Synthesis and properties of fluorosilicon compounds for protection of cultural monuments from harmful environmental exposure*

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Methods for the synthesis of perfluorocarboxylic acid derivatives with reactive trialkoxysilyl groups soluble in organic and organofluorine (1,1,2-trichlorotrifluoroethane, *etc.*) solvents have been developed. The contact angles of water and decalin, water absorption, resistance to freezing, and salt-resistance of limestone and plaster samples treated with these compounds were determined. Fluorosilicon organic compounds impart more hydro- and oleophobic properties to the protected surfaces than known organosilicon agents and reliably protect sculptures and architectural monuments from mold and algae deposition.

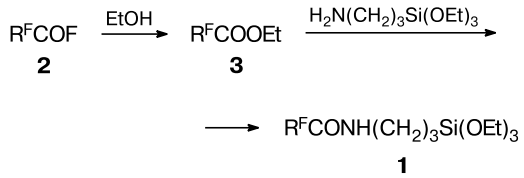
Key words: synthesis, fluorosilicon organic compounds, hydrophobization, oleophobization, contact angles, resistance to freezing, salt resistance.

Cultural monuments are most often protected from harmful environmental exposure using formulations based on organosilicon compounds, which impart water-repellent properties to the protected surfaces. However, these coatings have no oleophobic properties, because they swell or are partially soluble in organic compounds, which appear in the atmosphere due to automotive exhausts and other man-made factors. Perfluorinated organic compounds have very low surface tension, they are poorly soluble in organic solvents, and have higher hydro- and oleophobic properties than organosilicon compositions. A drawback of perfluorinated compounds is that, unlike functional organosilicon compounds, they most often do not react with Group 2 metal oxycarbonates present on the surface of structural materials.

The purpose of this study is development of methods for the synthesis of compounds containing both organosilicon and organofluorine moieties. These compounds are able to be firmly attached to the surface of constructional materials through the organosilicon moiety containing trialkoxysilyl groups, while the organofluorine moiety provides hydro- and oleophobic protection of the item.

The synthesis of perfluoro-2,5-dimethyl-3,6-dioxanonanoic γ-triethoxysilylpropylamide **1** was performed in two steps. The reaction of perfluoro-2,5-dimethyl-3,6-dioxanonanoyl fluoride **2** (hexafluoropropylene oxide trimer) with ethanol gave ester **3**, which then reacted with γ-aminopropyltriethoxysilane[1—3] to give the target compound **1** (Scheme 1).

Scheme 1



$R^F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

The completion of the reactions was checked by IR spectroscopy. Successive disappearance of the absorption bands at 1870 cm^{-1} (acyl fluoride C=O) and 1780 cm^{-1} (ester C=O) and appearance of a band at 1740 cm^{-1} (amide C=O) were observed. The yield of compound **1** was ~70% in relation to the starting acyl fluoride. The ^1H and ^{19}F NMR spectra confirm the structures of the products (see Experimental).

Treatment of samples of constructional materials was performed by immersion into 5% solutions of amide **1** in Freon-113 or ethyl acetate. The efficiency of the formed organofluorosilicon coating was estimated from the contact angles of water and decalin and the sample resistance

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to freezing, salt resistance, steam tightness, and water absorption. The organosilicon liquid GKZh-94 (research and production company PENTA, Russia) and the organosilicon product Disboxan-450 (Lacufa, Germany), which were applied on limestone samples in a similar way, served as the reference samples. The water, freezing, and salt resistances of the samples hydrophobized by compound **1** were determined according to the procedures NORMAL, RILEM 11.8a, RILEM 11.8b, GOST 7025-67, and GOST 2309-80 and other procedures used by restorers.[4,5]

The application of hydrophobic coatings on constructional materials gives rise to a surface protective layer, which prevents penetration of condensed moisture inside. This coating can partially prevent removal of the evaporated water from the material; therefore, steam tightness of the hydrophobized and untreated samples were compared. The steam tightness was measured in accordance with GOST 25898-83. A decrease in the steam tightness of plaster samples hydrophobized by compound **1** was 5.14%, which complies with the requirements imposed on hydrophobizing coatings.

Water absorption of hydrophobized samples of brick-rubble plaster. The hydrophobic effect was calculated as the ratio of the difference of water absorption between the initial and treated samples after they have been kept in water for 8 h (Table 1).

Determination of the resistance to freezing, salt resistance, and biological stability of hydrophobized samples of brick-rubble plaster. By resistance to freezing is meant the ability of the water-saturated material to withstand repeated alternative freezing in air and thawing in water. Water that freezes in the pores of the constructional material destroys the material. It was found that even after 90 freezing—thawing cycles, the lime wash did not drop off from plaster samples treated with 5% solutions of compound **1**, whereas the reference samples already lost the staining after two cycles and were destroyed after 15 cycles.

Table 1. Water absorption, hydrophobic effect, and contact angles (θ) of water and decalin for limestone samples pretreated with 5% solutions of hydrophobizing agents

Hydrophobic effect	Water absorption (%)			Hydrophobic effect	θ/deg	
	2 h	8 h	24 h		Water	Decalin
Reference*	6.34	6.62	6.96	0	0	0
GKZh-94	0.39	1.36	1.83	79.45	98	51
Disboxan-450	0.25	2.00	—	69.79	120	54
Compound **1**	0.18	0.38	1.38	94.26	138	115

* The sample untreated with the hydrophobizing agent.

A similar situation was also observed in the salt resistance testing of the samples. The salt resistance of constructional materials is defined as the ability to withstand repeated immersion of samples into a 14% solution of sodium sulfate at room temperature for 2 h followed by drying at 60°. The reference samples started to be intensively deteriorated after three testing cycles, while samples treated with compound **1** were destroyed only after 27—28 cycles. The samples treated with the Disboxan-450 product were already destroyed after 15 cycles of similar salt resistance testing.

The biological stability was assessed in collaboration with employees of the State Research Institute of Restoration using a six-point score. The biological stability of treated limestone samples 58 days after they were infected by microflora (see Experimental) corresponded to 1 or 2 two points, *i.e.*, although compound **1** does not exhibit fungicidal properties, it is not digested or is poorly digested by fungi. Hence, the compound can be recommended for long-term protection of constructional materials from infestation by molds, fungi, and algae. Together with employees of the State Research Institute of Restoration and the Central Scientific Restoration and Design Workshop (Moscow), a number of cultural monuments were treated with the developed agent, in particular, some grave-stones in the Donskoy Monastery and Novodevichy Convent, whitestone graves of Symeon of Polotsk and the dukes Ilya and Ivan Suleshovs from the collection of the Moscow State Integrated Museum-Reserve Kolomenskoye and some other. The field tests demonstrated that algae and fungi do not grow on the protected pieces of art even 8 years after their treatment.

Several water-emulsion compositions based on compound **1** were formulated. They contained hexane, octane, butanol, and xylene as the organic phase and oxyethylated isononylphenols[6] or perfluorocarboxylic acid $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)COOH$[7] prepared by hydrolysis of hexafluoropropylene oxide tetramer as the surfactant. The application of these compositions on structural materials gives rise to the same hydrophobic effect as the use of solutions of compound **1**.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker 300SF spectrometer (operating at 300.13 and 282.40 MHz, respectively). IR spectra were measured on a Bruker Alpha-T spectrometer. The high-resolution electrospray ionization (ESI) mass spectrum was run on a Bruker micrOTOF II instrument. The measurements were carried out in the positive ion mode (capillary voltage of 4500 V). The range of mass scanning m/z was 50 to 3000 D, the calibration was both external and internal (Electrospray Calibrant Solution, Fluka). Samples were injected by a syringe as acertonitrile solutions, the flow rate was 3 μL min^{-1}, nitrogen served as the nebulizer gas (4 L min^{-1}), and the interface temperature was 180 °C.

Perfluoro-2,5-dimethyl-3,6-dioxanonanoyl fluoride (**2**) was prepared by a known procedure[8] by polymerization of hexafluoropropylene oxide in the presence of CsF in diglyme.

Ethyl perfluoro-2,5-dimethyl-3,6-dioxanonanoic acid (3). Compound **2** (27.9 g, 56 mmol) was placed into a flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel, and ethanol (2.2 g, 58 mmol) was added with stirring. The reaction mixture was heated for 2 h at 50 °C, washed with a 5% solution of sodium carbonate, dried with calcined $MgSO_4$, and distilled. This gave ester **3** in a 80% yield, b.p. 165 °C. ^{1}H NMR (DMSO-d_6, δ): 1.53 (t, 3 H, Me, J = 6.0 Hz); 4.64—4.57 (q, 2 H, OCH_2, J = 6.0 Hz). ^{19}F NMR ($CFCl_3$, δ): −(80—83) (m, 9 F, CF_3); −(85—86) (m, 4 F, CF_2O); −(132.7—133.4) (m, 2 F, CF_2); −134.6 (q, 1 F, $OC\underline{F}(CF_3)C{=}O$); −144 (t, 1 F, $C\underline{F}(CF_3)CF_2O$). Found (%): C, 25.11; H, 0.97; F, 61.53. $C_{11}H_5F_{17}O_4$. Calculated (%): C, 25.19; H, 0.95; F, 61.64.

Perfluoro-2,5-dimethyl-3,6-dioxanonanoic γ-triethoxysilylpropylamide (1). γ-Aminopropyltriethoxysilane (b.p. 79—80 °C (3 Torr), research and production company PENTA) (11 g, 50 mmol) was added with stirring at room temperature to compound **3** (25.6 g, 50 mmol). The mixture was stirred for 2 h, and the product was isolated by vacuum distillation. The yield of compound **1** was 90—95%, b.p. 121—123 °C (1 Torr). ^{1}H NMR (DMSO-d_6, δ, J/Hz): 0.77 (t, 2 H, CH_2Si, J = 7.0 Hz); 1.34—1.29 (t, 9 H, 3 Me, J = 6.0 Hz); 1.97—1.92 (m, 2 H, CH_2CH_2 CH_2, J = 6.0 Hz); 3.51—3.46 (q, 6 H, OCH_2CH_3, J = 6.0 Hz); 8.23 (s, 1 H, HN). ^{19}F NMR ($CFCl_3$, δ): −(80—83) (m, 9 F, CF_3); −(85—86) (m, 4 F, CF_2O); −(132.7—133.4) (m, 2 F, CF_2); −134.6 (q, 1 F, $OC\underline{F}(CF_3)C{=}O$); −144 (m, 1 F, $OC\underline{F}(CF_3)CF_2O$). MS (ESI): m/z 722.0838; calculated for $C_{18}H_{22}F_{17}NO_6Si$, $[M + Na]^+$: m/z 722.0837. Found (%): C, 30.78; H, 3.23; N, 1.97; F, 45.98; Si, 3.62. $C_{18}H_{22}NF_{17}SiO_6$. Calculated (%): C, 30.90; H, 3.15; N, 2.0; F, 46.21; Si, 4.0.

Testing procedure. Cylindrical brick-rubble plaster samples (3 cm in diameter and 5 cm long) were immersed for 1 min in 5% solutions of compound **1** in Freon-113 or ethyl acetate. The samples were dried to a constant weight.

***Water absorption*.** The samples were placed in water for 2, 8, and 24 h and then weighed (GOST 2309-80). The results are given in Table 1.

***Resistance to freezing*.** The testing was performed in accordance with GOST 7025-67. The samples were placed in water for 2 h, then placed into a freezing chamber and kept for 2 h at −20 °C, then immersed again into water for thawing and weighed. The testing results are given above.

Biological stability was estimated at the State Research Institute of Restoration. The limestone samples with dimensions 5×5×1 cm pretreated with 5% solutions of compound **1** in Freon-113 or ethyl acetate and reference samples were infected with a suspension of the fungal spores *Ulocladium sp., Aspargillus versicolor*, and *Aspargillus niger*. The infected samples were placed in a dessicator with the bottom covered with water and kept in a thermostat at 27 °C and a relative air humidity of 90%. The development of the fungi on the samples was monitored by a MBS-9 microscope. After 58 days, the reference limestone samples were completely covered by the branched mycelium, while only limited spore growth was noted on the treated samples. According to GOST 9.048-89, these results correspond to resistance of 1—2 points.

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