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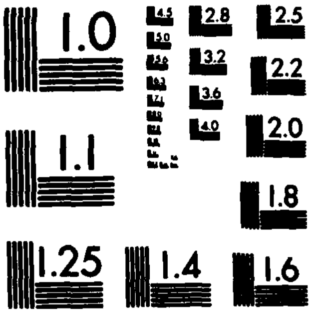

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FLUOROALKYL SILOXANES AS LIQUID-REPELLENT FABRIC FINISHES

PART 111:

THE DURABILITY OF THE COPOLYMERS AND COMPARISONS WITH COMMERCIALLY AVAILABLE FINISHES

by

J.W. Bovenkamp and B.V. Lacroix

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE [illegible]

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ABSTRACT

In this report the durability of liquid repellency properties imparted to fabrics by solutions of the copolymers of fluoroalkyl-substituted silanes and non-fluorinated silanes is examined. The best available commercial finishes were examined at the same time and the results compared with those of the experimental finishes. The durability testing encompassed wear, washing, dry cleaning, and weathering. Although the siloxane copolymers wear well, they are somewhat inferior to the commercial finishes after a number of washes. Much better durability to washing was obtained when a small amount of resin was added to the finish, following the normal commercial practice. The properties found for the siloxane finishes indicate that they could be useful in some circumstances.

RÉSUMÉ

On examine dans ce rapport la durabilité des propietéés hydrofuges et oléofuges des tissus traités avec des solutions de copolymeres contenant des substituts fluoroalkyles silanes et des silanes non fluores. Par la meme occasion, on a fait l'evaluation des meilleurs finis commerciaux disponibles et on en a comparé les resultats avec ceux qui ont été obtenus dans le cas des finis expérimentaux. Les essais de durabilité englobaient l'usure, le blanchissage, le nettoyage a sec et la résistance aux intemperies. Quoique les copolymeres siloxanes sont assez efficaces contre l'usure, ils sont quelque peu inférieurs aux finis commerciaux après un certain nombre de blanchissage. L'addition de petite quantité de resine aux finis augmente sensiblement la résistance au blanchissage, comme c'est le cas pour les finis commercials. Les propriétés trouvées dans le cas des finis siloxanes indiquent qu'ils pourraient être utiles en certaines circonstances.

INTRODUCTION

The present Canadian Chemical Warfare (CW) protective overgarment utilizes an outer layer of nylon/cotton (50/50 wt %) fabric which needs to be treated with a fluorocarbon finish to give it liquid repellent properties (oil and water repellency and resistance to penetration by liquid phosphorus esters (phosphate resistance)). In an earlier report (1), a state-of-the-art literature review of these finishes was presented. The finish currently in use is Zepel B (E.I. Dupont De Nemours & Co. (Inc.)). This and most other commercial oil-and water-repellent finishes utilize a series of fluoroalkyl-substituted acrylates and methacrylates having a carbon-carbon backbone (2). Due to the importance of the liquid-repellent barrier in the CW suit, it became desirable to evaluate and extend a number of publications on fluorokyl-substituted siloxanes (3-9). It was felt that these inorganic polymers having a silicone-oxygen backbone could have properties which would be more in keeping with a multi-purpose finish for military use.

Ten fluoroalkyl silane monomers comprising the best of those found in the literature as well as some new ones whose molecular structure appeared to hold promise were synthesized (1). Polymer solutions were then formed and applied to nylon/cotton (50/50 wt %) and to cotton (10). Copolymers of the fluoroalkyl silanes with non-fluorinated silanes were found to be especially effective. It was indeed found (10) that the initial liquid-repellency values of some of the experimental finishes were better than those obtainable from the best of the commercial finishes.

The requirements for a good military finish, however, include that of durability. The literature contains very little information on this topic and thus, as described in this technical note, the best of the siloxane polymers were submitted to extensive wear, washing, dry cleaning, and weathering tests. A brief summary of the results obtained at DREO for the durability of the oil-and water-repellency properties of the siloxane polymers has been published recently in the open literature (11). In this technical note, the durability of phosphate resistance is examined. Also, the siloxane-durability results are compared with those obtained with some excellent commercial finishes. The effects of added resin and of curing catalysts were assessed in a number of cases. Weathering tests were carried out.

Concluding statements are made regarding the usefulness of fluoroalkyl substituted siloxanes as liquid-repellent fabric finishes.

EXPERIMENTAL

The synthesis of the silanes F1,F2,F3,C1, and C2 (see Table 1 for structures) have been described previously (1). The commercial finishes Zepel B and Zepel RN were obtained from E.I. Dupont De Nemours and Co. (Inc.) while Scotchgard FC 232 was obtained from 3M Co. The following were obtained from Cyanamid of Canada, Inc. - Aerotex Resin MW, a melamine formaldehyde condensate; Aerotex Accelerator MX, a buffered magnesium salt; Aerotex Resin P-225, a hexamethoxymethylmelamine (solvent soluble); and Aerotex Accelerator Cycat 4040, an organic acid (solvent soluble). Mykon MRW-4 is a nonionic non-rewetting surfactant obtained from Sun Chemical Corporation. The fabric used in this durability study was a nylon/cotton twist (50/50 blend, 170 grams per square meter). It was designated as X74-438 (treated with olive green 107 dye).

APPLICATION OF FINISH AND CURING OF FABRICS

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. For commercial finishes, a 5 min drying time at 135°C was used followed by a curing time of 3 min at 171°C. Fabrics treated with siloxanes were inserted into the oven at room temperature and the oven temperature set at 150°C. Upon attaining 150°C, the samples were removed after 15 min. The treated fabrics were allowed to stand at room temperature overnight and then tested for oil-and water repellency and phosphate resistance.

DURABILITY TO WASHING, WEAR, DRY CLEANING, AND WEATHERING

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 (12). In this method, the samples (50 x 100 mm) 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.

The effect of wear on fabric properties was examined using a wear machine developed at DREO (13). Fabric samples (18 x 375 cm) were sewn into an endless belt and passed over the brushes and rollers of the machine under one-pound tension.

TABLE 1

Structures of the Silane Monomers and the Fluorinated Component of the Commercial Finishes

A. Structures* of the Silane Monomers

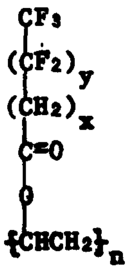
Fluoroalkyl-Substituted Monomers

F1	$CF_3(CF_2)_8CONH(CH_2)_3Si(OC_2H_5)_3$
F2	$CF_3(CF_2)_8CONH(CH_2)_3Si(OC_2H_5)_2(CH_3)$
F3	$CF_3(CF_2)_6CONH(CH_2)_3Si(OC_2H_5)_3$

Non-fluorinated Co-monomers

C1	$CH_3Si(OC_2H_5)_3$
C2	$CH_3(CH_2)_5Si(OC_2H_5)_3$

B. Structures of the Fluorinated Component of the Commercial Finishes



$$\begin{array}{l} CF_3 \\ | \\ (CF_2)_y \\ | \\ (CH_2)_x \\ | \\ C{=}O \\ | \\ O \\ | \\ \{CHCH_2\}_n \end{array}$$

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* Silane monomers with three replaceable ethoxy silane substituents form network polymers whereas F2 with only two replaceable silane substituents forms linear polymers.

Dry cleaning was performed by slight modification of Canadian Standard Textile Test Method 29.1-M77 (12). The samples (6" x 6") 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 container was drained and the samples were dried between two paper towels. After air drying, the samples were dried at 90°C for 10 min.

Weathering was carried out on swatches (8 x 12 inches), exposed on a stand on the roof of a three story building, inclined at 45° to the horizontal and facing south. They were fixed securely at each corner.

PAD FORMULATIONS

(i) Zepel B

The padding emulsion consisted of 23 g of Zepel B (13% solids) to which 77 g of water had been added with stirring.

(ii) Zepel B + Resin

This emulsion consisted of 23 g Zepel B, 3.75 g Aerotex Resin MW, 0.75 g Aerotex Accelerator MX, 0.3 g Mykon NRW-4, and 72.2 g water.

(iii) Zepel RN and Zepel RN + Resin

Same as above, except that Zepel B is replaced with Zepel RN emulsion (13% solids).

(iv) Scotchgard FC 232

This finish consisted of 10 g FC 232 (30% solids) to which 90 g of water had been added with stirring.

(v) Scotchgard FC 232 + Resin

Added together with stirring were 10 g FC 232 (30% solids), 87.3 g water, 2.0 g Aerotex Resin MW, 0.4 g Aerotex Accelerator MX, and 0.3 g Mykon NRW-4.

(vi) Formulations of F1 + C1 and F1 + C2

F1 (5.22 g) and C2 (0.78 g) (70/30 mole % ratio of F1/C2, weights were adjusted accordingly when C1 were used) were weighed into a 250 mL round-bottom flask. Tetrahydrofuran (120 mL) was added to dissolve the monomers. Sodium hydroxide solution (3 mL, 40 mg NaOH/mL) was added dropwise during vigorous stirring. The solution was stirred for 24 h and then neutralized with 20% aqueous sulphuric acid solution. After filtering, the polymer solution was applied to the fabric.

(vii) Formulations of F2 + C1, F2 + C2, and F3 + C1

As above for (vi) except that isopropanol was used as the solvent and a stirring period of 2.5 h was utilized.

(viii) Formulations of Siloxanes + Resin

After polymerization of the copolymers in the usual fashion (5% wt/volume solids), the solution was diluted with the polymerization solvent to 4 g solids in 100 mL of solution. One gram of Aerotex Resin P-225 and 0.25 g of Aerotex Accelerator Cycat 4040 (active catalyst 40% in isopropanol) was then added with stirring.

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) (14) were employed in this study. The oil repellency test was modified to include half levels. A short summary of these tests has been included in ref. 10.

PHOSPHATE RESISTANCE TEST

The resistance of treated fabrics to wetting by organo-phosphorus liquids was evaluated using a test developed at DREO by Hart and Fuoco (15). Small drops of the model test liquids trimethyl phosphate, triethyl phosphate and tri-n-propyl phosphate were placed on a flat fabric sample. After one hour, the appearance of each drop was noted visually and a rating assigned to the fabric based on the overall appearance of the three types of droplets (rating scale 0-9). A rating of 7 or above is considered good and means that only one of the liquids exhibits spreading or wicking. A rating of 3 or less indicates that all three of the liquids exhibit wetting to some extent.

RESULTS AND DISCUSSION

Only the most promising experimental finishes (described in ref.10) were subjected to durability testing. These were the copolymers of the fluoroalkyl substituted silanes, F1, F2 and F3 with the non-fluorinated alkyl silanes C1 and C2 (see Table 1 for structures). The exact structures of the commercial polymeric finishes were proprietary information. From patents and reviews (2, 16, 17), it was known that these are fluoroalkyl substituted esters as shown in Table 1. Generally x was 1 or 2 and y could be 5, 6, or 7. They could be copolymerized with or added to non-fluorinated acrylates.

All of the values discussed in this report were for nylon/cotton (50 weight %) fabric. Table 2 gives the initial liquid repellencies obtained with the siloxane copolymers and with the best of the commercial polymeric finishes. The siloxane copolymers P1, P2 and P3 all had equal or slightly better initial repellencies than the commercial finishes P8-P13. When 60% of the non-fluorinated alkyl silane C2 was utilized in P4, the phosphate resistance dropped from 9 to 4. When a linear siloxane was used, P5, the phosphate resistance dropped to zero while the water and oil repellencies were unchanged at 100 and 6/7. This is an interesting finish since water and oil repellency could be obtained while the wicking principle[1] could be used with phosphate. This is the reason for the inclusion of this material in this durability study. When 60% C1 was used, P6 (compare with P5), the oil repellency remained at 6/7, however, the water repellency had degraded to 90. As observed before (10), when the fluoroalkyl substituent was shortened by two CF_2 groups (P7 (compare with P1)), the phosphate resistance dropped to zero while the water and oil repellencies dropped to the next lower values.

The commercial finishes Zepel B, Zepel RN, and FC 232 all had water repellencies of 100, oil repellencies of 5/6 and 6, and phosphate resistance values of 9. The use of a resin had no effect on the initial repellencies but was important in providing durability (vide infra).

DURABILITY TO WASHING

Table 3 gives the durability to washing of P1-P13. The durability of all of the siloxane copolymers, P1-P7, to washing was unsatisfactory. By the sixth wash or earlier, water repellency had dropped to values as low as 0 and no values higher than 70 were obtained. The oil-repellency values after six washes for P1-P4 and P7 generally had dropped to the 1 or 2 level. The linear copolymers, P5 and P6, on the other hand, maintained reasonable oil-repellency values of 4/5-5/6. For the siloxanes, no values of phosphate resistance higher than 1 were found after six washes.

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[1] For the Canadian CW protective overgarment, the outer layer must be phosphate resistant. The CW protective garments of other countries utilize a wicking principle which requires that nerve agent droplets be spread to facilitate evaporation.

TABLE 2

Initial Liquid Repellencies

Designation	Composition of Copolymer	% Add-on	Water Repellency	Oil Repellency	Phosphate Resistance
	A. Siloxane Copolymers				
P1	F1 70% - C1 30%	4.2	100	6/7-7	9
P2	F1 40% - C1 60%	4.4	100	6/7	9
P3	F1 70% - C2 30%	2.4	100	6/7	9
P4	F1 40% - C2 60%	4.5	100	6	4
P5	F2 70% - C1 30%	2.8	100	6/7	0
P6	F2 40% - C1 60%	2.8	90	6/7	0
P7	F3 70% - C1 30%	2.8	90	6	0
	B. Commercial Finishes*				
P8	Zepel B	4.0	100	5/6	9
P9	Zepel B + resin	5.4	100	5/6	9
P10	Zepel RN	4.2	100	5/6	9
P11	Zepel RN + resin	6.6	100	5/6	9
P12	FC 232	4.7	100	6	9
P13	FC 232 + resin	5.2	100	6	9

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* Zepel B and Zepel RN are trade names of E.I. Dupont De Nemours & Co. (Inc.). FC 232 is a trade name of 3M Co.

TABLE 3

Durability to Washing

Designation	% Add-On	Composition of Copolymer	Number of Launder-Ometer Washings* 0	1	2	3	4	5	6
P1	4.4	F1 70%-C1 30%	100** 6/7 9	90 5/6 6	70 5/6 6	70 4 5	50 4 4	0 2 4	0 1/2 1
P2	4.4	F1 40%-C1 60%	100 6/7 9	80 5/6 5	70 5 1	70 3 1	50 3 1	50 2 1	0 1 1
P3	6.2	F1 70%-C2 30%	100 6/7 9	90 5/6 6	80 5/6 6	80 5/6 6	70 4/5 6	70 4/5 5	70 4/5 1
P4	4.5	F1 40%-C2 60%	100 6 4	90 4/5 0	70 4/5 0	70 4/5 0	70 3/4 0	50 3 0	50 2 0
P5	3.2	F2 70%-C1 30%	100 6/7 0	100 6/7 0	80 6/7 0	80 6/7 0	80 6 0	80 6 0	70 5/6 0
P6	3.4	F2 40%-C1 60%	90 6/7 0	90 6/7 0	80 6/7 0	70 6/7 0	70 5/6 0	70 4/5 0	70 4/5 0
P7	5.3	F3 70%-C1 30%	90 6 0	80 6 0	70 5/6 0	70 5/6 0	50 4/5 0	50 4 0	50 4 0
P8	4.0	Zepel B	100 5/6 9	100 5 9	100 5 9	100 5 9	100 5 9	100 4/5 9	100 4/5 9

TABLE 3 (Cont'd)

Designation	% Add-On	Composition of Copolymer	Number of Launder-Ometer Washings* 0	1	2	3	4	5	6
P9	5.4	Zepel B + Resin	100 5/6 9	100 5/6 9	100 5/6 9	100 5/6 9	100 5/6 9	100 5 9	100 5 9
P10	4.2	Zepel RN	100 5/6 9	100 5/6 9	100 5/6 9	100 5/6 9	100 5/6 6	100 5 6	100 4/5 6
P11	6.6	Zepel RN + Resin	100 5/6 9	100 5 9	100 5 9	100 5 9	100 5 7	100 5 4	100 4/5 4
P12	4.7	FC 232	100 6 9	100 5 9	100 5 9	100 5 9	100 5 6	100 5 6	100 5 6
P13	5.2	FC 232 + Resin	100 6 9	100 5 9	100 5 9	100 5 9	100 5 9	100 5 9	100 5 9

* One washing using this accelerated method approximates five launderings using a domestic washing machine.

** In Tables 3 to 7, liquid repellency values are given as horizontal rows of three values (water repellency, oil repellency, and phosphate resistance) arranged vertically.

In comparison, the commercial finishes, P8-P13, maintained water repellencies of 100 in all cases and after six washes lost no more than one level of oil repellency. Zepel B maintained a perfect reading of 9 for phosphate resistance both with and without added resin. Zepel RN, however, suffered a degradation in phosphate-resistance to 6 (P10) and 4 (P11) by the sixth wash. FC 232 alone had a phosphate resistance value of 6 (P12) at the sixth wash while a level of 9 was maintained if added resin was utilized (P13).

Thus, in comparison to the commercial finishes, the siloxanes were definitely inferior when applied without added resin. As shown in Table 4, however, much better results were obtained for durability to washing when a small amount of resin was added to the siloxane copolymer solutions. The values shown for P1′(Table 4) were a great improvement over that found for P1 (Table 3). Water repellency was unchanged from 100 after 6 washes while oil repellency dropped from 6 to only 5/6. These values were as good or better than those found for the commercial finishes P8-P13. The phosphate resistance, however, had degraded to 6 after six washes. This was better than that found for some of the commercial finishes but not as good as the value of 9 maintained by P8, P9 and P13. Although P3′ was much better than P3 it was not as good as P1′. P5′ was dramatically better than P5 and the values of 100 and 6/7 after six washes were the best of any in this study. The phosphate-resistance value was zero with or without resin. Even the values found for P7′ were a considerable improvement over the values found when no resin was used.

DURABILITY TO WEAR

Table 5 shows the values obtained when nylon/cotton fabrics treated with P1-P13 were subjected to wear tests. All of the finishes suffered serious degradation following wear. In terms of oil and water repellency, the results showed degradation after 20 h wear time to values generally in the range of 70-80 for water and 3/4-5 for oil repellency with the silanes retaining somewhat better oil repellencies than the commercial samples. The commercial finishes were superior in phosphate resistance, the best having degraded to 6 (P9), 4 (P11) and 3 (P13). The best siloxane finish, P1, still had a value of 4 at 16 h wear time but had decreased to 1 at 20 h. No significant improvement in durability to wearing was obtained when 1% of the siloxane copolymer was replaced by resin.

DURABILITY TO DRY CLEANING

As shown in Table 6, the siloxanes had good durability to dry cleaning. Most values dropped only a level or two even after six dry cleanings. The effect of resin in both the commercial and the siloxane finishes was minimal. The best siloxane, P1′, and the best commercial finishes P8 and P9, had nearly identical values of 90, 4/5-5/6, and 8 after six dry cleanings.

TABLE 4

The Effect of Added Resin on the Washing Durability of Siloxane Copolymers

Designation	Composition of Copolymer	% Add-On	Number of Launder-Ometer Washings 0	1	2	3	4	5	6
P1'	F1 70%-C1 30% + Resin	4.0	100 6 9	100 6 8	100 5/6 5	100 5/6 5	100 5/6 6	100 5/6 6	100 5/6 6
P3'	F1 70%-C2 30% + Resin	3.9	100 6 9	100 6 6	100 5/6 6	100 5/6 6	100 5/6 5	100 5/6 5	100 5 4
P5'	F2 70%-C1 30% + Resin	2.9	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0
P7'	F3 70%-C1 30% + Resin	5.6	100 5/6 0	90 5/6 0	90 5/6 0	90 5/6 0	90 5/6 0	90 5/6 0	80 5/6 0

TABLE 5

Durability to Wear

Designation	Composition of Copolymer	Wear Time (hours)					
		0	4	8	12	16	20
P1	F1 70%-C1 30%	100	80	80	80	80	80
		7	6	5/6	5	5	4/5
		9	5	4	4	4	1
P2	F1 40%-C1 60%	100	80	80	70	70	70
		6/7	4/5	4/5	3	2	2
		9	1	1	1	0	0
P3	F1 70%-C2 30%	100	80	80	80	70	70
		6/7	6	5/6	5	5	4/5
		9	4	4	1	1	1
P4	F1 40%-C2 60%	100	80	80	70	70	70
		6	5/6	5	4/5	4/5	4
		4	1	0	0	0	0
P5	F2 70%-C1 30%	100	80	80	70	70	70
		6/7	6/7	6	5/6	5/6	5
		0	0	0	0	0	0
P6	F2 40%-C1 60%	90	70	70	70	70	70
		6/7	6	5/6	5	5	4/5
		0	0	0	0	0	0
P7	F3 70%-C1 30%	90	80	80	70	70	70
		6	6	5/6	5	5	4/5
		0	0	0	0	0	0
P8	Zepel B	100	100	90	80	80	80
		5/6	5	4/5	4	3/4	2
		9	4	4	4	4	1
P9	Zepel B + Resin	100	100	100	100	90	80
		5/6	5/6	5	4	3/4	3/4
		9	8	8	6	6	6
P10	Zepel RN	100	80	80	80	80	70
		5/6	5	4/5	4	3	3
		9	6	5	5	5	2
P11	Zepel RN + Resin	100	100	100	90	80	80
		5/6	5	4/5	4/5	4	3/4
		9	7	5	5	5	4
P12	FC 232	100	80	80	80	80	70
		6	5	4/5	4/5	4	4
		9	4	4	4	1	1
P13	FC 232 + Resin	100	100	90	80	80	80
		6	5/6	5/6	5	4	4
		9	6	6	6	3	3

TABLE 6

Durability of Siloxanes, Siloxanes with Resin and Commercial Finishes to Dry Cleaning

Designation	Composition of Copolymer	% Add-On	Number of Dry Cleanings 0	1	2	3	4	5	6
P1	F1 70%,C1 30%	4.4	100 6 9	100 6 8	90 6 8	90 5/6 8	90 5/6 8	90 5/6 8	90 5 8
P1'	P1 + Resin	4.0	100 6 9	100 6 9	100 5/6 9	90 5/6 9	90 5/6 9	90 5/6 9	90 5/6 8
P3	F1 70%,C2 30%	4.2	100 6/7 4	100 6/7 4	90 5/6 4	90 5/6 4	90 5/6 4	90 5/6 4	90 5/6 4
P3'	P3 + Resin	3.9	100 6 9	100 5/6 9	100 5 9	90 5 9	90 5 5	90 5 5	90 5 5
P5	F2 70%,C1 30%	3.1	100 6/7 0	100 6 0	90 6 0	90 6 0	90 6 0	90 6 0	90 6 0
P5'	P5 + Resin	2.9	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0	100 6/7 0
P7	F3 70%,C1 30%	5.3	90 5/6 0	90 5/6 0	80 5/6 0	80 5/6 0	80 5/6 0	80 5/6 0	80 5/6 0
P7'	P7 + Resin	5.6	100 5/6 0	90 5/6 0	80 4/5 0	80 4/5 0	80 4/5 0	80 4/5 0	80 4/5 0
P8	Zepel B	4.0	100 5/6 9	100 4/5 8	100 4/5 8	100 4/5 8	100 4/5 8	100 4/5 8	90 4/5 8
P9	Zepel B + Resin	5.4	100 5/6 9	100 4/5 9	100 4/5 8	100 4/5 8	100 4/5 8	100 4/5 8	90 4/5 8
P10	Zepel RN	4.2	100 5/6 9	100 4/5 9	90 4/5 8	90 4/5 8	80 4/5 7	80 4/5 4	80 4 4
P11	Zepel RN + Resin	6.6	100 5/6 9	100 4/5 5	100 4/5 4	90 4/5 4	90 4/5 4	90 4 4	80 3/4 4
P12	FC 232	4.7	100 6 9	100 6 9	90 5/6 9	90 5/6 9	90 5/6 9	90 4/5 6	80 4/5 6
P13	FC 232 + Resin	5.2	100 6 9	100 5/6 6	100 5/6 6	100 5/6 6	100 5/6 6	100 5/6 6	100 4 6

DURABILITY TO WEATHERING

As shown in Table 7 noticeable degradation in both oil and water repellency was experienced by the treated fabrics when subjected to weathering. For the siloxanes, water repellencies generally fell from 100 to 70 (P5 and P5′ fell to 50) while oil repellency fell to 4 or 4/5 after three months. Note that nearly all of the degradation occurred during the first month and the values were essentially stable after that. Phosphate resistance for P1, P1′, P3 and P3′ fell from 9 to the medium range values of 4-6. Fabrics treated with siloxane finishes utilizing resin maintained the same water repellencies and the same or slightly lower oil and water repellencies than those without.

In comparing the commercial finishes, P9 and P13, with the siloxane finishes, P1′ and P3′, it is seen that P9 maintained better values at the one and two month stages, however, at the three month stage, the liquid-repellency values were essentially the same. For P13, the results over the three month period were comparable for water and oil repellency but were poorer for phosphate resistance, having dropped to 1-2 at three months.

INORGANIC CURING CATALYSTS

The inorganic curing catalysts zinc chloride (18), stannous octoate (18) and tetrabutyl orthotitanate (19,20), upon occasion, have been used with both fluoroalkyl and non-fluoroalkyl substituted siloxanes. It was found in this work that the use of each of these catalysts with the copolymer solutions of <u>F1</u> + <u>C1</u>, <u>F1</u> + <u>C2</u>, AND <u>F2</u> + <u>C1</u> made little or no difference to the eventual properties of the treated fabrics.

FIRE RESISTANCE TESTING

Fabric samples treated with the siloxane copolymers P1-P7 (see Table 2) were tested for flame resistance using a vertical burning test (Canadian Standard Textile Test Methods, Method 27.1-M77 (12)).. It was found that at these add-ons (2.8-4.5%) little or no fire resistance was imparted to the fabrics. It must be noted that this test is a severe one because the procedure creates conditions favourable to combustion.

CONCLUSIONS

1. The durability of the fluoroalkyl substituted siloxanes as liquid-repellent finishes on nylon/cotton (50/50 wt %) to washing, wear, dry cleaning, and weathering has been examined. Several excellent commercial finishes were examined at the same time.

TABLE 7

Durability to Weathering

Designation	Composition of Copolymer	% Add-on	Initial	Weathering Period 17-06-80 17-07-80	21-07-80 21-08-80	26-08-80 26-09-80
P1	F1 70%, C1 30%	4.9	100	70	70	70
			6/7	4/5	4	4
			8	6	6	6
P1'	P1 + Resin	4.7	100	70	70	70
			6/7	4/5	4/5	4
			9	5	5	5
P3	F1 70%, C2 30%	4.8	100	70	70	70
			6/7	4/5	4	4
			9	6	6	6
P3'	P3 + Resin	4.8	100	70	70	70
			6/7	4/5	4/5	4
			9	5	4	4
P5	F2 70%, C1 30%	3.2	100	70	70	50
			6/7	4/5	4	4
			0	0	0	0
P5'	P5 + Resin	3.2	100	70	70	50
			6/7	4/5	4/5	4
			0	0	0	0
P7	F3 70%, C1 30%	3.0	90	70	70	70
			5/6	5	4/5	4/5
			0	0	0	0
P7'	P7 + Resin	3.5	100	70	70	70
			5/6	4/5	4/5	4
			0	0	0	0
P9	Zepel B + Resin[1]	4.8	100	80	80	70
			5	4/5	4	4
			9	9	9	6
P13	FC 232 + Resin[1]	5.2	100	70	70	70
			5/6	5	4/5	4
			9	6	3	1-2

[1] The results for P9 and P13 in this table were provided by R.P. Fuoco and were carried out in the same time periods indicated.

2. It has been found that the siloxanes do not exhibit satisfactory durability to washing when used alone, but much better properties were found when a resin was used. It is customary to use a resin with polymer finishes, and when a resin was used, the best network siloxane finish maintained a slightly better oil repellency but a slightly lower phosphate resistance than the best commercial finish. The linear siloxane maintained perfect water resistance and the excellent oil repellency of 6/7 remained unchanged throughout the six washings. This finish, however, had an initial phosphate resistance of zero.

3. All finishes, both experimental and commercial, experienced serious degradation of properties following wear. The best of the siloxanes retained slightly better oil repellencies while the commercial finishes retained better phosphate resistance.

4. The best experimental finishes and the best commercial finishes exhibited identical liquid repellency values upon being subjected to repeated dry cleanings.

5. In terms of oil and water repellency, the linear siloxane finish (<u>F2</u> 70%, <u>C1</u> 30%), when used with added resin, had nearly ideal values. It maintained unchanged values of 100 and 6/7 (water and oil repellencies respectively) upon repeated washings and dry cleanings and had values of 70 and 4/5 after 20 h of severe wear. This finish, however, would not be suitable for use on the Canadian CW protective overgarment since the present concept requires a finish with phosphate resistance. The CW protective garments of other countries, however, utilize a wicking principle in which it is required that nerve agent droplets be spread to facilitate evaporation. In this circumstance, this could be an excellent finish. It could also be used in commercial situations where only oil and water repellency is required.

6. In general, the experimental siloxane finishes are not significantly better than the commercial finishes currently in use. They could be considered desirable when either a disposable protective suit is utilized and/or when only oil and water repellency are required.

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In this report the durability of liquid repellency properties imparted to fabrics by solutions of the copolymers of fluoroalkyl-substituted silanes and non-fluorinated silanes is examined. The best available commercial finishes were examined at the same time and the results compared with those of the experimental finishes. The durability testing encompassed wearing, washing, dry cleaning, and weathering. Although the siloxane copolymers wear well, they are somewhat inferior to the commercial finishes after a number of washes. Much better durability to washing was obtained when a small amount of resin was added to the finish, as is the usual commercial practice. The properties found for the siloxane finishes indicate that they could be useful in some circumstances.

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