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Siloxanes as Liquid  
Repellent Fabric Finishes**

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# Fluoroalkyl-Substituted Siloxanes as Liquid Repellent Fabric Finishes<sup>1</sup>

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The liquid repellencies imparted to fabrics by solutions of a family of ten fluoroalkyl-substituted siloxanes are described. Fluoroalkyl substituents with varying structures were employed. Both the amide function and the ether function were used to attach fluoroalkyl substituents. Five of the siloxanes were network polymers while the remaining five were the corresponding linear polymers. In general, those polymers bearing the longer straight-chain fluoroalkyl substituents and attached to the siloxane backbone with the amide group gave the best repellencies. In some cases, the longer fluoroalkyl-substituted silanes could be copolymerized with nonfluorinated alkyl silanes without affecting the liquid repellencies imparted to the fabric. The durability of these copolymers to laundering, wearing, and dry cleaning were examined for the most promising finishes. The use of added resin was advantageous.

## Introduction

Silicones are important commercial materials and are becoming more so. Owen (1980) has recently reviewed the surface activity of silicones and has made comparisons to other low surface energy hydrocarbon- and fluorocarbon-containing polymer systems. He predicts the commercialization of silicones containing more fluorine than those presently available. Zisman and others have examined the properties of fluorinated materials in the form of monomolecular films or as smooth, solid fluoropolymer surfaces (see, for example, Zisman, 1964). In this paper, a practical approach has been taken to the examination of fluoroalkyl-substituted siloxanes as liquid-repellent fabric finishes.

The commercial importance of fabric treatment to impart oil and water repellency is evident from recent reviews and books published on this subject (Sodano, 1979; Lichstein, 1977; Palmer, 1977). A pioneering paper in the use of fluorochemicals to impart both water and oil repellency to treated fabrics was that of De Marco et al. (1960). A combination application of a pyridinium-type water repellent with a fluorochemical was described. In the search for good oil and water repellents, fluoroalkyl groups have been attached to various functional groups and polymer backbones to impart high levels of repellencies and other desirable properties to textile materials.

Several patents have been issued on the use of fluoroalkyl-substituted siloxanes as oil- and water-repellent finishes (e.g., Holbrook and Steward, 1961, 1962; Pittman and Wasley, 1967, 1969, 1970, 1974; Nalco Chemical Co., 1972; Boerner et al., 1974). The values for liquid repellency imparted to fabrics reported in some of these patents indicate that they could be useful in the treatment of protective military garments. Due to the different methods

Table I. Structures and Numbering System of the Silane Monomers

$\text{CF}_3(\text{CF}_2)_3\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2$	1 <sup>a</sup>
$\text{CF}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	2 <sup>a</sup>
$\text{CF}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2$	3
$\text{CF}_3(\text{CF}_2)_6\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	4
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2$	5
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	6
$(\text{CF}_3)_2\text{CFO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2$	7
$(\text{CF}_3)_2\text{CFO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	8
$(\text{CF}_3)_2\text{CO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2$	9
$(\text{CF}_3)_2\text{CO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	10
$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$	C1
$\text{CH}_3(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$	C2

<sup>a</sup> During the study of initial repellencies, the trimethoxy derivative was used. In the copolymerizations with the nonfluorinated alkyl triethoxysilanes and in the durability study, the triethoxy derivative, as shown in the formula, was used.

of formulating the polymer solutions as well as variance in the fabrics treated and the test methods used, it is difficult to compare results achieved from one patent to another.

This paper reports a systematic study of fluoroalkyl-substituted siloxanes as oil- and water-repellent fabric finishes. The most promising monomers reported in the literature as well as others synthesized at this establishment (see Table I for structures of the monomers) were polymerized under as identical conditions as possible. The hydrocarbon bridge,  $(\text{CH}_2)_3$ , between the siloxane backbone and the fluorinated substituent is necessary to achieve stability (Owen, 1980; Haszeldine, 1968). Nylon/cotton fabric (50/50 wt %) was treated with the polymer solutions and the oil and water repellency of the treated fabric was measured. Also evaluated were copolymer solutions of the best of the fluoroalkyl-substituted silanes with the much cheaper nonfluorinated alkyl silanes. The durability of these copolymers to washing, wearing,

<sup>1</sup> DREO Report No. 825.

and dry cleaning was also examined. The effect of added resin was determined.

### Experimental Section

The synthesis of the monomers has been reported (Bovenkamp, 1979a). Some were new compounds. For others, the synthesis of the compound or that of a derivative was available from the literature. All of the monomers were carefully distilled and had narrow boiling point ranges. They were shown to be pure by proton and fluorine nuclear magnetic resonance as well as by infrared spectroscopy. The fabric used was a nylon/cotton twist (50/50 blend, 170 g/m<sup>2</sup>, dyed olive green). Methyltriethoxysilane, C1, was obtained commercially whereas hexyltriethoxysilane, C2, was derived from the trichloro derivative.

Using a two dip/two nip procedure, fabric samples were padded on an Atlas padding machine (Type LW-5) to a wet pick-up of 70–100%. After padding, the fabric samples were cured in a forced-air oven. They were placed in the oven at room temperature and the temperature was then set at 150 °C. Upon attaining 150 °C, the samples were removed after 15 min. Percent add-on of polymer finish was obtained by weighing each sample before treatment and weighing again after the cured samples had been allowed to sit undisturbed overnight.

Washing was carried out using an Atlas Launder-Ometer, Model B5, according to Canadian Standard Textile Test Methods, Method 19.1-M77, Wash Test 1, 1977. In this method, the samples (5 × 10 cm) are agitated in hot soap solution containing stainless steel balls to provide mechanical action. One washing using this accelerated method approximates five launderings using a domestic washing machine. Dry cleaning was performed by a slight modification of Canadian Standard Textile Test Methods, Method 29.1-M77, 1977. The samples (15.2 × 15.2 cm) were placed individually in the containers of the Launder-Ometer. Perchloroethylene (150 mL) and 100 steel balls were added. After running at 27 °C for 30 min, the containers were drained and the samples were dried between two paper towels. After air drying, they were dried at 90 °C for 10 min. The effect of wearing on fabric properties was examined using a wearing machine developed at DREO (Hart, 1964). Fabric samples (18 × 375 cm) were sewn into an endless belt and passed over the brushes and rollers of the machine under 1 lb tension.

A detailed study has been made of the polymerization conditions for each monomer in terms of add-on and liquid-repency properties imparted to the fabric (Bovenkamp, 1979b). Variables included solvent, polymerization times, and amount of aqueous sodium hydroxide. For example, fairly short polymerization times were necessary for 1 since at longer times the polymer begins to precipitate.

**Polymerization of the Copolymers.** (i) **Polymerization of 1 + C2.** The monomers 1 (5.22 g) and C2 (0.78 g) (70/30 mol % ratio) were weighed into a 250-mL round-bottom flask. Tetrahydrofuran (120 mL) was added to dissolve the monomers. Aqueous sodium hydroxide solution (3 mL, 40 mg of NaOH/mL) was added dropwise during vigorous stirring. The solution was stirred for 24 h and then neutralized with 20% aqueous sulfuric acid solution. After filtering, the polymer solution was applied to the fabric. The same procedure was used for 1 + C1.

(ii) **Polymerization of 2 + C1, 2 + C2, and 3 + C1.** The procedure was the same as above except that 2-propanol was used as the solvent and a stirring period of 2.5 h was utilized.

(iii) **Formulations of the Siloxane Copolymers Plus Resin.** After polymerization of the copolymers as de-

Table II. Initial Oil- and Water-Repellency Results for Each Homopolymer

monomer	% add-on	oil repellency	water repellency
1	2.0	6/7	100
2	2.7	6/7	90
3	1.5	6/7	90
4	4.1	6	70
5	2.9	5/6	80
6	2.6	0	50
7	3.3	0	50
8	2.6	0	0
9	2.0	1	70
10	3.9	0	50

scribed above (5% wt/vol of solids), the solution was diluted with the polymerization solvent to 4 g of solids in 100 mL of solution. One gram of Aerotex Resin P-225 (liquid form of hexamethoxymelamine) and 0.25 g of Aerotex Accelerator Cycat 4040 (active catalyst 40% in 2-propanol) (both obtained from Cyanamid of Canada, Inc.) were then added with stirring.

**Water- and Oil-Repellency Tests.** The American Association of Textile Chemists and Colorists (AATCC) Test Methods 118-1966 (oil repellency), 1970, and 22-1967 (water repellency), 1970, were employed in this study. In the oil-repellency test, the fabric is placed flat on a smooth, horizontal surface. Drops of the standard test liquids consisting of a selected series of hydrocarbons with varying surface tensions are placed on the fabric surface and observed for wetting. The oil-repellency rating is the highest-numbered test liquid which does not wet the fabric surface within a period of 30 s. At DREO two modifications have been made to the standard oil-repellency test. For experimental purposes, half levels were used. Thus 5/6 represents a situation where liquid 6 would wet the fabric whereas a 50/50 mixture of liquids 5 and 6 would not. The second modification was the use of a 5-min test period instead of the normal 30 s since the requirements for military fabrics are more stringent than those for normal consumer use. In some cases this longer time period resulted in a lower rating of half a grade.

In the water-repellency spray test, water is sprayed against the taut surface of a test specimen under controlled conditions. This produces a wetting pattern whose appearance depends on the repellency of the treated fabric. Evaluation is accomplished by comparing the wetting pattern with pictures on a standard chart.

### Results and Discussion

**Initial Repellencies Imparted to Treated Fabric.** Table II shows the initial repellencies obtained when nylon/cotton (50/50 wt %) is treated with the polymer solutions of each of 1 to 10. Only with the longer straight-chain fluoroalkyl substituents (1 to 5) are repellencies of any interest obtained. When the results for the network polymers from the monomers 1, 3, 5, 7, and 9 are compared with those of the corresponding linear polymers (even numbered), it is seen that the network polymers give superior results in every case. The effect of increasing chain length is clearly revealed by comparing the values for 1 and 2 (9 fluorinated carbons) with those of 3 and 4 (7 fluorinated carbons). The water repellency drops from 100 to 90 for 1 to 3 and from 90 to 70 for 2 to 4. The effect on oil repellency is much smaller with 1 and 3 having equal values of 6/7 while there is a slight drop of 6/7 to 6 for 2 to 4.

The monomers 3 to 6 all contain the perfluoro *n*-heptane substituent. The monomers 3 and 4 utilize the amide function while 5 and 6 utilize the ether function to attach

Table III. Initial Oil- and Water-Repellency Results For Copolymers of 1, 2, and 3 with C1 and C2

compn of copolymer	% add-on	water repellency	oil repellency
1 70%, C1 30%	4.2	100	6/7
1 40%, C2 60%	4.4	100	6/7
1 70%, C2 30%	2.4	100	6/7
1 40%, C2 60%	4.5	100	6
2 70%, C1 30%	2.8	100	6/7
2 40%, C1 60%	2.8	90	6/7
3 70%, C1 30%	2.8	90	6

the perfluoro *n*-heptyl group. In comparing 3 and 5 it is seen that both oil and water repellencies have decreased a full level. The degradation is even more pronounced for 4 and 6 (6 → 0 for oil and 70 → 50 for water repellency).

The low level of repellencies obtained with the branched perfluoro substituents (isopropyl, 7 and 8; *tert*-butyl, 9 and 10) were somewhat surprising (see Table II). It has been stated that the heptafluoroisopropoxy group can give an oil repellency equivalent to a straight-chain substituent bearing approximately twice the number of fluorines (Pittman and Wasley, 1969, 1970, 1974; Wasley and Pittman, 1977). It is believed that the medium-range values obtained by Pittman and Wasley were due to the isolation of their perfluoroisopropoxy-substituted siloxane polymers and subsequent cross-linking for several hours at high temperature. The resultant polymer is then dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane. Since it was our intention to keep the polymerization process simple and to use as uniform a procedure for the monomers 1 to 10 as possible, this procedure was not utilized. Although very low, the repellencies obtained with the perfluoro *tert*-butyl substituent were slightly better than the values obtained with the 2-propanol substituent.

Since only the polymers of 1, 2, and 3 have repellencies in the range of interest, only these will be considered further. The copolymerization of these monomers with the nonfluorinated monomers, methyltriethoxysilane (C1) and hexyltriethoxysilane (C2), resulted in better add-ons due to increased solubility of the copolymer in the solvent. Also the nonfluorinated silanes are much cheaper. Table III shows the results obtained. In comparing the results for the polymers (Table II) with those of the copolymers (Table III), it is seen that the addition to 1 of 30–60 mol % C1 and 30% C2 has no effect on the repellencies obtained. The use of 60% C2 results in a slight degradation in oil repellency. On the other hand, the use of 30% C1 with 2 actually increases the water repellency from 90 to 100. This is believed to be due to the fact that C1 has three

replaceable silane substituents and the resultant copolymer has some network character. The use of tetraethoxysilane as a comonomer was tried with 3. However, the resultant copolymer soon precipitated out of solution.

**The Durability of the Treated Fabrics to Washing, Wearing, and Dry Cleaning.** (i) **Durability to Washing.** The durability to washing of the copolymers shown in Table III was found to be below that expected for a good finish. The first two entries shown in Table IV represent what was generally found. When 1 g of the copolymer was replaced with a resin, however, not only were the same initial repellencies obtained but these values were very durable to repeated washings (see Table IV). Only a small amount of degradation of properties was found even after six washings. It is common practice to include a resin in commercial finishes.

(ii) **Durability to Wearing.** Table V shows the results obtained when the treated fabrics were subjected to wear testing. Reasonable levels of repellency were maintained even after 20 h of wearing. No significant improvement in durability to wearing was obtained when 1 g of the siloxane copolymer was replaced by resin. After 20 h of wearing time, the finish with the higher nonfluorinated alkyl silane content has a slightly lower oil repellency in each case.

(iii) **Durability to Dry Cleaning.** Table VI shows that the siloxane copolymers have good durability to dry cleaning. Most values drop only one level even after six dry cleanings. No significant improvements were obtained by the use of a resin.

The inorganic curing catalysts zinc octoate, stannous octoate (Watt, 1960), and tetrabutyl orthotitanate (Cockett et al., 1954; Monsanto Chemicals Ltd., 1955) have been used with nonfluorinated siloxanes. It was found in this study that the use of these catalysts with the copolymers of 1 and C1, 1 and C2, and 2 and C2 made little or no difference to the properties of the treated fabrics.

A survey was also made of available commercial finishes utilizing fluoroalkyl-substituted acrylates and methacrylates. Lichstein (1977) includes a summary of commercial finishes. On treating the nylon/cotton fabric used in this study with the best of these finishes, the results for water repellency were generally similar. The oil-repellency values for the siloxane copolymers, however, were somewhat better initially, and this difference was generally maintained during the washing, wearing, and dry cleaning tests.

To summarize the foregoing results, the best oil and water repellencies are obtained with fluoroalkyl siloxanes

Table IV. The Durability of the Siloxane Copolymers to Washing

compn of copolymer	% add-on	no. of washings							
		0	1	2	3	4	5	6	
Copolymers without Resin									
1 70%, C1 30%	4.2	100	90	70	70	50	0	0	
		6/7	5/6	5	4	3/4	2	2	
2 70%, C1 30%	2.8	100	90	80	70	70	70	50	
		6/7	6/7	6	6	6	6	5/6	
Copolymers with Resin <sup>a</sup>									
1 70%, C1 30%	4.0	100	100	100	100	100	100	90	
		6/7	6	5/6	5/6	5/6	5/6	5	
1 70%, C2 30%	3.9	100	100	100	100	100	90	80	
		6/7	6	5/6	5	5	4	4	
2 70%, C1 30%	2.9	100	100	100	100	100	100	100	
		6/7	6/7	6	6	6	6	6	
3 70%, C1 30%	5.6	90	90	90	90	90	90	80	
		6	5/6	5/6	5/6	5/6	5/6	5/6	

<sup>a</sup> One gram of the copolymer replaced by one gram of resin.

Table V. Durability of the Siloxane Copolymers to Wearing

compn of copolymer	wearing time, h					
	0	4	8	12	16	20
1 70%, C1 30%	100	80	80	80	80	80
	6/7	6	5/6	5	5	4/5
1 40%, C1 60%	100	80	80	70	70	70
	6/7	4/5	4/5	3	2	2
1 70%, C2 30%	100	80	80	80	70	70
	6/7	6	5/6	5	5	4/5
1 40%, C2 60%	100	80	80	70	70	70
	6	5/6	5	4/5	4/5	4
2 70%, C1 30%	100	80	80	70	70	70
	6/7	6/7	6	5/6	5/6	5
2 40%, C1 60%	90	70	70	70	70	70
	6/7	6	5/6	5	5	4/5
3 70%, C1 30%	90	80	80	70	70	70
	6	6	5/6	5	5	4/5

Table VI. Durability of the Siloxane Copolymers to Dry Cleaning

compn of copolymer	no. of dry cleanings						
	0	1	2	3	4	5	6
1 70%, C1 30%	100	100	90	90	90	90	90
	6/7	6	6	5/6	5/6	5/6	5
1 70%, C2 30%	100	100	90	90	90	90	90
	6/7	6/7	5/6	5/6	5/6	5/6	5/6
2 70%, C1 30%	100	100	90	90	90	90	90
	6/7	6	6	6	6	6	6
3 70%, C1 30%	90	90	80	80	80	80	80
	5/6	5/6	5/6	5/6	5/6	5/6	5/6

having perfluorinated straight-chain substituents with seven or more carbons. The amide function is superior to the ether function for attachment of the perfluorinated substituent to the polymer backbone. Nonfluorinated alkyl-substituted silanes can be used in moderate amounts

with 1, 2, and 3 to increase the solubility properties of the polymers and to reduce cost without affecting the repellency properties imparted to the fabric. The use of a resin with these copolymers is recommended since it is necessary to achieve good durability to laundering and it also reduces the overall cost. Good durability to wearing and dry cleaning are exhibited by these finishes.

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