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Surface Chemical Displacement of Organic Liquids from Solid Surfaces

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ABSTRACT

An investigation has been made of the various factors operative in the displacement by organic liquid compounds of a bulk layer of any nonaqueous liquid from a solid surface. Although the solid surfaces used in the experiments were SAE 1020 steel and borosilicate glass, the results are readily applied to any solids. The nonaqueous pure liquids displaced were selected to cover the surface tension range and included n-hexadecane, ar-dibromoethylbenzene, tricresyl phosphate, and propylene carbonate. A large number of well-defined displacing agents were investigated, of which the most efficient proved to be those where an optimum balance could be achieved between low surface tension, high equilibrium spreading pressure, and good solubility with respect to the organic substrate to be removed. Agents which were particularly effective for long-lasting or permanent displacement were certain classes of highly fluorinated organic compounds and low-molecular-weight dimethyl silicones. Low-surface-tension polar hydrocarbons, such as n-alkanols, were effective for temporary displacement. The several mechanisms operative in liquid-liquid displacement from solid surfaces have been investigated. It was shown that these results and generalizations include our earlier results on water displacement as a special (and extreme) case.

PROBLEM STATUS

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

AUTHORIZATION

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SURFACE CHEMICAL DISPLACEMENT OF ORGANIC LIQUIDS FROM SOLID SURFACES*

INTRODUCTION

When a small drop of a pure liquid b is placed upon the horizontal surface of another pure liquid a, spontaneous spreading of b will occur if a decrease in the surface free energy will result. This means, as Harkins and coworkers pointed out (1-5), that the initial spreading coefficient per unit area, $S_{b/a}$, is positive, where

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{b'a'}); \tag{1}$$

γ_a and γ_b are the surface tensions of liquids a and b, respectively, and $\gamma_{b'a'}$ is the interfacial tension of b and a, the prime superscript indicating that a is saturated with b and vice versa. It was also shown that Eq. (1) is equivalent to

$$S_{b/a} = W_{b/a} - W_{b/b} \tag{2}$$

where $W_{b/a}$ is the reversible work of adhesion per unit area of liquids b and a, and $W_{b/b}$ is the reversible work of adhesion of b to itself (i.e., the reversible work of cohesion), or twice the surface tension of liquid b.

If both liquids had previously been mutually saturated, the resulting liquid b' would spread upon a' if the "final spreading coefficient" $S_{b'/a'}$ satisfied the condition that

$$S_{b'/a'} > 0 \tag{3}$$

where

$$S_{b'/a'} = \gamma_{a'} - (\gamma_{b'} + \gamma_{b'a'}). \tag{4}$$

An intermediate condition will occur if a small drop of b spreads on a much larger volume of a, because b will change rapidly during spreading to b' before a can saturate with b to become a'. The spreading coefficient for such a system is "the Harkins semi-initial spreading coefficient," $S_{b'/a}$, where

$$S_{b'/a} = \gamma_a - (\gamma_{b'} + \gamma_{b'a'}). \tag{5}$$

Hence,

$$S_{b'/a} - S_{b'/a'} = \gamma_a - \gamma_{a'}. \tag{6}$$

If, after film spreading from the drop has occurred, some of the drop b remains as a lens on the film-covered surface a', the resulting surface tension decrease, or surface pressure $(\gamma_a - \gamma_{a'})$, is the equilibrium spreading pressure of b on a, and is denoted by $F_{b/a}$,

$$F_{b/a} = \gamma_a - \gamma_{a'} \tag{7}$$

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which is simply a generalization by Ellison and Zisman (6) of Cary and Rideal's (7) concept of the equilibrium spreading pressure of a surface-active liquid lens on water. From this definition and Eqs. (6) and (7), it follows that

$$F_{b/a} = S_{b'/a} - S_{b'/a'}. \tag{8}$$

Experimental data reveal that usually $F_{b/a} > S_{b/a}$. As $F_{b/a}$ becomes large, it approaches $S_{b/a}$; for example, in the system isoamyl alcohol spreading on water at 20°C, $F_{b/a}$ = 46.8 dynes/cm, and $S_{b/a}$ = 44.0 dynes/cm.

Harkins and co-workers (3-5) have pointed out that liquid b can even be devoid of polar or hydrophilic groups and yet have the ability to spread spontaneously on water as a duplex film. Relations (1) through (8) were used by Harkins et al. to discuss the spreading of a wide variety of pure liquids over bulk water and mercury.

Langmuir (8,9) and later Zisman (10) investigated the effects of modifying the spreading properties on water of a nonspreading liquid, such as a higher hydrocarbon, with a dissolved solute having a hydrophobic-hydrophilic structure. More recently, Ellison and Zisman (6) and Jarvis and Zisman (11) have shown that even if b and a are both organic liquids, spreading of b on a can occur; many such pairs of pure liquids were described, and others will be presented here.

Conditions affecting the spreading of a liquid upon a clean, smooth, solid surface have been extensively investigated at this Laboratory and summarized in various publications (12-16). Comparatively little has been published on the spreading of liquids over solid surfaces previously coated with a thin layer of a different liquid. Baker and Zisman (17,18) studied many solid hydrophilic surfaces coated with a thin layer of water and found that certain types of pure organic liquids were able not only to spread rapidly on the water but also to displace it from the solid. In each instance the organic liquid had a hydrophobic-hydrophilic (or amphipathic) molecular structure. The most effective compounds were somewhat soluble in water and had large initial spreading coefficients on water (or high equilibrium spreading pressures). When a drop of such an organic liquid was placed gently on the surface of the water, it spread rapidly on the water, a hole formed in the water layer, and it grew in diameter while exposing a dry surface of area Σ. Ultimately Σ attained a maximum value Σ_{max} which was a function of the mass and constitution of the drop of the water-displacing liquid. It was shown that some water-displacing liquids deposited a hydrophobic film on the exposed solid surface such that after the water layer had been displaced it would not respread. By the addition of a suitable solute, any water-displacing liquid could be made to behave in that way.

Baker (19-21) subsequently prepared emulsions of hydrocarbon solvents in water which were effective in displacing thin layers of oils from solid surfaces. By the successive applications of oil- and water-displacing agents, Baker, Leach, Singleterry, and Zisman (22-24) developed an economic and efficient process for salvaging equipment previously damaged by water and/or smoke.

In the past decade, investigations by Zisman and co-workers of surface-activity in nonaqueous liquid systems and of the surface chemistry of fluorocarbon derivatives have established that (a) surfaces of close-packed adsorbed perfluoromethyl groups have the lowest surface energies known at ordinary temperatures (12-16) and (b) suitably constituted fluorocarbon derivatives are the most effective compounds for depressing the surface tensions of any nonfluorocarbon liquids at such temperatures (6,11,25-32). This report will present recent work using such concepts to demonstrate the existence of agents capable of displacing a great variety of organic liquids from solid surfaces.

Since a large value of $S_{b/a}$ and some solubility in water had been found by Baker and Zisman (17) to be essential for the effective displacement of water from solid surfaces,

a somewhat soluble pure liquid compound b was also sought at first, which, when placed on the surface of the organic liquid a to be displaced, would exhibit the largest possible values of $S_{b/a}$ (or $F_{b/a}$). Inspection of Eq. (1) reveals that if liquid b is to be effective in displacing liquid a it should have a surface tension (γ_b) as much below γ_a as possible. This is obvious when a and b are such that the interfacial tension ($\gamma_{a'b'}$) is small when compared with either γ_a or γ_b. Where a and b are somewhat soluble, Pound's interfacial tension rule (33,34) reveals that $\gamma_{a'b'}$ will be small or negligible. Equation (7) shows that $F_{b/a}$ will be greater, the smaller the value of $\gamma_{a'}$, i.e., the greater the surface tension depressant ability of b when dissolved in a. Since certain types of fluorocarbon derivatives are now known to be the most efficient surface tension depressants (25,26,32), any liquid member of such homologous families of compounds was assumed to be suitable as the displacing liquid b. However, the maximum spreading pressure of b on a and the optimum liquid displacing effect would be determined by some upper and lower limits to the allowable solubility of b in a. Liquid b will hereafter be referred to as the oil-displacing "agent" and liquid a as the displaced "oil."

EXPERIMENTAL CONDITIONS, MATERIALS, AND TECHNIQUES

In the experiments described here, the ability of many pure compounds to displace each of a selected group of pure organic liquids from clean smooth horizontal plates of steel and glass was investigated. However, it will later be made evident that the results can be extended to any solid surface. Panels of SAE 1020 cold-rolled steel, 15.0 cm long and 7.5 cm wide, were used after having been polished with #4/0 sandpaper and then rinsed repeatedly with ACS-grade benzene. The borosilicate (Pyrex) plates of the same dimensions were soaked in a hot sulfuric acid-nitric acid (ratio 1:2) bath and then were rinsed repeatedly with distilled water. All specimens were dried in a clean oven at 100°C for several hours. Each test plate was mounted on a leveling table with the plane face horizontal and was then covered to a depth of 0.2 mm with the oil or organic liquid to be displaced. Unless stated otherwise, an 0.01-ml drop of the oil-displacing agent was delivered gently to the wet surface from a freshly flamed platinum wire tip, and the speed, extent, and mode of spreading and oil displacement were observed, through a low-power lens when necessary. During these observations each panel was completely enclosed and observed through a glass cover plate to avoid disturbances by dust or air currents. This precaution was helpful also in observing the behavior of the more volatile oil-displacing agents. Unless indicated otherwise, all experiments were conducted at 25°C and 50% R.H.

Organic liquids displaced from the panels are listed in the first row of Table 1, and the pure liquid compounds used to displace them are given in the first column. The former liquids were selected to cover a wide range in surface tensions at 25°C and a promising variety of chemical compositions. Each organic liquid or oil-displacing agent, however previously prepared and purified, was finally purified by being percolated slowly at room temperature through an adsorbent column of activated alumina and Florisil just prior to each experiment in order to remove any traces of polar adsorbable impurities.

Surface tensions were measured by the ring method with a du Noüy tensiometer (6-cm-circumference platinum ring), using the corrections of Harkins and Jordan (35) for conventional liquids and the corrections of Fox and Chrisman (36) for liquids of high density and low surface tension. The solubility of an oil-displacing agent in an oil was obtained by measuring the equilibrium surface tension of a progressively more concentrated solution and by finding that point in the curve of surface tension versus concentration at which an additional quantity of solute did not further depress the surface tension.

Equilibrium spreading pressures were calculated from Eq. (7) by obtaining the difference of the surface tension of the pure oil and that of the oil saturated with the oil-displacing agent.

Table 1
Behavior of Oil-Displacing Agents on Steel Substrates at 25°C

Agent				Behavior on Displacement of Oil			
Compound	γ (dynes/cm)	d (g/cc)	bp (°C/mm)	Hexadecane γ = 27.0 d = 0.775 bp = 287	ar-Dibromoethylbenzene γ = 38.2 d = 1.738 bp ≈ 260	Tricresyl Phosphate γ = 40.4 bp ≈ 410 d	Propylene Carbonate γ = 41.1 d = 1.198 bp ≈ 240
Fluorinated Esters							
Perfluorooctyl-ethanesulfonate	19.1	1.709	100/2.8	Good	Excellent	Good	Good
Hexyl perfluorobutyrate	19.2	1.231	74/20	Excellent	Excellent	Excellent	Excellent
Bis (perfluorooctyl)-α-n-dodecenyl succinate	19.4	1.484	185/0.3	—	—	Good	Good
Bis(perfluorooctyl)-3-methyl glutarate	19.5	1.689	145/0.5	Good	Good	Good	Good
Bis(perfluorohexyl)-3-methyl glutarate	19.7	1.539	115/0.5	Good	Good	Good	Good
1,2,3-Trimethylolpropane tris(perfluorobutyrate)	21.4	1.614	120/0.2	Fair	Fair	Good	Good
Bis(ω-hydrogen perfluoroheptyl)-3-methyl glutarate	25.6	1.648	147/0.5	Poor	Poor	Good	Good
Bis(ω-hydrogen perfluoroheptyl) phenyl succinate	25.9	1.640	165/0.25	Inactive	Poor	Fair	Fair
Bis(ω-hydrogen perfluoroheptyl) phenyl glutarate	26.2	1.654	180/0.5	Inactive	Poor	Fair	Fair
(ω-Hydrogen-perfluoroheptyl)-hydrogen-3-methyl glutarate	26.4	1.557	143/0.5	Inactive	Poor	Fair	Fair
$C_7F_{15}CONH(CH_2)_3N^+(CH_3)_2(CH_2)_2COO^-$	—	1.5	Viscous	Fair	Good	Good	Good
Silicones							
Bis(t-butoxy)-bis(perfluorooctoxy) silane	18.4	1.525	108/0.3	Good	Good	Good	Good
Bis(t-butoxy)-bis(ω-hydrogen-perfluoroheptoxy) silane	20.8	1.474	125/0.3	Good	Good	Fair	Fair
Silicone DC 200, 0.65 poise	15.9	0.761	100	Fair*	—	—	Fair
Silicone DC 200, 1.0 poise	17.4	0.818	152	Fair*	—	—	Fair
Silicone DC 200, 1.5 poise	18.0	0.853	192	Fair*	—	—	Fair
Silicone DC 200, 2.0 poise	18.7	0.873	230	Fair*	—	—	Fair
Silicone DC 200, 3.0 poise	19.2	0.900	70-100/0.5	Good	Good	—	Fair
Fluoro silicone QF 1-0065	25.7	1.24	—	Inactive	Poor	Poor	Poor
Fluorocarbons							
$C_3F_7[CF_2CF(CF_3)]_2Cl$ PPCl 2	15.1	1.915	134	Fair	—	Poor	Fair
$C_3F_7[CF_2CF(CF_3)]_{3A}F$ PPF 3A	16.3	1.992	115/98	Fair	Fair	—	Good
$C_3F_7[CF_2CF(CF_3)]_{4A}F$ PPF 4A	17.8	—	143/95	Fair	Fair	—	Good
$\{C_3F_7[CF_2CF(CF_2)]_{2A}\}_2$ PPCA 2	18.5	1.996	127/10	Poor	—	—	—
FCD-330	20.2	1.996	—	Poor	Fair	Fair	Inactive

*Area recovered after 15 minutes.

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CONDITIONS FOR OIL DISPLACEMENT FROM METAL SURFACES

Observations made of the various materials on steel panels revealed distinctive patterns of oil-displacement behavior which were dependent upon several parameters. Baker and Zisman (17) had observed that maximum water displacement was a function of the solubility of the agent in water, the initial spreading coefficient (or else the equilibrium spreading pressure) on water, and the speed of spreading. The present investigation showed that displacement of the oil by the agent was determined by its solubility in the oil, the difference $(\gamma_a - \gamma_b)$ in the surface tension of the agent and the oil, and the volatility of the agent. Table 1 lists the fluorinated esters, silicon-containing compounds, and halogenated hydrocarbons examined as oil-displacing agents, along with selected physical constants and a qualitative statement of the oil-displacement characteristics observed.

Certain spreading properties were observed. These were Σ_{max} (the maximum value of the approximately circular area of oil displaced), t_{max} (the time required to attain Σ_{max}), and the ultimate condition of the cleared solid surface. In Table 1 a combination of these properties was expressed in a single statement. The most efficient oil-displacing liquids had an appreciably smaller surface tension (γ_b) than that of the oil displaced (γ_a); however, solubility in the oil as well as other physical properties were also involved. Oil displacement proceeded at various speeds and the resulting cleared area could (a) be perfectly dry and clean, (b) be covered with a thin layer of oil, or (c) show a combination of both properties in various proportions.

OIL DISPLACEMENT BY AGENTS HAVING FUNCTIONAL POLAR GROUPS

Effect of Homology and Molecular Weight of Displacing Agent

In Tables 2 and 3 are given the observations made on the homologous series of liquid n-alkanols, n-perfluoroalkanols, and ω-monohydrogen perfluoroalkanols when a drop of each is placed on a 0.2-mm layer of hexadecane or propylene carbonate covering a steel or Pyrex panel. When the molecular weights (M) in the homologous series of perfluoroalkanols were plotted against Σ_{max} (as represented in Fig. 1 for propylene carbonate), it was found that Σ_{max} increased with M, the slope becoming steeper with higher values of M. The family of ω-hydrogen perfluoroalkanols behaves similarly at high values of M, but the lower members were not as efficient as the lower perfluoroalkanols in displacing the propylene carbonate. In contrast to the fluorinated alcohols, the lower n-alkanols were less effective in displacing propylene carbonate and, when M exceeded 100, became essentially ineffective. Whereas the surface tensions of the perfluoroalkanols decrease with increased molecular weight, the opposite occurs in the family of n-alkanols (see Fig. 2). Hence, Σ_{max} can be directly related to $\gamma_a - \gamma_b$, the difference in surface tension of the oil and the displacing agent. The interfacial tension $\gamma_{b'a'}$ is smaller than the surface tension (γ_a) of the organic liquid; it decreases as the solubility of the agent increases, and it approaches zero at infinite solubility. Thus, the value of $\gamma_{b'a'}$ can be neglected in Eq. (1), so that $(\gamma_a - \gamma_b)$ becomes equal to the initial spreading coefficient $S_{b/a}$ and also approximates the spreading pressure $F_{b/a}$. Plots of Σ_{max} against $(\gamma_a - \gamma_b)$ are given in Fig. 3 for each of the three homologous series of alcohols when placed on specimens coated with propylene carbonate or with n-hexadecane. For comparison purposes, results obtained on specimens coated with water are also included. Displacement of propylene carbonate or of hexadecane by the same agent made it evident that greater oil-displacing ability was observed the higher the surface tension of the oil. It was also evident that the fluoroalcohols have higher displacing ability than the n-alkanols.

Table 2
Behavior of Aliphatic n-Alkanols as Oil Displacing Agents at 25°C

Agent			Substrate	Oil					
				Hexadecane γ_a = 27.0 d = 0.775			Propylene Carbonate γ_a = 41.1 d = 1.198		
Compound	γ_b (dynes/cm)	d (g/cc)		Σ_{max} (cm^2)	t_{max} (min)	Area Condition	Σ_{max} (cm^2)	t_{max} (min)	Area Condition
Ethanol	22.3	0.785	Steel	2.5	Imm.	—	7.1	Imm.	—
			Pyrex	2.5	Imm.	—	6.3	Imm.	—
1-Butanol	23.9	0.810	Steel	3.1	Imm.	—	7.1	Imm.	Moist
			Pyrex	1.0	Imm.	—	3.1	1	Dry
1-Pentanol	24.9	0.814	Steel	2.5	1	Dry	4.2	1	Moist center
			Pyrex	4.5	1	Center drop	12.6	1	Moist center
1-Hexanol	24.9	0.819	Steel	0.8	Imm.	—	1.2	2	Center drop
			Pyrex	7.5	1	Dry	4.2	1	Center drop
1-Heptanol	26.2	0.822	Steel	0.8	1	Moist	2.0	3	Center drop
			Pyrex	19.6	5	Dry	2.0	1	Center drop
1-Octanol	26.9	0.825	Steel	Inactive		—	0.5	5	Large drop
			Pyrex	Inactive		—	0.5	1	Large drop
1-Nonanol	27.4	0.827	Steel	Inactive		—	0.8	10	Large drop
			Pyrex	Inactive		—	0.1	1	All drop
1-Decanol	27.4	0.833	Steel	Inactive		—	1.2	15	Large drop
			Pyrex	Inactive		—	0.2	5	All drop
1-Undecanol	28.1	0.833	Steel	Inactive		—	0.8	30	Large drop
			Pyrex	Inactive		—	0.8	5	Large drop
1-Dodecanol	28.7	0.831	Steel	Inactive		—	0.8	60	Large drop
			Pyrex	Inactive		—	0.8	5	Large drop

Table 3
Behavior of Fluorinated n-Alkanols as Oil-Displacing Agents at 25°C

Agent			Substrate	Oil					
				Hexadecane γ_a = 27.0 d = 0.775			Propylene Carbonate γ_a = 41.1 d = 1.198		
Compound	γ_b (dynes/cm)	d (g/cc)		Σ_{max} (cm²)	t_{max} (min)	Area Condition	Σ_{max} (cm²)	t_{max} (min)	Area Condition
Perfluoroethanol	19.5	1.374	Steel	0.8	1	Small drop	12.6	Imm.	Dry
			Pyrex	0.8	1	Small drop	4.7	Imm.	Dry
1-Perfluorobutanol	17.2	1.600	Steel	1.7	1	Small drop	23.6	1	Droplets
			Pyrex	1.2	1	Small drop	15.7	Imm.	Dry
1-Perfluorohexanol	17.4	1.686	Steel	0.8	5	Large drop	47.1	2	Droplets
			Pyrex	4.9	1	Small drop	9.5	1	Center drop
1-Perfluorooctanol	17.0	1.734	Steel	2.3	30	Large drop	65.9	5	Droplets
			Pyrex	4.5	1	Large drop	9.5	1	Center drop
ω-Hydrogen-perfluoropropanol-1	26.0	1.485	Steel	0.2	5	Large drop	12.6	20	Droplets
			Pyrex	0.2	5	Large drop	7.5	Imm.	Dry
ω-Hydrogen-perfluoropentanol-1	23.5	1.665	Steel	0.2	5	Large drop	22.0	30	Droplets
			Pyrex	0.8	5	Large drop	18.8	5	Dry
ω-Hydrogen-perfluoroheptanol-1	22.7	1.753	Steel	0.5	5	Large drop	56.5	60	Dry
			Pyrex	0.5	5	Large drop	57.0	60	Dry

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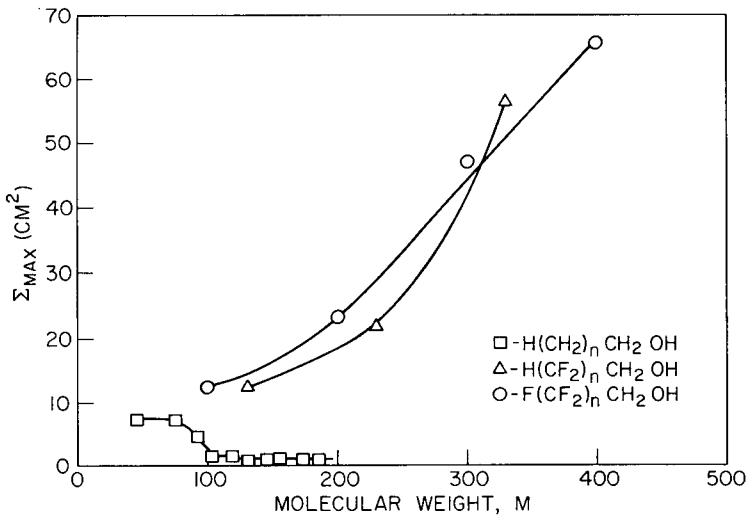

Fig. 1 - Effect of molecular weight of oil-displacing agent on maximum area displaced of propylene carbonate (substrate steel)

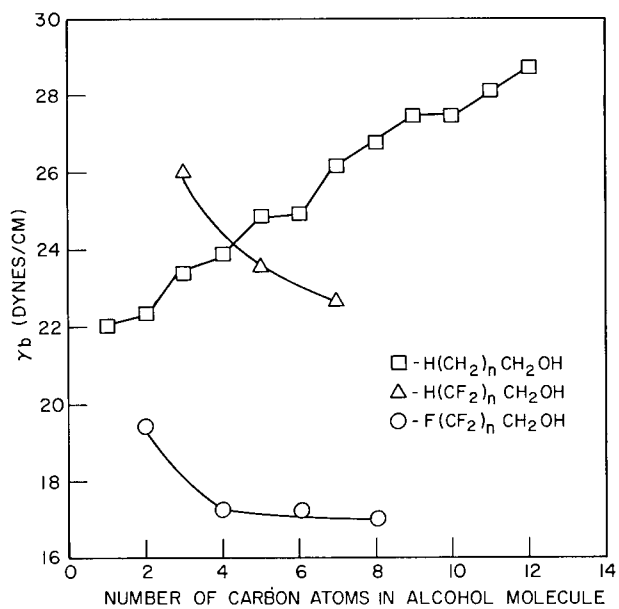

Fig. 2 - Surface tensions of n-alkanols at 25°C

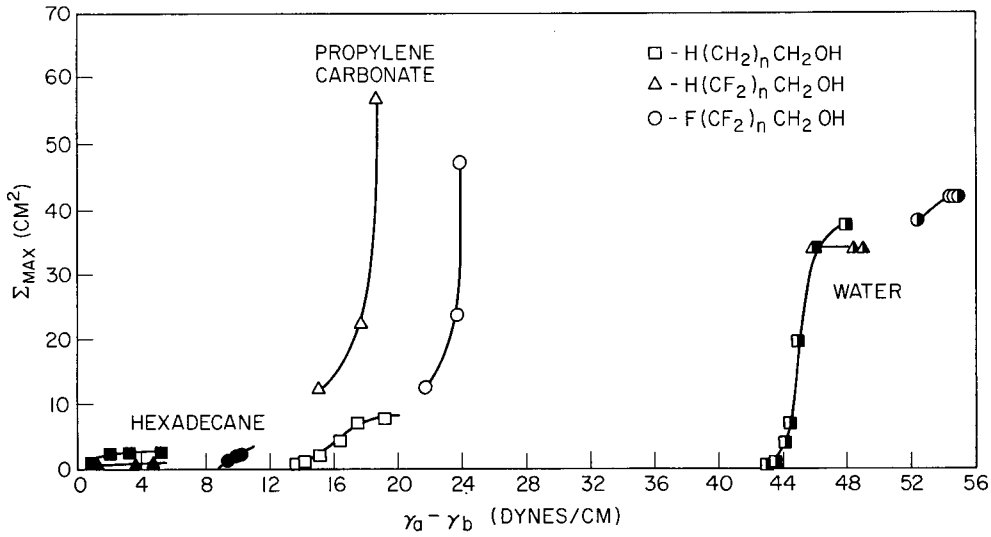

Fig. 3 - Effect of surface tension difference of liquid and agent on maximum area displaced of liquid (substrate steel)

Another measure of the efficiency of the oil-displacing agent is t_{max} which is plotted in Fig. 4 against the boiling point of the agent. As in any homologous series, an increase in the molecular weight raises the boiling point and lowers the vapor pressure. The increase in t_{max} of Fig. 4 may be regarded as the result of the decrease in the vapor pressure of the agent or a lower rate of agent diffusion in the oil.

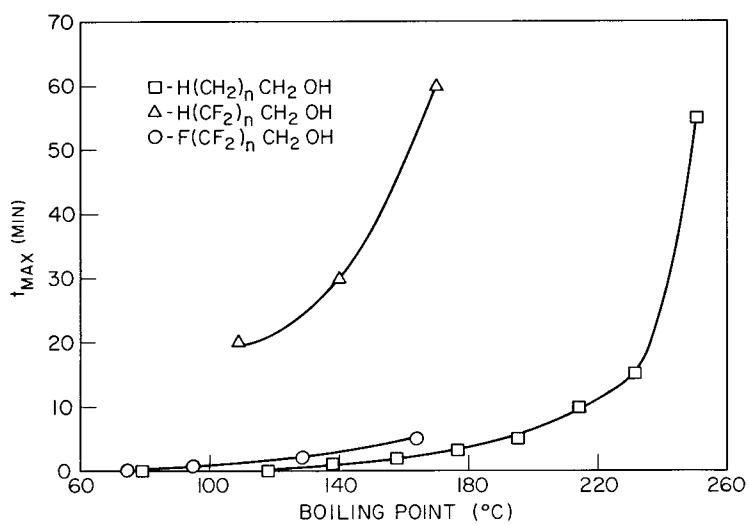

Fig. 4 - Effect of boiling point on time necessary to reach maximum area when n-alkanols are spread on propylene carbonate (substrate steel)

Effect of Solubility of Displacing Agent in Oil

The effectiveness of water-displacing agents was found by Baker and Zisman (17,23, 24) to be roughly proportional to the solubility in water. This is reasonable because in each homologous series of such agents, higher water solubility corresponds to lower molecular weight, higher volatility, higher rate of spreading, and higher equilibrium spreading pressure. In order to observe the effect of agent solubility in oil-displacing mechanisms, several agents having large differences in solubility in oils of nearly equal surface tensions were examined. Ar-dibromoethylbenzene (Alkazene 42) and propylene carbonate, which have surface tensions at 25°C of 38.2 and 41.1 dynes/cm, respectively, are two such oils. Here, the value of $\gamma_a - \gamma_b$ of the oil-displacing agent with respect to each oil is nearly the same and, therefore, of negligible influence. Any difference in oil-displacing properties must then necessarily be due to solubility properties only. Table 4 summarizes the results obtained with these oils. For purposes of comparison, the results observed on displacing hexadecane (γ_a = 27.0 dynes/cm) are also given in Table 4. Where the solubility of the agent (for example, that of any fluorinated alcohol) is greater in propylene carbonate than in ar-dibromoethylbenzene, the value of Σ_{max} is always greater for propylene carbonate; where the agent solubility is in reverse order (n-decanol or the methyl silicones are examples), Σ_{max} is always greater for ar-dibromoethylbenzene than for propylene carbonate.

The influence of solubility is even more striking in the case of the two methyl silicone fluids, because each is insoluble in propylene carbonate but soluble in hexadecane. Values of $\gamma_a - \gamma_b$ for the two methyl silicones are 25.2 and 21.9 dynes/cm with respect to propylene carbonate, and only 11.1 and 8.8 dynes/cm with respect to hexadecane. Yet the corresponding values of Σ_{max} are only 7.1 and 9.1 cm^2 for propylene carbonate and 19.6 and 32.0 cm^2 for hexadecane. A comparison of the values of Σ_{max} for the same two methyl silicones spread on ar-dibromoethylbenzene as well as on hexadecane, in both of which these silicones are soluble, reveals that Σ_{max} increased with $\gamma_a - \gamma_b$. Thus, if the oil solubilities of the displacing agents are approximately the same, the dominant variable is the value of $\gamma_a - \gamma_b$.

In miscible systems, $\gamma_{a'}$ approaches γ_b, and thus $F_{b/a}$ approaches $\gamma_a - \gamma_b$; when the agent is insoluble, however, the value of $F_{b/a}$ is small as compared to $\gamma_a - \gamma_b$. The relationship is thus shown to be more simple between $F_{b/a}$ and Σ_{max} than that between $\gamma_a - \gamma_b$ and Σ_{max} (compare the methyl silicones in Table 4). Thus, under these circumstances both the equilibrium spreading pressure of $F_{b/a}$ and the oil solubility of the agent are the principal factors determining the oil displacement; furthermore, $F_{b/a}$ decreases with the solubility of the agent in the organic liquid.

Effect of Volatility of Displacing Agent

In those systems where $\gamma_a - \gamma_b$ is large and the oil-displacing agent has a high vapor pressure, the drop of the agent does not have to be in direct contact with the oil in order to cause oil displacement. When a drop of any of the fluorinated alkanols or fluorocarbons was held just above the surface of the oil-coated panel, the vapor molecules of the agent adsorbed on the liquid surface and created a large enough local surface tension gradient to cause formation of a growing hole in the oil layer. The oil-displacing action continued as long as the drop was held above the oil. The area cleared of oil grew to a maximum size which was larger the nearer the drop of agent was held relative to the panel and the higher its vapor pressure. When the suspended drop was removed to a great distance, the displaced oil flowed back over the cleared area to completely cover it once more. Thus the attractive forces between the solid surface and the vapor molecules of the agent were not strong enough, for the systems studied, to promote irreversible adsorption on the solid surface of an oleophobic monolayer (one on which no oil respreading could occur).

Table 4
Effect of Solubility, Spreading Pressure, and Surface Tension Difference on Behavior of Oil-Displacing Agents

Agent	Oil*	Solubility (moles/l)	$F_{b/a}$ (dynes/cm)	$\gamma_a - \gamma_b$ (dynes/cm)	Σ_{max} (cm^2)	t_{max} (min)	Composition of Residual Mound*
1-Perfluorobutanol	P	>2	17.6	23.9	23.6	1	P + Some alkanol†
	B	Insol.	8.0	21.0	9.4	30	B (Center)
	H	<0.02	0.6	9.8	1.7	1	H (Ridge)
1-Perfluorooctanol	P	>1	21.7	24.1	65.9	5	P + Alkanol†
	B	Insol.	11.9	21.2	12.6	30	B (Center)
	H	<0.01	0.6	10.0	2.3	30	H (Ridge)
ω-Hydrogen-perfluoroheptanol-1	P	Sol.	12.9	18.4	56.5	60	No remains
	B	Insol.	8.9	15.5	33.0	60	B (Center)
	H	<0.02	0.3	4.3	0.5	5	Alkanol (center)
1-Butanol	P	Sol.	16.4	17.2	7.1	Imm.	—
	B	Sol.	12.8	14.3	6.3	Imm.	—
	H	Sol.	1.8	3.1	3.1	Imm.	Alkanol + some H (moist)
1-Decanol	P	<0.3	12.5	13.7	1.7	5	P (Center)
	B	Sol.	10.5	10.8	12.7	10	B + Alkanol (ridge)
	H	—	—	0.2	Inactive	—	—
PPF3 A	P	<0.02	—	24.8	12.6	5	—
	B	Insol.	—	21.9	7.5	5	—
	H	Insol.	—	10.7	0.8	30	—
Dimethyl silicone (DC 200, 0.65 poise)	P	Insol.	2.4	25.2	7.1	1	P (Center)
	H	Sol.	8.7	11.1	19.6	1	—
Dimethyl silicone (DC 200, 3.0 poise)	P	Insol.	4.8	21.9	9.1	60	P (Center)
	B	Sol.	18.8	19.0	56.5	60	Silicone + some B (ridge)
	H	Sol.	6.8	8.8	32.0	60	—

*P = propylene carbonate; B = ar-dibromoethylbenzene; H = hexadecane.
†Ridge during displacement process. Final Σ_{max} dry.

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When the suspended drop of the agent was placed on the cleared area of the solid, it continued to cause displacement of the oil if insoluble in it, but Σ_{max} was less than the value observed when the agent was placed directly on the oil layer to be displaced. When the agent was soluble in the oil to be displaced, Σ attained about the same maximum as that caused by an insoluble agent, but it thereafter gradually diminished in size; it was concluded that some of the agent was dissolving in the oil around the cleared periphery.

Mechanisms of Oil Displacement

Oil-Soluble Agent — From the data and the qualitative observations made during many spreading and oil-displacement experiments, it was obvious that several mechanisms participate in the displacement of oils by liquid organic agents, but their relative importance depended upon the experimental conditions. Of special importance was the oil solubility of the displacing agent. When a drop of an oil-soluble spreadable agent was placed on the surface of a layer of organic liquid not over a few tenths of a millimeter thick, it dissolved as it spread (Fig. 5a). Since the surrounding area of the liquid had a higher surface tension than the oil solution in the immediate vicinity of the spreading oil drop, a localized and large surface tension gradient developed which was equivalent to a large spreading pressure directed radially and outwards. The result was a flow of the surface layer of the liquid in the same direction. The so-called Marangoni effect (37,38) is the same radial pressure effect occurring on the surface of water. The movement of the spreading surface film dragged along the bulk oil immediately beneath it (39), and therefore the local, radial, outward movement of the oil tended to form a circular depression of the oil level with a central mound (see Fig. 5b). A central mound resulted because the radial gradient in surface tension must be greatest at the periphery of the drop and least at the center. The greater the rate of spreading of the agent, the deeper the circular depression. However, during this spreading process the agent continued to dissolve in the central oil mound and contacted the solid/oil interface to adsorb as a monolayer. This solution process also caused continued spreading of the central mound and eventually its disappearance, leaving a circular hole in the oil layer and so exposing the dry surface of the solid.

Whenever the oil-spreading movement was sufficiently rapid, inertial effects of the flowing oil mass were manifested. An annular oil ridge usually appeared around the central spreading drop; eventually this ring broke up into a circular array of oil mounds (see Fig. 5c). Such a breakup process is familiar evidence of the characteristic instability of a toroidal liquid mass, which is the result of the system striving to minimize its surface energy. Infrared analysis of the oil residue left by the breakup of the oil ridge revealed that it consisted of the oil and a low concentration of the dissolved agent (see last column of Table 4). The rate at which the oil ridge broke up into discrete oil mounds depended upon the density, viscosity, and surface tension of the oil, and also on the molecular weight, viscosity, and volatility of the agent. For example, an oil-displacing agent of relatively high volatility and low surface tension (such as perfluorobutanol) spread very rapidly on propylene carbonate while piling up a well-defined oil ridge which subsequently broke up into a modest number of oil mounds. The entire spreading and breakup process was completed in a minute. When the oil-displacing agent had such a chemical structure as to be strongly adsorbed on the solid surface to form an oleophobic film, a completely dry solid surface area remained exposed after the spreading process has been completed (see Fig. 5d); this dry area was found to exhibit a large and characteristic contact angle with a drop of the oil.

If the oil-displacing agent exerted a low spreading pressure (i.e., if γ_b was only slightly less than γ_a), the central oil mound did not disappear; instead, the central area remained covered by a thin residual layer of oil. Some examples of such behavior are given in Table 4. However, this residual layer of oil usually retracted slowly to leave a disk-shaped bare area on which were located a few scattered drops of oil. Since γ_b was

only a little less than γ_a, any residual adsorbed film of agent modifying the solid surface imparted to the solid a critical surface tension of wetting (γ_c) only slightly lower than γ_a. Thus the contact angle of the residual film of oil had to be small. Although the bulk oil had been swept back vigorously in the initial spreading process, the residual oil layer retracted slowly, but completely, until a dry oleophobic surface remained.

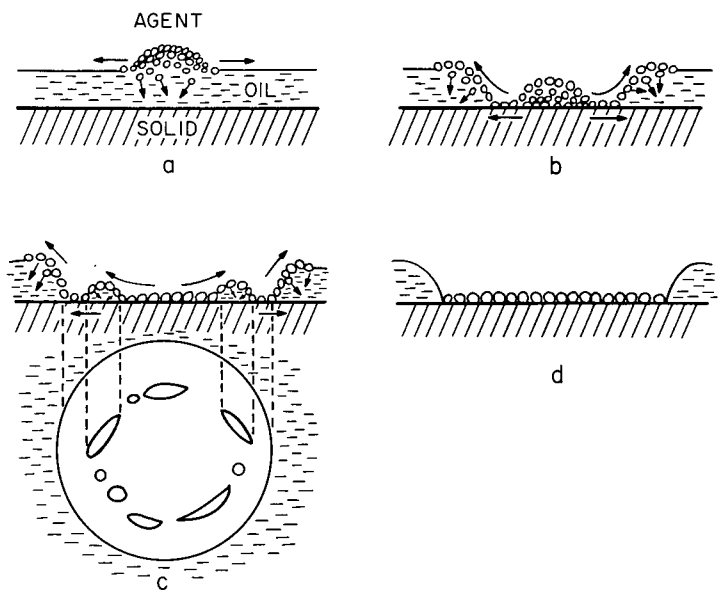

Fig. 5 - Displacement mechanism by agent soluble in oil ($\gamma_a - \gamma_b$ is large)

Oil-Insoluble Agent — When the agent was insoluble in the oil upon which it spread, several new and interesting stages appeared in the oil-displacement process. If $\gamma_a - \gamma_b$ was large, the drop of agent spread rapidly and radially over the surface of the oil (Fig. 6a). An oil hole was not created immediately below the area of original contact, but instead a widening circular dry band appeared (Fig. 6b). Where the agent had become adsorbed on the dry solid surface, an oleophobic monolayer remained which prevented the oil from respreading. Thus, an oil disk remained in the center, surrounded either by a thinner circular oil layer or by a dry annulus which in turn was surrounded by a thin toroidal mound of oil (see Fig. 6c). Somewhat later the thin oil layer often broke up to form a number of small scattered drops. Under any condition the residual thin film of oil retracted into the large center mound or into the displaced bulk liquid (Fig. 6d). Infrared analysis showed that the residual oil mounds consisted of the pure oil (Table 4), as would be expected because of the insolubility of agent and oil.

An example of effective oil-displacement for an insoluble system in which $\gamma_a - \gamma_b$ is small is that of ω-hydrogen-perfluoroheptanol and n-hexadecane (Table 4). When a drop of the alkanol was placed upon the layer of hexadecane, it first remained there in the shape of a lens. After about 2 to 3 minutes, the drop completely sank through the oil layer, and on contacting the solid/oil interface it spread radially over this interface displacing the hexadecane through adsorption on the solid as a monolayer of ω-hydrogen-perfluoroheptanol. At the site of initial contact, there remained a drop of pure displacing liquid (Table 4). The alkanol drop displaced the oil by a combination of gravitational, hydrodynamic, and surface chemical mechanisms. The effect of gravity is significant because the densities at 25 °C of hexadecane and of the alkanol are 0.775 and 1.753 g/ml,

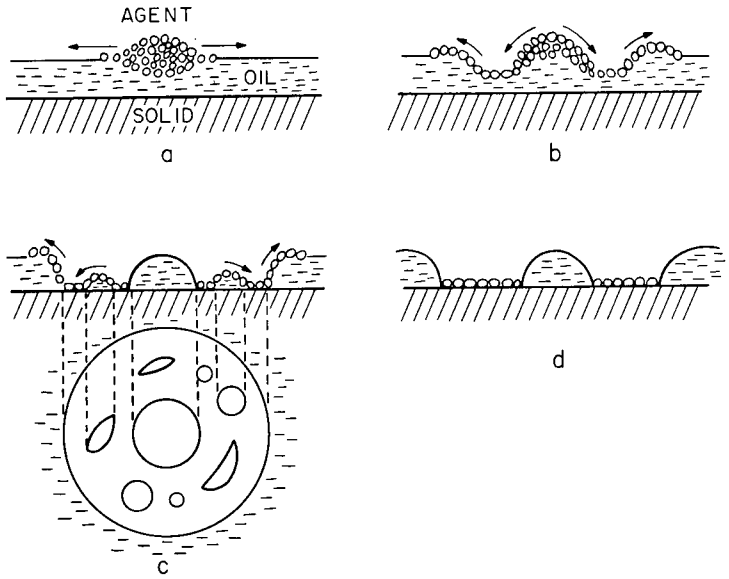

Fig. 6 - Displacement mechanism by agent insoluble in oil ($\gamma_a - \gamma_b$ is large)

respectively. As the lens traveled through the oil, its lower surface assumed a concave configuration. On reaching the solid/oil interface, it displaced the oil beneath but entrapped a layer of hexadecane between it and the solid below the center region of the drop; only the periphery of the lens was in actual contact with the solid and spreading of the alcohol started at that site. An oil layer several thousand angstroms thick may have been present initially trapped beneath the bulk alkanol drop. Baker, Bascom, and Singleterry (40) have made similar observations in their study on water drops approaching solid/oil interfaces.

Effect of Injecting Agent at Solid/Oil Interface

In order to understand better the mechanisms involved, several systems were studied by injecting the displacing agent below the oil layer in direct contact with the solid/oil interface.

When a drop of an oil-soluble agent was deposited directly at the solid/oil interface, the results were the same as though the drop were deposited at the oil/air interface. This could have been predicted since the agent was able to reach the solid/oil interface through solution in the oil. In such a system, monolayer formation at the solid/oil interface is the dominant mechanism rather than viscous drag as in the case of agent spreading at the air/oil interface.

When a drop of an oil-insoluble agent was deposited directly at the solid/oil interface, a different mechanism was operative. After the drop of agent contacted the solid/oil interface, it spread radially along that interface depositing a monolayer on the solid and dragging the layer of oil immediately above it toward the periphery. The oil layer became thinner, and, if the critical surface tension γ_c of the modified solid/oil interface was sufficiently low and the oil not too viscous, a hole formed at the site of the drop from which the oil retracted spontaneously to leave a dry solid surface area coated with an oleophobic film. When the oil could not be carried fast enough toward the periphery

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of the spreading drop, it retracted into droplets with well-defined, nonzero contact angles. In systems where $\gamma_a - \gamma_b$ was small, the rate of spreading was slow.

These experiments revealed that the net oil displacement we had observed was the resultant of two processes, (a) the Marangoni effect on an organic liquid/air interface and (b) the additional effect of permeation of the agent through the oil layer to adsorb as an oleophobic film at the solid/oil interface and its effect on destabilizing the thin layer of oil adhering to the solid.

OIL DISPLACEMENT BY AGENTS FREE OF FUNCTIONAL POLAR GROUPS

Monolayer adsorption of the agent is easily understood for the polar-nonpolar displacing agents mentioned since they always contained an adsorbable functional polar group. The polar functional end of the agent molecules adsorbed at the solid/oil interface exposing, in the case of the fluorinated alkanols, the fluorocarbon (or organophobic) portion of the molecule to the oil. The metal surface coated with close-packed fluorinated paraffin chains became a surface of low free energy for which γ_c was much smaller than γ_a; therefore, it became oleophobic to the oil displaced. When the polar agents were unfluorinated, as was true of the fatty alcohols, the solid surface was coated by the methyl terminal groups of the oriented paraffin chains. If the value of γ_c of the resulting film-covered surface was not appreciably lower than γ_a, oil displacement was only temporary, i.e., the oil (such as hexadecane) spread back eventually as the alcohol disappeared to recover the cleared area. If γ_a was higher than γ_c, as in the case of liquids such as ar-dibromoethylbenzene, tricresyl phosphate, or propylene carbonate, then permanent oil displacement occurred, but the areas displaced were small and some remained partially covered by oil.

Agents free of functional polar groups, such as the perfluoroalkanes and chloroperfluoroalkane prepared by Hauptschein et al. (41), were also found capable of permanently displacing oil from a steel plate (see, for example PPF3A in Table 4). Thus some adsorption at the solid/oil interface must have occurred. It is pertinent to note here that adsorption of even a nonpolar compound occurs readily at metal/air interfaces through the polarization induced by the surface forces emanating from the metal (42). In displacing oils, the perfluoroalkanes behaved somewhat differently than the other agents. The peripheral front of the oil-displacing drop propagated in an irregular waving manner, i.e., a small section was cleared but immediately was re-covered by the oil and an adjacent section was cleared; this one, in turn, was re-covered by the oil and the initial section was cleared. This waving propagation continued for long periods of time, until evaporation of the drop, except for the adsorbed portion, had been completed. When the oil-coated steel panel was fully exposed to the atmosphere, rather than covered by a glass plate, the waving action was enhanced, and the final Σ_{max} was smaller. Oil displacement by these compounds was thus primarily the result of surface tension gradients between the agent and the oil layer and of the high volatility of the agent.

Bascom, Cottington, and Singleterry (43) had found that, in a mixture of hydrocarbons, constituents of high volatility capable of lowering the surface tension of the mixture would increase the rate of spontaneous spreading of these hydrocarbons. In the present study an analogous but somewhat modified process occurred. The rate of spreading of these highly volatile nonhydrophilic agents was very rapid; since adsorption at the solid/oil interface did not take place readily, the oil of higher surface tension respread over the solid surface but was displaced in turn by the highly volatile and, therefore, better spreading compound of lower surface tension. This dynamic process continued until evaporation of the agent in excess of the adsorbed fraction was completed and equilibrium conditions had been reached. The ease and efficiency of oil displacement were thus dictated by $\gamma_a - \gamma_b$ and the difference in volatility of oil and displacing agent.

OIL DISPLACEMENT BY DIMETHYL SILICONES

The volatile open-chain dimethyl silicone fluids, when used as oil-displacing agents, behaved similarly to the perfluoroalkanes. Specimens of high volatility displaced the oil rapidly, but eventually the oil respread over the area; the rate and completeness of rewetting depended upon $\gamma_a - \gamma_b$. As the molecular weight of the silicones increased, and therefore the volatility decreased, Σ_{max} increased (Fig. 7); eventually the film remained adsorbed on the solid, making the surface oleophobic even with respect to oils of such low γ_a as hexadecane (Table 4). In systems such as these, the vapor pressure of the agent plays a significant part in the oil-displacement mechanism as was proven by the contraction to smaller values of Σ_{max} when the systems were exposed to the open atmosphere.

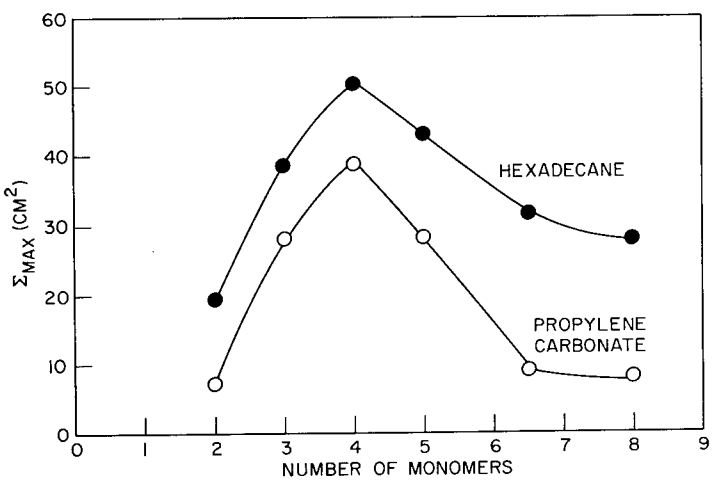

Fig. 7 - Effect of degree of polymerization of dimethyl silicones on maximum area displaced of oil (substrate steel)

Figure 7 shows the effect of degree of polymerization of the dimethyl silicones on the extent to which they displace hexadecane and propylene carbonate. The value of Σ_{max} was greatest in either case for the tetramer, which apparently combines the optimum features of volatility and molecular weight; silicones of lower molecular weight were too volatile to be efficient, while those of higher molecular weight were too viscous. Higher solubility of the silicone in the hexadecane than in propylene carbonate accounted for the larger Σ_{max} obtained by displacement from hexadecane than from propylene carbonate (see Table 4). Results in Fig. 8 also confirmed the conclusions about the effect of solubility on oil displacement, as evidenced by the larger Σ_{max} observed with hexadecane, although the surface tension differences between the silicones and hexadecane were much smaller than those between the silicones and propylene carbonate. The smaller values of Σ_{max} with increasing $\gamma_a - \gamma_b$ were again the manifestations of the high viscosity of the high-molecular-weight silicones.

These observations were made using the linear dimethyl silicones. Studies carried out with cyclic (44) and branched dimethyl silicones gave essentially the same results and showed the same trends.

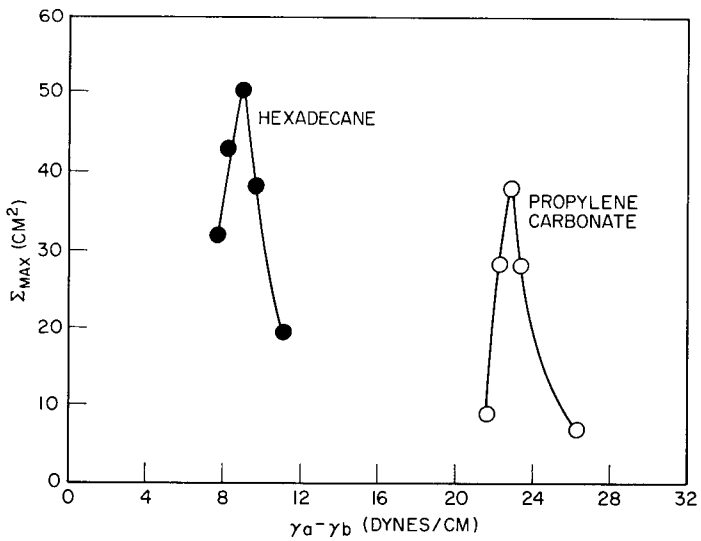

Fig. 8 - Effect of surface tension difference of oil and dimethyl silicones on maximum area displaced of oil (substrate steel)

OIL DISPLACEMENT FROM BOROSILICATE GLASS OR OTHER SOLID SURFACES

The same series of experiments on oil-coated borosilicate (Pyrex) glass panels resulted in essentially the same oil-displacement phenomena observed with steel panels. In Tables 2 and 3 will also be found the results obtained on Pyrex substrates for drops of alkanols and fluorinated alkanols placed on hexadecane and propylene carbonate. Usually, the values of Σ_{max} caused by the alkanols on Pyrex were approximately the same or slightly larger than those on steel. The fluorinated alkanols displaced areas of hexadecane which were equal to, or slightly larger than, those on steel and areas of propylene carbonate which were smaller. Hence, the mechanisms of oil displacement and the final condition of the cleared solid surfaces were the same regardless of whether the solid surface was steel or borosilicate glass. Studies by Levine and Zisman (45) and Cottington, Shafrin, and Zisman (46) of the physical properties of adsorbed alkanol monolayers at the glass/air and steel/air interfaces concluded that the adhesion of the alcohol polar group to glass and steel were about the same. The present observations were in agreement with theirs.

It has been shown that the mechanism involved in liquid/liquid displacement is not strongly dependent on the nature of the underlying solid surface. The bulk of the oil is displaced by any suitable agent without a specific solid-liquid interaction. Only when the agent molecules reach the oil monolayer adsorbed at the solid surface does it have to compete with the oil molecules for the available adsorption sites. Thus liquid/liquid displacement can apply to any solid surface for which there is not an extremely unfavorable competitive adsorption situation. For example, such an unfavorable situation would occur if the adjacent monolayer of oil (or liquid to be displaced) is chemisorbed on the solid.

GENERAL CONCLUSIONS

This investigation has extended the knowledge of the surface-chemical displacement of water from solid surfaces to the displacement of <u>any</u> liquid from such surfaces. It is concluded that:

1. The most suitable liquid displacement agents are polar-nonpolar compounds capable of adsorbing readily at the solid/oil interface. Certain nonpolar compounds can also act as displacing agents, but their efficiencies are not as high.

2. It is preferable that the nonpolar portion of the molecule of the displacement agent be a long aliphatic chain for maximum cohesion between adjacent molecules in the adsorbed monolayer; for maximum organic liquid-displacing ability (oleophobicity) the aliphatic chain should be fully fluorinated.

3. For optimum results the liquid-displacing agent should have a large initial spreading coefficient on the liquid to be displaced.

4. The agent should also exhibit a high equilibrium spreading pressure. For achievement of the two preceding properties, it is necessary that the displacing agent (a) have a surface tension as low as possible when compared to that of the oil to be displaced, (b) have a high solubility in the oil to be displaced, and (c) be efficient in depressing the surface tension of the oil to be displaced.

5. High volatility (high vapor pressure) is advantageous when the agent must displace the oil rapidly; where long-lasting oleophobicity of the area cleared of oil is more important than the speed, compounds of low volatility (but high solubility) are more suitable.

6. Low-molecular-weight dimethyl silicones (dimers, trimers, and tetramers) are also good displacing agents for liquids in which they are highly soluble.

7. The results presented here (for example, Figs. 3, 5, and 6) include the previous conclusions of Baker, Singleterry, and Zisman (24) on water displacement.

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13. ABSTRACT

An investigation has been made of the various factors operative in the displacement by organic liquid compounds of a bulk layer of any nonaqueous liquid from a solid surface. Although the solid surfaces used in the experiments were SAE 1020 steel and borosilicate glass, the results are readily applied to any solids. The nonaqueous pure liquids displaced were selected to cover the surface tension range and included n-hexadecane, ar-dibromoethylbenzene, tricresyl phosphate, and propylene carbonate. A large number of well-defined displacing agents were investigated, of which the most efficient proved to be those where an optimum balance could be achieved between low surface tension, high equilibrium spreading pressure, and good solubility with respect to the organic substrate to be removed. Agents which were particularly effective for long-lasting or permanent displacement were certain classes of highly fluorinated organic compounds and low-molecular-weight dimethyl silicones. Low-surface-tension polar hydrocarbons, such as n-alkanols, were effective for temporary displacement. The several mechanisms operative in liquid-liquid displacement from solid surfaces have been investigated. It was shown that these results and generalizations include our earlier results on water displacement as a special (and extreme) case.

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Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Liquid spreading						
Liquid-liquid displacement						
Surface tension						
Fluorinated alkanols						
Dimethyl silicones						
Surface chemical displacement						

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