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Solution Systems for the Displacing of Organic Liquids from Solid Surfaces

MARIANNE K. BERNETT AND W. A. ZISMAN

*Surface Chemistry Branch
Chemistry Division*

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CONTENTS

Abstract	1
Problem Status.....	1
Authorization	1
INTRODUCTION.....	1
EXPERIMENTAL CONDITIONS AND TECHNIQUES.....	1
“OIL”-DISPLACEMENT BY SOLUTIONS OF FLUORINATED ALCOHOLS	2
“OIL” DISPLACEMENT BY SOLUTIONS OF FLUORINATED ACIDS	5
“OIL” DISPLACEMENT BY SOLUTIONS OF OTHER TYPES OF FLUORINATED COMPOUNDS.....	9
SILICONES AS “OIL”-DISPLACING SOLUTES.....	9
CONCLUSIONS AND RECOMMENDATIONS.....	10
REFERENCES.....	11

Solution Systems for the Displacing of Organic Liquids from Solid Surfaces

MARIANNE K. BERNETT AND W. A. ZISMAN

*Surface Chemistry Branch
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Many liquid organic compounds that are effective in surface chemically displacing an adhering layer of a nonaqueous liquid from a solid surface are also effective when used in a solution in an appropriate nonaqueous solvent. Besides reducing the necessary quantity of active solute, the use of a solvent also greatly increases the variety of compounds effective in surface-chemical displacement by including compounds which are either solid (or very viscous) at ordinary temperatures. These principles were established by experiments on displacing hexadecane, propylene carbonate, and Navy Special Fuel Oil from the solid, clean surfaces of SAE 1020 steel, borosilicate glass, and a variety of polymeric organic solids used as insulating materials. Solvents used included common hydrocarbons, fluorinated hydrocarbons, or a combination of either. It was found that highly fluorinated alkanols and low-molecular-weight dimethyl silicones were especially well suited for temporary oil displacement when used in concentrations of only 0.05 to 5.0 wt-%. The duration of liquid displacement could be increased greatly by adding small concentrations (0.1 wt-%) of a compound capable of adsorbing from solution to form an oleophobic film on the solid surface; stearic acid and the higher molecular weight dimethyl silicones are good examples. Permanent oil-displacement from *any* type of surface was obtained by using concentrations as low as 0.02 wt-% of certain types of progressively fluorinated fatty acids. Applications of the solutions were equally effective whether they were by a dynamic means, such as by spraying or flushing, or by a combination of solution and subsequent competitive adsorption, such as by dipping or immersion.

INTRODUCTION

In a previous study we described the principles and experimental conditions under which a spreading liquid compound can displace an organic liquid from a solid surface by a dynamic surface-chemical mechanism (1). The most efficient compounds for such purposes were shown to be those having the following simultaneous properties: low surface tensions, high equilibrium spreading pressures, and some solubility in the liquid to be removed. Other physical properties such as the volatility, viscosity, and density of the organic liquid (the "oil") and of the liquid-displacing compound (the "agent") were also factors determining the speed and mode of liquid displacement.

This report is concerned with the "oil"-displacing properties of solutions with a minor proportion of an effective "oil"-displacing compound (the solute) dissolved in a major proportion of one or more less effective "oil"-displacing

constituents (the solvent). The solvent may be used to reduce the necessary quantity of the more expensive solute or to decrease the viscosity. The use of a solvent also greatly increases the variety of promising "oil"-displacing solutes by making possible the use of compounds which by themselves are either solid or too viscous for use at ordinary temperatures.

EXPERIMENTAL CONDITIONS AND TECHNIQUES

The solid surfaces used in the experiments described below were panels of SAE 1020 cold-rolled steel 15.0 cm long, 7.5 cm wide, and 1 mm thick. Each was polished before use with No. 4/0 sandpaper, after which it was repeatedly rinsed with ACS-grade benzene and then was dried in a clean oven at 100°C for several hours. Each panel was mounted horizontally on a leveling table and then was covered with a 0.2-mm layer of the "oil" to be displaced. A 0.010-ml drop of the "oil"-displacing solution was placed on the liquid-coated surface from a freshly flamed platinum wire tip, and the extent, speed,

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and mode of drop spreading and liquid displacement were observed. During these experiments the panel was completely enclosed and observed from above through a window to avoid disturbances by dust or air currents and to retard evaporation of the more volatile "oil"-displacing solutions. To evaluate the oleophobicity and hydrophobicity of the cleaned panel, slowly advancing contact angles of sessile drops of hexadecane, propylene carbonate, and water on the clean area were measured with a goniometer described previously (2).

In addition to the steel panels, various solid resins, which were selected because they are much used as insulating materials in electrical or electronic equipment, were also studied in the "oil"-displacement experiments. The resins were NELCO 100 (epoxy glass), Taylor Fiber XXXP-242 (paper base phenolic), Taylor Fiber XY-1 (paper base epoxy), Formica (glass epoxy), Bakelite (paper reinforced), and Bakelite (fiber reinforced).

The method of "oil" displacement described above involves a surface-chemical dynamic spreading and displacement effect whose principles and mechanisms were discussed in a previous investigation (1). However, "oil" can also be removed from solid surfaces by other means, such as by a combination of solution and surface-chemical displacement. For this purpose an "oil"-coated steel panel, 7.5 by 2.5 cm, was suspended in the solution for varying intervals of time. After withdrawal from the solution, the oleophobicity of the cleaned panels was evaluated in the same manner as above.

Ultrasonic wave agitation was employed to see if it would improve removal of the "oil" film; this method was found especially useful for objects displaying normally inaccessible recesses and crevices. The equipment used for such purposes was a Crest ultrasonic 100-watt generator, Model 701, connected to a 1-gallon tank, Model 511. A 500-ml flask equipped with a condenser and containing the appropriate displacing agent solution was lowered into the water-filled tank, and an "oil"-coated steel panel, 7.5 by 2.5 cm, was suspended in the solution. The ultrasonic waves were generated for varying lengths of time.

Organic liquids which were displaced in these experiments were hexadecane (Eastman Practical),

propylene carbonate (Eastman Practical), and Navy Special Fuel Oil (NSFO). The first two liquids were percolated just before use through a long adsorbent column of activated alumina and Florisil to remove any traces of polar impurities. These two liquids were selected from the group investigated in our earlier report (1), because the former represents a nonpolar liquid of low surface tension and the latter a polar liquid of high surface tension. Petroleum fuel oil NSFO was chosen because it represents an important class of oils encountered widely in naval operations and applications.

Tables 1 and 2 list the "oil"-displacing solutes and solvents investigated, respectively, along with convenient code designations. The melting or freezing points, boiling points, and densities given were determined by the producer of each liquid. The two perfluoroalcohols listed were obtained from the Columbia Chemicals Company of South Carolina. Each was purified further by being percolated through adsorbent columns of alumina and Florisil just before use. The various members of the family of progressively fluorinated acids having the general molecular structural formula $F(CF_2)_m(CH_2)_nCOOH$ were exceptionally pure compounds prepared by Brace (3) and investigated by us in several previous surface-chemical studies (4,5). All solvents in Table 2 were commercial materials identified by producers' designations and used as received. The hydrocarbon solvents were selected for their comparatively low flash points and rapid rates of evaporation.

Surface tensions given in the tables were measured by the ring method with a Cenco du Noüy tensiometer after applying the corrections of Harkins and Jordan (6) to conventional liquids and the corrections of Fox and Chrisman (7) to liquids of high density and low surface tension. All experiments reported here were carried out at 25°C in the air at 50% R.H.

"OIL"-DISPLACEMENT BY SOLUTIONS OF FLUORINATED ALCOHOLS

Since our previous study (1) showed that the liquid perfluoroalcohols were very effective agents for displacing organic liquids, they were the first compounds investigated as the "oil"-displacing solutes. Table 3 gives the values of Σ_{max} , the

TABLE 1
Organic Solutes Studied

Compound	Identification Code	mp (°C)	bp (°C/mm)	d ²⁵	γ_{LV}^{25} (dynes/cm)
F(CF ₂) ₃ CH ₂ OH	3F-1H alcohol	—	95/749	1.600	17.2
F(CF ₂) ₇ CH ₂ OH	7F-1H alcohol	27	164	1.734 ²⁷	17.0 ²⁷
F(CF ₂) ₂ (CH ₂) ₁₆ COOH	2F-16H acid	70-71	—	—	—
F(CF ₂) ₅ (CH ₂) ₁₆ COOH	5F-16H acid	77-79	—	—	—
F(CF ₂) ₇ (CH ₂) ₁₆ COOH	7F-16H acid	91-92	—	—	—
F(CF ₂) ₂ (CH ₂) ₁₀ COOH	2F-10H acid	48-50	—	—	—
F(CF ₂) ₆ (CH ₂) ₁₀ COOH	6F-10H acid	67-69	—	—	—
F(CF ₂) ₁₀ (CH ₂) ₁₀ COOH	10F-10H acid	111-112	—	—	—
(CH ₃) ₃ SiOSi(CH ₃) ₂ OSi(CH ₃) ₃	Silicone DC 200, 1.0 cs	—	150	0.818	17.4
Dimethyl polysiloxane, MW = 1150	Silicone DC 200, 10 cs	—	>200/0.5	0.940	20.1

TABLE 2
Solvents Studied

Compound	Identification Code	fp (°C)	bp (°C)	d ²⁵	γ_{LV}^{25} (dynes/cm)
Fluorinated:					
CCl ₃ F*	Freon-11	-111	23.8	1.476	20.2
CCl ₂ F-CCl ₂ F*	Freon-112	26	92.8	1.634 ³⁰	23.3 ²⁷
CCl ₂ F-CClF ₂ *	Freon-113	-35	47.6	1.565	18.0
CBrF ₂ -CBrF ₂ *	Freon-114B2	-110.5	47.3	2.163	17.3
CCl ₃ -CF ₂ -CF ₃ *	Freon-215	-80	74	1.643	17.2
CCl ₃ -CF ₂ -CF ₂ Cl*	Freon-214	-92.8	114	1.694	21.9
Fluorinated Polyether*	Freon-E3	-115**	152	1.723	13.7
CF ₃ -CCl ₂ -CFCl-CF ₃ †	Halocarbon-437	3.2	98	1.748	18.1
Unfluorinated:					
Aliphatic Solvent‡	AMSCO 140	—	60††	0.7835	24.8
Aliphatic Naphtha§	Varsol 1	—	40.2††	0.7887	24.8
(CH ₃) ₃ SiOSi(CH ₃) ₂ OSi(CH ₃) ₃ ¶	Silicone DC 200, 1.0 cs	—	150	0.818	17.4

*du Pont Company.

†Halocarbon Products Corporation.

‡American Spirits Company.

§Humble Company.

¶Dow Corning Corporation.

**Pour point.

††Flash point.

TABLE 3
 "Oil"-Displacing Efficiency of Solutions Containing Perfluoroalcohol

Displacing Solution	γ_{LV} (dynes/cm)	Hexadecane $\gamma_{LV} = 27.0$		Prop. Carb. $\gamma_{LV} = 41.1$		NSFO $\gamma_{LV} = 30.9$	
		Σ_{max} (cm ²)	Remarks	Σ_{max} (cm ²)	Remarks	Σ_{max} (cm ²)	Remarks
Freon 11 + 3F-1H alc.*	20.0	2	fast;contracts	4	fast;contracts	—	—
Freon 11 + 7F-1H alc.*	19.9	3	fast	9	fast	—	—
Freon 11	20.2	1	recovers immed.	1	recovers immed.	—	—
Freon 112 + 3F-1H alc.*	23.0	2	slow	9	fast;contracts	1	recovers
Freon 112 + 7F-1H alc.*	22.8	2	fast	16	fast;contracts slightly	1	recovers
Freon 112	23.3	1	recovers immed.	4	recovers immed.	4	recovers
Freon 113 + 3F-1H alc.*	18.0	0.5	slow	4	fast;contracts	0.2	recovers
Freon 113 + 7F-1H alc.*	17.8	3	faster;dry;best	9	fast;dry;best	1	recovers slowly
Freon 113	18.0	1	recovers immed.	3	recovers immed.	0.2	recovers
Halocarbon 437 + 7F-1H alc.*	18.0	2	fast;contracts	—	—	—	—
Halocarbon 437	18.1	0.5	recovers immed.	—	—	—	—
Hexadecane + 3F-1H alc.†	26.4	—	—	—	—	9	remains partially covered
Hexadecane + 7F-1H alc.†	26.4	—	—	—	—	16	remains partially covered; clears slightly
Hexadecane	27.0	—	—	—	—	4	thin solvent film remains
Hexane + 3F-1H alc.†	—	—	—	—	—	4	remains mostly covered
Hexane + 7F-1H alc.†	18.1	—	—	—	—	4	remains partially covered
AMSCO 140 + 3F-1H alc.†	—	—	—	—	—	9	remains mostly covered
AMSCO 140 + 7F-1H alc.†	—	—	—	—	—	12	remains partially covered
AMSCO 140	24.8	—	—	—	—	6	remains partially covered

*1 vol-% alcohol.

†Saturated; <1 vol-% alcohol.

maximum area from which "oil" was displaced when a 0.01-ml drop of a solution of 1-vol-% perfluoroalcohol in Freon was placed on the "oil"-covered surface of a clean steel panel. Remarks are also given in Table 3 about the speed of the "oil" displacement and the final appearance of the cleared area. Similar observations were also made on the "oil"-displacing properties of perfluoroalcohol solutions in hydrocarbon solvents. Since these alcohols are not soluble enough in unfluorinated solvents to allow making up 1-vol-% solutions, saturated solutions of the solutes were

employed instead; the results obtained are also given in Table 3. The "oil" displacement action of each pure solvent is also included in Table 3 for comparative purposes.

The data in Table 3 show that a solution of 7F-1H alcohol, in any one of the three Freon solvents, is a better "oil"-displacing material than a solution of lower molecular weight 3F-1H alcohol. Solutions of the perfluoroalcohols in Freon 112 as the sole solvent displace "oils" from somewhat larger areas than solutions in either Freon 11 or 113. Since a freezing point of 26°C, however,

prevents the use of Freon 112 at ordinary room temperatures, a solution of Freon 112 and 113 in a 1:1 volume ratio ($\gamma_{LV} = 20.4$ dynes/cm), which behaves much like a solution of Freon 112 only, can be substituted. The fluorinated liquids were more effective as solvents for "oil"-displacement compositions than the hydrocarbons, since the area (although smaller) was nearly entirely cleared of "oil," whereas the area displaced by a hydrocarbon solvent remained covered to a varying extent with a thin film of the "oil." The observed poor "oil" displacement results from the low "oil"-displacing ability of the hydrocarbon solvent and the low solubility of the perfluoroalcohol in this type of solvent.

To investigate whether a process of solution combined with surface-chemical displacement is more effective, a small "oil"-coated panel (2.5 by 7.5 cm) was partially immersed into the solution. In this method the solvent dilutes and removes the "oil" coating adhering to the surfaces until only a weakly adsorbed monolayer remains. The strength with which the monolayer adheres depends upon the molecular structure of the "oil," but even a nonpolar liquid adheres weakly to a metal because of induced polarization in the local field emanating from the metal (8). If the solute is chosen to be of such a molecular configuration as to be strongly adsorptive on the metal, competitive adsorption between the weakly held monolayer of "oil" and the solute will eventually result in the displacement of the "oil." When the metal is withdrawn from the solution, it will exhibit the surface properties of the adsorbed monolayer of the solute. The ability of the solute to act as an "oil"-displacing agent by adsorbing as a monolayer can be studied by measuring the contact angles of selected liquids on the solid surface.

The "oil"-coated panels were partially immersed in the solution for time intervals ranging from 1 minute to 64 hours; after a panel was slowly retracted from the liquid, it was placed in the horizontal position and the contact angles of sessile drops of hexadecane, propylene carbonate, and water were measured on the exposed surface to characterize the residual film. The results, summarized in Table 4, were unaffected by the time of immersion. The first four columns of Table 4 indicate the solute; the solvent, which was either a Freon, an aliphatic naphtha, or a mixture of both

in the volume ratio of 1:1; and whether the steel panel was clean or coated with a layer of hexadecane when immersed into the displacing solution. The observed contact angles (last three columns) reveal that the perfluoroalcohols somewhat modify the wetting properties of the steel surface.

Experiments on solutions of ω -hydrogen perfluoroalcohols (9) revealed essentially the same phenomena as the perfluoroalcohols. Similar results were obtained with solutions of fluorinated alcohols having the general structure $H(CF_2)_m-CH(CH_3)CH_2OH$ and $H(CF_2)_mC(CH_3)_2CH_2OH$ (10). Furthermore, our observations can be extrapolated to include any class of highly fluorinated alcohols, as long as they have the following essential properties: low surface tension (if liquid), adsorptivity on the solid substrate, and low surface energy when adsorbed as a condensed oriented monolayer.

"OIL" DISPLACEMENT BY SOLUTIONS OF FLUORINATED ACIDS

An oleophobic film may be desirable which will be more able to persist even after "oil" displacement has occurred; either a higher molecular weight perfluoroalcohol or a more firmly adsorbed solute such as a fluorinated fatty acid, amine, or amide will suffice. But perfluoroalkyl carboxylic acids are strong acids and hence corrode most metals. Recent studies by Shafrin and Zisman (5) on the homologous family of progressively fluorinated fatty acids have shown that these weak acids, especially the higher homologs, adsorb as stable, condensed, oleophobic monolayers on solid surfaces. These properties make such compounds desirable candidates as "oil"-displacing agents.

Solutions of such an acid, the 10F-10H acid, can be prepared by dissolving the acid first in a fluorinated solvent (such as one of the Freon formulations) followed by the addition, where desired, of an aliphatic hydrocarbon (such as commercial naphtha) to produce a 1:1 volume ratio of the two solvents. The adsorptivity of this acid and the oleophobicity of its adsorbed monolayer on steel and Pyrex were observed by the same methods used to study the fluorinated alcohols, *i.e.*, by the dynamic liquid-displacement method or by partially immersing clean (or "oil"-covered) panels in the

TABLE 4
Oleophobic Properties of Steel Panels After Immersion in Solutions
Containing Various Solutes and Solvents

Solute	Solvent	Conc. of Solute (wt-%)	"Oil" Coating	Contact Angle (deg)		
				Hexadecane	Propylene Carbonate	Water
7F-1H alc.	Freon 113	1.1	None Hexadecane	spr spr	30 33	55 60
7F-1H alc.	AMSCO 140	(sat.)	None Hexadecane	spr spr	35 45	55-60 60-62
7F-1H alc.	Freon 113 AMSCO 140	4.6	None Hexadecane	spr spr	26 30	55-60 60
2F-10H acid	AMSCO 140	0.3	None Hexadecane	46 46	60 60	96-98 96-98
2F-16H acid	AMSCO 140	0.2	None Hexadecane	46 42	62 56	98-100 96-98
7F-16H acid	Freon 113 AMSCO 140	0.05	None	44	68-70	85
Silicone DC 200 (1 cs)	Freon 113 AMSCO 140	3.3	None	spr	35	60-65
Silicone DC 200 (1 cs)	Freon 113 AMSCO 140 Stearic acid*	3.3	None Hexadecane	18 18	58-60 58-60	95 95
Silicone DC 200 (1 cs)	AMSCO 140	50.0	None Hexadecane	spr spr	30 30	65 65
Silicone DC 200 (1 cs)	AMSCO 140 Stearic acid*	50.0	None Hexadecane	25 22	60 60	95 95
Silicone DC 200 (10 cs)	Silicone DC 200 (1 cs)	5.0	None Hexadecane	spr spr	55 55	75-80 75
Silicone DC 200 (10 cs)	Silicone DC 200 (1 cs) Stearic acid†	5.0	None Hexadecane	12 10	60-62 60-62	105 105

*0.1 wt-%.

†Saturated, <0.1 wt-%.

displacing solutions for various time intervals and measuring contact angles of hexadecane and propylene carbonate as well as water on the dry surface after panel retraction. The results obtained are summarized in Table 5. The first five columns give the solvent used (in some experiments Varsol 1 was substituted for AMSCO 140 because of its more rapid evaporation from the solid surface); the concentration of 10F-10H acid; the "oil" coating (if any) to be displaced from the steel panel; the time interval of immersion of the panel; and whether or not ultrasonic agitation was used. From these measurements and observations it was concluded that the 10F-10H acid acted as an efficient "oil"-displacing agent in the fluorinated solvents examined and that it would be similarly effective in any volatile fluorinated solvent or mixture with a hydrocarbon solvent so long as the resulting solvent would be liquid at room temperature.

Complete "oil" displacement occurred by a combined solvent action and competitive adsorption which was usually completed in 1 minute or less. Physical agitation, like that caused by ultrasonic wave action, was not necessary to speed or complete the "oil"-displacement process, but it was a useful aid where all portions of the surface of the object were not quickly accessible to the liquid during a brief immersion. Atomizer-spraying the panel, while it was inclined at 45 degrees from the vertical, also produced rapid "oil" displacement. Here the solvent acted as a vehicle for transporting away the "oil" droplets, which were unable to respread over the surface of the monolayer coating of acid that displaced the "oil" to form them. Solvents consisting of a mixture of a Freon and hydrocarbon were slightly more effective than those consisting of Freons alone.

The large contact angles observed with hexadecane, propylene carbonate, and water proved that the added 10F-10H acid did displace the "oil" and adsorb on the panel as an oriented close-packed monolayer. Hexadecane contact angles above 70 degrees have only been found on extremely low-energy surfaces, such as adsorbed monolayers of closely packed, well-adlinedated, terminally fluorinated acids (5,11) and on condensed films of the perfluorooctyl ester of poly(methylmethacrylic) acid (12). Even on the smooth, clean surface of polytetrafluoroethylene (Teflon)

the contact angle of hexadecane was only 46 degrees. The large contact angles observed in sessile test drops on retracted panels also revealed that the monolayer of acid had not been desorbed from the metal surface by the fluorinated solvents, as was the case with adsorbed monolayers of the lower perfluoroalkanols. The metal surface was so modified by the adsorbed monolayer of 10F-10H acid that any liquid with a surface tension above 16 or 17 dynes/cm at 25°C would be unable to spread over it (5). After the monolayer-coated panel had been partially immersed in water for at least several hours, rust formation of the steel panels was observed. No rusting was observed in 200 hours after the panel had been partially immersed in an aqueous emulsion of the solute and the mixed fluorinated and aliphatic hydrocarbon solvents. Hence, we conclude that these weakly acidic, but highly oleophobic, compounds can be useful rust-inhibitive coatings for iron and steel; this is a familiar property of the fatty acids and salts (13,14).

Shorter-chain members of the same family of progressively fluorinated acids were also effective "oil"-displacing solutes which adsorbed on steel surfaces to form oleophobic monolayers. Table 4 gives several examples of the properties of such acids. Although the contact angles of the same three liquids were comparable to those observed on polytetrafluoroethylene (and thus were somewhat lower than those obtained on the adsorbed monolayer of 10F-10H acid), these lower homolog (shorter chain) acids had the advantage of being sufficiently soluble in volatile hydrocarbon solvents (such as naphtha) to permit their use as "oil"-displacing solutes in small quantities without the necessity of also including a Freon as mutual solvent. In the two series of progressively fluorinated acids investigated, all of the lower homologs below the 3F-16H and 6F-10H acids were soluble in aliphatic hydrocarbon solvents. Fluorinated solvents had to be used with the acids containing longer fluorinated segments. The low members of each homologous family of acids were also slightly soluble in the low-molecular-weight silicones (such as the 1-cs DC 200 fluid), and each such acid could therefore be used with such a silicone solvent to form an effective "oil"-displacing solution.

TABLE 5
Oleophobic Properties of Steel Panels After Immersion in
a Solution Containing 10F-10H Acid

Solvent	Conc. of 10F-10H Acid (wt-%)	"Oil" Coating	Immersion (min)	Ultrasonic Agitation	Contact Angle (deg)		
					Hexadecane	Propylene Carbonate	Water
Freon 113 AMSCO 140	0.03	None	1	No	58-60	80-82	110
		None	2	No	58-60	80-84	110
		None	2	Yes	54-58	82-84	114
		None	64 hr	No	54-58	80-84	112
		Hexadecane		2	No	54-58	80-82
		Hexadecane	2	Yes	54-58	80-82	112
		Hexadecane	10	No	62	82-84	115
		Hexadecane	10	Yes	60-62	82-84	114
		Prop. Carb.	2	No	56	77-79	105
		Prop. Carb.	2	Yes	57	79-80	110
Freon 113 Varsol 1 (mixed ultrasonically, including oil washed off from panels)	0.03	Hexadecane	1	No	73	84	115
		Hexadecane	1	Yes	74	85	115
		Hexadecane	2	No	73	84	115
		Hexadecane	2	Yes	73	85	115
		Prop. Carb.	1	No	74	84	115
		Prob. Carb.	1	Yes	72	84	115
Freon 113 Varsol 1 (not mixed ultrasonically)	0.03	Hexadecane	5	No	60-63	78-80	110
		Prop. Carb.	5	No	57	77	107
		None	5	No	65-68	82-85	107
Freon 112 Varsol 1	0.05	None	5	No	55	68	100
		Hexadecane	5	No	58-60	75	110
Freon 114B2 Varsol 1	0.03	None	2	No	68-70	84-85	108
		Hexadecane	2	No	68-70	84	110
Freon 215 Varsol 1	0.05	None	5	No	68	82-85	110
		Hexadecane	5	No	65	80	110
Freon 214 Varsol 1	0.05	None	5	No	52-55	70	105
		Hexadecane	5	No	55	72-75	105
Halocarbon 437 Varsol 1	0.03	None	5	No	60-62	75	110
		Hexadecane	5	No	55-60	75	110
Freon 113 AMSCO 140 Water	0.02	None	5	No	78-80	92	120
		None	2	No	70	82	110
		Hexadecane	5	No	78	90	115
Freon 113	0.08	None	5	No	70	82-84	110
		Hexadecane	5	No	70	80-84	114
Freon 112	0.08	None	5	No	62	75	105
		Hexadecane	5	No	63	75	105
Freon 215	0.08	None	5	No	71	84-86	115
		Hexadecane	5	No	70	85	115
Freon 214	0.08	None	5	No	52	70	94
		Hexadecane	5	No	48	68	94
Halocarbon 437	0.04	None	5	No	65	83-85	110
		Hexadecane	5	No	66	83-85	110

"Oil"-displacement experiments were tried on the solid resins and plastics listed earlier because of interest in using such a process to remove liquid films adsorbed on insulating housing materials used in electrical and electronic equipment. These test panels were also each 2.5 by 7.5 cm, and each was covered with a 0.2-mm-thick layer of the petroleum fuel oil NSFO. Each panel was inclined at 45 degrees from the vertical before being sprayed with each of the above-mentioned solutions of a progressively fluorinated acid. Every such solution tried was found effective in removing the "oil"; the results were generally the same as those obtained with steel panels.

"OIL" DISPLACEMENT BY SOLUTIONS OF OTHER TYPES OF FLUORINATED COMPOUNDS

The following classes and types of compounds in Freon solutions in concentrations from 0.1 to 5 wt-% were also examined for their "oil"-displacing ability: partially fluorinated esters, partially fluorinated silanes, fully and partially fluorinated hydrocarbons, chloro-substituted fluorocarbons, and miscellaneous structures (1). It was found that among these classes were many good "oil"-displacing agents. As a general rule, the compounds that were efficient "oil"-displacing agents in the pure state were also able to displace "oils" effectively when used as solutes in small concentrations in a Freon.

SILICONES AS "OIL"-DISPLACING SOLUTES

Dimethyl silicones of low molecular weight (linear, branched, or cyclic) had been shown earlier (1) to be efficient "oil"-displacement agents; they were especially effective with "oils" in which they were soluble. The hexadecane displacing action of several Freon solutions of silicone DC 200 (1.0 cs at 25°C) were therefore investigated, since the lower-molecular-weight silicones were soluble in hexadecane. Not only were the resulting solutions efficient at removing the hexadecane coating on the panels, but values of Σ_{max} were comparable to those obtained with the perfluoroalcohols in the same solvents. However, the displaced hexadecane did spread back to cover the cleared areas within 30 minutes. Similar

observations resulted when the silicone was dissolved in either naphtha or a lower alkane.

Solutions of Freon and AMSCO 140 in a 1:1 volume ratio to which low-molecular-weight dimethyl silicones had been added in small concentrations were used in steel panel immersion and retraction experiments. Although the "oil" coating had been displaced, the cleaned steel surface was not very oleophobic (see Table 4). "Oils" of low surface tension, such as hexadecane, respread readily over the cleared surface, and even the liquids of higher surface tension were not completely prevented from respreading.

Since a low-molecular-weight dimethyl silicone has a boiling point of 150°C, its adsorbed monolayer evaporates from the surface after a short time; hence the displaced "oil" is able to spread back over the cleared area. If only 5.0 wt-% of a dimethyl silicone of higher molecular weight was added to the low-molecular-weight silicone, the adsorbed solute remained on the solid surface because of its extremely low vapor pressure, and the displaced hexadecane "oil" could not spread back even after 6 hours. Dimethyl silicones having average molecular weights of 1200 or 15,000 (viscosity grades 10 cs and 350 cs at 25°C, respectively) produced nearly identical results as the oleophobic solute.

Another method of obtaining long-lasting "oil" displacement with silicone solutes was to add 0.1 wt-% or less of a polar-nonpolar long-chain compound such as stearic acid. Table 4 shows that the addition of this concentration of stearic acid to a low-molecular-weight silicone dissolved in a hydrocarbon or fluorinated solvent, or else along with a high-molecular-weight silicone dissolved in a low-molecular-weight silicone solvent, increased the duration of the oleophobic property of the cleared solid surface.

Certain organosilicones with the general formula $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_m\text{Si}(\text{CH}_3)_2\text{C}_3\text{H}_6\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{CH}_3$, or similar types (15) obtained from Union Carbide Company (16), exhibited the same general behavior and acted as promising "oil"-displacing agents when dissolved in Freon or in Freon and AMSCO 140 in concentrations of about 5 wt-%. However, they permitted the displaced "oil" to spread back over the cleared area; therefore a small concentration of a more permanently adsorbed oleophobic agent, like a higher

dimethyl silicone or stearic acid, was added to prevent respreading.

Fluorosilicones, such as those with the monomer $-\text{SiO}(\text{CH}_3)(\text{C}_3\text{H}_4\text{F}_3)-$, were also effective "oil"-displacing agents when used in Freon solutions; they had about the same effectiveness as the unfluorinated dimethyl silicones of higher molecular weight. Organic liquids having surface tensions at 20°C higher than 30 dynes/cm were displaced readily, although a few moist areas remained.

CONCLUSIONS AND RECOMMENDATIONS

This investigation has demonstrated amply that "oil"-displacing systems composed of suitable solvent-solute combinations are very effective. The use of such systems is preferable to the application of a pure liquid agent because: (a) the variety of "oil"-displacing agents is vastly increased by the possibility of including compounds having the appropriate chemical structure but existing in the solid state or a highly viscous state at ordinary temperatures, and (b) the use of a solvent can greatly reduce the necessary quantity of the effective "oil"-displacing compound, which often is expensive or in very limited supply. The use of any specific solution system appears limited mainly by considerations of toxicity, flammability, and softening effects on other solid materials present.

When the primary objective was displacement of the "oil" for a short time, small amounts of fluorinated alcohols or low-molecular-weight dimethyl silicones dissolved in fluorinated or other solvents were very effective "oil"-displacing agents. The fluorinated solvent, however, could also serve to desorb the alcohol and thus leave the surface subject to subsequent wetting by the respreading of the "oil" or water. The low-molecular-weight silicones were volatile enough to evaporate quickly from the solid surface, and thus they did not offer permanent protection. The duration of protection against respreading, however, could be increased greatly by adding a small concentration (0.1 wt-%) of stearic acid or other polar-nonpolar compounds, which adsorbed on the solid surface and acted as an effective and durable oleophobic and protective coating. A combination of these constituents in a solution of hydrocarbons or other mixed solvents

thus offers an effective and economic means for obtaining long-lasting "oil" displacement with protection from subsequent "oil" respreading or water contamination. A small concentration of a dimethyl silicone of high molecular weight, dissolved in one of low molecular weight, also increased the time of protection from respreading.

When it is desirable to displace the "oil" permanently, the solid surface can be modified by adsorption from solution in such a manner as to prevent subsequent respreading by the displaced "oil" or any other organic or aqueous liquid. For use on noncorrosive solid surfaces, solutions of fluorinated acids in fluorinated solvents were suitable displacing agents. Of more general application, however, are dilute solutions of one or more of the progressively fluorinated fatty acids, which are ideally suited for permanently displacing "oils" from *any* solid surface. As little as 0.02 wt-% of such an efficient fluorochemical solute in an appropriate solvent will displace the bulk organic liquid or "oil" from any smooth solid surface; the most efficient of these solutes left a residual monolayer adsorbed on the solid such that no liquid with a surface tension higher than 15 to 16 dynes/cm at 20°C could spontaneously spread over it. Where solid surfaces had only to be protected from respreading by liquids with surface tensions above 30 dynes/cm at 20°C, the low-molecular-weight (short-chain) progressively fluorinated acids are very effective; these acids are quite soluble in hydrocarbon solvents and are especially attractive economically.

Many of the oleophobic films deposited on the steel surface by the "oil"-displacing solutes investigated are effective in preventing or inhibiting subsequent corrosion by the humid atmosphere. However, if the effective "oil"-displacing solute itself was not such an inhibitor, an oleophobic and inhibitive compound such as stearic acid could be added to the solution in low concentration.

Various procedures for applying the "oil"-displacing solution to solid surfaces were found effective: spraying and flushing, which are examples of the previously discussed dynamic surface-chemical displacement, as well as the methods of dipping or immersion (or immersion with ultrasonic agitation). Other methods of application more adaptable to the object to be

cleaned or the circumstances of application can be devised readily.

The results of this investigation show that the mechanisms responsible for the surface-chemical displacement of organic liquids from solid surfaces by nonaqueous solvent-solute systems are, in principle, generalizations of the solvent-solute systems employed in the displacement of water (17-20).

These nonaqueous solutions are useful for liquid-displacing applications where the presence of water or aqueous solutions would prove detrimental or injurious, such as in cleaning watches, meters, or other fine mechanisms, or electronic and electrical apparatus containing parts damaged by water such as sodium-bromide windows in spectroscopic and optical equipment.

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13. ABSTRACT <p>Many liquid organic compounds that are effective in surface chemically displacing an adhering layer of a nonaqueous liquid from a solid surface are also effective when used in a solution in an appropriate nonaqueous solvent. Besides reducing the necessary quantity of active solute, the use of a solvent also greatly increases the variety of compounds effective in surface-chemical displacement by including compounds which are either solid (or very viscous) at ordinary temperatures. These principles were established by experiments on displacing hexadecane, propylene carbonate, and Navy Special Fuel Oil from the solid, clean surfaces of SAE 1020 steel, borosilicate glass, and a variety of polymeric organic solids used as insulating materials. Solvents used included common hydrocarbons, fluorinated hydrocarbons, or a combination of either. It was found that highly fluorinated alkanols and low-molecular-weight dimethyl silicones were especially well suited for temporary oil displacement when used in concentrations of only 0.05 to 5.0 wt-%. The duration of liquid displacement could be increased greatly by adding small concentrations (0.1 wt-%) of a compound capable of adsorbing from solution to form an oleophobic film on the solid surface; stearic acid and the higher molecular weight dimethyl silicones are good examples. Permanent oil-displacement from any type of surface was obtained by using concentrations as low as 0.02 wt-% of certain types of progressively fluorinated fatty acids. Applications of the solutions were equally effective whether they were by a dynamic means, such as by spraying or flushing, or by a combination of solution and subsequent competitive adsorption, such as by dipping or immersion.</p>		

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