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CONTENTS

ABSTRACT

Adsorbed films having a wide range of wettabilities have been formed on silica, Pyrex, aluminosilicate, α-alumina, steel, and gold by trialkoxysilane (and trichlorosilane) compounds. These compounds had the general formulas $RSi(OR')_3$ or $RSiCl_3$, where R- was a fluorocarbon or a chlorocarbon group and -OR' was $-OCH_3$ or $-OCH_2CH_3$. The fluorocarbon films had γ_c values of 20 dynes/cm and water contact angles of 100 to 118 degrees. The chlorocarbon films had γ_c values of 40 dynes/cm and water contact angles of 80 to 90 degrees. Film thickness, determined by ellipsometry, was consistently greater than a monolayer of the trialkoxysilane. Desorption experiments suggest that the films were composed of a polysiloxane network along with unhydrolyzed adsorbate, small polysiloxane molecules, and solvent. The fluorocarbon compounds have potential for forming oleophobic barrier films in lubricated devices.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE WETTABILITY OF FLUOROCARBON AND CHLOROCARBON TRIALKOXYSILANE FILMS ADSORBED ON GLASS AND METAL SURFACES

INTRODUCTION

The scientific basis for controlling the wettability or oil and water repellency of surfaces has been established by Zisman and coworkers in their extensive studies of the relationship between chemical constitution and wettability (1). They have shown that specific wettabilities, i.e., specific values of the critical surface tension for wetting γ_c, are characteristic of the chemical groups forming the surface. For example, a surface which exposes closely spaced fluorocarbon groups will be both hydrophobic and oleophobic ($\gamma_c <$ 20 dynes/cm), whereas a surface rich in covalently bonded chlorine atoms will be hydrophobic but oleophilic ($\gamma_c >$ 40 dynes/cm). Hydrocarbon-containing surfaces are hydrophobic and have intermediate critical surface tensions ($\gamma_c =$ 20 to 40 dynes/cm). Previous work (2,3) has shown that alkyltrialkoxysilanes form films on silica or α-alumina surfaces having critical surface tensions in this range.

This report describes the wettability of the films formed by certain trialkoxysilanes (and trichlorosilanes) having the general formulas RSi(OR') and $RSiCl_3$ in which the R-group was either a fluorocarbon or a chlorocarbon group and the ester group was either $-OCH_3$ or $-OCH_2H_5$. The study was designed to extend the range of γ_c values obtainable with trialkoxy (or trichloro) silanes so that hydrophobic films which were either strongly oleophobic or oleophilic could be produced as desired. Also, the range of substrates has been expanded to include stainless steel, gold, and borosilicate and aluminosilicate glasses. It was suggested in the earlier work here (3) and by Tutas, Stromberg, and Passaglia (4) that the films formed by trialkoxysilanes are polymeric. Therefore, the films reported here were studied by ellipsometry to detect evidence of polymer formation.

EXPERIMENTAL PROCEDURE

Materials

The organosilicon compounds studied are listed in Table 1 with their refractive indices and the temperatures and pressures at which they were distilled. For simplicity, these compounds and their films are referred to by their fluorocarbon or chlorocarbon group; e.g., $CF_3(CF_2)_6CH_2OCH_2CH_2Si(OCH_2CH_3)_3$ is designated as the fluorooctyl compound and its films as fluorooctyl films. The author is indebted to Mr. J. G. O'Rear of NRL for the synthesis of the p-chlorophenyl compounds (5), to Dr. A. G. Pittman, U.S. Dept. of Agriculture, Western Utilization and Development Division, for the synthesis of the fluorocarbon compounds (6,7), and to Mr. S. Sterman, Silicones Division, Union Carbide Corp., for providing the γ-chloropropyltrimethoxysilane. Bicyclohexyl and α-chloronaphthalene were used as the solvents from which the organosilicon compounds were adsorbed. These liquids and the organic test liquids used for determining critical surface tensions were percolated through activated adsorbents to remove more polar contaminants.

The solid substrates on which the films were formed were small disks or plates of fused silica (A. H. Thomas Co., Philadelphia, Pa.), a borosilicate glass (Corning Pyrex), an aluminosilicate glass (Corning 1720), α-alumina (synthetic sapphire, Linde Division, Union Carbide Corp.), stainless steel (18% Cr and 8% Ni), and gold (99.9%). The nonmetallic

Table 1
Refractive Indices and Boiling Points of Some Organosilicon Compounds

Adsorbate	Refractive Index, n_D^{25}	Boiling Point (°C)	Pressure (mm Hg)
γ-Perfluoroisopropoxypropyltrimethoxysilane, $(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3$	1.3461	34	0.5
3-(1,1-Dihydroperfluorooctoxy)propyltriethoxysilane, $CF_3(CF_2)_6CH_2OCH_2CH_2CH_2Si(OCH_2CH_3)_3$	1.3530	130	1.5
γ-Fluoropropyltrimethoxysilane, $CFH_2CH_2CH_2Si(OCH_3)_3$	1.3977	95	0.5
β-(p-Chlorophenyl)ethyltrimethoxysilane, $p\text{-}ClC_6H_4CH_2CH_2Si(OCH_3)_3$	1.4863	107	0.5
β-(p-Chlorophenyl)ethyltriethoxysilane, $p\text{-}ClC_6H_4CH_2CH_2Si(OCH_2CH_3)_3$	1.4737	114	0.5
β-(p-Chlorophenyl)ethyltrichlorosilane, $p\text{-}ClC_6H_4CH_2CH_2SiCl_3$	1.5293	95	0.5
γ-Chloropropyltrimethoxysilane, $ClCH_2CH_2CH_2Si(OCH_3)_3$	1.4183	195	750
γ-Chloropropyltrichlorosilane, $ClCH_2CH_2CH_2SiCl_3$	1.4654	*	-

*Used as obtained from Pierce Chemical Co., Rockford, Ill.

substrates were cleaned in hot concentrated H_2SO_4-HNO_3 (1:1) and thoroughly rinsed in boiling, distilled water. The surfaces were then dried in an all glass oven at 150 to 200°C for 1/2 hour. The metal surfaces were cleaned by metallographic polishing (8) and then dried in the glass oven. The final polishing step was on an abrasive-free cloth to remove the alumina polishing agents. These cleaning and drying procedures left the surfaces completely wettable by water, indicating that they were free of organic contamination.

Methods

The various organosilicon films were formed by adsorption from either the solution or the vapor. For adsorption from the vapor, clean test surfaces were suspended over a few drops of the adsorbate liquid in a closed cell. The exposure time and temperature are specified for each case.

From solution, the adsorbed fluorocarbon films were isolated by retraction, i.e., the film-covered test plates emerged from the solution dry. In the case of the chlorocarbon films, retraction usually did not occur; the test plates emerged from the solutions with liquid adhering to the surface, and this liquid was removed by rinsing the plates with acetone. In all the solution adsorption experiments, concentrations of 0.1, 0.25, and 1% were tried. Generally, the choice of concentration had no measurable effect on the film wettabilities if 20 hours was allowed for the films to form. At the lowest concentration, 0.1%, the rates at which the films reached steady values of γ_c and θ_{H_2O} were somewhat slower than at the higher concentrations. The effect of adsorbate concentration on film thickness was not studied. All solution preparations and the adsorption experiments at 25°C were done in polyethylene "dry" manipulation bags maintained at about 3% RH (50 ppm of water) by a continuous flow of dried air. Adsorption experiments at 50°C and 70°C were done in a small oven at about 5 to 10% RH.

The films were tested for their stability toward prolonged contact with water and toward certain organic solvents. The water stability was measured by allowing water to fall dropwise for 1 hour over the film-covered substrate held at a small angle to the horizontal (3). The stability of the films to organic solvents was determined by rinsing the surfaces in a gentle stream of acetone or, in the case of fluorooctyl films, with Freon TF (CCl_2F-$CClF_2$, purified grade, du Pont).

The wettability characteristics determined for each film were the critical surface tension γ_c and the water contact angle θ_{H_2O}. The critical surface tensions were measured by the Zisman method (1) with a series of n-alkanes, namely, hexadecane (27.6 dynes/cm), tetradecane (26.7 dynes/cm), dodecane (25.4 dynes/cm), decane (23.9 dynes/cm), and octane (21.8 dynes/cm). The surface tensions γ_{LV}, given in parentheses, were measured at 25 ± 2°C by the duNouy ring method with the appropriate corrections. For the films that had γ_c values too high to measure with the n-alkanes, a nonhomologous series of test liquids was used, namely, bicyclohexyl (33.0 dynes/cm), α-chloronaphthalene (42.9 dynes/cm), methylene iodide (50.8 dynes/cm), thiodiglycol (54.0 dynes/cm), and formamide (58.2 dynes/cm). To distinguish between the critical surface tensions obtained with the two series of liquids, the values for the nonhomologous series are designated $\gamma_c{}^*$. In earlier work it was found that for surfaces on which both sets of liquids could be used $\gamma_c{}^*$ was less than γ_c, but the difference between these parameters probably becomes smaller as $\gamma_c{}^*$ increases (3). All contact angle measurements were made at 25 ± 2°C and about 45% RH.

The thicknesses of certain of the organosilicon films were determined by ellipsometry. This is a sensitive method for determining the thickness d_f and, in some cases, the refractive index n_f of adsorbed films (9). The method is based on the change in polarization that the film produces in light reflected from the substrate. The parameters that express the effect of the film on the polarization can be related to the film thickness and refractive index. However, the equations relating these quantities cannot be solved for n_f and d_f explicity. This difficulty has been surmounted by solving the equations iteratively on a high-speed computer using a computer program developed by McCrackin and Colson at the National Bureau of Standards (10,11).

Determination of both thickness and refractive index are not always possible. On metal surfaces, when d_f is less than 100 Å, only the film thickness can be determined from the experimental parameters. For these films, the thickness was calculated by assuming reasonable values for n_f. Fortunately, the spread in film thickness for the assumed range of refractive index was small. In each case the range assumed is indicated in the tables.

An ellipsometry study of the films on Pyrex and the aluminosilicate glass was made using prism-shaped specimens through which the light was multiply reflected. This method is many times more sensitive than the conventional method of a single external reflection (12). Unfortunately, determinations could be made of either d_f or n_f but not both, and when a small range of n_f values is assumed, the calculated values of d_f may extend over an order of magnitude.

The ellipsometer used was an O. C. Rudolph and Sons (Caldwell, N.J.) Model 436-200E. In this instrument the substrate was held vertically, and the quarter-wave plate and analyzer were located in the reflected beam. All ellipsometric determinations were made at 25 ± 2°C and 45 to 50% RH. To partially compensate for instrumental errors, each measurement was made by reading the optical components in all four quadrant positions (10).

RESULTS

Fluorocarbon-Silicon Films

The properties of the films formed from the fluorooctyl adsorbate $CF_3(CF_2)_6CH_2OCH_2CH_2CH_2Si(OCH_2CH_3)_3$ and from the perfluoropropoxy adsorbate $(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3$ are given in Tables 2 to 4. Critical surface tensions of 14 to 16 dynes/cm and water contact angles of 111 to 118 degrees were obtained for the fluorooctyl films on Pyrex, stainless steel, and gold (Table 2) when the films were formed at an adsorption temperature of 70°C using acetic acid as a catalyst. The wettability of these films was essentially unaltered by rinsing with water, acetone, or Freon, although Freon did reduce the film thickness and refractive index (Table 2). After the first treatment with Freon, further rinsing with Freon, water, or acetone had no effect on the film properties. Although reasonably oleophobic-hydrophobic fluorooctyl films were obtained at 25°C with acetic acid or at 70°C without a catalyst, the most stable films were formed by the combined use of the higher adsorption temperature and the acid catalyst. A strong base catalyst, n-propylamine, produced somewhat less oleophobic-hydrophobic films than did the acid.

The perfluoropropoxy films had γ_c values of 16 to 18 dynes/cm and θ_{H_2O} values of 104 to 110 degrees (Table 3). However, these films did not retain these wettability characteristics when rinsed with organic solvents (Table 4), even when the films had been adsorbed in the presence of a catalyst and at adsorption temperatures above 25°C. Note in Tables 3 and 4 that the initial films deposited from the vapor or solution had to be rinsed with water before determining γ_c. Otherwise, the test liquids gave unstable contact angles which did not show a linear relationship in the cos-θ-vs-γ_{LV} plots used to determine γ_c. After the water rinse, the test liquids gave stable and reproducible data. When rinsed with acetone, the perfluoropropoxy films were much less oleophobic and hydrophobic than the films left after the water rinse (Table 4). This was so even when the initial film was given a water rinse before the acetone treatment.

Ellipsometric measurements of the fluorooctyl and perfluoropropoxy films on stainless steel, given in Tables 2 and 4, indicate that the films were considerably thicker than can be accounted for by a monolayer of the adsorbates. A monomolecular film of $CF_3(CF_2)_6CH_2OCH_2CH_2Si(OCH_2CH_3)_3$ would have a thickness of 14 to 15 Å if each molecule were adsorbed with the oxygens on the silicon held against the surface and the fluorocarbon group oriented normal to and away from the surface. A monolayer of $(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_2$, similarly oriented, would be 11 Å thick.

The monofluoropropyl compound $CFH_2CH_2CH_2Si(OCH_3)_3$ did not give strongly oleophobic films; γ_c· was 20 to 25 dynes/cm. On stainless steel, the film thickness was about 20 Å assuming n_f = 1.3 to 1.5.

Chlorocarbon-Silicon Compounds

Both the chlorophenyl compounds and the chloropropyl compounds formed stable films that were hydrophobic and yet oleophilic. However, to secure such films from the trialkoxysilanes it was necessary to use somewhat elevated temperatures and an acid or base catalyst. The films of $p-ClC_6H_4CH_2CH_2Si(OCH_3)_3$ had γ_c values of 44 to 47 dynes/cm and θ_{H_2O} values of 85 to 88 degrees (Table 5). These results are comparable

Table 2
The Properties of Films Formed by $CF_3(CF_2)_6CH_2OCH_2CH_2Si(OCH_2CH_3)_3$
on Stainless Steel, Pyrex, and Gold*

Substrate	Initial Film				Rinsed Film†			
	d_f (Å)	n_f	γ_c (dynes/cm)	θ_{H_2O} (degrees)	d_f (Å)	n_f	γ_c (dynes/cm)	θ_{H_2O} (degrees)
Stainless steel	401	1.34	14	112	233	1.23	14	116
Gold	-	-	14	112	-	-	16	118
Pyrex	-	-	14	111	-	-	14	111

*0.25% solution in α-chloronaphthalene at 70°C with an acetic acid/adsorbate mole ratio of 1/10.

†The film-covered substrates were rinsed with Freon TF.

Table 3
The Wettability of Films Formed by
$(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3$

Substrate	Wettability	
	γ_c (dynes/cm)	θ_{H_2O} (degrees)
Obtained From 0.25% Solution in α-Chloronaphthalene at 25°C; Films Had Been Water Rinsed		
Silica	17	109
Pyrex	18	104
Stainless steel	17	110
Obtained by Vapor Deposition at 25°C with a 5-min Exposure Time; Films Had Been Water Rinsed		
Silica	16	108
Stainless Steel	17	105

Table 4
The Effect of Acetone and Water on the
Initial Film Formed by
$(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3$
on Stainless Steel

d_f* (Å)	γ_c (dynes/cm)	θ_{H_2O} (degrees)
Initial Film†		
59 ± 9	indeterminate	80
Water-Rinsed Film		
34 ± 5	18	105
Acetone-Rinsed Film		
25 ± 4	20	96

*Calculated assuming n_f = 1.3 to 1.5

†0.25% solution of α-chloronaphthalene at 25°C.

Table 5
The Wettability of Films Formed by p-$ClC_6H_4CH_2CH_2Si(OCH_3)_3$†

Substrate	Wettability	
	γ_c* (dynes/cm)	θ_{H_2O} (degrees)
Silica	44	85
Pyrex	45	85
Aluminosilicate glass (Corning 1720)	47	88
α-Alumina	44	85
Stainless steel	47	86
Gold	47	87

†0.25% solution in bicyclohexyl at 70 °C with an acetic acid/adsorbate mole ratio of 1/10; film was isolated by rinsing with acetone (or water).

to the γ_c and θ_{H_2O} data reported earlier for films of p-$ClC_6H_4CH_2CH_2Si(OCH_2CH_3)_3$ (with an n-propylamine catalyst) and p-$ClC_6H_4CH_2CH_2SiCl_3$ (from the vapor) on silica and alumina (3). It was necessary to use an acetic acid catalyst and a 70°C adsorption temperature to obtain water-stable, oleophilic-hydrophobic films of the trimethoxy adsorbate. Since these films were so oleophilic, the adsorbate solution failed to retract from the test surfaces. However, immediately after the surfaces were removed from the solution, the adhering liquid could be rinsed off with water or a stream of acetone. The resulting film had the same wettability regardless of whether acetone or water was used. Furthermore, films obtained by the acetone rinse were unchanged when given a subsequent water rinse and, conversely, the water-rinsed films were unchanged even by multiple acetone washes.

The wettabilities of the adsorbed films of γ-chloropropyltrimethoxysilane are indicated in Table 6. The γ_c* values, 43 to 45 dynes/cm, and the θ_{H_2O} values, 80 to 82 degrees, were somewhat lower than the values obtained with the p-chlorophenyl compounds. As with the p-chlorophenyl adsorbates, an acid catalyst and an adsorption temperature of 70°C were needed to produce the most oleophilic and hydrophobic films. All of the films indicated in Table 6 were obtained by rinsing the test surfaces with water or acetone to remove adhering adsorbate solution; these rinsed films were stable toward further contact with acetone or water. Lee (13) obtained slightly less oleophilic (γ_c = 41 dynes/cm) and slightly less hydrophobic films (θ_{H_2O} = 75 degrees) of γ-chloropropyltrimethoxysilane when deposited by evaporation of acidic alcohol-water solutions.

The films formed by p-$ClC_6H_4CH_2CH_2Si(OCH_3)_3$ and $ClCH_2CH_2CH_2Si(OCH_3)_3$ on stainless steel at 70°C with acetic acid as a catalyst were about 60Å and 233 Å thick, respectively (Table 7). The thickness of a monolayer of the chlorophenyl compound would be 11 Å and of the chloropropyl compound would be 7 Å. The chloropropyl film was thick enough that the film refractive index as well as the thickness could be calculated from the ellipsometry data. Repeated rinsing of the films in Table 7 with acetone produced no changes in wettability or thickness, and in the case of the chloropropyl film there was no change in refractive index.

The chlorocarbon-silicon films on Pyrex and aluminosilicate (formed as were the films in Tables 5 to 7) were consistently thicker than a monolayer. For example, the calculated values of d_f for a p-chlorophenyl film on Pyrex were 30 to 150 Å assuming

n_f to be 1.2 to 1.4. This uncertainty in d_f was typical of these determinations. However, d_f values corresponding to a monolayer could be calculated only if n_f was assumed to be 1.1 or less.

The trichlorosilane $ClCH_2CH_2CH_2SiCl_3$, when applied from the vapor, formed a film having a $\gamma_c{}^*$ value of 42 dynes/cm and a θ_{H_2O} value of 77 degrees on Pyrex at 25°C. This film was thick enough to be a visible coating on the test surface. Rinsing with acetone left the surface free of visible material but did not change the wettability.

Table 6
The Wettability of Films Formed by
$ClCH_2CH_2CH_2Si(OCH_3)_3$†

Substrate	Wettability	
	$\gamma_c{}^*$ (dynes/cm)	θ_{H_2O} (degrees)
Pyrex	43	80
α-Alumina	45	81
Stainless steel	45	82

†0.25% solution in α-chloronaphthalene at 70°C with an acetic acid/adsorbate mole ratio of 1/10; film was isolated by rinsing with acetone (or water).

Table 7
The Properties of the Chlorocarbon-Silicon Films
Formed on Stainless Steel†

Adsorbate	Film Properties			
	d_f (Å)	n_f	$\gamma_c{}^*$ (dynes/cm)	θ_{H_2O} (degrees)
$p\text{-}ClC_6H_4CH_2CH_2Si(OCH_3)_3$	51-65	1.4-1.6‡	47	85
$ClCH_2CH_2CH_2Si(OCH_3)_3$	233	1.35	44	84

†0.25% solution in bicyclohexyl at 70°C with an acetic acid/adsorbate mole ratio of 1/10; film was isolated by rinsing with acetone.

‡Assumed.

DISCUSSION

This work shows that oleophobic-hydrophobic films can be obtained from fluorocarbon-trialkoxysilanes and oleophilic-hydrophobic films from chlorocarbon-trialkoxysilanes.

The films generally appear to be three-dimensional polysiloxane networks. The organic-liquid and water rinses would have reduced the thickness to a monolayer or less if these films had been entirely composed of unhydrolyzed (or partially hydrolyzed) monomer or small, polymer molecules. As discussed below, the rinses did remove small amounts of low-molecular-weight material from the film but left behind the cross-linked, high-molecular-weight polymer. These polymer networks resisted desorption partly because of their low solubility in the rinse liquids and partly because the polymer segments in contact with the surface form multiple bonds to the surface. It is true the adsorbed polymer may form siloxane bonds to the silica and the glasses and metallosiloxane bonds to the α-alumina and stainless steel. However, the strongly ionic metallosiloxane bonds are susceptible to hydrolysis (14), and chemical bonding to the gold is doubtful. Hence, the stability of these films to water and the organic solvents cannot be attributed to chemical bonding to the surface.

The water required for the hydrolysis-polymerization reaction (one molecule of water for each polymer siloxane bond formed) was probably available from the substrate surfaces and the adsorbate solution. It can be reasonably argued that the acid-washed glass, silica, and alumina surfaces (15,16) and the mechanically polished stainless-steel surfaces (17) held enough water to generate polysiloxane films up to 100 Å thick (approximately ten equivalent monolayers). Each monolayer of polymer would require somewhat less than a monolayer of water. It is doubtful that the gold surface had enough water to form more than a monolayer of polysiloxane or that any of the surfaces held the water needed to form more than a 100-Å-thick film. In the cases of the thicker films, at least, the adsorbate solution must be assumed to be the principal source of water, particularly when an acid or base catalyst had been added to the solution. The acetic acid and the n-propylamine were reagent-grade chemicals, but they had not been given any special drying treatment.

The water, acetone, and Freon treatments of the fluorocarbon films indicated that all of the films were composed of materials having different degrees of stability toward these agents. First, there was usually present in the initial films a material so weakly held that it interfered with the wettability test liquids. This material could be removed by the water or the organic-liquid rinses. In addition to these very weakly adsorbed components, there was present a more strongly held material that resisted removal by water but was removed by the organic liquids (Tables 2 and 4). Finally, a highly stable structure remained that resisted both the water and the organic liquids. The weakly held materials that interfered with the initial contact angle measurements and could be dissolved out of the polymer structure probably included solvent molecules, partially hydrolyzed and unhydrolyzed adsorbate monomer, and some small polysiloxane molecules. Note in Table 2 that the Freon rinse of the fluorooctyl film lowered the refractive index, as would be expected if traces of the α-chloronaphthalene solvent ($n_D^{25} = 1.6306$) were extracted during the rinse. The rinse may also have left the remaining polymeric structure slightly porous, which would further depress the apparent refractive index.

The perfluoropropoxy film was particularly susceptible to the acetone rinse (Table 4), which may have been due to steric hindrance to crosslinking in the perfluoropropoxysiloxane polymer (7).

The chloropropyl and chlorophenylethyl films were too oleophilic to allow retraction of the adsorbate solution so that comparisons cannot be made between initial and rinsed films. However, it is reasonable to believe that these films, like the fluorocarbon films, initially contained entrapped low-molecular-weight molecules that were removed along with the adsorbate solution by the acetone or water rinses.

The polysiloxane films studied, although they appear to expose predominately fluorocarbon or chlorocarbon groups at the air/film interface, are not considered to achieve maximum close packing and orientation of these groups. The literature reports a γ_c value of 6 dynes/cm for close-packed perfluorooctyl groups (1) as compared with values of 13 to 16 dynes/cm characteristic of the fluorooctyl films reported here. This latter range of γ_c values is still typical of a fluorocarbon surface, so it is doubtful that the underlying oxypropyl chain or siloxane network were significantly exposed to the test liquids. Similar conclusions follow from the data for the perfluoropropoxy films in Table 4; the 16 to 18 dynes/cm were significantly higher than the 13 to 15 dynes/cm reported for surfaces of closely spaced $(CF_3)_2CF$ groups (18). For the chlorophenyl films, the observed range of γ_c was again higher than literature values, 44 to 47 dynes/cm compared to 39 to 45 dynes/cm for surfaces of closely spaced p-ClC_6H_4 groups (19).

The oleophobic-hydrophobic character of the fluorocarbon-silicon films suggests their use in a number of practical situations where durable, oil-resistant and water-resistant coatings are needed. The use of the fluorooctyl compound to form coatings that act as barriers to the migration of lubricants is described in the Appendix of this report.

The films produced by $ClCH_2CH_2CH_2Si(OCH_3)_3$ and p-$ClC_6H_4CH_2CH_2Si(OCH_3)_3$ meet the two basic requirements for adhesion promoters (19-21): (a) they form stable films on adherend surfaces and (b) the films are sufficiently oleophilic (γ_c [illegible] 40 dynes/cm) to be readily wet by most adhesive resins.

When considering the functioning of the chlorocarbon-silicon films at the adhesive/adherend interface, it must be kept in mind that they are three-dimensional polymer networks into which the liquid resin may or may not penetrate. If the resin liquid fails to penetrate the polysiloxane coating, there is a good chance that the coating will act as a weak boundary layer between the adhesive and the adherend. To a first approximation, penetration is most likely to occur when the surface tension of the liquid resin and the critical surface tension of the film are nearly equal, because there will then be a reasonable match between the solubility parameters of the liquid and the film. Although the properties of the interfacial zone formed by penetration of resin into the polymer film have not been studied, there is a good probability that such penetration will improve the bond between resin and substrate (21,22).

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Appendix

BARRIER FILMS FROM PERFLUOROOCTYLPROPYLTRIETHOXYSILANE

The possible use of the fluorocarbon silanes as oleophobic barrier films in lubricated devices is of particular interest to the Navy. The use of barrier films to prevent oil from creeping out of the bearing races of miniature ball bearings was developed at NRL.* The coating materials presently in use are fluorinated methacrylate polymers and are applied along the bearing edges to form an oleophobic coating past which the oil in the race cannot pass. Another use of the barrier film is to prevent oil from creeping onto electrical contacts in lubricated instruments. There are two important requirements for a useful barrier film material besides the ability to render the surface oleophobic: (a) the coating material must not spread from the area of application and contaminate other areas and (b) the barrier film must not be dissolved by the cleaning fluids used to clean the component. Even if desorption does not reduce the oleophobic character of the coating, the film material removed could contaminate other surface areas.

Tests were made to determine if the fluorooctyltriethoxysilane compound could be used to form useful barrier films. Freon solutions of this compound and its polymerization products were painted onto steel surfaces; the surfaces were then heated at 60 to 70°C for about an hour to crosslink the coating material. Coatings were then tested for their oil repellency and resistance to removal by solvents. To determine if a coating would spread from the area of application or could be transferred by desorption, only half of the stainless-steel surface was coated. Contamination of the uncoated area was examined by determining if there were changes in wettability of the uncoated portion. Three lubricants were used as wetting test liquids–a diester oil [bis(2-ethylhexyl)sebacate], a chlorinated silicone oil, and a hydrocarbon (squalane).

The most successful barrier films were obtained from solutions of the fluorooctyl polymer that had been prepared by adding fluorooctyltriethoxysilane dropwise to a 0.1% aqueous solution of acetic acid. The precipitate of polymer that formed was dissolved in Freon TF. Fluorooctyl polymer that had been formed in water without the acid catalyst was less soluble in Freon and did not give as satisfactory a barrier film as the acid-precipitated polymer.

The properties of the barrier films prepared using solutions of the fluorooctyl monomer, the acid-precipitated polymer (polymer A), and the neutral-precipitated polymer (polymer N) are contrasted in Table A1. The acid-precipitated polymer solution gave the most oleophobic film and had little tendency to contaminate the adjacent surface. Contact angle data for the three model lubricants on the polymer A film are given in Table A2. Coatings of the polymer A were tested for durability by (a) repeated rinsing with Freon, methyl ethyl ketone, and carbon tetrachloride and (b) by soaking for a week in these solvents and in the model lubricants. None of these treatments caused any evident transfer of material to the uncoated area and only soaking in the chlorinated silicone oil decreased the oleophobicity of the coating.

It is recommended that fluorooctyl silane barrier films be tested on actual ball bearings. The acid-precipitated polymer appears to be the most promising film former and should be prepared and applied in the following manner. One milliliter of fluorooctyltriethoxysilane is added dropwise into 100 ml of water containing 0.05 to 0.1 ml of

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*V.G. FitzSimmons, C.M. Murphy, J.B. Romans, and C.R. Singleterry, J. Am. Soc. Lub. Eng. 24:35(1968).

water containing 0.05 to 0.1 ml of glacial acetic acid. A finely divided precipitate of the polymer is obtained by stirring rapidly as the silane is added. When the addition is complete, the suspension is allowed to stand for at least an hour with occasional stirring to allow all of the silane monomer to polymerize. The water is decanted and the precipitate dissolved in 100 ml of Freon TF (Freon, Precision Cleaning Agent grade, du Pont). Any precipitate that does not dissolve or water left after decanting can be easily separated from the Freon solution. The concentration of this final solution is about 0.1% based on the amount of monomer. This Freon solution is painted onto the bearing edges with a soft artist's brush. The solvent evaporates rapidly leaving an invisible polyfluorooctyl siloxane film. The coated piece is then heated at about 60°C (140°F) for 1/2 to 1 hour to complete polymerization which enhances film durability.

The metal surface on which the barrier film is to be formed should be completely free of organic contamination. If at all possible, the bearings should be degreased using acetone in a soxlet extractor or a comparable apparatus that contacts the bearings with hot, clean solvent.

Table A1
A Comparison of the Wettability of Fluorooctylsiloxane Barrier Films Formed on Stainless Steel Using the Monomer and the Polymer

Coating Solution		Diester Oil Contact Angle (degrees)	
Solute*	Concentration (vol-%)	Coated Area	Adjacent Area†
Monomer	0.05	20	5
Monomer	0.25	35	15
Polymer (A)	0.1	73	10
Polymer (N)	0.1	50	5

*The solvent was Freon TF.

†The adjacent, uncoated area was considered contaminated if the contact was <10 degrees.

Table A2
The Wettability of Fluorooctylsiloxane Barrier Films by Representative Lubricating Oils

Wetting Test Liquid	Contact Angle (degrees)	
	Coated Area	Adjacent Area
Diester oil, bis-(2-ethylhexyl)sebacate	73	10
Chlorosiloxane oil	56	8
Hydrocarbon oil, squalane	77	spreads

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13. ABSTRACT

Adsorbed films having a wide range of wettabilities have been formed on silica, Pyrex, aluminosilicate, α-alumina, steel, and gold by trialkoxysilane (and trichlorosilane) compounds. These compounds had the general formulas $RSi(OR')_3$ or $RSiCl_3$, where R- was a fluorocarbon or a chlorocarbon group and -OR' was $-OCH_3$ or $-OCH_2CH_3$. The fluorocarbon films had γ_c values of < 20 dynes/cm and water contact angles of 100 to 118 degrees. The chlorocarbon films had γ_c values of > 40 dynes/cm and water contact angles of 80 to 90 degrees. Film thickness, determined by ellipsometry, was consistently greater than a monolayer of the trialkoxysilane. Desorption experiments suggest that the films were composed of a polysiloxane network along with unhydrolyzed adsorbate, small polysiloxane molecules, and solvent. The fluorocarbon compounds have potential for forming oleophobic barrier films in lubricated devices.

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