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FLUOROALKYL SILOXANES AS LIQUID-REPELLENT FABRIC FINISHES.

PART II.

THE HOMOPOLYMERS AND THEIR COPOLYMERS WITH ALKYL SILANES

by

J.W. Bovenkamp

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PART II
THE HOMOPOLYMERS AND THEIR COPOLYMERS WITH ALKYL SILANES

by
J.W. Bovenkamp
Environmental Protection Section
Protective Sciences Division

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ABSTRACT

In this report the liquid-repellent properties of the homopolymers and selected copolymers of ten fluoroalkyl-substituted silane monomers of varying structures are evaluated. The homopolymers of the silanes are synthesized, applied to nylon/cotton (50:50 weight per cent) and cotton as finishes, and the oil and water repellency imparted to these fabrics ascertained by standard tests. In this manner it is possible to compare the effects of (i) length and degree of branching of the fluorinated alkyl chains, (ii) the use of network (three replaceable silane substituents in the monomer) versus linear (two replaceable substituents) siloxane polymers, and (iii) the use of either an amide or an ether function to bond the fluoroalkyl group to the polymer backbone.

Due to the expense of these fluorinated materials, a study was conducted of the copolymerization of the best fluoroalkyl-substituted silanes with much cheaper non-fluorinated alkyl silanes. Among the latter were those with varying alkyl chain lengths and number and orientation of the replaceable silane substituents. The oil and water repellencies obtained with both the homopolymers and copolymers ranged from outstanding to essentially none. Explanations are advanced for the values obtained and literature comparisons are made.

RÉSUMÉ

Le présent rapport évalue les propriétés hydrofuges et oléofuges des homopolymères et de certains copolymères de dix monomères de fluoroalkylsilanes. Après synthèse, les homopolymères des silanes sont appliqués, comme fini, sur des tissus de nylon/coton (50/50 en masse) et de coton. Le caractère hydrofuge et oléofuge des tissus ainsi traités est évalué à l'aide de méthodes normalisées. De cette façon il est possible de comparer les effets de (i) la longueur et du degré de ramification des chaînes alkyles fluorées, (ii) l'emploi de polymères siloxanes en réseau (trois substituants échangeables dans le silane monomère) plutôt que linéaires (deux substituants échangeables), et (iii) l'emploi d'une fonction amide ou éther pour lier le groupement fluoroalkyle au silane.

En raison du coût élevé des produits fluorés, on a étudié la copolymérisation des meilleurs fluoroalkylsilanes avec des alkylsilanes non-fluorés moins chers. Parmisces derniers il y en avait avec des substituants du silane différent en nombre et en orientation, ainsi que par la longueur de la chaîne alkyle. La résistance à l'huile et à l'eau obtenue avec les homopolymères et les copolymères variait d'excellente à nulle. On propose des explications des valeurs obtenues et on fait des comparaisons avec des travaux publiés.

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INTRODUCTION

The military requires good liquid-repellent fabric finishes which are capable of performing a variety of functions (1). Liquid repellency (particularly for water and oil) is also very important commercially and it is for this reason that much of the work dealing with these topics is to be found in patents. In fact, the structures of the commercially available oil- and water-repellent compositions are proprietary information and are generally mixtures of a number of compounds which are very difficult to separate and analyze (especially without the actual pure compounds in hand). Usually the best way to obtain an idea of the structures of these commercial repellents is from patents which have been granted to the particular company. However, due to the nature of patents only a guess at the formulation actually used can be ascertained (2).

The pioneering paper in the use of fluorochemicals as fabric finishes, which raised much interest, was that of DeMarco et al (3). In this article the development of "Quarpel", a combination application of a pyridinium-type water repellent with a fluorocarbon, was announced. This was a durable treatment lending good water repellency and some oil resistance (the actual value in terms of today's standard test cannot be ascertained). The granting of a series of patents (4, 5, and 6) to Dupont in 1966 was another highlight. These patents describe the use of a series of acrylates and methacrylates with straight-chain fluorinated alkyl substituents. Good water and oil repellency levels were claimed for these materials. It is believed that these polymers still form the backbone of the commercial formulations available today (7).

Another series of patents granted to various organizations as far back as 1961-62 (8, 9) concerned fluoroalkyl-substituted siloxanes. The main activity concerning the development of these most interesting polymers has mainly taken place in the 1970's (10 - 14). The siloxanes, in general, are known to have many desirable properties (see part I (1) for a full discussion). In particular non-fluorinated siloxanes are known to be (i) durable as water repellents, (ii) stable to both low and high temperatures, and (iii) stable to sunlight. It is possible that these properties are also present in the fluoroalkyl substituted siloxanes.

The present project was undertaken as a result of the following considerations:

(i) The commercial finishes currently in use each have at least one deficiency, such as a somewhat low oil repellency or instability to sunlight. Also improvements in the important properties of durability to laundering, dry cleaning, and wearing characteristics could perhaps be obtained.

(ii) The more recently developed siloxane polymers may have properties more in keeping with a multi-purpose finish for military use.

(iii) The patents on the fluoroalkyl-substituted siloxane polymers leave many questions unanswered. In some cases the standard test methods were not used. The best methods of preparing the polymer finishes were often not spotlighted and, in some cases, data were not given for what could have been the best structures.

(iv) It was also thought desirable to increase our knowledge and contribution to this field so that DREO would be in a better position to monitor new developments emanating from commercial firms and other sources of expertise in the field.

The approach in this project was to synthesize the most promising structures used in the patents and then to add to this group several new compounds not studied previously (the synthesis of these compounds has been described in Part I (1)). In this way a family of ten fluoroalkyl silanes was obtained (see Table 1) from which the effects of various structural features should become evident. First it can be seen that the odd numbered monomers have three replaceable silane substituents and thus can lead to what are called network polymers (see Figure 1). The even-numbered silanes have only two replaceable substituents and thus can lead to only linear polymers (Figure 1). The main difference between 1 and 3 (and 2 and 4) is that 1 has a longer fluoroalkyl substituent (by two CF_2 groups). The only difference that would be caused by the replaceable methoxy groups in 1 and 2 would be a somewhat faster polymerization reaction. Comparing 3 and 5 (and 4 and 6), it is seen that 5 has the fluoroalkyl chain attached to the rest of the molecule with an ether function while 3 utilizes the amide group. The monomers 1 to 6 all contain straight-chain fluoroalkyl substituents while in 7 to 10 these substituents are branched.

The effect of branching in the fluoroalkyl chain appears to be somewhat controversial. The main proponents of branching, Wasley and Pittman (10, 11, 13, 14) claim that a perfluoroisopropoxy group has an oleophobicity equivalent to six or seven fluorinated carbon atoms in a straight chain. On the other hand, Lichstein in a recent publication (7), states that the main purpose in the synthesis of derivatives containing the perfluoroisopropoxy group appears to be avoidance of infringement on patents which are based on straight-chain fluorocarbons. The monomers 7 and 8 contain the perfluoroisopropoxy group (two CF_3's) and in order to test the effect of branching even further, the monomers 9 and 10 which contain the perfluoro-t-butyl group (three CF_3's) have been included in the study.

A close look was also taken at the copolymerization of the best fluorinated monomers (1, 2, 3 and 4) with the much cheaper non-fluorinated alkyl silanes C1-C4 and polymethylhydrogensiloxane C5 (see Table 1). In actual fact, the triethoxy derivatives of 1 and 2, E1 and E2 (Table 1) were used since C1-C4 were triethoxy derivatives. The trimethoxy derivatives are more reactive and it was desired to have approximately equal reactivity for the comonomers. The monomers C1 to C3 differ only in the length of the alkyl chain (one, six and twelve carbon atoms respectively). Four replaceable silane substituents are present in C4, thus allowing a greater degree

Table 1. Structure and Numbering System of the Silane Monomers

A. Fluoroalkyl Silane Monomers

$CF_3(CF_2)_8CONH(CH_2)_3Si(OCH_3)_3$	1
$CF_3(CF_2)_8CONH(CH_2)_3Si(OCH_3)_2CH_3$	2
$CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_3$	3
$CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_2CH_3$	4
$CF_3(CF_2)_6CH_2O(CH_2)_3Si(OC_2H_5)_3$	5
$CF_3(CF_2)_6CH_2O(CH_2)_3Si(OC_2H_5)_2CH_3$	6
$(CF_3)_2CFO(CH_2)_3Si(OC_2H_5)_3$	7
$(CF_3)_2CFO(CH_2)_3Si(OC_2H_5)_2CH_3$	8
$(CF_3)_3CO(CH_2)_3Si(OC_2H_5)_3$	9
$(CF_3)_3CO(CH_2)_3Si(OC_2H_5)_2CH_3$	10

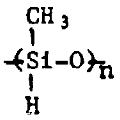
B. Ethoxy Derivatives of 1 and 2

$CF_3(CF_2)_8CONH(CH_2)_3Si(OC_2H_5)_3$	E1
$CF_3(CF_2)_8CONH(CH_2)_3Si(OC_2H_5)_2CH_3$	E2

C. Unfluorinated Alkyl Silanes (Comonomers)

$CH_3Si(OC_2H_5)_3$	C1
$CH_3(CH_2)_5Si(OC_2H_5)_3$	C2
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$	C3
$Si(OC_2H_5)_4$	C4

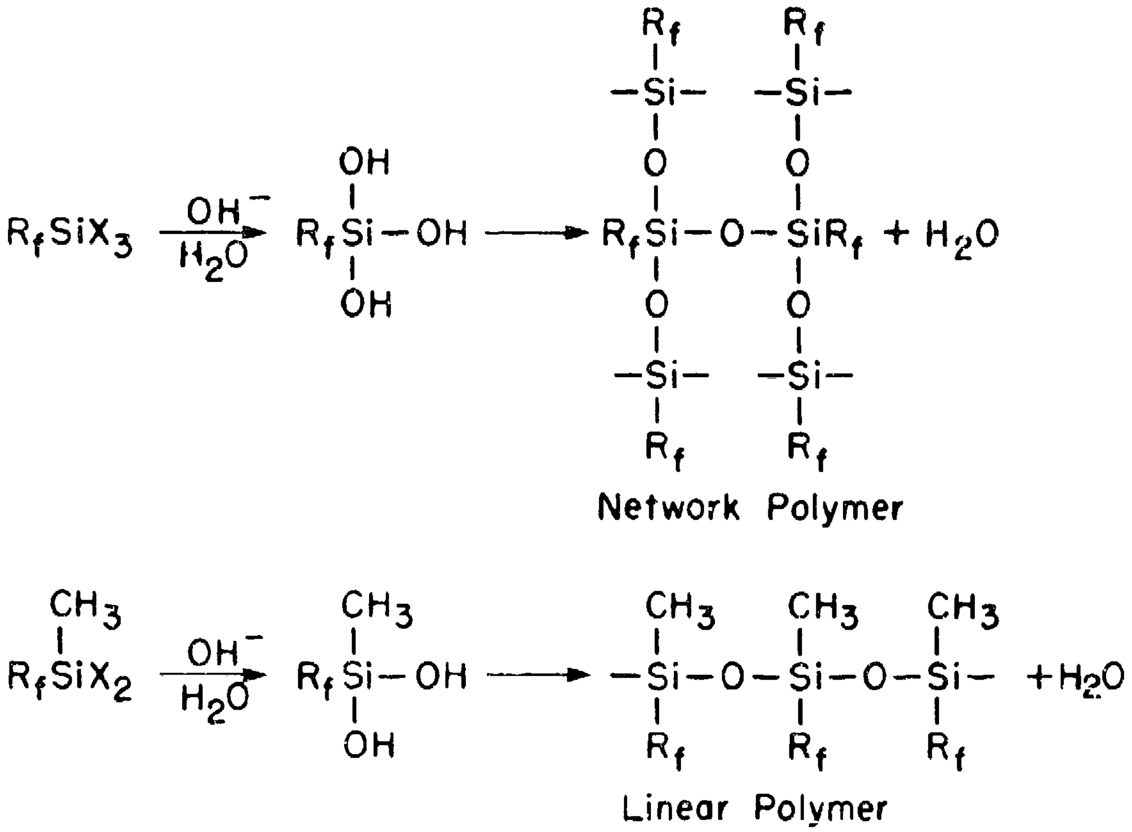
Polymethylhydrogensiloxane



$$\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ H \end{array}\right)_n$$

C5

Figure 1. The Formation of Network and Linear Siloxanes



- X is a replaceable group such as halogen or alkoxy
- R_f contains the fluoroalkyl group
- hydroxide is used as a catalyst
- The polymer chain is formed by the condensation of two SiOH groups to form Si-O-Si plus water.

of cross-linking. In basic solution, the hydrogens of the polymer C5 are readily replaced by hydroxyl groups in the presence of water. These hydroxyls can then condense with the replaceable silane substituents to attach the fluoroalkyl substituted monomer to the chain. The remaining hydroxyl substituents can either condense with substituents on the fabric or crosslink with other polymer chains.

EXPERIMENTAL

Synthesis of the Monomers

The synthesis of the monomers used in this study has been described in Part I(1). Other chemicals and the solvents used in this project were reagent grade or better.

The Standard Method of Polymerization, Application of Finish, and Curing Conditions

Unless stated otherwise the following standard procedures were followed. The weight of monomers used was 2g or a total of 2g in the case of comonomers. In some cases, when the amount of monomer available was limited, the scale of the polymerization was reduced to three-quarters or one-half of that described.

The monomer(s) was weighed into a 50-ml round-bottom flask containing a magnetic stirring bar. Isopropanol (40 ml) was then added to dissolve the monomer(s). One millilitre of aqueous sodium hydroxide solution was pipetted in. The amount of sodium hydroxide used ranged from 5-60 mg per millilitre depending on the particular polymerization requirements. The polymerization solution was allowed to stir for an indicated period of time and was then neutralized with 20% aqueous sulfuric acid. The mixture was filtered through a medium-porosity sintered-glass funnel, then applied directly to the fabric.

Using a two dip/two nip procedure, fabric samples were padded on an Atlas laboratory padding machine (Type LW-5) to a wet pick-up of 70-100% with each finish. After padding, the fabric circles were cured in a forced-air oven at 150°C for 15 min. The fabrics were allowed to stand at room temperature overnight and then tested for oil and water repellency.

Fabric Circles

Duplicate samples (8.5-cm circles) of two fabrics were tested with each finish. The first was nylon/cotton twist fabric (50/50 blend; 170 grams per square meter; designated as X74-438 (olive green 107 dye)). The second was a bleached cotton fabric of plain weave (152 g/m^2).

WATER- AND OIL-REPELLENCY TESTS

The American Association of Textile Chemists and Colorists (AATCC) Test Methods 118-1966 (oil repellency) and 22-1967 (water repellency)(15) 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 (Table 2), 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 seconds. At DREO two modifications have been made to the standard oil-repellency test. One is the use of half grades. That is, a rating of 5/6 would be assigned to a fabric which was not wet by a solution consisting of 50% by volume of each of n-dodecane and n-decane. The second is the use of a 5-min test period instead of the normal 30 seconds 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 wetted pattern whose appearance depends on the relative repellency of the treated fabric. Evaluation is accomplished by comparing the wetting pattern with pictures on a standard chart. A written description of the wetting patterns and their associated grades is given in Table 3.

Table 2. Standard Liquids for the Oil-Repellency Test (15)

AATCC Oil Repellency Rating Number	Composition	Surface Tension of Liquid (16)[a]
1	Nujol	31.5
2	65:35 Nujol:n-hexadecane by volume	29.6
3	n-hexadecane	27.3
4	n-tetradecane	26.4
5	n-dodecane	24.7
6	n-decane	23.5
7	n-octane	21.4
8	n-heptane	19.8

[a] dynes/cm

Table 3. Water-Repellency Spray Test Ratings (15)

AATCC Rating	Description
100	No sticking or wetting of upper surface
90	Slight random sticking or wetting of upper surface
80	Wetting of upper surface at spray points
70	Partial wetting of whole of upper surface
50	Complete wetting of whole of upper surface
0	Complete wetting of whole upper and lower surfaces

RESULTS AND DISCUSSION

The Fluoroalkyl-Substituted Homopolymers

In Table 4 are summarized the results obtained for nylon/cotton fabric with each fluoroalkyl-substituted homopolymer when the optimum stirring times and catalyst concentrations are utilized in the synthesis of the polymer solutions. Table 5 gives the variations in liquid repellency and add-on with stirring time and concentration of catalyst. If the structures of the monomers given in Table 1 are matched with the summarized results in Table 4, several trends become immediately apparent. Only with the longer straight-chain fluoroalkyl substituents (1 to 5) are repellencies of any interest obtained. In fact, excellent values which certainly meet the requirements for a military finish are obtained with 1 which has nine fluorinated carbons in a straight chain.

On comparing the network polymers from the monomers[1] 1, 3, 5, 7, and 9 with those from the corresponding linear ones, it is seen that network polymers are superior in every case and the size of the difference between the two systems depends on the initial values. That is the difference between 1 and 2 consists of only a slight decrease of water repellency for 2. The difference between 3 (network) and 4 (linear) is somewhat more pronounced (a decrease of half an oil repellency level and two water repellency levels). The change from 5 to 6 is even more drastic in that the oil repellency for the linear polymer has dropped to zero and the water repellency has decreased by two levels. Where branched-chain monomers are used it is again observed that the network polymers from 7 and 9 give superior values to the linear analogues from 8 and 10 respectively.

The effect of increasing chain length is very clearly revealed by comparing the values for 1 and 2 (9 straight-chain fluorinated carbons) with those for 3 and 4 (7 straight-chain fluorinated carbons). The water repellency drops from 100 to 90 for 1 vs 3 and from 90+ to 70 for 2 vs 4. The oil repellencies are quite similar except for that of 4 which has dropped to 6 from 6/7. The effect of chain length will be discussed further when the copolymerizations with non-fluorinated silanes are presented.

The monomers 3 to 6 all contain a fluoroalkyl substituent of 7 carbons. The essential difference between 3 and 5 and between 4 and 6 is that in each case the former utilizes the amide group to attach the fluoroalkyl group to the rest of the molecule while in the latter the ether function is used. This

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[1] For the balance of this report the reader can readily infer from the context of the discussion whether a numbered substance refers to a polymer or to the corresponding monomer.

Table 4. Oil- and Water-Repellency Results for Each Homopolymer with Nylon/Cotton[a]

Monomer	Oil Repellency	Water Repellency[b]
1	6/7	100
2	6/7	90^{+}
3	6/7	90
4	6	70
5	5/6	80
6	0	50
7	0	50
8	0	0
9	1	70
10	0	50^{-}

[a] The results reported here are for polymer solutions produced at the optimum reaction time and catalyst concentrations. For variations in these two variables, see Table 5.

[b] The 90^{+} indicates a very good 90 which is just short of 100. The 50^{-} indicates (for purposes of the discussion) a fabric that upon being turned over immediately after the test was still dry on the bottom but soaked through a few seconds later.

seemingly minor difference causes a great change in the liquid-repellent properties of the resultant polymers. In comparing the values for the network polymers 3 and 5 it is seen that both the oil (6/7 → 5/6) and water (90 → 80) repellencies decrease. The change is even more pronounced in the case of the linear analogues. In fact the oil repellency decreases from 6 (for 4) to 0 (for 6) and the water repellency drops from 70 to 50.

In relation to the straight chain fluoroalkyl-substituted polymers, the branched chain ones 7 - 10 have extremely poor values. In each case the network polymer is better than the linear one and the perfluoro-t-butyl-substituted polymer is somewhat better than the corresponding perfluoroisopropyl substituted polymer (7 vs 9 and 8 vs 10). The values corresponding to those in Table 4 but for cotton instead of nylon/cotton fabric are found in the Appendix (Table 4A). The values obtained for oil repellencies on cotton are essentially unchanged from those obtained on nylon/cotton while water repellency values are generally a level lower.

Table 5 gives for each monomer a set of polymerizations utilizing various stirring times and catalyst concentrations. Using these data, which are for the nylon/cotton fabric (results with cotton are found in Table 5A in the Appendix), the chemistry associated with these polymerizations can be described and a number of trade offs operating in these systems can be mentioned. With the network polymer 1, solubility is a major problem. At 14 min stirring time (20 mg NaOH) so much of the polymer had already precipitated that a negative add-on was obtained. At 5 min stirring time (5 mg NaOH), little or no polymer precipitate was present but the molecular weight of the polymer was not sufficiently high to produce a good add-on (only 0.55%; see Table 5). At 5 min stirring time, with twice the catalyst, significant precipitation (0.7 g) occurred but the material was of sufficiently high molecular weight to give a good add-on (2.04%) at a curing temperature of 150°C for 15 min. It should be noted that, with the initial monomer concentration at 5%, add-ons between 3 and 4% should be obtained if no material is lost due to precipitation or removal in the curing step. As will be shown later, the solubility problem can be eliminated by the addition of a small amount of non-fluorinated alkyl silane monomer.

The solubility of the polymer of 2 was much greater. In fact at a stirring time of 14 min (20 mg NaOH) and 42 min (20 mg NaOH) identical add-ons of 3.7% were obtained. At 63 min (40 mg NaOH); however, a polymer precipitate was observed. With 3 no polymer precipitate was observed at 14 min; however, the add-on was low, indicating that the molecular weight of much of the resulting material was not high enough to survive curing at 150°. With 42 min stirring time, a little precipitate was present when 20 mg NaOH (1.49% add-on) was used, while a significant amount of precipitate was present with 40 mg NaOH (1.69% add-on). In contrast, the polymer of the linear analogue, 4, had very good solubility and 4% add-ons were obtained with no polymer precipitate.

The polymer of the ether 5 proved to be less soluble (or more reactive) than its analogue with the amide function (the polymer of 3). At 28 min (20 mg NaOH), no add-on was obtained because essentially all of the polymer had precipitated while only a low add-on was obtained at 14 min. At 7 min (10 mg NaOH), no polymer precipitate was observed, however, the add-on and the liquid-repellency values were still quite low. A slow-cure procedure was utilized (as detailed in footnote b, Table 5) to give the polymer time to cross link further

Table 5. Sets of Results for Each Homopolymer with Nylon/Cotton

Stir Time (min)	Weight NaOH (mg)	Oil Repel.	Water[a] Repel.	% Add-on	Stir Time (min)	Weight NaOH (mg)	Oil Repel.	Water[a] Repel.	% Add-on
Polymer of 1					Polymer of 2				
5	5	6	90-100	0.55	14	20	6/7	90^+	3.74
5	10	6/7	100	2.04	42	20	6/7	90^+	3.65
14	20	4/5	90	-	63	40	6/7	90^+	2.67
Polymer of 3					Polymer of 4				
14	20	6/7	90^+	0.87	14	20	5/6	50	1.91
42	20	6/7	90	1.49	63	40	5/6	50-70	3.88
42	40	6	90	1.69	5.5 h	40	5/6-6	50-70	4.10
					20 h	40	5/6-6	70	4.13
Polymer of 5					Polymer of 6				
7	10	3	70	1.56	14	20	0	0	0.94
7[b]	10	5/6	80	2.89	42	20	0	50	2.56
14	20	1	70	0.61	63	40	0	0	2.50
28	20	0	50	-					
Polymer of 7					Polymer of 8				
14	20	0	50	0.51	14	20	0	0	-
63	40	0	50	1.66	126	60	0	0	-
20.5 h	40	0	50	3.29	42[c]	20	0	0	0.77
					42[d]	20	0	0	2.56
					63[e]	40	0	0	1.60
					63[f]	40	0	0	3.05
Polymer of 9					Polymer of 10				
14	20	0	50	0.37	56[e]	40	0	50^-	1.19
28	20	0	50	0.75	56[f]	40	0	50^-	3.92
63	40	1	50	1.16					
63[b]	40	1	70	2.04					

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[a] See footnote b in Table 4.

[b] Same solution and technique was applied as in the above entry in the table except that a slow cure (5 min at 100°; temperature raised to 150° in 8-9 min; 15 min at 150°) was applied.

[c] Standard technique gave zero add-on. Reasonable add-ons were obtained by using an initial polymerization solution of 2 g monomer, 10 ml of isopropanol, and 1 ml of aqueous NaOH. After the noted stirring time and neutralization, a further 20 ml of solvent was added.

[d] Same polymer solution used as in the above entry in the table except that the fabric was dried overnight at room temperature and then cured 0.5 h at 120°.

[e] Same as in footnote c except that only 10 ml of solvent were added after neutralization.

[f] Same as the above table entry except that the fabrics were cured at 120°/0.5 h.

with both itself and the fabric. This procedure almost doubled the add-on (from 1.6 to 2.9%). The data in Table 5 show that not only are the best liquid-repellency values substantially inferior to those of the corresponding network polymers of 1 and 3 but these values are developed only at much higher add-on levels. For both 1 and 3 liquid repellencies obtained at less than 1% add-on are nearly identical to those obtained with much higher add-ons. That is, maximum values are approached quickly. This is not so in the case of 5. The dramatic climb in oil-repellency values from 1 to 3 to 5/6 with add-ons of 0.6 to 1.6 to 2.9% indicates a high dependence on the percentage add-on. Hence this finish would probably lose its repellency properties very quickly upon wearing.

At first glance the liquid-repellent properties for the polymer of 6 are very surprising. Here is an example of a polymer which confers no oil repellency and yet contains seven fluorinated carbons. When this behaviour is considered in the light of the results which have already been discussed, however, it is clear that the polymer of 6 contains some quite undesirable structural features. First, it is a linear polymer and these have already been shown to be inferior to the network polymers. Secondly, it has been shown in the case of the polymer of 5 that, with this particular fluoroalkyl substituent containing the ether function, lower liquid-repellency values are obtained than with the similar polymer containing the amide group. Thirdly it is clear that, with this fluoroalkyl substituent, maximum repellency values are not obtained until a high add-on level is reached. Thus it appears that these three factors have combined in the polymer of 6 to give a finish with essentially no liquid-repellent properties.

The polymer of 7 has good solubility properties and can achieve a high enough molecular weight so that good add-ons are achieved. Thus, no precipitate appeared with 7 even after a stirring time of 20.5 h (40 mg NaOH) and an add-on of 3.3% was obtained. With the polymer of 8 no precipitate is observed even after stirring 126 min (60 mg NaOH). No add-on was obtained with this solution even after utilizing the slow-cure procedure. Thus, the resultant polymer must be of low molecular weight. It is apparent in this case that either the polymerization reaction is very slow or that the equilibrium between polymerization and depolymerization favours the low molecular weight material. In order to obtain a higher molecular weight, the polymerization was carried out in only 10 ml of solvent instead of 40, while the amount of aqueous sodium hydroxide solution was not altered. After the polymerization a further 10 ml of solvent was added. This method had the desired effect of producing a polymer with a high enough molecular weight to give reasonable add-ons. With a 63-min stir (40 mg NaOH), 1.6% add-on was obtained with a cure at 150° for 15 min and a 3.1% add-on with a cure at 120° for 0.5 h.

With 9, no polymer precipitate was observed even at 63 min stirring time (40 mg NaOH). The normal cure (150°/15 min) gave an add-on of 1.2% whereas a slow cure (starting at a lower temperature and then a normal cure) gave an add-on of 2.04%. The molecular weight of the polymer formed from 9 is thus less than that formed from the network polymer 7 when equal reaction times are used. Using the same polymerization technique as described for 8 (see above) in order to obtain a reasonable molecular weight, the polymer of 10 gave an add-on of 1.2% on normal curing technique and of 3.9% on curing at 120° for 0.5h.

Copolymerization of Fluoroalkyl-Substituted Monomers With Non-Fluorinated Alkyl Silanes

It is apparent that only the homopolymers of 1, 2, 3, and 4 have liquid-repellent properties of interest. A practical concern which always arises with fluorinated materials is their high cost. It was decided to copolymerize the four best fluorinated monomers with three much cheaper alkyltriethoxysilanes carrying straight-chain hydrocarbon substituents of one (methyl (C1)), six (hexyl (C2)), and twelve (dodecyl (C3))carbons respectively (see Table 1). Also used, to a lesser extent, was tetraethoxysilane, a monomer which has four replaceable substituents and thus can form polymer chains in four directions, as well as polymethylhydrogensiloxane (C5) a polymer which, in aqueous sodium hydroxide solution, reacts with water in such a manner that the hydrogen on the silane is replaced by hydroxyl. The fluoroalkyl-substituted monomer or polymer can then attach to this polymer chain by condensation with loss of water.

With copolymerizations of this type it is important that the comonomers involved do not have widely different reactivities and it is for this reason that the triethoxy derivatives of 1 and 2, i.e. E1 and E2 (see Table 1) were used. Another requirement is that no polymer precipitate be formed during the reaction since precipitation of copolymer with a high preponderance of fluorinated comonomer would make the results meaningless in terms of initial monomer concentrations. A minimum of two hours stirring time (40 mg NaOH) was used with each polymerization. In this way add-ons near 3% or better were achieved in all cases but those with the highest concentration of alkyl silanes. It was necessary to use tetrahydrofuran as the solvent in the copolymerizations of E1 and C1, C2 and C3 since with the standard solvent (isopropanol), a precipitate was obtained.

In Table 6 the results obtained when the triethoxy derivative of 1 was copolymerized with C1, C2, C3 and C5 are presented. A significant practical result from Table 6 is that the add-ons are as expected from the percentage wet pick up. That is, little or no polymer is lost due to precipitation in the polymerization reaction or due to removal during curing. This was a major problem with the homopolymers of 1 and 3 and this alone would be sufficient reason to add some alkylsilane monomer to the polymerization reaction. No decrease in oil or water repellency is observed with C1 at either the 30 or 60 mole % levels. Only at the 90% level does a slight decrease in oil and water repellency occur. The results are similar for C2 except for a slightly lower oil repellency at 60%, while a perceptible decrease to a rating of 5 has taken place at 90%. With the long twelve-carbon alkyl chain (C3), the oil repellency has fallen to a value of 4/5 at the 90% level. The effect of alkyl chain length of the copolymer on oil repellency is shown graphically in Figure 2. The slight increase in oil repellency with the C1 and C2 copolymers at the 30% level is most likely caused by the increased add-on over that attainable by the homopolymer (see Table 4). Two main conclusions are evident from Fig. 2. First, with the monomer E1, large amounts (e.g. as much as 90 mole % C1) of unfluorinated monomer can be added with little or no effect on the oil repellency. Second, the packing of the fluorocarbon chains is such that even 60 mole % of the dodecyl silane monomer C3 does not cause an appreciable loss in oil repellency. This is quite remarkable when it is considered that the substituent chain for the fluorinated monomer E1 (14 atoms long) is only 2 atoms longer than that of the non-fluorinat

Table 6. Copolymerization of $CF_3(CF_2)_8CONH(CH_2)_3Si(OC_2H_5)_3$ E1 with Non-Fluorinated Monomers (Nylon-Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-on
$CH_3Si(OC_2H_5)_3$ C1			
30	6/7-7	100	4.2
60	6/7	100	3.5
90	6	90-100	2.7
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7-7	100	3.5
60	6-6/7	100	4.3
90	5	100	2.9
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	6-6/7	100	3.8
60	6	100	2.5
90	4/5	90	0.6
Polymethylhydrogensiloxane C5			
0.3 g C5/1.7 g E1	6/7	90	3.6
0.6 g C5/1.4 g E1	5/6	80	3.5
1.4 g C5/0.6 g E1	0	70	4.9

[a] The standard method of polymerization and curing was used as described in the experimental section except that tetrahydrofuran was used as the solvent with C1, C2 and C3. All polymerizations with C1, C2 and C3 were stirred for 2 h (40 mg NaOH). With C5, the 0.3g solution was stirred for 1h with 20 mg NaOH while the 0.6 and 1.4 g C5 solutions were stirred 1.5 h with 40 mg NaOH. With C5, it is necessary to add the aqueous NaOH slowly since a large amount of hydrogen is produced initially.

Figure 2. Oil Repellency Ratings of Copolymer Finishes of E1 and Alkyl Silanes

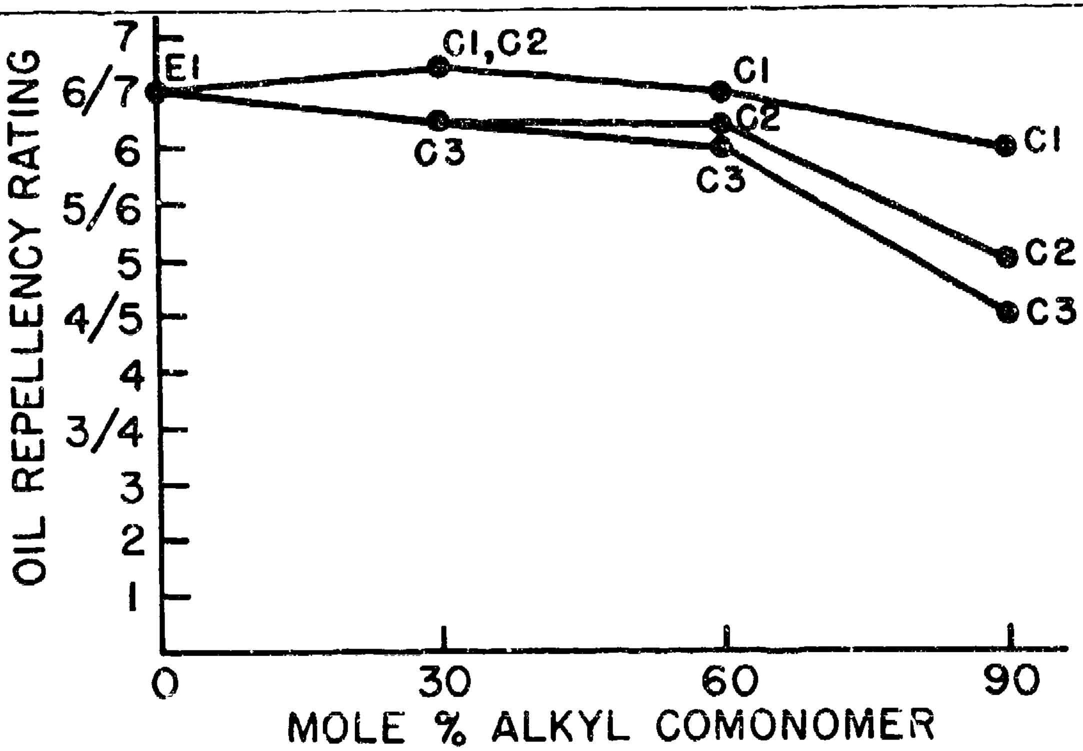
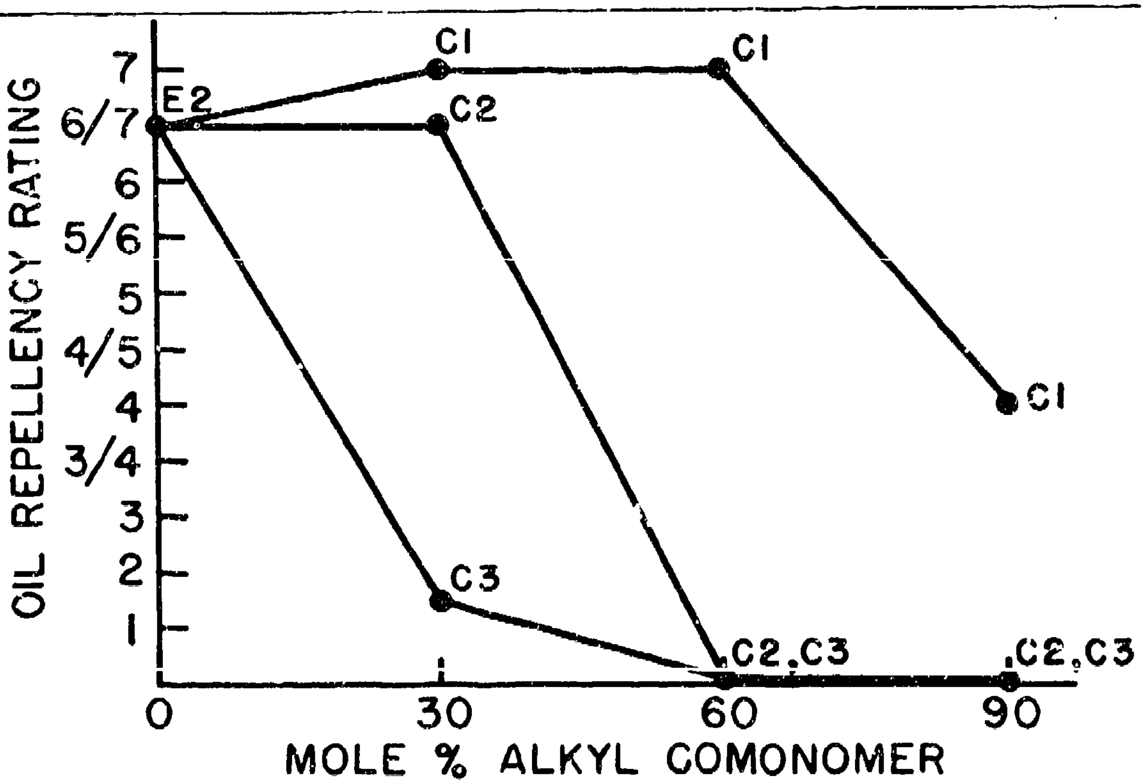


Figure 3. Oil Repellency Ratings of Copolymer Finishes of E2 and Alkyl Silanes



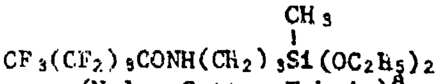
C3 (12 atoms long) and indicates tight packing.

In the above polymerizations, the copolymer is formed by the reaction of monomer units. It was thought of interest to obtain the results for the situation where the fluoroalkyl monomer reacts with a preformed unfluorinated polymer which has active sites on which to attach the monomer. Thus E1 was reacted with polymethylhydrogensiloxane (C5, see Table 6) in the presence of base (the Si-H of C5 is converted to Si-OH in the presence of base with the evolution of hydrogen). It is clear, however, that much better results, especially at the higher concentrations of non-fluorinated monomer, are obtained when the comonomers C1 and E1 are allowed to react intimately to produce a polymer containing the same functional groups. For example, the 90 mole % C1 entry in Table 6 (1.39 g C1) still has an oil repellency of 6 while the 1.40-g C5 entry has a value of 0.

Table 7 contains the results of the copolymerization of E2 with C1, C2 and C3. The small increase in oil and water repellency (from 6/7 to 7 and 90$^+$ to 100 of the 30% C1 copolymer over that of the homopolymer is probably due to the tighter packing of fluorinated groups caused by the addition of a monomer with three replaceable functional groups to E2 which only contains two replaceable groups. This benefit outweighs the detrimental effect of the addition of unfluorinated methyl groups along the chain. Even at 60% C1 the oil-repellency rating in still slightly better. At 90% C1 both oil and water repellency have dropped considerably. As shown graphically in Figure 3, the effect of alkyl chain length is very much greater in copolymers with E2 than with E1 (compare with Figure 2). Oil repellency values for C2 are only of interest at the 30% level, while at 30% C3 the values have already dropped to 1-2. Thus, E2 with only two replaceable silane substituents does not orient its fluorinated functional groups in such a way as to prevent the longer alkyl groups from being in the surface.

The copolymer results with 3 are shown in Table 8 and graphically in Figure 4. The oil repellency remains unchanged from that of the homopolymer (6/7) with 30% of C1, C2 or C3. But at 60% C1 slight deterioration to 6 has taken place and at 60% C2, it has fallen to 5/6. At 60% C3, 90% C1, and 90% C2 the oil repellency has fallen to 1 or less. A comparison of Figures 2 and 4 shows how important the extra two CF_2's are in resisting deterioration in oil-repellency levels with both higher proportion and length of the alkyl silanes. When the tetraethoxysilane monomer, C4, (four replaceable silane substituents) was copolymerized with 3 at 30, 60 and 90 mole % C4, essentially all of the polymer precipitated out of the polymerization solution in each case. Also, the two entries in Table 8 for polymerization of the monomer 3 with the preformed polymer C5 in the presence of base indicate again that it is better to react the monomers themselves since the results are poorer than that obtained with the comonomers of 3 and C1.

The last three entries in Table 8 indicate further that the polymerization of the monomers separately, then adding them together does not produce results which are as good as copolymerization of the monomers. In these experiments 3 is polymerized separately and is then added to individual solutions of the polymer of C2, C5 and polydimethylsiloxane. The proportion of the polymers were such as to approximately correspond to the corresponding 30% alkyl monomer entries. In each case, the results obtained were poorer than those with the related copolymerizations.

Table 7. Copolymerization of  $CF_3(CF_2)_5CONH(CH_2)_3\overset{CH_3}{Si}(OC_2H_5)_2$ E2 With Non-Fluorinated Monomers (Nylon-Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	7	100	3.3
60	7	90+	3.1
90	4	70	1.3
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7	90	3.6
60	0	80	2.9
90	0	70	2.4
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	1-2	90	3.1
60	0	80	2.9
90	0	70	1.4

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred for 2 h and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

Table 8. Copolymerization of $CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_3$ 3 With Non-Fluorinated Monomers (Nylon-Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	6/7	90	3.1
60	6	70	3.0
90	1	50	1.1
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7	80-90	2.5
60	5/6	70	2.6
90	0	50	2.0
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	6/7	80-90	2.6
60	1	90	2.7
$Si(OC_2H_5)_4$ C4			
30,60,90	N/A[b]	N/A[b]	0
Polymethylhydrogensiloxane C5			
0.3g	5/6	80	3.5
0.6g	4	70	3.8
Polymer Solutions of 3[c]			
0.8 g 3 + 0.2 g C2 polymer	5/6	80	1.8
0.8 g 3 + 0.2 g C5	4/5	90	2.2
0.8 g 3 + 0.2 g polydimethlsiloxane	4	80	2.2

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred for 2.5 h and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

[b] Not applicable. At the conditions stated in the above footnote, the polymer had precipitated out of solution to the point where no add-on was obtained. Thus only modest values were obtained which can not be related to the initial monomer concentrations.

[c] The individual monomers were polymerized separately and the solutions were added together in such ratios that comparisons could be made with data where the monomers were copolymerized.

Figure 4. Oil Repellency Ratings of Copolymer Finishes of 3 and Alkyl Silanes

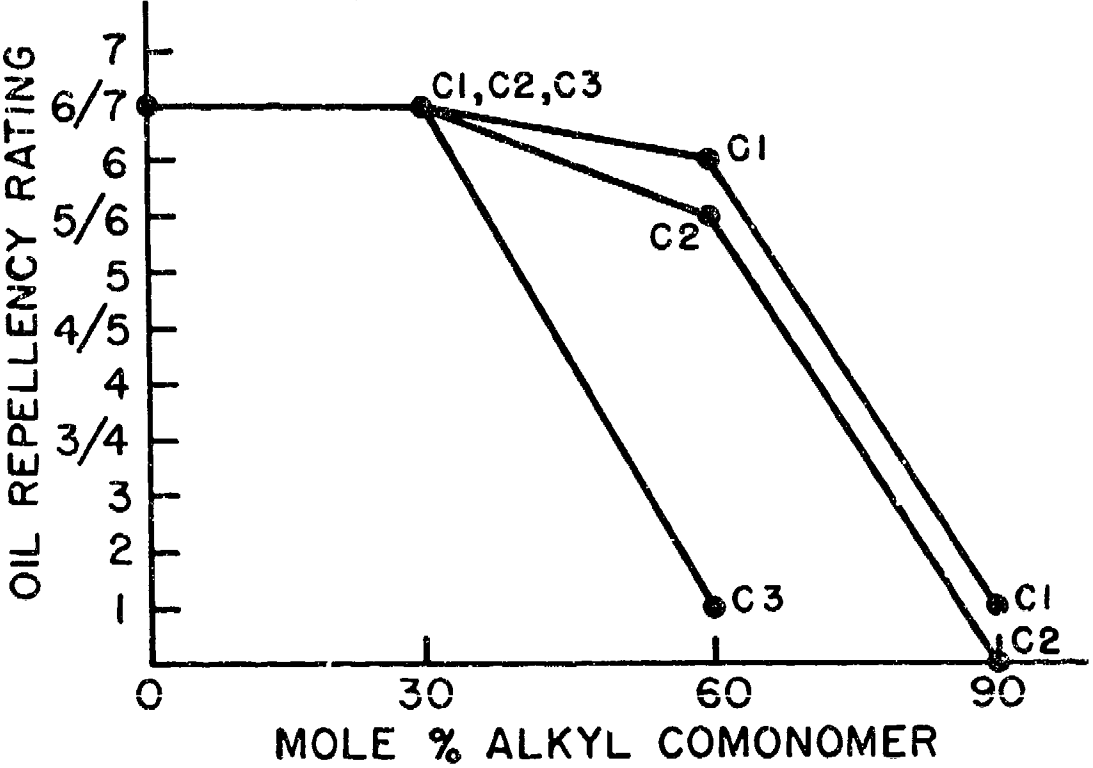
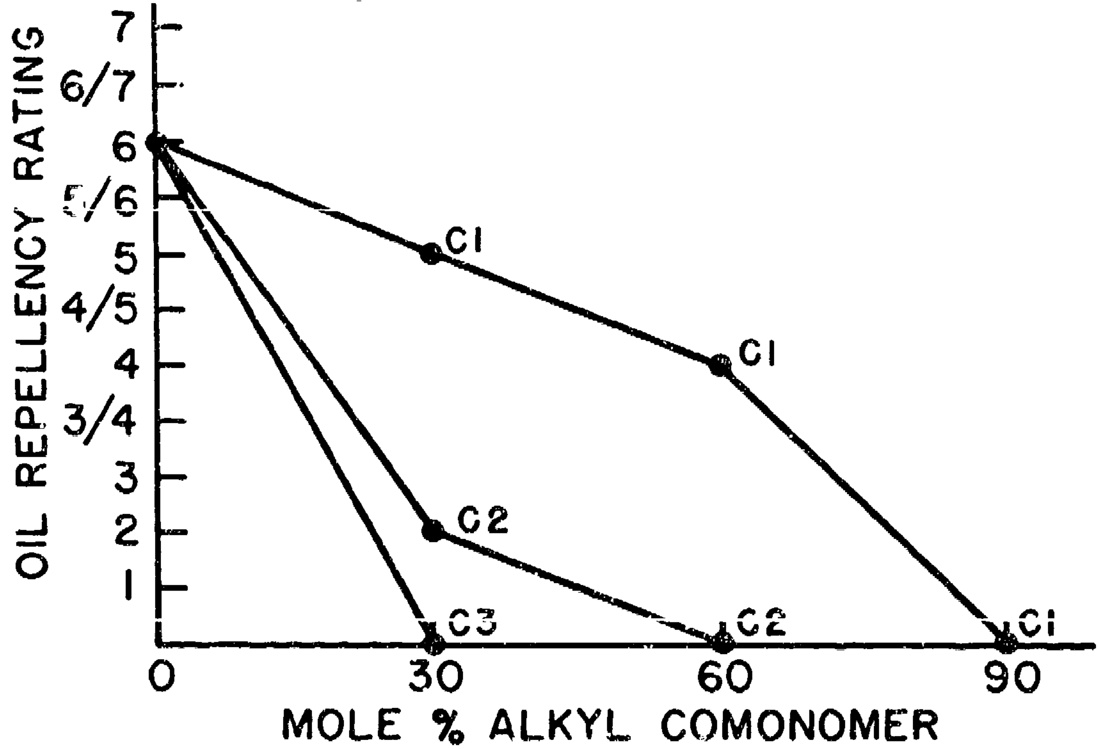


Figure 5. Oil Repellency Ratings of Copolymer Finishes of 4 and Alkyl Silanes



The results for the copolymerization of the monomer 4 with alkyl silanes are found in Table 9 and graphically in Figure 5. With 4 it is seen that even small amounts of alkyl silane comonomer significantly reduce the oil repellency. For example 30 mole % of C1 and C2 reduces the oil repellency rating from 6 to 5 and 2 respectively. This is in contrast to the corresponding copolymers with E1, E2 and 3 (Figures 2, 3 and 4) where 30 mole % of C1 and C2 did not reduce the oil repellency. When 30% of C3 is copolymerized with 4, no oil repellency at all is observed.

Results with similar trends to those of Tables 6-9 for nylon/cotton fabric were obtained with cotton fabric when the same copolymer solutions were applied. These results are found in the Appendix in Tables 6A-9A.

Phosphate Resistance

A very brief look was taken at the phosphate resistance of the copolymers of E1 and E2 with 30% of methyltriethoxysilane (C1). On a scale of 0 to 9, it was found that the copolymer of E1 gave a perfect rating of 9 while the copolymer of E2 gave a rating of 0. This test again shows the overall superiority of network polymers.

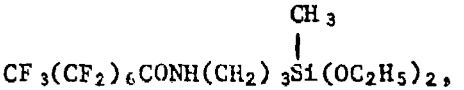


Table 9. Copolymerization of $CF_3(CF_2)_6CONH(CH_2)_3\overset{CH_3}{\overset{|}{Si}}(OC_2H_5)_2$, 4 With Non-Fluorinated Monomers (Nylon-Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	5	50	3.8
60	4	50	2.7
90	1	50	1.1
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	2	70	3.5
60	0	50	3.0
$CH_3(CH_2)_{11}Si(OC_2H_5)$ C3			
30	0	70	3.3
$Si(OC_2H_5)_4$ C4			
30	5/6-6	50	2.6
60	6	70	0.6[b]
Polymethylhydrogensiloxane C5			
0.3 g	4-4/5	50	3.9
0.6 g	1	50-70	3.7

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred overnight and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

[b] Polymer had precipitated out in the reaction solution and thus the values are not meaningful in terms of initial monomer concentration.

CONCLUSIONS

1. It has been shown that the length of the fluoroalkyl substituent in siloxane polymers is an extremely important variable with respect to the liquid-repellency properties imparted to fabrics. The best results are obtained with a fluoroalkyl substituent of 9-carbon length (1 and 2), although good results were obtained with monomer 3 which contains 7 fluorinated carbons. The results reported for 3 are the same as those reported in the literature (12) except for the slightly lower water repellency of 90 instead of 100. This may be due to the use of nylon/cotton fabric in this study instead of wool fabric (12) since the latter has an inherent water repellency of 50.

2. The results show very clearly that network siloxane polymers exhibit liquid-repellency properties superior to those of their linear analogues.

3. The functional group used to attach the fluoroalkyl substituent to the polymer backbone can make a large difference to the liquid-repellency values obtained. This was shown by the superior values for 3 and 4 (amide group) compared to those for 5 and 6 (ether group).

4. In this study, no advantage could be seen to using branched-chain substituents. Using our standard polymerization method, very poor liquid-repellency values were obtained with the branched-chain-substituted monomers 6-10. It is believed that the medium range values obtained by Pittman and Wasley (10, 11, 17) were due to the isolation of their perfluoroisopropoxy-substituted siloxane polymers and subsequent cross-linking for several hours at high temperature. These steps complicate the experimental procedure and also their resultant polymer is soluble only in exceptional solvents such as freon. These results and a literature search (see Part I(1)) lend credence to Lichstein's statement (7) that the branched-chain work appears to have been undertaken in order to avoid infringements on patents which are based on straight-chain fluorocarbons.

5. Copolymerization of some of the fluorinated monomers (E1 and 3) with the much cheaper non-fluorinated alkyl silanes has led to materials with excellent liquid repellencies. It has been shown for example, that as much as 60 mole per cent methyltriethoxysilane can be copolymerized with E1 with no decrease in liquid repellency values, while 60% of C2, 60% of C3 and 90% of C1 cause only a small decrease. Even a small amount of alkyl silane comonomer causes a beneficial increase in the solubility of the network polymers E1 and 3 resulting in much better add-ons to the fabric.

6. Better results are obtained if the fluorinated and non-fluorinated monomers are copolymerized rather than being merely mixed as separate polymer solutions. Another method whereby the fluorinated monomer is attached to the preformed non-fluorinated polymer is also inferior.

RECOMMENDATIONS

Liquid repellencies have been obtained which meet the requirements of a military finish. It is considered that the best way to proceed from this point is as follows:

(i) Information on the durability of these finishes (wearing, washing, and dry cleaning) should be obtained. The best candidates would most likely be the copolymers of E1 with 30 and 60 mole % methyltriethoxysilane (C1). These finishes should be durable since covalent bonds can be formed to the fabric and good durability to washing and dry cleaning has been achieved with non-fluorinated siloxanes (18).

(ii) Data on stability to sunlight and fire resistance would be useful, as well as a more comprehensive look at phosphate resistance.

(iii) Finally comparisons must be made with the two finishes currently used for armed forces fabrics. Other modern finishes, such as those listed in the recent article by Lichstein (7), might also be included in the comparisons.

ACKNOWLEDGEMENTS

The author is grateful to Dr. R.A.B. Bannard for helpful discussions during the preparation of these reports. Dr. J.M. McAndless and Mr. B.V. Lacroix carried out some preliminary experiments in this area. These experiments and some initial discussions with Dr. McAndless were valuable in the selection of the approach to this project.

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APPENDIX

Table 4A. Oil- and Water-Repellency Results for Each Homopolymer With Cotton[a]

Monomer	Oil Repellency	Water Repellency
1	6/7	80
2	7	80
3	6/7	80
4	6	70
5	5	70
6	0	0
7	0	50
8	0	0
9	1	50
10	0	0

[a] The results reported here are for polymer solutions produced at the optimum reaction time and catalyst concentration. For variations in these two variables, see Table 5A.

Table 5A. Sets of Results for Each Homopolymer with Cotton

Stir Time (min)	Weight NaOH (mg)	Oil Repel.	Water[a] Repel.	% Add-on	Stir Time (min)	Weight NaOH (mg)	Oil Repel.	Water[a] Repel.	% Add-on
Polymer of 1					Polymer of 2				
5	5	6	70	0.07	14	20	6/7-7	70	3.22
5	10	6/7	80	1.53	42	20	6/7	80	2.89
14	20	4/5	70	-	63	40	7	80^{+}	2.33
Polymer of 3					Polymer of 4				
14	20	6/7	70-80	0.47	14	20	5/6	50	0.66
42	20	6/7	80	0.77	63	40	5/6	50	2.70
42	40	6/7	80	1.39	5.5 h	40	6	70	3.94
					20h	40	6	70	3.49
Polymer of 5					Polymer of 6				
7	10	1	50	0.62	14	20	0	0	0.29
7[b]	10	5	70	1.93	42	20	0	0	1.54
14	20	1	50	-	63	40	0	0	1 94
28	20	0	50	-					
Polymer of 7					Polymer of 8				
14	20	0	50	0.21	14	20	0	0	-
63	40	0	50	1.19	126	60	0	0	-
20.5 h	40	0	50	2.53	42[c]	20	0	0	-
					42[d]	20	0	0	1.62
					63[e]	40	0	0	1.08
					63[f]	40	0	0	2.34
Polymer of 9					Polymer of 10				
14	20	0	50	-	56[e]	40	0	0	0.48
28	20	0	50	0.25	56[f]	40	0	0	2.55
63	40	1	50	0.77					
63[b]	40	1	50	1.75					

[a] The 80^{+} indicates a very good 80 which is just short of 90.

[b] Same solution and technique was applied as in the above entry in the table except that a slow cure (5 min at 100°; temperature raised to 150° in 8-9 min; 15 min at 150°) was applied.

[c] Standard technique gave zero add-on. Reasonable add-ons were obtained by using an initial polymerization solution of 2 g monomer, 10 ml of isopropanol, and 1 ml of aqueous NaOH. After the noted stirring time and neutralization, a further 20 ml of solvent was added.

[d] Same polymer solution used as in the above entry in the table except that the fabric was dried overnight at room temperature and then cured 0.5 h at 120°.

[e] Same as in footnote c except that only 10 ml of solvent were added after neutralization.

[f] Same as the above table entry except that the fabrics were cured at 120°/0.5 h.

Table 6A. Copolymerization of $CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_3$, E1 with Non-Fluorinated Monomers (Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	7	100	4.3
60	6/7	80	2.8
90	5/6	80	2.6
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7	90	2.9
60	6	100	3.5
90	6	90-100	2.1
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	6/7	90-100	2.9
60	5/6-6	80	2.1
90	4/5	70	0.4
Polymethylhydrogensiloxane C5			
0.3g	6/7	70	3.6
0.6g	5-5/6	70	2.8
1.4g	0	50	4.5

[a] The standard method of polymerization and curing was used as described in the experimental section except that tetrahydrofuran was used as the solvent with C1, C2 and C3. All polymerizations with C1, C2 and C3 were stirred for 2 h (40 mg NaOH). With C5, the 0.3 g solution was stirred for 1 h with 20 mg NaOH while the 0.6 and 1.4 g C5 solutions were stirred 1 5 h with 40 mg NaOH. With C5, it is necessary to add the aqueous NaOH slowly since a large amount of hydrogen is produced initially.

Table 7A. Copolymerization of $CF_3(CF_2)_8CONH(CH_2)_3\overset{CH_3}{\overset{|}{Si}}(OC_2H_5)$ E2 with Non-Fluorinated Monomers (Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	7-7/8	90	2.8
60	7	80	3.0
90	2-3	50	0.7
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7	80-90	3.0
60	1	80	2.4
90	0	50	2.1
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	5/6	90	2.6
60	0	80	2.2
90	0	50	0.9

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred for 2 h and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

[redacted]

Table 8A. Copolymerization of $CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_3$ 3 with Non-Fluorinated Monomers (Cotton Fabric)[a]

Comonomer (mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	6/7	80	2.8
60	6	50	2.6
90	1	50	0.6
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	6/7	80	1.7
60	6	70	2.2
90	0	50	1.3
$CH_3(CH_2)_{11}Si(OC_2H_5)_3$ C3			
30	6	80	1.9
60	3/4	70	2.3
$Si(OC_2H_5)_4$ C4			
30,60,90	N/A[b]	N/A[b]	
Polymethylhydrogensiloxane C5			
0.3 g	5/6	70	3.2
0.6 g	4	50	3.3
Polymer Solutions of 3[c]			
0.8 g 3 + 0.2 g C2	5/6	70-80	1.5
0.8 g 3 + 0.2 g C5	0	70-80	1.8
0.8 g 3 + 0.2 g polydimethylsiloxane	0	70	1.8

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred for 2.5 h and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

[b] Not applicable. At the conditions stated in the above footnote, the polymer had precipitated out of solution to the point where no add-on was obtained. Thus, only modest values were obtained which can not be related to the initial monomer concentrations.

[c] The individual monomers were polymerized separately and the solutions were added together in such ratios that comparisons could be made with data where the monomers were copolymerized.

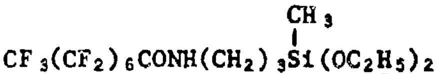

Table 9A. Copolymerization of $CF_3(CF_2)_6CONH(CH_2)_3\overset{CH_3}{\overset{|}{Si}}(OC_2H_5)_2$ 4 with Non-Fluorinated Monomers (Cotton Fabric)[a]

Comonomer (Mole %)	Oil Repellency	Water Repellency	% Add-On
$CH_3Si(OC_2H_5)_3$ C1			
30	5	50	3.2
60	4	50	2.0
90	1	50	0.6
$CH_3(CH_2)_5Si(OC_2H_5)_3$ C2			
30	3	50-70	3.1
60	0	50	2.2
$CH_3(CH_2)_{11}Si(OC_2H_5)$ C3			
30	0	50	2.9
$Si(OC_2H_5)_4$ C4			
30	5	50	1.7
60	N/A[b]	N/A[b]	0
Polymethylhydrogensiloxane C5			
0.3 g	4	50	3.3
0.6 g	1	50	3.0

---

[a] The standard method of polymerization and curing as described in the experimental was used. The solution was stirred overnight and the aqueous sodium hydroxide solution contained 40 mg NaOH per millilitre.

[b] Polymer had precipitated out in the reaction solution and thus the values are not meaningful in terms of initial monomer concentration.

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In this report the liquid-repellent properties of the homopolymers and selected copolymers of ten fluoroalkyl substituted silane monomers of varying structures are evaluated. The homopolymers of the silanes are synthesized, applied to nylon/cotton (50:50 weight per cent) and cotton as finishes, and the oil and water repellency imparted to these fabrics ascertained by standard tests. In this manner it is possible to compare the effects of (i) length and degree of branching of the fluorinated alkyl chains, (ii) the use of network (three replaceable silane substituents in the monomer) versus linear (two replaceable substituents) siloxane polymers, and (iii) the use of either an amide or an ether function to bond the fluoroalkyl group to the polymer backbone.

Due to the expense of these fluorinated materials, a study was conducted of the copolymerization of the best fluoroalkyl substituted silanes with much cheaper non-fluorinated alkyl silanes. Among the latter were those with varying alkyl chain lengths and number and orientation of the replaceable silane substituents. The oil and water repellencies obtained with both the homopolymers and copolymers ranged from outstanding to essentially none. Explanations are advanced for the values obtained and literature comparisons are made.

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KEY WORDS

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SILOXANES
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LIQUID REPELLENCY
WATER REPELLENCY
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