IMPREGNATING EMULSION CONTAINING NANOPARTICLES (TiO_2, SiO_2 AND ZrO_2) REDUCING WEAR AND IMPROVING THE HYDROPHOBIC PROPERTIES OF VARIOUS SURFACES

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Abstract

The basic component of an impregnating liquid is methyl-silicon resin. An aqueous emulsion was formed using a suitable solvent (e.g. xylene) and water. The emulsion had to be further thickened to increase the viscosity of the resulting solution. The silicone component can be very effectively transported deep into the structure of the material via a carrier solvent of water and a residual solvent. To increase the utility properties (hydrophobic and antisoiling) of the emulsion nanoparticles were also added to the emulsion. The protective layer is developed on the basis of nanotechnology. Due to their nanometric dimensions (10 - 30 nm), nanoparticles can penetrate into the porous structure of the substrate. A thus prepared impregnating emulsion was applied onto the various substrates e.g. polycarbonate, automotive paint and a geopolymer material. The treated samples were further tested for changes in contact angles (changes in hydrophobic properties), abrasion resistance by means of tribological tests, and resistance to elevated temperatures.

Keywords: Hydrophobic, treatment, silicon, abrasion resistance, nanoparticles, transparent

1. INTRODUCTION

Hydrophobic impregnation is widely used for example for impregnation of textiles, lenses, and facades, etc. Its purpose is to provide water repellent properties to the substrate and also to promote its regeneration. The type of hydrophobic agent affects the quality of the modifications. These modifications can be made by applying a film-forming compound or compounds that repel water and have a high surface tension. The used compounds are e.g. hydrocarbons, silicates, fluorosilicates, fluorocarbonates and others. [1-4] Nanoparticles are also widely used for the hydrophobization of the surfaces of various materials. [5] The network of nanoparticles of silicon dioxide (SiO_2) is highly resistant to mechanical wear and has a high UV stability. Products with nanoparticles of silicon dioxide are also resistant to chemicals and gain a hydrophobic character. [6, 7] Nanoparticles of titanium dioxide (TiO_2) can be applied to materials or products which are suitable for photocatalysis, protective layers, preservation, cosmetic applications and carriers in catalysis. [8, 9] The content of zirconium oxide (ZrO_2) in materials has a visible effect on their microstructure and mechanical properties (flexural strength, hardness). The addition of ZrO_2 nanoparticles into products or materials increases the barrier properties and stabilizes the product. [10]

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Impregnating emulsion

An aqueous emulsion of methyl-silicon resin was mixed together with Adeps Lanae (lanolin) or 1-hexadecanol in a defined ratio. Both emulsifiers can be used separately or together. We then added the nanoparticles of metal oxides (TiO_2, SiO_2 and ZrO_2) to the emulsion during mixing. All of these nanoparticles can be used separately or together. All of the tested nanoparticles, titanium oxide (TiO_2, anatase, 99.5%, product #:

7910DL), silicon oxide (SiO_2, 99.5%, product #: 6807NM) and zirconium oxide (ZrO_2, 99.9%, product#: 8512QI) were supplied by 'SkySpring Nanomaterials', Inc., Houston, USA.

2.1.2. Tested substrates

The influence of the impregnating emulsion on utility properties was tested on various materials. The substrates selected for testing were car paints, glass, polycarbonate and geopolymer.

2.2. Structure and morphology characterization

The structure was determined using scanning electron microscopy - Zeiss Ultra Plus ultra-high-resolution field emission scanning electron microscope equipped with an EDS + WDS + EBSD microanalytic system (resolution: 1 nm @ 15 kV, 1.7 nm @ 1 kV, magnification 12x to 1000000x, possibility of 3D-imaging by the use of a four-quadrant AsB detector; Oxford). Samples were deposited with a thin layer of gold. A light optical microscopy was also used for the structure characterization.

2.3. Measurement of transparency

The testing of transparency of layers self-hardened at an ambient temperature was performed using a Haze-gard dual device from the company BYK. This device provides haze and transmission measurements according to ISO 13468 (compensated method) and ASTM D1003 (non-compensated method).

2.4. Measurement of abrasion resistance

The measurement of the friction coefficient was performed using a CETR UMI Multi-Specimen Test System - Scratch Tester (load 2N, speed of moving pin- 4 mm/sec, duration of the experiment - 1000 sec).

2.5. Wettability measurements

Wettability was measured by contact angle measurements. The equipment used for measuring the contact angles of liquids was a surface energy evaluation system known by the acronym See System. Another test consisted of immersing the sample with a defined mass (sample previously dried to a constant weight) into a defined volume of liquid (water) for a defined time. The absorption of liquid was determined from the weight gain.

3. RESULTS AND DISCUSSION

This study was focused on modifications of aqueous emulsions of methyl-silicon resin used for the surface treatment of porous materials. The purpose of this emulsion is to impart a hydrophobic character onto the materials. The resulting emulsion is suitable for use in paints (car paints), glass, plastics and others. The emulsion forms a film on the surface of the substrate, whereby smoothing out the surface of the substrate. This prevents debris from settling in uneven areas, which greatly contributes to protecting against scratching when the substrate is cleaned or washed. Only selected properties will be mentioned for the tested substrates.

3.1. Polycarbonate and glass

The surface of the polymer is quite porous and therefore has a tendency to collect dust and other contaminants. The purpose of this layer is to smooth out the surface and to increase the hydrophobicity and abrasion resistance, while creating an antistatic layer that prevents the accumulation of dirt on the surface of the polymer. Polycarbonate was impregnated with an emulsion made from methyl-silicon resin with Adeps Lanae. Untreated samples of laboratory glass were selected for testing due to the need to increase hydrophobicity and reduce soiling. The coating of the glass samples needed to be completely transparent.

3.1.1. Contact angle measurement [θ]

Table 1 and 2 Average values of the contact angle (from 10 measurements)

Sample - polycarbonate	[θ]
Without treatment	84.6 ± 1.48
Pure emulsion	84.4 ± 2.11
Emulsion with SiO_2	85.9 ± 3.21
Emulsion with SiO_2+ZrO_2	80.8 ± 1.65
Emulsion with ZrO_2	88.1 ± 3.85
Emulsion with TiO_2	88.7 ± 2.98

Sample - glass	[θ]
Without treatment	43.42 ± 1.48
Pure emulsion	81.50 ± 2.40
Emulsion with SiO_2	82.28 ± 4.21
Emulsion with SiO_2+ZrO_2	88.18 ± 3.65
Emulsion with ZrO_2	81.13 ± 2.52
Emulsion with TiO_2	79.41 ± 3.99

3.1.2. Measurement of transparency - ASTM

Table 3 and 4 Average values of transparency (from 10 measurements)

Sample - polycarbonate	
Without treatment	100±0.15
Pure emulsion	100±0.10
Emulsion with SiO_2	100±0.15
Emulsion with SiO_2+ZrO_2	100±0.21
Emulsion with ZrO_2	100±0.19
Emulsion with TiO_2	100±0.31

Sample - glass	
Without treatment	100±0.15
Pure emulsion	100±0.10
Emulsion with SiO_2	100±0.22
Emulsion with SiO_2+ZrO_2	100±0.31
Emulsion with ZrO_2	100±0.08
Emulsion with TiO_2	100±0.15

3.1.3. Antistatic effect (polycarbonate)

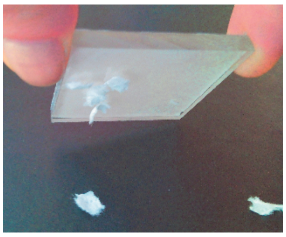
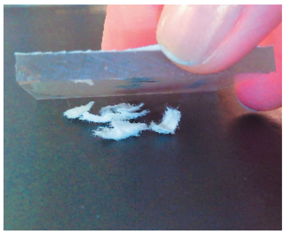

Fig. 1 The antistatic effect of the impregnating emulsion left) untreated sample, right) treated sample

3.1.4. Abrasion resistance

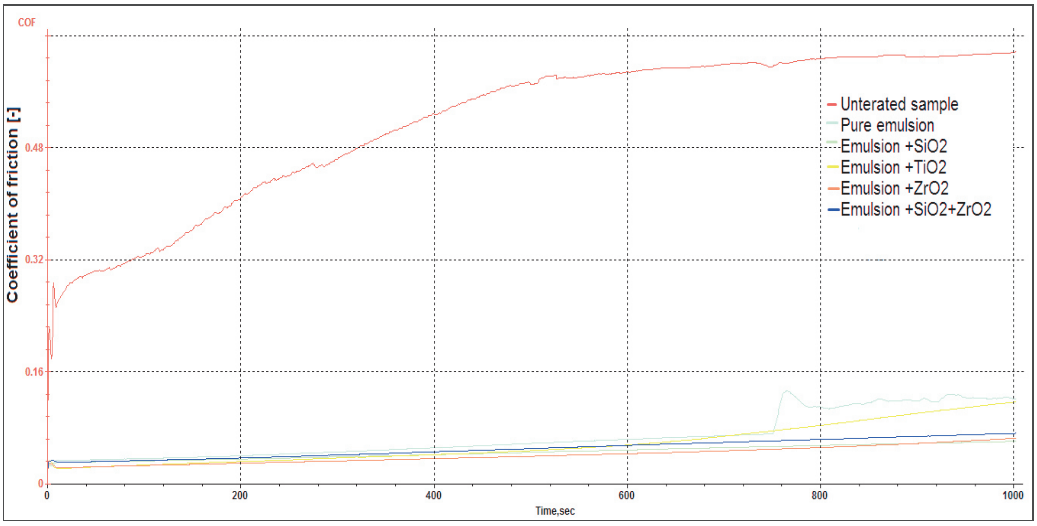

Fig. 2 Results of friction coefficient measurements

3.2. Automotive paint

Impregnating emulsion containing various emulsifiers was applied to samples of automotive paint. The effect of the emulsifier on the final properties of the treated surfaces was examined.

3.2.1. SEM analysis

Fig. 3 The difference in the structure of the surface left) before and right) after applying the impregnation (magnification 10 000x)

3.2.2. Contact angle measurement [θ]

Table 5 The average values of the contact angles (from 10 measurements)

Sample	[θ]
Untreated sample	64.99 ± 3.11
Emulsion with 1-hexadecanol	91.88 ± 2.42
Emulsion with Adeps Lanae	87.89 ± 3.20
Emulsion with a combination of both emulsifiers	68.01 ± 2.25
Emulsion with 1-hexadecanol +SiO_2	78.40 ± 1.42
Emulsion with 1-hexadecanol +TiO_2	79.09 ± 2.53
Emulsion with 1-hexadecanol +SiO_2+ZrO_2	79.64 ± 2.62
Emulsion with a combination of both emulsifiers +SiO_2	70.60 ± 1.53
Emulsion with a combination of both emulsifiers +TiO_2	71.18 ± 2.42
Emulsion with a combination of both emulsifiers +SiO_2+ZrO_2	83.02 ± 3.29

3.2.3. Abrasion resistance

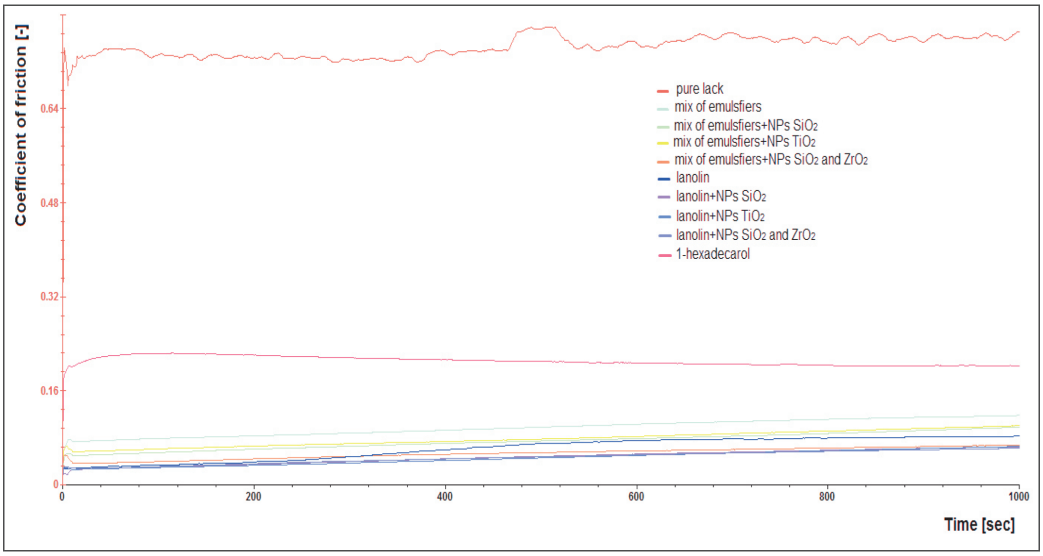

Fig. 4 Results of friction coefficient measurement

3.3. Geopolymer

The tested substrate was BAUCIS L 160 (purchased from České lupkové závody, a.s), which is a light gray geopolymeric binder based on fire clay. Alkalinisation was performed using a sodium solution.

3.3.1. Contact angle measurement [θ] and measurement of water absorption

*Samples weighing 15 g were immersed in 500 ml of water for 48 hours.

Table 6 The average values of the contact angle

Sample	[θ]
Without treatment	47.64 ± 1.63
Pure emulsion	103.18 ± 3.84
Emulsion with SiO_2+ZrO_2	105.39 ± 3.85

Table 7 Water absorption*

Sample	[%]
Without treatment	76.05
Pure emulsion	17.71
Emulsion with SiO_2+ZrO_2	17.03

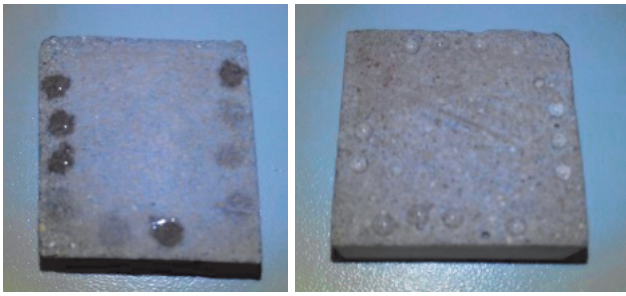

Fig. 5 The hydrophobicity effect of the impregnating emulsion left) untreated sample, right) treated sample

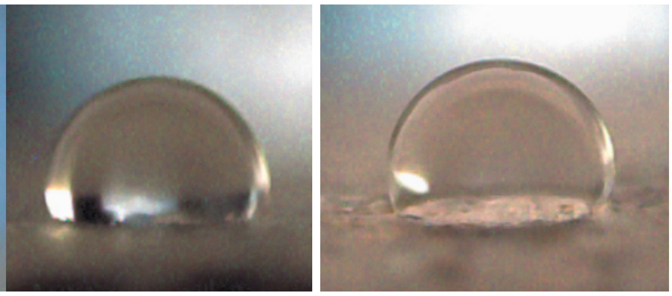

Fig. 6 left) pure emulsion, right) emulsion with nanoparticles

3.3.2. Behaviour of samples under elevated temperatures (LOM) - magnification 40x

The resistance of layers of the impregnating emulsion to elevated temperatures was also tested.

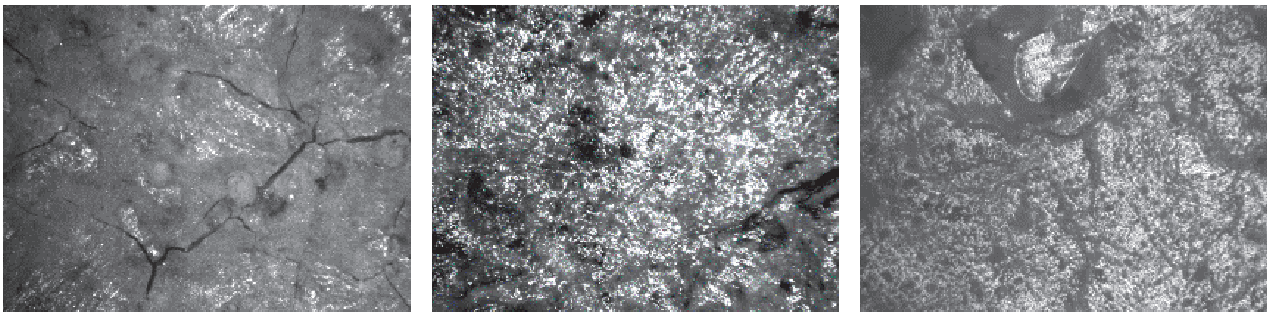

Fig. 7 200°C left) untreated sample, middle) pure emulsion, right) emulsion with nanoparticles

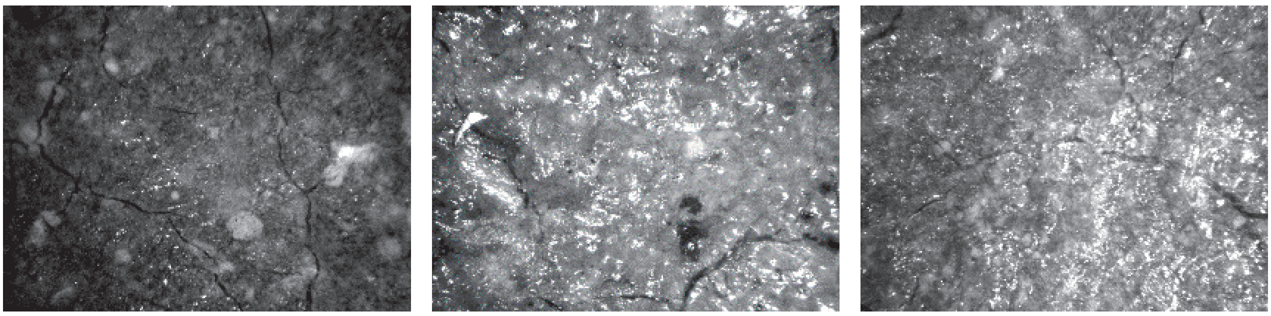

Fig. 8 500°C left) untreated sample, middle) pure emulsion, right) emulsion with nanoparticles

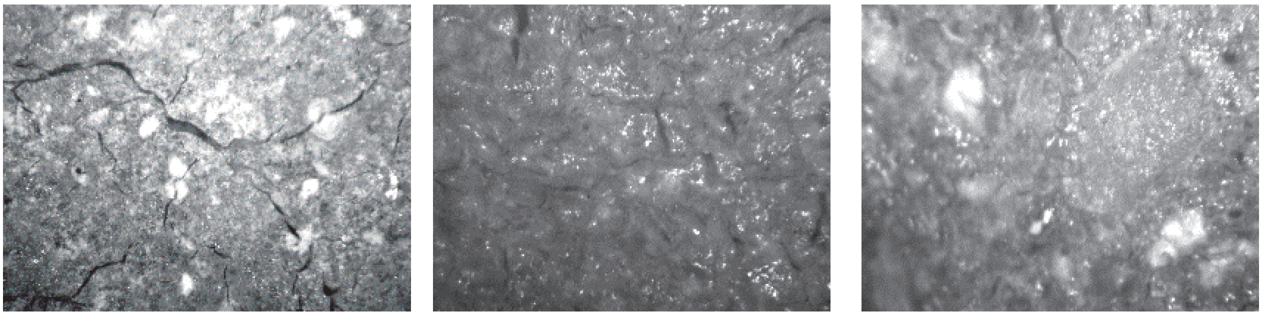

Fig. 9 700°C left) untreated sample, middle) pure emulsion, right) emulsion with nanoparticles

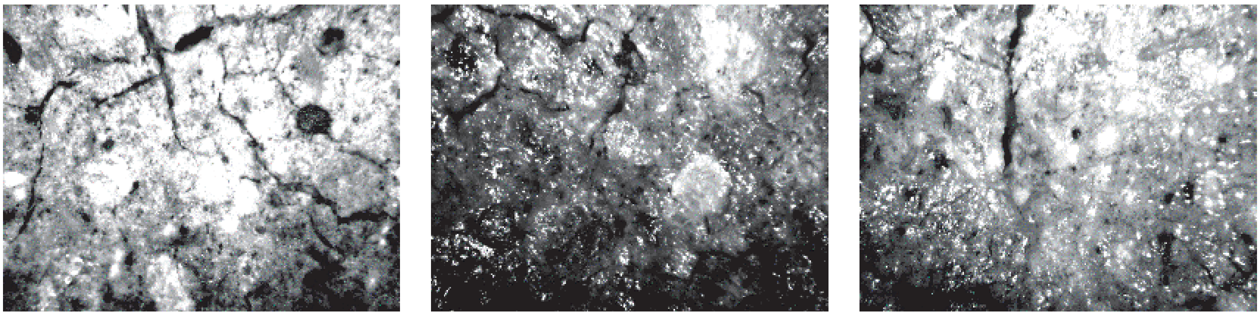

Fig. 10 900°C left) untreated sample, middle) pure emulsion, right) emulsion with nanoparticles

4. CONCLUSION

The use of a hydrophobic (water-repellent) treatment can significantly reduce the absorbency of a treated material (water rolls into balls that quickly run off the surface), whereby reducing soiling of the surface. This can lead to a significantly extend life and functionality of the treated material. Due to the high resistance of this silicone emulsion to weathering, sunlight and high temperatures this impregnation has a considerable service life.

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