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Synthesis of water- and oil-repellent organofluorosilicon compounds

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We have synthesised organofluorosilicon compounds that impart higher water- and oil-repellent properties to construction materials than known organosilicon compounds.

In most cases, cultural monuments and buildings are protected from adverse environmental effects by means of functionally substituted organosilicon compounds that impart water-repellent properties to protected surfaces. However, these compounds have no oil-repellent properties since they undergo swelling or dissolution in organic compounds that occur in the atmosphere due to motor-car exhausts and other anthropogenic emissions. Organofluorine compounds have low surface tension and are, as a rule, poorly soluble in organic solvents. Therefore, they possess higher hydrophobic and oleophobic properties than organosilicon compounds. However, organofluorine compounds cannot interact with the inorganic surfaces of construction materials in the same way as functionally substituted organosilicon compounds.

For this reason, compounds that incorporate both organosilicon and organofluorine fragments are of interest. Owing to the organosilicon fragment, they can be reliably attached to construction material surfaces, whereas the organofluorine fragment will ensure the hydrophobic and oleophobic protection of the object.

This paper presents several ways to synthesise organofluorosilicon compounds.[1–4]

Perfluoroacyloxyalkylethoxysilanes were obtained from perfluorocarboxylic acid fluorides and unsaturated alcohols followed by hydrosilylation (Scheme 1):[†]

$$\underset{\textbf{1a–c}}{R_fCOF} + \underset{\textbf{2}}{HOCH_2CH{=}CH_2} \rightarrow \underset{\textbf{3a–c}}{R_fCOOCH_2CH{=}CH_2}$$

$$\xrightarrow{HSi(OEt)_3} \underset{\textbf{4a–c}}{R_fCOOCH_2CH_2CH_2Si(OEt)_3}$$

a $R_f = C_6F_{13}$
b $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
c $R_f = CF_3O[CF(CF_3)O]_x(CF_2O)_y[CF(CF_3)CF_2O]_zCF(CF_3)$

Scheme 1

According to GLC data, the yields of esters **3a**–**c** were up to ~95%. The structures of the products were confirmed by NMR spectra.

The hydrosilylation of compounds **3a**–**c** with triethoxysilane was carried out in the presence of catalytic amounts of $H_2PtCl_6 \cdot 6H_2O$ at temperatures above 100 °C. The product yields were about 60%. An alternative method to obtain compounds **4a**–**c** is the hydrosilylation of compounds **3a**–**c** with trichlorosilane at 80 °C. Compounds **5a**–**c** were ethoxylated with triethyl orthoformate at room temperature (Scheme 2), yield 80%:

$$\underset{\textbf{3a–c}}{R_fCOOCH_2CH{=}CH_2} \xrightarrow{HSiCl_3} \underset{\textbf{5a–c}}{R_fCOO(CH_2)_3SiCl_3}$$

$$\xrightarrow{3\,HC(OEt)_3} \underset{\textbf{4a–c}}{R_fCOO(CH_2)_3Si(OEt)_3} + 3\,EtCl + 3\,HCOOEt$$

Scheme 2

Polyfluoroalkoxyalkylalkoxysilanes were synthesised from fluorinated alcohols and γ-chloropropyltriethoxysilane (Scheme 3):

$$H(CF_2)_2CH_2OH \xrightarrow{Na} H(CF_2)_2CH_2ONa$$

$$\xrightarrow{Cl(CH_2)_3Si(OEt)_3} \underset{\textbf{6}}{H(CF_2)_2CH_2O(CH_2)_3Si(OEt)_3}$$

Scheme 3

According to ^1H and ^{13}C NMR data, the ethoxy groups at the Si atom are replaced with polyfluoroalkoxy groups under the synthesis conditions of compound **6** to give compounds **7** and **8**:

$$\underset{\textbf{7}}{H(CF_2)_2CH_2O(CH_2)_3Si(OEt)_2(OCH_2CF_2CF_2H)}$$

$$\underset{\textbf{8}}{H(CF_2)_2CH_2O(CH_2)_3Si(OEt)(OCH_2CF_2CF_2H)_2}$$

An alternative method to obtain compound **6** (total yield 44%) involves the reaction of a fluoroalkoxide with allyl bromide and the hydrosilylation of compound **9** with trichlorosilane followed by ethoxylation with triethyl orthoformate (Scheme 4):

$$H(CF_2)_2CH_2ONa \xrightarrow{BrCH_2CH{=}CH_2} \underset{\textbf{9}}{H(CF_2)_2CH_2OCH_2CH{=}CH_2} \xrightarrow{HSiCl_3}$$

$$\underset{\textbf{10}}{H(CF_2)_2CH_2O(CH_2)_3SiCl_3} \xrightarrow{3\,HC(OEt)_3} \underset{\textbf{6}}{H(CF_2)_2CH_2O(CH_2)_3Si(OEt)_3}$$

Scheme 4

Perfluoroacylaminoalkylethoxysilanes were synthesised according to Scheme 5.[‡]

$$R_fCOF \xrightarrow{MeOH} R_fCOOMe$$

$$\xrightarrow{NH_2(CH_2)_3Si(OEt)_3} \underset{\textbf{11a–c}}{R_fCONH(CH_2)_3Si(OEt)_3}$$

a $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
b $R_f = CF_3O[CF(CF_3)O]_x(CF_2O)_y[CF(CF_3)CF_2O]_zCF(CF_3)$
c $R_f = CF_3O(CF_2CF_2O)_5CF_2$

Scheme 5

The reactions were monitored by IR spectroscopy. The gradual disappearance of bands at 1870 (acyl fluoride C=O) and 1780 cm^{-1} (ester C=O) was observed, along with the appearance of a band at 1740 cm^{-1} (amide C=O). The yield of compounds **11a**–**c** was ~70% with respect to the original acyl fluoride. The structures of the products were confirmed by ^1H and ^{13}C NMR spectra.

The protective properties of compounds **11a**–**c** were estimated with their 5% solutions in Freon-113, which were used to treat specimens of construction materials. The efficiency of these compounds was estimated by the contact angles of water and decalin on the specimens, frost resistance, salt resistance, vapour permeability and water absorption. The test results for certain compounds are presented in Table 1.[§] The organosilicon liquid

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[†] *Synthesis of compounds* **4a**–**c**. Acyl fluoride R_fCOF **1a**–**c** (56 mmol) was placed in a flask equipped with a stirrer, a condenser, a thermometer and a dropping funnel, and allyl alcohol (58 mmol) was added with stirring. The reaction was carried out for 2 h at 35 °C. The yields of compounds **3a**–**c** were 80–88%.

The hydrosilylation of compounds **3a**–**c** was carried out for 5 h at 50 °C in a stream of argon in the presence of $H_2PtCl_6 \cdot 6H_2O$ (20 mmol). The yields were 50–60%. Bp 82–85 °C (1 Torr) for **4a** and 125–128 °C (1 Torr) for **4b**. Compound **4c** was used without rectification.

For **4a**: ^{13}C NMR, δ: 9.24; 21.73 and 70.39 [$O(CH_2)_3Si$], 17.31 and 58.53 (EtOSi), 158.5 (C=O), 85–125 (carbon atoms of the fluorinated radical). ^{29}Si NMR, δ: –7.46. The ^{13}C and ^{29}Si NMR spectra of compounds **4b** and **4c** are identical and differ only in the ^{19}F NMR spectra characteristic of the corresponding organofluorine substituents.

[‡] *Synthesis of compounds* **11a**–**c**. Acyl fluoride R_fCOF (56 mmol) was placed in a flask equipped with a stirrer, a condenser, a thermometer and a dropping funnel, and MeOH (58 mmol) was added with stirring. The reaction was carried out for 2 h at 50 °C. The mixture was washed with a 5% solution of sodium carbonate and dried over calcined Na_2SO_4. After that, γ-aminopropyltriethoxysilane (60 mmol) was added at 20 °C. The yields of compounds **11a**–**c** were 90–95%. Bp 140–144 °C (1 Torr) for **11a** and 121–123 °C (1 Torr) for **4b**. Compound **11c** was used without rectification.

[§] *Tests with organofluorosilicon compounds.* Limestone specimens were immersed into a 5% solution of an organofluorosilicon compound in Freon-113 for 1 min, dried to constant mass and weighed.

Determination of water absorption. The specimens were immersed in water for 2, 8 and 24 h and weighed. The results on water absorption are presented in Table 1.

Determination of frost-resistance. The tests were carried out according to GOST (State Standard) no. 7025-67. The specimens were immersed in water for 2 h and then for 2 h into a freezing chamber at –20 °C, then again immersed in water for thawing, and weighed.

Bioresistance assessment. Limestone specimens (5×5×1 cm) were treated with 5% solutions of compounds **11a** and **11c** and then contaminated, along with blank specimens, with the suspensions of *Ulocladium sp*., *Aspargillius versicolor*, *Aspargillius niger* and other fungi spores. The contaminated specimens were placed in a desiccator containing water at the bottom and kept at a constant temperature of 27 °C and an air relative humidity of 90%. The growth of fungi on the specimens was monitored using an MBS-9 microscope. After 58 days, the blank limestone specimens were entirely covered with branching mycelium, whereas only limited spore production was observed on the pretreated specimens. According to GOST 9.048-89, these results correspond to a bioresistance of 1 to 2 grades.

Table 1 Physico-chemical characteristics of limestone specimens after treatment with 5% solutions of hydrophobising compounds.

Compound	Water absorption in 2 h (%)	Water absorption in 8 h (%)	Water absorption in 24 h (%)	Hydrophobic effect (%)	Water contact angle, $\theta/°$	Decalin contact angle, $\theta/°$
Original specimen	6.34	6.62	6.96	0	0	0
GKZh-94	0.39	1.36	1.83	79.45	98	51
Disboxan-450	—	2.0	—	69.79	120	54
Compound **11a**	0.36	0.48	1.88	92.75	130	110
Compound **11b**	0.18	0.38	1.38	94.26	138	115
Compound **11c**	0.58	0.95	2.24	85.64	128	110

GKZh-94 and the organosilicon composition Disboxan-450 (Lacufa, Germany) applied to limestone specimens were used for comparison. The water resistance, frost resistance and salt resistance of hydrophobised specimens were determined according to the NORMAL, RILEM 11.8a, RILEM 11.8b, GOST 7025-67, GOST 2309-80 and GOST 25898-83 procedures, as well as by other methods.[5–6]

When a hydrophobic coating is applied to construction materials, a protective layer that hinders the ingress of water is formed on their surfaces. Such a coating can partially prevent water evaporation from the material. Therefore, hydrophobised specimens are tested for changes in their vapour permeability in comparison with non-treated ones. The vapour permeability of the specimens was determined according to GOST 25898-83. The decrease in the vapour permeability of plaster specimens hydrophobised with compounds **11a**–**c** was ~5%, which complies with the requirements for hydrophobising coatings.

The hydrophobic effect was calculated by dividing (i) the difference between the values of water absorption for non-treated and treated specimens by (ii) the water absorption for the non-treated specimen after exposure to water for 8 h (Table 1).

The frost resistance is the ability of a material saturated with water to withstand repeated alternating freezing in air and thawing in water. Water freezing in the pores of a construction material causes its degradation. The salt resistance of construction materials is determined as the ability to withstand repeated immersion of specimens in a solution of salts at 20 °C followed by drying at 60°. Accelerated tests for frost resistance and salt resistance are carried out using hydrophobised specimens prepared from brick-cement plaster.

The hydrophobisation of plaster specimens coated with lime wash was carried out by analogy with the hydrophobisation of limestone. It was found that even after 90 freezing–thawing cycles on plaster specimens treated with 5% solutions of compounds **11a**–**c**, lime wash did not fall off, whereas blank specimens lost colour after 2 cycles and degraded after 15 cycles. A similar behaviour was observed in the salt-resistance tests of plaster specimens. Blank specimens started to degrade intensely after 3 test cycles, whereas the specimens pretreated with compounds **11a**–**c** started to degrade after 27–28 cycles. The specimens pretreated with Disboxan-450 degraded after 15 cycles in a similar salt-resistance test.

The laboratory assay for the bioresistance of new compounds was carried out in GosNIIRestavratsii (State Research Restoration Institute); the bioresistance was evaluated using a six-grade scale. It was found that the bioresistance of pretreated limestone specimens was 1 to 2 grades 58 days after the contamination. Compounds **11a**–**c** do not possess anti-fungal properties, but they are not digested or hardly digested by microorganisms. Hence, such compounds can be recommended for prolonged protection from attacks of construction materials with mould, fungi and algae. Environmental tests carried out with a number of cultural monuments made of limestone, cement, marble and granite showed that no algae and fungi grew on them even eight years after treatment with the test compounds.

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References

1 S. P. Krukovsky, A. A. Yarosh, V. M. Kotov, T. A. Pryakhina, V. N. Yarosh, B. G. Zavin, V. N. Pisarenko, V. M. Svetlakov and V. E. Blinov, *RF Patent 2,149,151*, 2000.

2 S. P. Krukovsky, A. A. Yarosh, V. M. Kotov, T. A. Pryakhina, V. N. Yarosh, B. G. Zavin, V. N. Pisarenko, V. M. Svetlakov and V. E. Blinov, *RF Patent 2,151,151*, 2000.

3 S. P. Krukovsky, A. A. Yarosh, A. A. Glazkov, D. V. Batizat and T. N. Redina, *J. Fluorine Chem.*, 1999, **96**, 31.

4 A. A. Yarosh, T. A. Pryakhina, V. M. Kotov, B. G. Zavin and S. P. Krukovsky, *The 2nd International Conference ‘Chemistry, Technology and Applications of Fluorocompounds’ (STAF-97)*, St. Petersburg, 1997, P2-24, p. 96.

5 A. A. Yarosh, S. P. Krukovsky, B. G. Zavin, V. M. Kotov, T. A. Pryakhina and V. N. Yarosh, *Abstracts of the 10th All-Russian Conference ‘Organosilicon Compounds: Synthesis, Properties and Applications’*, 2005, abstract 3C23 (in Russian).

6 A. A. Yarosh, S. P. Krukovsky, A. M. Sakharov, B. G. Zavin, V. M. Kotov, T. A. Pryakhina and V. N. Yarosh, *International Conference ‘Art et Chimie, Les Polymers’*, Actes du Congres, Paris, 2002, pp. 115–117.

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