

NRL Report 5957

UNCLASSIFIED

Effect of Polar-Nonpolar Additives on Oil-Spreading on Solids, with Applications to Nonspreading Oils

R. L. COTTINGTON, C. M. MURPHY,
AND C. R. SINGLETERRY

*Surface Chemistry Branch
Chemistry Division*

July 26, 1963



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Abstract	1
Problem Status	1
Authorization	1
INTRODUCTION	1
RESULTS AND DISCUSSION	2
Anomalous Spreading Behaviors	3
Effect of Organic Surface Contaminants	7
Pretreatment with Silicone Films to Prevent Oil-Spreading	9
EXPERIMENTAL MATERIALS AND PROCEDURES	11
CONCLUSIONS	12
REFERENCES	12

Effect of Polar-Nonpolar Additives on Oil-Spreading on Solids, with Applications to Nonspreading Oils

R. L. COTTINGTON, C. M. MURPHY,
AND C. R. SINGLETERRY

*Surface Chemistry Branch
Chemistry Division*

The work of Zisman and associates has established that most nonspreading oils do not spread because they deposit monolayers which modify the surface so that the critical surface tension for spreading is less than the surface tension of the oil. Nonspreading oils can be prepared from aliphatic and aromatic hydrocarbons and from many synthetic oils by the proper choice of an adsorbable additive, but an additive which makes one oil nonspreading may cause violent spreading of another oil of much higher surface tension. This anomalous spreading is produced by surface tension gradients that result from decreases in the concentration of additive at the oil/air interface as adsorption on the solid proceeds.

Oily contamination of a surface may cause spreading of an otherwise nonspreading oil because the contamination raises the critical surface tension of the surface above the surface tension of the oil. Such contamination rarely produces a critical surface tension above 30 dynes/cm. Consequently a practical nonspreading oil should have a surface tension above 32 dynes/cm so that oily contamination of the surface near the oil will not induce spreading.

Effective additives for producing nonspreading include the silicones, various fluoroesters, salts of organic amines with organic acids, high molecular weight organic acids, alcohols or amines, and some oil soluble soaps. A predeposited film of a dimethyl or methylphenyl polysiloxane is found to prevent the spreading of diester or hydrocarbon oils on stainless steel surfaces for as long as nine months. Such a treatment provides an alternative approach to the control of spreading.

INTRODUCTION

For an important group of applications the spreading characteristic of a lubricating oil may be as important as the viscosity, the oxidation stability, or the boundary lubricity of the oil. This has long been recognized by watchmakers, who require an oil that will not spread from jewel bearings to the hair spring, where it may alter the escapement rate. Jeweled bearings in meters for military electrical equipment require a similar lubricant. The nonspreading property of oil is also important because it minimizes evaporation; a drop of oil after spreading may expose as much as a thousand times the original surface. A drop of a good nonspreading oil will remain almost undiminished on a test plate for a year or more, whereas a spreading oil of equal volatility will be lost completely within one or two weeks. A spreading oil film is also undesirable because it promotes the collection of dust and lint which

wick up additional oil. The nonspreading characteristic of instrument lubricants may be expected to assume additional importance as problems emerge in maintaining highly instrumented missiles in instant readiness over a period of years. Nonspreading oils may also find critical uses in satellite instruments, which cannot be relubricated and are sometimes exposed to evaporation in a high vacuum.

On the other hand, there are some lubricant applications in which spreading under surface chemical forces is essential. An example is the grease-lubricated ball bearing, which is considered to depend upon creeping of oil from the grease reservoir to the race for sustained lubrication. The factors controlling this creep, or spreading, are not well understood and have been made the object of a study that will be reported elsewhere (1).

Nonspreading oils are not new (2) and there have been earlier investigations directed toward the production of better synthetic oils for this application (3-6). Earlier work in this Laboratory

NRL Problem C02-04, WEP TASK RRMA 04-021/652 1/R001 07-01. This is an interim report; work on the problem is continuing.

Manuscript submitted April 5, 1963.

(7) has established criteria for spreading or non-spreading of liquids on solid surfaces. This work, which has been summarized in a previous paper (8), explains the behavior of watch oils that have already been developed by empirical methods and provides the basis for a rational approach to the formulation of instrument oils to meet more exacting requirements.

Such an approach must choose between the attempt to synthesize a truly autophobic liquid having suitable physical properties and the search for additive-oil combinations that will be reliably nonspreading. The truly autophobic liquids reported to develop contact angles greater than three degrees are aromatic phosphates or halides. Since such compounds have large viscosity-temperature coefficients, the most promising approach to the preparation of nonspreading oils with better low temperature properties would appear to be a basic study of the effect of surface-active additives on the spreading behavior of nonautophobic oils. The results of such a study should provide rational guidance for the formulation of nonspreading oils from available low temperature lubricants of the spreading type.

There are many polar-nonpolar compounds which, when added to a spreading oil, will be adsorbed at metal or oxide interfaces to form a film over which the oil will not spread. The watch oils now in use are usually unrecognized applications of this principle.

The formula of the nonspreading oil now under military specification (Mil-L-3918) includes an antiwear agent (dodecylpiperidine stearate), the components of which may be expected to adsorb strongly at the oil/metal or oil/sapphire interface to give a low energy surface. The naturally occurring nonspreading oils, such as porpoise jaw oil or neat's foot oil, are mixtures of esters with free acids or alcohols which would give similar adsorption effects. This investigation has established that almost any oil can be made nonspreading on clean and smooth stainless steel or sapphire surfaces by the inclusion of a proper additive. However, unsuitable additives may sometimes accelerate rather than prevent spreading. This report describes the diverse wetting phenomena observed with oil solutions of polar-nonpolar molecules and identifies the properties favorable to the formulation of a stable nonspreading lubricant. It also examines new possibilities for the prevention of spreading by predepositing silicone

coatings in a manner somewhat analogous to the "epilame" treatment of bearings with stearates and/or stearic acid.

RESULTS AND DISCUSSION

Preliminary experiments revealed four typical patterns of behavior for oil solutions of additives strongly adsorbed at the oil/metal interface.

1. The solution was nonspreading and developed a reproducible contact angle which decreased only moderately during several months storage of the test assembly at room temperature (Fig. 1).

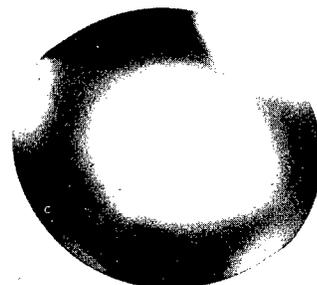


Fig. 1 - A nonspreading droplet of squalane containing 0.1% DC 510 silicone, after 30 days

2. The solution spread initially in the same way as a pure oil but eventually retracted from the wetted area to form many small drops with finite contact angles (Fig. 2).

3. The drop exhibited a substantial contact angle, but skated over the surface at a rate of several millimeters per minute. It refused, however, to cross any previous track in its gyrations.



Fig. 2 - Retraction after initial spreading of bis(2-ethylhexyl)sebacate containing 1% of sodium dinonylnaphthalene sulfonate



Fig. 3 - Dendritic spreading of bis(3,5,5-trimethylhexyl)sebacate containing 1% of DC 510 silicone

4. The drop spread "catastrophically" at a rate two or three orders of magnitude faster than the spreading of pure oils of comparable viscosity. In such cases, the spreading liquid formed an intricate dendritic pattern, a series of rapidly growing lobes about the drop circumference, or a reticulated pattern containing parallel threads of liquid obviously related to polishing directions on the solid surface. These patterns, after a few hours of development, were stable, and exhibited finite contact angles at the oil margins (Fig. 3).

Anomalous Spreading Behaviors

The anomalous spreading behaviors (types 2, 3, and 4) that are exhibited by some liquids containing strongly adsorbed additives need to be clearly understood if such effects are to be avoided in practical formulations of nonspreading oils. The information in Tables 1-3 and in Fig. 4 suggests the following explanations for the various behaviors.

1. Stable spreading behavior of type 1 results when the additive has only a small effect on the surface tension γ_{LV} of the oil but deposits a monolayer whose critical surface tension γ_c is smaller than γ_{LV} , so that the solution exhibits a substantial contact angle against the monolayer in air. Several such systems are shown in Tables 1-3 with data for the decrease in γ_{LV} of the liquid produced by the specified additive. Stable nonspreading compositions result when dimethyl (or lightly phenylated) silicones are added to aliphatic hydrocarbons and when fluoroesters are added to bis(2-ethylhexyl)sebacate. Other examples not included in the table are barium dinonylnaphthalene sulfonate in isopropyl biphenyl and a moderately phenylated DC 550 silicone in isopropyl 1,9-diphenylnonane. The significant common feature of these systems is that the additive lowers the surface tension of the pure liquid by not more than 5 to 6 dynes/cm.

2. Normal spreading with delayed retraction to droplets (type 2 spreading) is characteristic

of nonvolatile additives which do not lower the surface tension of the solution significantly and whose monolayers at the solid interface have γ_c only slightly smaller than γ_{LV} . Type 2 spreading is understandable if we recall that all of the oils studied with nonspreading additives spread normally on metals in the absence of the adsorbed monolayer. It must be assumed that at the instant of application a "foot" or meniscus of oils turns outward at the base of the drop to form a zero contact angle with the solid surface. If the adsorption of additive from this thin film is insufficient to make the critical surface tension of the surface less than the surface tension of the oil solution, spreading will continue. As the bulk of the droplet passes over the zone of unsaturated adsorption more additive will be deposited to saturate the monolayer, which will then have γ_c smaller than γ_{LV} although spreading still continues at the drop margin. The thin film of oil above the monolayer eventually breaks and retracts into irregular droplets. In other cases the ultimate nonspreading may result from *in situ* hydrolysis of an ester to give acids or alcohols which adsorb to form a low energy oil/solid interface after the drop has spread.

3. Type 3 behavior, in which nonspreading drops moved about spontaneously over the surface, is observed for several oils containing amine salts of fluorinated acids. Since there may be some free amine present in the oil, it is suspected that the evaporation of amine vapor from the drop is nonuniform because of air convection; this nonuniformity causes slight differences in the surface tension so that the surface film flows toward the point of higher surface tension. Such a flow carries along the bulk oil underneath and produces a self-propagating movement of the drop along a straight path. The self-propagation results because the new surface generated on the trailing side of the drop will have a lower surface tension than the surface on the advancing edge. The significance of additive evaporation for this phenomenon is supported by the fact that the second sample, when held at 60°C for two weeks, lost its nonspreading property and its mobility and spread normally. Such mobile behavior has also been noted for drops of squalane and isopropyl 1,9-diphenylnonane supported on the adjacent faces of a polished metal disc and a glass cover slip one millimeter above it. If the drop of squalane (surface tension = 27.8 dynes/cm) is

TABLE I
Spreading of Oils Containing DC 510 Silicone
on Clean Stainless Steel

Oils	Silicone (percent)	Spreading Behavior	Surface Tension, γ_{LV} at 25°C		
			Base Oil	Solution	$-\Delta\gamma_{LV}$
Pristane	1.0	Nonspreading	25.5	23.4	2.1
n-hexadecane	1.0	Nonspreading	27.3	23.6	3.7
Squalane	1.0	Nonspreading	27.8	22.7	5.1
1010 petroleum oil	1.0	Nonspreading	28.7	23.6	5.1
Bis(3,5,5-trimethylhexyl) sebacate	1.0	Slight spreading	28.4	22.5	5.9
Polypropylene glycol	1.0	Rapid dendritic	29.2	-	-
Trimethylol propane tri-n-alkanoate	1.0	Rapid dendritic	29.6	22.8	6.8
Bis(2-ethylhexyl)sebacate	1.0	Slight dendritic	30.3	23.2	7.1
Isopropyl biphenyl	0.1	Strong dendritic	34.8	24.1	10.7

TABLE 2
Effect of Surface-Active Solutes on the Spreading Behavior
of Bis(2-ethylhexyl)sebacate* on Polished Stainless Steel

Additive	Additive Conc. (wt. %)	Spreading Behavior	$-\Delta\gamma_{LV}$ of Solution
DC 200 silicone (70 cs)	0.01	Nonspreading (low θ)	4.9
DC 200 silicone (70 cs)	0.1	Nonspreading (low θ)	
DC 200 silicone (20 cs)	0.1	Dendritic spreading	
DC 200 silicone (5 cs)	1.0	Dendritic spreading	
DC 510 silicone (50 cs) stripped sample	0.1	Dendritic spreading	5.9
DC 510 silicone (50 cs) stripped sample	1.0	Nonspreading (low θ)	7.1
DC 510 silicone (50 cs) stripped sample	10.0	Slow spreading	8.6
DC 510 silicone (50 cs) stripped sample	40.0	Moderate spreading dendritic	9.1
DC 550 silicone (100 cs)	1.0	Slow spreading	
Fluorosilicone (1000 cs)	0.01 (sat.)	Slow spreading	
Fluoroester I†	1.0	Nonspreading (low θ)	0.4
Fluoroester I†	5.0	Nonspreading (low θ)	0.9
Fluoroester II‡	1.0	Nonspreading ($\theta = 17^\circ$)	2.3
Fluoroester III§	1.0	Nonspreading	
Barium dinonylnaphthalene sulfonate	2.0	Normal spreading, then retracts to irregular drops	0.2
11H-eicosofluoroundecylic acid plus dimethyldodecylamine	1.0	Nonspreading - self- mobile drops which leave oleophobic trail	0.2
Pentadecafluoro-octanoic acid plus dimethyldodecylamine	1.0	Nonspreading - self- mobile drops $\theta = 50^\circ$. Spreads after 2 weeks at 60°C	0.0

* $\gamma_{LV} = 30.3$ dynes/cm.

†Bis(1H,1H,7H-dodecafluoroheptyl)3-methylglutarate.

‡Bis(1H,1H-undecafluorohexyl)3-methylglutarate.

§Tris(1H,1H,4H-hexafluorobutyl)tricarallylate.

TABLE 3
Effect of Additives on the Spreading Behavior
of Squalane* on Stainless Steel

Additive	Conc. Additive (wt. %)	Spreading Behavior	$-\Delta\gamma_{LV}$
DC 510 silicone	0.01	Marginal - 2 of 3 tests were nonspreading	2.0
DC 510 silicone	0.1	Nonspreading	
DC 510 silicone	1.0	Nonspreading ($\theta = 21^\circ$)	5.1
DC 510 silicone	9.5	Nonspreading	
Fluoroester II†	0.5	Nonspreading	1.5

* $\gamma_{LV} = 27.8$

†Bis(1H,1H-undecafluorohexyl)3-methylglutarate

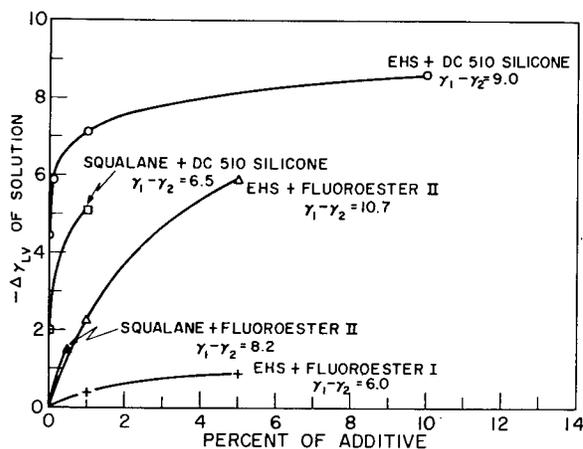


Fig. 4 - Surface tension lowering in squalane and in bis(2-ethylhexyl)sebacate as a function of concentration of surface-active solute

centered on the disk and the drop of the aromatic hydrocarbon (surface tension = 34.4 dynes/cm) on the underside of the cover slip above it is displaced from the center by two millimeters, the interchange of vapor between the two drops will lower the surface tension of the isopropyl 1,9-diphenylnonane and raise the surface tension of the squalane on the sides of the drops nearest each other. As a result of the surface tension disbalance across each drop the aromatic hydrocarbon will move away from the squalane drop,

but the latter will move in the same direction, so that one drop appears to pursue the other. Since both of these compounds have vapor pressures low enough to permit their use as the stationary phase in gas-liquid chromatography, this experiment shows that extraordinarily small differences in surface tension are sufficient to produce bulk movements of oil if the surface tension gradient can be maintained over an interval of minutes or hours.

4. The rapid dendritic (or lobar) spreading of type 4 is characteristic of oils containing a strongly surface-active additive which lowers the surface tension of the additive-containing oil by 5 dynes/cm or more, and which is also strongly adsorbed at the oil/solid interface. The dendritic pattern usually follows the direction of microscratches produced during polishing. It is believed that spreading occurs initially along these capillary scratches, which are effectively open capillaries with a radius of curvature of only a few hundred angstroms. A liquid forming a contact angle of less than 90 degrees with the solid will spread along such a capillary even though it may be nonspreading on a plane surface. The filling of such capillaries is not directly observable with an optical microscope, but indirect evidence is obtainable after the oil has had time to diffuse over the metal surface adjacent to the scratches. A breath pattern of the surface then reveals a network of hydrophobic bands which eventually fuse into a

continuous hydrophobic ring outside the drop. Capillary spreading occurs with all nonspreading oils, but in the absence of unusual surface tension effects the process slows or stops within a millimeter as the oil reaches dead ends in the scratch structure or as the viscous drag on oil moving through long capillaries starves the advancing front. The total volume of oil removed from the drop is then negligible. However, if the surface tension lowering agent originally present is strongly adsorbed at the metal surface, the surface-to-volume ratio in the tiny capillary may be so great as to permit extensive depletion of additive from the oil advancing through the capillary. This raises the surface tension of the oil in the capillary with respect to the central drop which produces a surface flow outward along the capillary. The viscous drag of this flowing film carries additional oil beneath it toward the tip of advancing liquid (Marangoni effect) (9,10). This flow may lead to the formation of an actual mound of oil near the outer end of the capillary. Thus surface tension gradients produced by adsorption from thin advancing films of liquid provide a powerful mechanism for the transport of bulk oil along a solid surface. The changes in surface tension which may result from adsorption can be estimated from Fig. 4, in which the change in surface tension of the solution ($\Delta\gamma_{LV}$) is plotted against the concentration of additive present.

The whole dendritic spreading process is relatively rapid; after one or two hours the pattern becomes nonspreading and usually remains unchanged for weeks. In the absence of scratches, a related depletion process may occur along the edge of the main drop in a random way to initiate lobes which spread most rapidly at the point furthest from the main drop. Such lobar spreading is usually slower and less extensive than the typical dendritic spreading along scratches. Oils which show dendritic spreading on polished stainless steel or sapphire are either nonspreading or develop lobar patterns when applied to scratch-free surfaces of blown or melt-drawn glass.

It is clear from the foregoing that the formulation of a nonspreading oil requires a discerning choice of the amount and nature of the adsorbable additive. The additive should be appreciably soluble in the base oil over the temperature range contemplated, it should adsorb promptly from the leading edge to give a film from which the oil retracts, and it should lower the surface

tension of the base oil by less than 5 dynes/cm. In addition, it should not be more volatile than the base oil and should not be altered by hydrolysis or oxidation in such a way as to increase the free surface energy of the adsorbed film. Polydimethyl siloxanes and their slightly phenylated analogs are useful only with aliphatic oils having surface tensions below about 29 dynes/cm. The moderately phenylated DC 550 silicone, on the other hand, was found to produce a stable nonspreading composition giving a contact angle of 14 degrees when added to isopropyl 1,9-diphenylnonane ($\gamma_{LV} = 34.4$). Although bis(2-ethylhexyl)sebacate is nonspreading on a predeposited film of the DC 510 silicone (Table 4), a 1% solution of this silicone in the same ester spreads on clean steel; the film initially adsorbed from this solution is clearly not equivalent to one prepared from the silicone in a volatile hydrocarbon solvent. The behavior of the fluoroesters as additives probably depends upon trace hydrolysis to give strongly adsorbed fluorinated alcohols or half esters. The purified ester was nonspreading even shortly after percolation, but it has been shown (7) that esters are readily hydrolyzed by the water normally adsorbed at an alumina surface; a similar behavior on the oxidized stainless steel surface is probable. The fluoroesters are promising additives for the ester type oils most likely to satisfy low-temperature requirements because they produce much smaller lowerings of the surface tension of the diesters than the methyl silicones give, but nevertheless deposit low-energy adsorbed films. The present work has examined representatives of a few classes of additives; further work using the guidelines set forth may be expected to produce more nearly optimum combinations than are reported.

Effect of Organic Surface Contaminants

An examination of the behavior of nonspreading formulations on oil-contaminated, shop-soiled, or abraded surfaces (Table 5) indicates that practical nonspreading oils must have surface tensions above 30 dynes/cm. This restriction is understandable in terms of the concept of the critical surface tension γ_c , the established laws for spreading pressure, and the spreading of one liquid on another. These relations are illustrated in Table 6, which records spreading data for a variety of liquids on some low energy surfaces. If a solid

TABLE 4
Contact Angles of Various Liquids on Silicone Films
Over a Stainless Steel Substrate*

Liquid	Contact Angle (degrees)		
	On DC 200	On DC 510	On DC 550
DC 200 silicone	-	-	spreads
DC 510 silicone	9	-	-
DC 550 silicone	26	11	-
DC 710 silicone	47	31	12
Squalane	43	25	-
Bis(2-ethylhexyl)sebacate	48	25	ca 3
Isopropyl 1,9-diphenylnonane	56	31	25
Methylene iodide	77	-	48
Water	95		
n-octane	6		
n-decane	13		
n-dodecane	24		
n-tetradecane	30		
n-hexadecane	35		

*Films were prepared by adsorption from bulk silicone oil followed by repeated washing with benzene.

surface is covered with a thin film of organic material which exposes aromatic or oxygenated structure at the air interface, the critical surface tension γ_c may readily exceed 30 dynes/cm. Since aliphatic hydrocarbon liquids do not have surface tensions above 30 dynes/cm, any oil having such a base must spread upon the contamination. The behavior of aliphatic diester oils, which usually have surface tensions in the range of 30 to 32 dynes/cm, will be marginal in the presence of organic contaminants. Oils having higher surface tensions than the aliphatic esters do not spread on such surfaces.

One significant feature of Table 6 is the anomalous behavior of fluoroesters I and II on an octa-

decylamine monolayer. Both liquids show higher contact angles on this surface than on Teflon, although the latter has a significantly lower critical surface tension. This anomaly results because these esters, even after percolation, contain minute amounts of fluoroalcohols and fluorinated acid esters produced by hydrolysis. These hydrolysis products displace octadecyl amine from the stainless steel surface giving a fluorinated surface of lower critical surface tension. The data show that monolayers of phenylstearic acid and of barium dinonylnaphthalene sulfonate are not displaced in similar circumstances. The fluorinated esters are nonspreading on clean stainless steel because of the same hydrolysis products.

TABLE 5
Effect of Surface Contamination or Roughness
on Behavior of Nonspreading Oils

Surface	Spreading Behavior				
	Bis(2-ethylhexyl)sebacate		Squalane +1% DC 510	P_1 †	Mil-L-3918‡
	+1% Fluoroester II*	+5% Fluoroester II			
Polished stainless steel	Nonspreading	-	Nonspreading	Nonspreading	Nonspreading
Sapphire	-	-	Nonspreading	Nonspreading	Nonspreading
Pyrex plate	-	-	-	Nonspreading	Nonspreading
Naval Brass (clean)	Slight spreading	Nonspreading	Nonspreading	Slight lobes	Nonspreading
Abraded stainless steel (600 A paper)	Slight spreading	Slight spreading	Slight spreading	Slight spreading	Nonspreading
Brass—not cleaned	Nonspreading	Slight spreading	Slight spreading	Nonspreading	Nonspreading
Chrome plate—not cleaned	Slight spreading	Lobes	Lobes	Slight spreading	Nonspreading
1020 steel—not cleaned (smooth)	Nonspreading	Slight spreading	Slight spreading	Slight spreading	Nonspreading
Nickel—not cleaned	Nonspreading	Nonspreading	Nonspreading	Nonspreading	Nonspreading
Surface tension of solution (dynes/cm)	28.0	24.4	22.7	28.3	32.3

*Bis(1H,1H-undecafluorohexyl)3-methylglutarate.

†Experimental nonspreading oil containing 97.75% bis(2-ethylhexyl)sebacate, 1.0% barium dinonylnaphthalene sulfonate, 1.0% fluoroester II, and 0.25% phenolic oxidation inhibitor.

‡Military specification nonspreading oil.

Pretreatment with Silicone Films to Prevent Oil-Spreading

Films of stearic acid or metal stearates have been used previously to prevent spreading of oil in watch and clock mechanisms (11-13). In connection with the present work it has been noted that silicones are readily and rapidly adsorbed on stainless steel, brass, sapphire, quartz, and glass to form films over which none of the oils studied will spread. The silicones have been reported to adsorb to give films several times as thick as a stearic acid monolayer (14). The sili-

cones are much more resistant to oxidation than are aliphatic carbon structures, and have low volatility, so that silicone films may be expected to have long useful lives. The critical surface tension of a dimethyl silicone film is about 23 dynes/cm, which is closely comparable with the critical surface tension for stearic acid or stearate films. Tests showed that nonspreading behavior persisted for test drops that had been in contact with the silicone treated surface for nine months. All of the base oils studied were nonspreading on a film adsorbed from DC 510, a lightly phenylated methylphenyl polysiloxane.

TABLE 6
Spreading Behavior of Various Oils and Reference Liquids
on Some Low Energy Surfaces

Liquid	Surface Tension	Contact Angle (degrees)						On Thin Film EHS† on SS
		On Teflon	On Octadecylamine Monolayer on SS	On Phenylstearic Monolayer on SS	On BaDNNS Monolayer on SS	On Polyethylene		
Fluoroester II*	19.6	Spreads	26	Spreads	Spreads	Spreads	-	
Squalane + 1% DC 510	22.7	42	18	Spreads	Spreads	Spreads	-	
Fluoroester	24.3	19	49	18	16	4	-	
n-Hexadecane	27.3	46	39	Spreads	Spreads	Spreads	-	
EHS‡ + 1% Fluoroester II*	28.0	58	41	Spreads	Spreads	Spreads	-	
EHS‡ + 1% Fluoroester I†	29.9	62	45	ca 4	12	Spreads	-	
Mil-L-3918	32.3	68	50	17	20	8	7	
Isopropyl 1,9-diphenylnonane	34.4	73	53	29	31	9	13	
Methylene iodide	50.3	88	69	55	-	52	-	
Critical surface tension dynes/cm		18	22	ca 28	29	32	ca 31	

*Bis(1H,1H-undecafluorohexyl)3-methylglutarate
†Bis(1H,1H,7H-dodecafluoroheptyl)3-methylglutarate
‡Bis(2-ethylhexyl)sebacate

Films of the silicones having different degrees of phenylation can be arranged in a series according to increasing γ_c of the treated surface. DC 550 and DC 710 silicones spread on their own films, but not on films from silicones having a lower degree of phenylation (Table 4).

Silicone films are readily deposited from extremely dilute benzene solutions, so that films of submicron thickness can be formed uniformly and reproducibly either by dipping the instrument into a very dilute solution and draining, or by applying a light film of the dilute solution as an aerosol spray. Such films could be renewed at the time of cleaning the instrument by including a very small amount of a suitable silicone in the cleaning solvent.

It was also shown that the silicone film responsible for the nonspreading was not removed by repeated washing in benzene. It appears desirable to use a silicone of relatively high molecular weight to reduce volatility and to decrease the rate of lateral flow. The film should be kept below 300Å to reduce lateral flow as well as to minimize dust collection by the treated surface. The utilization of thicker resin-type films for the control of oil spreading is described in another report from this Laboratory (15).

EXPERIMENTAL MATERIALS AND PROCEDURES

The bis(2-ethylhexyl)sebacate (EHS) used in this study was prepared from lubricant grade diester by fractionation in a molecular still and percolation through Florosil adsorbent before use. The other aliphatic esters were research preparations which were percolated through Florosil before use. The fluoroesters were pure materials prepared at this Laboratory for other purposes (16-18). They were repercolated through Florosil before use. The fluoroester prepared from a telomer alcohol, bis(1H,1H,7H-dodecafluoroheptyl)3-methylglutarate, is referred to as fluoroester I, that prepared from an alcohol terminated by a perfluoromethyl group (1H,1H-undecafluorohexylalcohol) is designated as fluoroester II, and tris(1H,1H,4H-hexafluorobutyl)tricarallylate as fluoroester III.

The squalane (2,6,10,15,19,23-hexamethyltetracosane) was material represented to have an iodine number of 7.5 or less (Eastman No. 7311). It was treated with concentrated sulfuric acid, washed, and percolated through silica gel and

Florosil before use. The absence of polar impurities was shown by its nonspreading on clean water. The pristane (2,6,10,14-tetramethylpentadecane) was a commercial sample which was twice percolated through silica gel and Florosil. The cetane (η -hexadecane) was a high purity material which was percolated through silica gel and Florosil before use. Isopropylbiphenyl, supplied by the Monsanto Corporation, was percolated through alumina and Florosil before use. The isopropyl 1,9-diphenylnonane was a research sample supplied by the California Research Corporation (19) and was percolated through alumina and Florosil before use. It was a mixture of the meta and para isomers. The grade 1010 petroleum oil was a light aircraft engine oil supplied under specification Mil-O-6081/B(ASG). It was percolated through alumina, fuller's earth, and Florosil.

The DC 510 silicone was material supplied commercially by the Dow Corning Corporation. It was used after percolation through Florosil except in the cases where the use of the nonvolatile residue from stripping in a molecular still is specified. This residue was also percolated through Florosil before use. The dimethyl silicone DC 200, the moderately phenylated DC 550, and the highly phenylated DC 710 were obtained from Dow Corning; they were percolated through alumina and Florosil before use. The fluorosilicone was a sample supplied by Dow Corning Company under the designation QF-1-0065. It had a nominal viscosity of 1000 cs and was percolated through alumina and Florosil.

Wetting behavior was studied mostly on stainless steel surfaces (304 SS: 18% Cr, 8.0% Ni, 2.0% Mn, 0.75% Si) which formed the ends of short cylinders, 3/4 in. in diameter by 1/2 in. long. Special care was exercised to prepare the test pieces from bar stock containing a minimum of microscopic inclusions and voids. The cylinders were ground to exact height and polished on a pitch lap to a high mirror finish. The surface was cleaned immediately before use by a light polishing with gamma alumina on a metallographic wheel, rinsed with hot distilled water, and dried at room temperature. Sapphire and fused quartz surfaces were cleaned in the same manner before use. Oil droplets were applied to test surfaces with a freshly flamed platinum wire. The drops commonly had initial diameters 0.03 to 0.10 cm and were observed under a metallurgical microscope with vertical incident illumination.

Contact angles of five degrees or more were measured with a contact angle goniometer. Angles of less than five degrees were determined by measurement of the spacing of interference bands generated by monochromatic light on the slope adjacent to the drop edge. This technique permits a precision of 0.1 degree or better with such small angles. True nonspreading edges were readily distinguished from the edges of slowly spreading drops by the different appearance of the first interference band; this band was sharp and spaced uniformly with the adjacent bands for true nonspreading, but was widened and displaced outwards from uniform spacing in the case of slow-spreading liquids.

The test surface with the oil drop in place was protected from aerosols and dust during observation and storage by enclosing it in a glass cylinder three millimeters larger in diameter and two millimeters higher than the test piece. The upper end of the glass cylinder was covered with a standard microscope cover slip through which observations were made. The small volume of air enclosed and the very low head room between the test surface and the cover slip reduced aerosol contamination so that test drops could be studied over storage periods of as long as 12 months. Experience indicates that oily aerosols, e.g., from tobacco smoke, are a major source of contamination for clean surfaces.

CONCLUSIONS

1. A wide variety of hydrocarbon oils ranging in surface tension from 25 to 45 dynes/cm can be rendered nonspreading on clean smooth stainless steel, sapphire, or glass by the inclusion of a suitable additive.

2. A wrong choice of surface-active additive may lead to rapid spreading in characteristic branched or lobed patterns. This behavior is caused by surface tension gradients resulting from extensive adsorption of the additive out of thin films at the edge of the drop or in capillary scratches leading away from the edge.

3. A useful nonspreading additive should not favor the development of surface tension gradients in the liquid surface. Gradients will be prevented if the additive has a minor effect on the surface tension of the liquid or if it is not depleted from thin films in sufficient amount to change the surface tension of the oil-additive solution significantly. In general, additive liquids whose surface

tensions are less than five dynes/cm lower than that of the base oil are unlikely to give anomalous spreading.

4. A nonspreading oil should have a surface tension above 32 dynes/cm to prevent its spreading when the adjacent surface is contaminated with organic matter. Such contamination rarely raises the critical surface tension for spreading above 31 dynes/cm.

5. All ordinary instrument oils are nonspreading on a preadsorbed film of a dimethyl silicone or a lightly phenylated phenylmethyl silicone. Such films are readily deposited from dilute solution in a cleaning solvent. They are nonvolatile, oxidation resistant, and not readily removed by solvents.

REFERENCES

1. Bascom, W.D., Cottington, R.L., and Singleterry, C.R., "Dynamic Surface Phenomena in the Spontaneous Spreading of Oils on Solids," NRL Report 5963, in press
2. Peterman, R., *Schweiz. Arch. Angew. Wiss. Tech.* **26**:45 (1960)
3. Barker, G.E., Alter, G.E., Jr., McKnight, C.E., McKlveen, J.R., and Hood, D.M., ASTM Bull. No. 139, p. 25, Mar. 1946
4. Barker, G.E. (to Elgin Watch Co.), U.S. Patent 2,355,616, Aug. 15, 1944, U.S. Patent 2,412,956, Dec. 24, 1946, U.S. Patent 2,583,200, Jan. 22, 1952
5. O'Rear, J.G., "Synthesis and Characterization of Esters and Ethers for Nonspreading Lubricants," NRL Report 3891, Dec. 14, 1951
6. Portnoy, S., Verderame, F.D., Messina, J., and Gisser, H., *Chem. Engr. Data Ser.* **3**:287 (1958)
7. Fox, H.W., Hare, E.F., and Zisman, W.A., *J. Phys. Chem.* **59**:1097 (1955)
8. Zisman, W.A., "Relation of Equilibrium Contact Angle to Liquid and Solid Constitution," presented before "Symposium on Contact Angle, Wetting, and the Adhesion of Liquids to Solids," American Chemical Society, Los Angeles, Apr. 2, 1963
9. Scriven, L.E., and Sternling, C.V., *Nature* **187**:186 (1960)
10. Thomson, James, *Phil. Mag.* **10**(Ser. 4):330 (1855)
11. Bulkley, R., and Snyder, G.H.S., *J. Am. Chem. Soc.* **55**:194 (1933)
12. Woog, P., *Compt. Rend.* **181**:772 (1925)
13. Woog, P., "Contribution a l'etude du Graissage Onctuosite," Delagrove, Paris (1926)
14. Perkel, R., and Ullman, R., *J. Polymer Sci.* **54**:127 (1961)
15. Bennett, M.K., and Zisman, W.A., "Prevention of Liquid Spreading or Creeping," presented before "Symposium on Contact Angle, Wetting, and the Adhesion of Liquids to Solids," American Chemical Society, Los Angeles, Apr. 2, 1963
16. Faurote, P.D., Henderson, C.M., Murphy, C.M., O'Rear, J.G., and Ravner, H., *Ind. Eng. Chem.* **48**:445 (1956)
17. Romans, J.B., and Singleterry, C.R., *J. Chem. Engr. Data* **6**:56 (1961)
18. Jarvis, N.L., and Zisman, W.A., *J. Phys. Chem.* **64**:150,157 (1960)
19. Wilgus, D.R., Ettling, A.C., and Pino, M.A., *J. Chem. Engr. Data* **6**:106 (1961)