical exposures. solvent 646 is a mixture containing 50% of toluene, 15% of ethanol, 10% of butanol, 10% of butyl or amyl acetate, 8% of ethyl cellosolve, and 7% of acetone. Hydrophobic soot was produced at the Institute of Combustion Problems by applying a 1 kV electric field during the combustion of a propane, butane, and isobutene mixture. The size of the soot particles was in the range of 30–40 nanometers with the main chain formation and a tertiary structure, and the contact angle was about 146° [10].

The 1 mm diameter nozzle supplied a working mixture at a gas flow rate of 425–500 cm^3/min. Electric field voltage ranging from 0.01 to 1 kW was applied to the system. According to the polarity of the applied electric field, the cylinder may have connected to an anode or a cathode. Soot was placed on the surface of a stainless steel cylinder, which rotated at 1 rotation per second and was collected into the soot collector. After removing it from the surface of the rotating drum with a mounted scraper, it was collected into a soot container (Fig. 1.).

The wetting angle of the obtained soot was tested and controlled by drop shape analyzer (DSA25 KRÜSS). The soot was investigated by SEM, Raman spectroscopy, and EDS. Figure 2**.** shows SEM images of the soot samples.

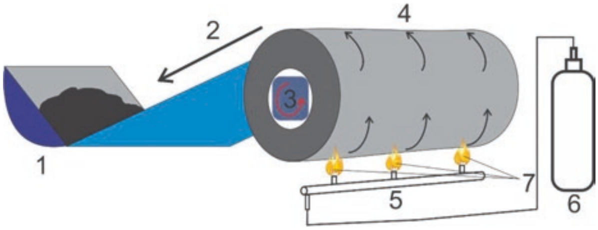


Fig. 1 The scheme of the apparatus for obtaining hydrophobic soot. (1) Soot collector, (2) carbon black tape, (3) retainer, (4) rotating drum, (5) tube, (6) propane-butane mixture, (7) flame

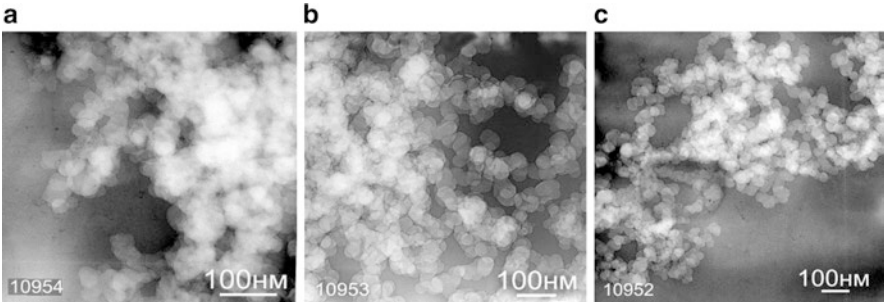


Fig. 2 Electron diffraction patterns of morphostructures

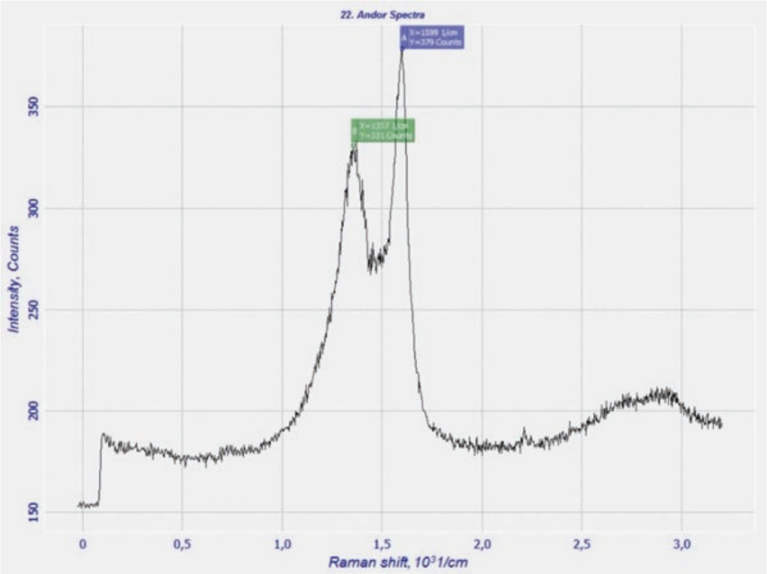
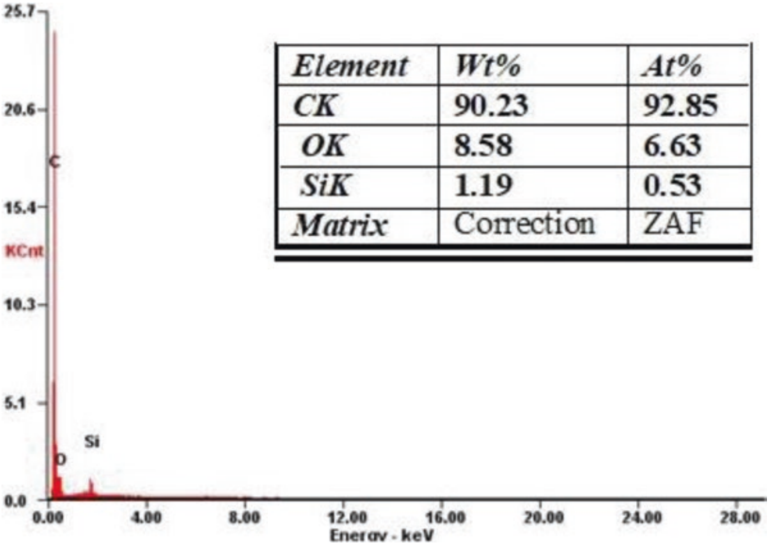


Fig. 3 Raman spectrum of soot

The sample substance is fairly homogeneous, the bulk of which consists of aggregates (Fig. 2a) of flattened rounded particles with fairly distinct boundaries. The visible particle diameter was 30–40 nm (Fig. 2b, c). Cloud and film particles were relatively rare.

Figure 3**.** illustrates the Raman results of the samples. The Raman spectra illustrate that the samples contain two peaks – 1350 cm^{-1} (D – amorphous) and 1590 cm^{-1} (G – graphite) – that corresponds to an amorphous carbon phase, which have been described in the literature [7, 12].

The existence of these two peaks with a comparable intensity is characteristic of graphitized materials consisting of disordered micro-crystallites with a size of up to 10 nm.



Element	*Wt%*	*At%*
CK	90.23	92.85
OK	8.58	6.63
SiK	1.19	0.53
Matrix	Correction	ZAF

Fig. 4 EDAX analysis of soot

To determine the composition of the resulting soot, an elemental analysis was carried out. Figure 4 shows the elemental determination analysis of the composition of the resulting soot that had hydrophobic properties.

EDAX analysis of the soot samples showed that the resulting carbon material consisted of 90.23% of carbon atoms, 6.37% of oxygen, and 1.19% of silica atoms.

2.2 Preparation of Coatings and Dispersion of Soot in the Resin

Polyurethane and solvent 646 were mixed very well. Originally, polyurethane and solvent 646 were weighed and blended, and then the obtained soot was rapidly dispersed into the liquid mixture by an ultrasonic homogenizer (Fig. 5a) under various conditions. As illustrated in Fig. 5a), the ultrasonic homogenizer dispersed the hydrophobic soot without flocculation to polyurethane-solvent 646 mixtures. The instrument power and the time of mixing soot were changed by the control panel (Fig. 5b). To transmit ultrasonic waves to the mixture, a probe (Fig. 5c) was utilized.

Table 1 shows three samples of a coating composed of polyurethane resin (“Elakor-PU” lacquer, TU 2312-009-18891264-2009), solvent 646, and hydrophobic soot.

Samples were prepared in different containers and then applied on paper, tile, metal, and wood surfaces. To measure the wetting angle, a surface shape analyzer (DSA25 KRÜSS GmbH) was used. Three or four water drops were applied on the sample, and then the sample was measured and the average was calculated.

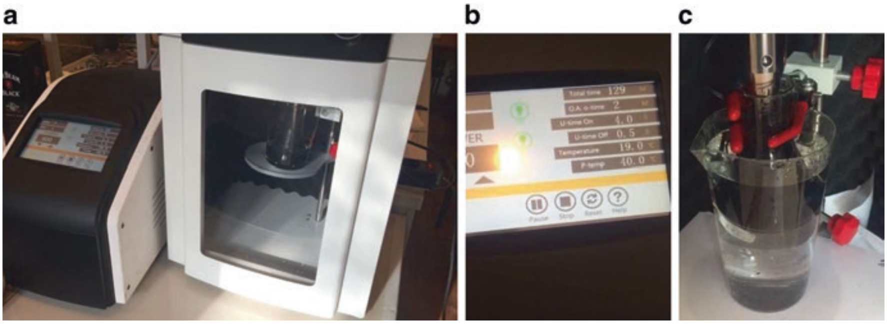


Fig. 5 Ultrasonic mixer (homogenizer) (**a**), control panel (**b**), ultrasonic probe (**c**)

Table 1 Different samples under different conditions

Number of the sample	Polyurethane, gr.	Solvent 646, gr.	Carbon soot, gr.	Ultrasonic power (25 Hz), watt	Ultrasonic on time (second working)	Ultrasonic off time (second not working)	Min
Coating-1	5	30	1	600	2	1	5
Coating-2	5	30	2	600	3	1	15
Coating-3	4	40	3	600	5	0.5	30

3 Results and Discussion

3.1 Comparison of Wetting Angle by Drop Shape Analyzer (KRUSS)

The wetting angle was measured on the surfaces of materials, such as tile, paper, wood, and metal without coating. The results of the wetting angle for the materials are shown in Table 2.

The obtained results show that the wetting angle is lowest on the metal surface and is greatest on the paper surface. Coating-1, coating-2, and coating-3 were applied onto tile, paper, wood, metal surfaces, and then the wetting angle was determined with data shown in Table 3.

The results of the comparison of different coating compositions, wetting angle, and soot concentrations are given in Table 3.

3.2 Comparison of Wetting Angle by Drop Shape Analyzer (KRUSS) Before and After Applying Coating-3

Figure 6 shows the comparison results of wetting angles on the tile surface before and after applying hydrophobic coating-3.

Table 2 The wetting angle of the tile, paper, wood, and metal surfaces without coating

Number of the sample	Measurement of contact angle on different materials without applying hydrophobic coating	Wetting angle
1.	Tile	47.8°
2.	Paper	98.6°
3.	Wood	40°
4.	Metal	29.9°

Figure 6 shows that before applying the hydrophobic coating on the tile surface, the wetting angle was 49.4°, whereas after applying hydrophobic coating-3, it rose significantly until reaching 141°. This rise is explained by adding 3 grams of soot to the polyurethane and solvent 646. Figure 7**.** illustrates the comparison of wetting angle on the wood surface before and after applying hydrophobic coating-3.

As Fig. 7 demonstrates before the application of coating-3, the wetting angle amounted to 53.6°, and then after applying coating-3, it changed to 137.3° because coating-3 created hydrophobic surface which enhances the wetting angle. Figs. 6 and 7 illustrate the adhesive ability of the wood and tile surfaces. By comparing the results presented in both figures, the adhesive ability of the tile surface is worse than that of the wood surface because wood is a porous material which possesses good adsorption properties, whereas tile is a smooth material that cannot adsorb coating-3. Figure 8 shows the comparison of wetting angle on the paper surface before and after applying hydrophobic coating-3.

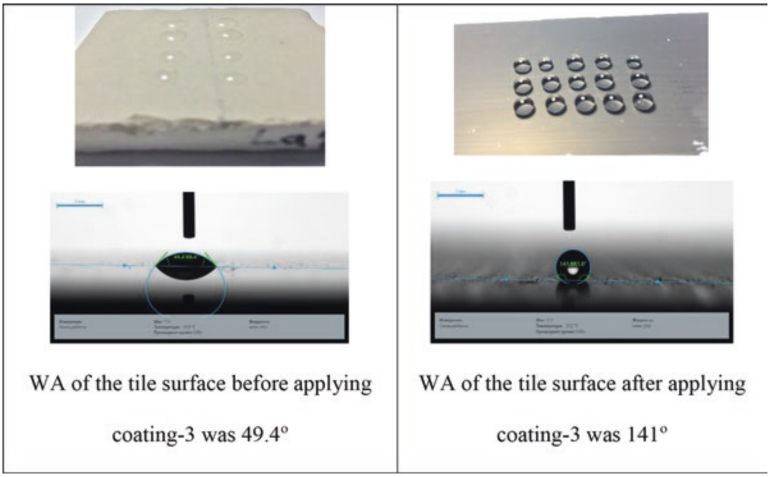
Figure 8 shows that the wetting angle on the paper before applying hydrophobic coating was 96.1°, and after applying hydrophobic coating-3, the wetting angle was 143.6°. Hydrophobic coating-3 increased the wetting angle on the paper surface by adding 3 grams of soot to the composition of the polyurethane-solvent 646 mixture. Figure 9 illustrates the results of the wetting angle on the metal surface before and after applying hydrophobic coating-3.

Figure 9**.** reveals that the wetting angle on the metal surface before applying hydrophobic coating was 58.4°, and after applying hydrophobic coating-3, the wetting angle reached 135°, which was possible by adding 3 grams of soot to coating-3. Therefore, hydrophobic coating-3 on the paper surface has a better adhesive ability than on the metal surface. Figure 10**.** presents the results of WA on pure polyurethane and soot.

As it is seen from Fig. 10, when applied, the polyurethane lacquer imparts a good adhesive ability not only to glass but also to paper, metal, tile, and wood surfaces, whereas hydrophobic soot cannot be applied to any surface because of the lack of adhesive ability. The results of adding nanostructured soot showed that the hydrophobic properties of the surface increase due to the presence of carbon nanobeads in the soot.

Table 3 Comparison of different coating compositions, wetting angle, and soot concentrations

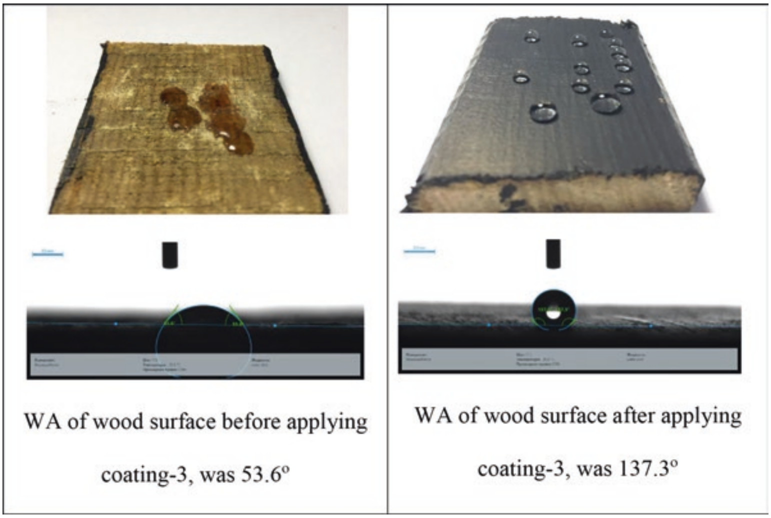
Number	Polyurethane, gr	Solvent 646, gr	Soot, gr	Ultrasonic action, min	Soot concentration, %	Wetting angle on the tile surface, degree	Wetting angle on the paper surface, degree	Wetting angle on the wood surface, degree	Wetting angle on the metal surface, degree
Coating-1	5	30	1	5	2.7	93	115	105	100
Coating-2	5	30	2	15	5.4	137	136	130	128
Coating-3	4	40	3	30	6.3	141	142	136	135. .



WA of the tile surface before applying coating-3 was 49.4°

WA of the tile surface after applying coating-3 was 141°

Fig. 6 Comparison of two tile surfaces without and with hydrophobic coating-3



WA of wood surface before applying coating-3, was 53.6°

WA of wood surface after applying coating-3, was 137.3°

Fig. 7 Comparison of wood surfaces without and with hydrophobic coating-3

3.3 Comparison of Different Coatings by the Presence of the Thixotropic Properties

“Thixotropy” is a rheological phenomenon mainly found in many complex chemical materials. These materials are usually colloidal solutions. It is linked with different rheological properties during a certain time period, even when the applied stress rate is constant [11].

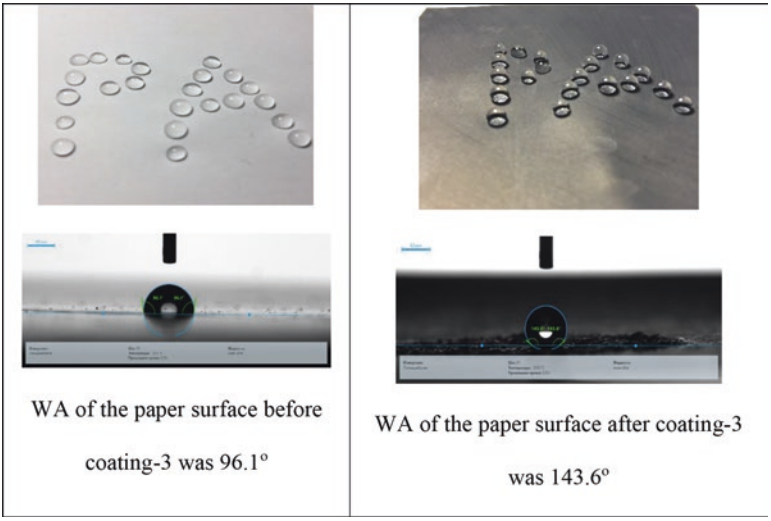


Fig. 8 Comparison of two paper surfaces without hydrophobic coating and with hydrophobic coating-3

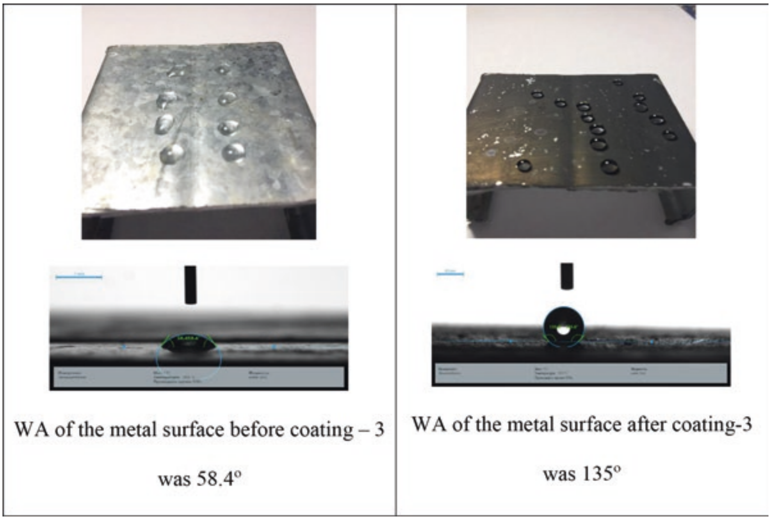
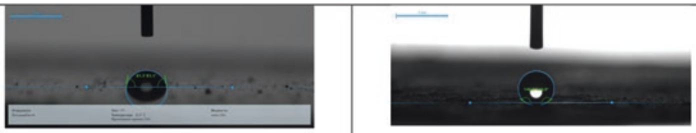


Fig. 9 Comparison of two metal surfaces without hydrophobic coating and with hydrophobic coating-3

This study showed that coating-2 and coating-3 have good thixotropic properties, and additionally, when these coatings were applied, settling and flocculation of soot were not observed (Table 4.).



WA of the glass surface covered with pure polyurethane without adding any soot was 81.1°

WA of pure hydrophobic soot was 146.9°

Fig. 10 Comparison of wetting angle of pure polyurethane and hydrophobic soot

Table 4 Comparison of soot concentration and thixotropic properties

Number	Soot, gr.	Flocculation	Use of dispersing agent	Thixotropic properties	Settling	Liquid stability	Concentration of soot in the composition, %
Coating-1	1	No	No	No	Yes	No	2.7
Coating-2	2	No	No	Yes	No	Yes	5.4
Coating-3	3	No	No	Yes	No	Yes	6.3

4 Conclusions

The addition of carbon soot to coating-3 improved the hydrophobicity of wood, tile, metal, and paper surfaces. Pure polyurethane was found to be acid and alkali material-resistant and had a good adhesive ability when applied to any surface. The mixing of polyurethane with hydrophobic soot in an ultrasonic homogenizer resulted in obtaining two hydrophobic coatings: coating-2 and coating-3. These coatings had good thixotropic properties which make the application of paint on wood, tile, paper, and metal surfaces efficient.

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