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The new water-emulsion compositions for the cultural monuments proofing from the environmental hazards

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Abstract:*A new water-emulsion compositions, generally intended for the proving of different building materials against environmental hazards were obtained based on organofluorosilicon compound «Fluorosam-39» and a range of emulsifiers. After different building materials were applied with such compositions, the limiting wetting angles by water and engine oil achieved 105° - 144° and 116° accordingly. The worked up chalk stone samples got the high freezing and salt resistance, and the lowered water adsorption.*

Keywords:water emulsion, triethoxysilylpropylamide perfluoro-2,5-dimethyl-3,6-dioxanonanoic acid, organic solvents, non-ionic emulsifiers, limiting wetting angles, water adsorption, freezing resistance, salt resistance, building materials proof against destruction.

All kinds of the natural (chalk stone, sandstone, wood) and the manufactured building materials (brick, bonding plaster, designed protective coverings) are connected with the moisture migration in the building constructions and the cultural monument constructions. The sources and the reasons of watering may be different: atmospherical condensation (the water direct hit on the surface); ground waters and melt waters, or rain-waters intake by the monument's socular part, as well as the condensate formation on the surfaces of the interior structures. The variable environmental temperature-moisture conditions existence is one of the reasons of the landmarks destruction. The thermal shocks and air swings appears in the midland of Russia. The water is one of the main factors. That is why it is important to know the moisture influence on the mechanical and physicochemical properties of the architectural monument's materials [1-3].

Under the moisture of condensation influence in the near-surface layer through phasing freezing and defrosting internal stresses arise, disbanding between the different building materials' elements happens, that leads to it's splitting and further destruction. The material's water adsorption depends on it's component elements porosity and hygroscopic property. The surface condition: hygroscopicity (water affinity), septic conditions and mat surface destruction depth are also important [4-7].

For the nonce there are known many water-emulsion compositions, created on the base of the organosilicon compounds and that are used for the building structures defense. The known methods of the cultural monuments defense are either not effective enough or change it's look substantially. That is why the investigations of new protective means and there appliance for the objects of cultural heritage is the relevant objective.

There are known many water-emulsion compositions, created on the base of the organosilicon compounds and that are used for the building structures defense. For example, 50% - water emulsions of organosilicon compounds type «Penta – 814 and Penta – 812» are used for the surface treatment of plaster stones, cement, plaster, faux stones, mineral cotton and mineral inks. When attenuating concentrate with water, the emulsion flow rate is 1 litre/m^2[9]. After this emulsion is applied at chalk stone or plaster, they get hydrophobic properties. The limiting wetting angles by water and decalin are ~ 120° and 68° accordingly.

« Disboxan-450» - the product that is available in Germany, is a mixture of organosilanes and organosiloxanes and is used as 10% - water emulsion. The length of this water emulsion life is not more than 8 hours, because after the concentrate is attenuated with water in 8 hours it's destruction and residue take place because of organoalkoxysilanes hydrolysis [10].

Organosilicon compounds, and oligomers and polymers based on them are able to solute and plump in organic solvents, that is why oil resistance (oleophobic qualities) of such cover is not high.

The 1,1-dihydropolyfluorinated alcohols water-emulsion in the presence of ammonium salts of perfloropolyether acids is known. Such emulsion was used for building materials from atmospherical condensation covering. The hydrophobic effect of such cover used to attain 56.7% [11].

Among the advanced protectors for the different natural and man-made materials the produced within Russia product «Fluorosam-39» was given a good account. The «Fluorosam-39» is based on fluorosilicon compounds. «Fluorosam-39» has good optical and hygienical properties: it doesn't change the look of the material and lets the object to «breathe», that is also good for the product's mechanical characteristics.

This compounds were successfully applied by the State Institute of Restoration (Moscow) stuff for hydro- and oil-repellent proving for a variety of landmarks. It was found out that when the articles made from marble, chalk stone, brick and ciment were treated with this compound, in this case stone's vapour permeability nearly didn't change, while fouling of the stone dipped down [4,7].

However, the fluorine-containing hydrophobizated compositions based on the «Fluorosam-39» were applied only in the form of solution in the organic solvent. In terms of the environmental safety the water-emulsion compositions have the advantages over the «based on solution». This work is related to produce new fluoro-containig water-emulsion compositions and the summing up the hydrophobic properties of appeared covers.

Generally, the fluororganic compounds are poorly soluble in common organic solvents and oils, that is why the oleophobic properties of the surfaces covered with such compounds are high (the limiting wetting angles by oils are higher than 80°).

An original compound that contains triethoxysilylpropylamide perfluoro-2,5-dimethyl-3,6-diocanonanoic acid $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)NH(CH_2)_3Si(OC_2H_5)_3$, organic solvent and emulsifier was developed by us [8].

Although applying of this compound by way of solution in organic solvents allows to make restoration works around the clock, it should be used only in well-ventilated places or outside.

The aim of this work is to outspread an assortment of environmentally safe water-emulsion compositions that consist of organosilicon amide perfluorocarboxylic acid $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)NH(CH_2)_3Si(OC_2H_5)_3$, organic solvent (butyl acetate, butanol, p-xylene, octane), hydroxyethylated non-ionic emulsifier (iso-nonylphenols marks AF-9-12, AF-9-16, C-12) and water.

After the water-emulsion composition was prepared, it was proportionally carried on the chalk stone's surface. The quality control of the cover was measured by the limiting wetting angles by water. The maximum *limiting wetting angles date (144*°) *was attained in ten days after the*water-emulsion composition was covered. «A capillary intake by water» coefficient (K_B) was determined by comparison of time of the disappearance of water drops that were applied at the chalk-stone sample and at the matte glass. The water evaporation area from the glass is bigger because the water drop channeled on the glass, while on the chalkstone it got the sphere form. That is why in case of absence of water absorption in the covered chalkstone, the «capillary intake by water coefficient» (K_B) may be larger than one. The water is applied at the glass with the aim to exclude water evaporation. In this case K_B = 1.5. The covered surface *limiting wetting angles by the engine oil M6-12g was equal to 133*°.

The obtained emulsions remain its functional during a couple of days and provide reliable hydro- and oil-repellent protection of the building materials and constructions. After the chalk stone and wood samples were applied with the pointed out compositions, the *limiting wetting angles by water were equal to 105*°*-144*°, while the capillary intake by water coefficient (K_B) attained 1,55. The *limiting wetting angles by engine oil M6-12g were equal to 116*° [12].

There were made the investigations of the created compositions protection properties. The chalkstones samples were tested on water absorption, freezing resistance and salt resistance. The water absorption was tested through dipping the cultivated and not cultivated samples in water for 2 and 8 hours at *20*°C and weighting. Before weighting all dropping water was removed from the samples' surface [13]. The sample's water adsorption after its cultivation decreased in 13 times (the hydrophobic effect 97%).

The freezing resistance is the material's capability after it was water storage, pass the multiple then it freezes, that causes the destruction of the building material. For measuring the freezing resistance the chalkstone samples were dipped into water at 20°C for 1 hour, then all dropping water was removed, the samples was weighted and then placed into the deep-freeze at *-15*°C, then the samples were dipped into water again for 1 hour and again weighted. These operations were repeated until the mass lost because of its destruction decreased on 10% [14]. It was found out that the sample got through without the noticeable destruction 80 circles of freezing and defrosting. The water adsorption in this case was less than 12%. Similar tests were made for measuring salt resistance capability, but instead of water 14% sodium sulfate solution was used. In this case the sample after being hold in the salt solution during 2 hours then was dried at 60°C during 6 hours [15]. The test sample was ruined after 7 circles, while the covered sample didn't visibly suffer a change even after 40 circles.

Experimental

A method for the manufacture of organosilicon amide perfluorocarboxylic acid that is used for the development of water emulsions was prepared according to the patent RF №2149151 by mixing $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)OCH_3$ and $NH_2(CH_2)_3Si(OC_2H_5)_3$ (Fluorosam-39). Organic solvents had classification "chemically pure" and were applied without previous cleaning. Emulsifiers were applied as a commercial product.

Preparation of water emulsions:

1. Obtainment of water emulsions compositions with the emulsifier C-12

Three neck flask equipped with magnetic stirrer, dropping funnel was loaded organosilicon amide perfluorocarboxylic acid (Fluorosam-39), butyl acetate, emulsifier C-12 and while stirring water is added. The composition content, % weight: Fluorosam-39 – 8.5, butyl acetate – 15, emulsifier C-12 – 0,5, water – 76. The white water emulsion composition was prepared, it didn't break down during 2 days. The water emulsion composition in amount of 0.16g straight after preparation was proportionally carried on the chalk stone's size 8.5 cm ² surface. While the chalk stone cultivation, the consumption of the F-39 component was 15g/1m² of the sample surface.

The maximum *limiting wetting angles date (144*°) *was attained in ten days after the*water-emulsion composition was covered. The *limiting wetting angles by the engine oil M6-12g was 133*°. K_B by water is 1.55.

2. The emulsion is prepared by analogy with the example 1 from the Fluorosam-39, butyl acetate, emulsifier AF-9-16 and water. The emulsion content, % weight: F-39 – 12.1, butyl acetate – 25.7%, emulsifier – 1.5%, water – 60.6 %. The white water emulsion composition doesn't decompose during 3 days. The chalkstone *limiting wetting angle by water 135*°. In 3 month after the emulsion was applied, the *limiting wetting angle attained 141*°. $K_B$by water is 1.55. The *limiting wetting angle by the engine oil M6-12g was 127*°.

3. The emulsion is prepared by analogy with 1 from the Fluorosam-39, n-butyl acetate, emulsifier AF-9-16 and water. The emulsion content, % weight: Fluorosam-39 – 12.5, butanol – 23.3%, emulsifier «Kanol» – 1.5%, water – 62.7. The white water emulsion composition does not

decompose during 3 days. The chalkstone *limiting wetting angle by water 135*°. In 3 month after the emulsion was applied, the *limiting wetting angle attained 144*°. $K_B$by water is 1.35. The *limiting wetting angle by the engine oil M6-12g was 117*°.

4. The emulsion is prepared by analogy with 1 from the Fluorosam-39, butyl acetate, emulsifier «Kanol» and water. The emulsion content, % weight: Fluorosam-39 – 8,0, butyl acetate – 15,4, emulsifier– 0,6, water – 76. The water emulsion composition did not decompose during 2 days. The chalkstone *limiting wetting angle by water 132*°. $K_B$by water is 133.

5. The emulsion is prepared by analogy with 4 from the Fluorosam-39, octane, emulsifier AF-9-12 and water. The emulsion content, % weight: F-39 – 12.9, octane – 21,4, emulsifier «Kanol» – 1.3, water – 64.4. The white water emulsion composition does not decompose during 15 hours. The sample made of aspen *limiting wetting angle by water 114*°. $K_B$by water is 0.80. The *limiting wetting angle by the engine oil M6-12g was 116*°.

6. The emulsion is prepared by analogy with 5 from the Fluorosam-39, p-xylene, emulsifier AF-9-12 and water. The emulsion content, % weight: F-39 – 11.4, p-xylene – 18.9%, emulsifier – 1.1%, water – 68.6. The white water emulsion composition does not decompose during 8 hours. The pine sample *limiting wetting angle by water 131*°. $K_B$by water is 0.90.

In the table there are shown the *limiting wetting angles by water of other wood samples, cultivated with this composition*

Table

Example #	Material	Sample *limiting wetting angle by water*, θ,°
9	Redwood	129
10	Larix	121
119	Oak	105
12	Linden	132

As can be seen from the above, the shown examples demonstrate the possibility of obtaining more environmentally safe water-emulsion composition on the basis of organosilicon amide perfluorocarboxylic acid, organic solvent, non-ionic emulsifier and water. The obtained emulsions remain its functional during a couple of days and provide reliable hydro- and oil-repellent protection of the building materials and constructions. After the chalk stone and wood samples were applied with the pointed out compositions, the *limiting wetting angles by water were equal to 105°-144*°, while the capillary intake by water coefficient attained 1,55. The *limiting wetting angles by engine oil M6-12g were equal to 116*°-135°.

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