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Dynamic Surface Phenomena in the Spontaneous Spreading of Oils on Solids

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*Surface Chemistry Branch
Chemistry Division*

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A detailed study has been made by interference microscopy and ellipsometry of the spontaneous spreading of a variety of nonpolar liquids on smooth, clean metal surfaces. Spreading is generally characterized by the advance from the bulk liquid of a primary film having a thickness of much less than 1000Å; this primary film is usually followed by a considerably thicker secondary film. The movement of the secondary film is the result of a surface tension gradient across the transition zone between the primary and secondary films. This gradient is produced by the unequal evaporative depletion from these two regions of a volatile contaminant having a lower surface tension. If the volatile contaminant has a higher surface tension than the main component the direction of this surface tension gradient may be reversed so that the liquid recedes rather than spreads. Removal of the relatively more volatile constituents from the test liquid eliminates the spreading of the secondary film but not the spreading of the primary film. Under some conditions movement of liquid onto the solid surface may also occur by vapor transport and by capillary flow of liquid through microscratches.

INTRODUCTION

The tendency of certain liquids to spread spontaneously, *i.e.*, "creep" over solid surfaces, is sometimes desirable and sometimes a distinct annoyance. Lubrication engineers must often rely upon the creep of oils to carry the lubricant to surfaces which otherwise would be inaccessible. On the other hand, the ease with which some liquids will creep out of a container and contaminate the surrounding area can be most disconcerting. The spontaneous spreading of liquids over solids is not simple, and it presents an intriguing problem in surface chemistry which has not received the detailed attention it deserves.

There have been three previous studies of spontaneous spreading which are pertinent to this present investigation; Sir William Hardy's studies in this area (1), the somewhat later work of Bangham and Saweris (2), and the recent studies by Zisman and coworkers (3) of liquids spreading on polar surfaces.

Hardy (1), in his classic study of boundary lubrication, gave careful attention to the spreading of drops of water and of various polar organic liquids on clean surfaces of glass and steel. He

observed that a film not sensibly visible of liquid about 1-micron thick spreads from a drop and that this primary spreading may or may not be followed by spreading of the drop itself. These two distinct processes Hardy termed the primary and secondary spreading respectively, and he arrived at some interesting conclusions concerning the nature of the primary film. It was his opinion that this film is usually many molecules in thickness and that it has a surface tension greater than that of the liquid itself. This primary film he termed "contractile" in that it pulls the liquid drop out to form a secondary spreading. He also concluded that the primary film is formed only by deposition of liquid from the vapor.

Bangham and Saweris (2) observed the behavior of various liquids on freshly cleaved mica. They found that of the many polar and nonpolar liquids observed on this surface in air, only a few would spread spontaneously and none of the substances would spread when the surrounding atmosphere was saturated or supersaturated with vapor. Their conclusions were essentially the same as Hardy's, except that they believed the primary film could be formed by surface diffusion of molecules from the drop edge as well as by deposition from the vapor.

Zisman and coworkers (3) studied the spreading of liquids on both the nonpolar surfaces of organic solids and the polar surfaces of metals,

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oxides, and glass. They have determined experimentally that for nonpolar surfaces of organic solids and for close-packed monolayers of organic molecules adsorbed on polar solids there exists a critical surface tension of wetting, γ_c , characteristic of the surface (4). Liquids having surface tensions greater than the value of γ_c of any given solid surface will not spread on that solid. Their experiments with polar solids demonstrate that organic liquids will usually spread on these surfaces unless it happens that the liquid forms a monolayer that has a γ_c value lower than the surface tension of the liquid itself (5).

The experimental work of the present investigation deals exclusively with hydrocarbons showing zero contact angles on the surfaces studied. Their spontaneous spreading behavior on both horizontal and vertical surfaces was observed by interference microscopy and ellipsometry, which allowed the study of the topography of the spreading films in considerable detail. The spreading of these liquids is characterized by the formation of an extremely thin primary film, much thinner than the 1 micron suggested by Hardy; the primary film is often but not invariably followed by a much thicker secondary film. An important aspect of the geometry of spreading films revealed by interference techniques is the development of a ridge between the primary and secondary regions of the film. This observation, along with a careful study of the effect on spreading of surface roughness, the chemical constitution of the solid surface, and the chemical composition of the liquid, permits us to propose a mechanism of spontaneous spreading. The proposed mechanism is entirely consistent with the experimental results and satisfactorily explains why certain liquids that have a zero angle with the solid show no tendency to spread spontaneously and why certain others actually show a receding behavior.

Any explanation of the observed spreading behavior must account for the fact that a film of liquid many hundreds of molecules deep can spread upward against gravity over an already developed primary film of the same liquid. Hardy (1) and Bangham (2) believed that spontaneous spreading of the secondary film occurs because the liquid in the primary film ahead of it has a higher surface tension. They attributed this higher surface tension to interaction between the molecules of the primary film and the solid substrate,

even though the surface of the primary film was many molecules away from the liquid/solid interface. The work of Zisman (3), however, shows that the exterior surface of a close-packed monolayer of a compound such as stearic acid on a polar solid has a critical surface tension characteristic of the exposed methyl end groups, and nearly the same as the critical surface tension of a paraffin crystal face exposing similar groups. This finding argues against long range effects of a polar solid on the surface tension of an overlying liquid. Experimental results reported by the authors in the present paper suggest an alternate source of surface tension gradients capable of producing the observed spreading phenomena and develop a mechanism for bulk transport in liquid films. It also describes further experiments designed to test the ability of the theory to predict spreading behavior.

EXPERIMENTAL METHODS

The Metal Surfaces

The stainless (18-8) steel plates used to study vertical spreading were 1/4-inch thick, cut in 1 × 2 inch rectangles, and were machine ground on all sides; one of the faces was polished to an optical mirror finish. Prior to each experiment all surfaces of the steel plate were cleaned of adsorbed polar contamination by polishing on a metallographic wheel with alumina powder suspended in water and then rinsed in a strong stream of distilled water to remove adhering particles. The plate was placed on end on a washed piece of filter paper, covered, and allowed to dry. The presence of surface contamination could be detected by the tendency of the water film to retract and drain irregularly from the affected area. In such an event the plate was recleaned. For studies of horizontal spreading, stainless steel disks 3/4 inch thick and 3/4 inch in diameter were prepared with one face highly polished. They were cleaned and handled in the same manner as the rectangular plates.

Evaporated films of Nichrome metal deposited on glass microscope slides were also employed. The glass slides were cleaned by chemical methods and then by glow discharge in the evaporation chamber. Nichrome wire was evaporated onto the glass to give an opaque coating.

The Spreading Liquids

The liquids, whose spreading behaviors were observed, are listed in Table 1 with their surface tensions and viscosities at 25°C. The surface tensions were determined by the ring method with appropriate corrections (5,6) and the viscosities were measured in an Ostwald-Cannon capillary viscometer.

Polar impurities were removed from the organic liquids by percolation through columns of activated Florisil adsorbent. The absence of polar contamination was assumed if a drop of the percolated liquid would not spread on a clean water surface. Passage of the alkyl aromatic liquids through Florisil did not always achieve sufficient purification; some required passage through fuller's earth adsorbent as well.

Soap Adsorbates

The barium salt of dinonylnaphthalene sulfonic acid $\text{Ba}(\text{DNNS})_2$ was prepared by metathesis of the sodium salt with barium chloride (7).

An aqueous solution of potassium perfluorodecanoate was prepared by dissolving 0.016 g of the free acid into 10 ml of distilled water and exactly neutralizing with aqueous potassium hydroxide. The resulting solution was diluted with distilled water to a concentration of 3×10^{-4} mol/l of the potassium salt.

The Observation of Spreading by Interference Microscopy

Profiles of the liquid films were plotted from photomicrographs of the interference bands taken with conventional microphotographic equipment. The light source was a mercury vapor lamp from which the mercury green line (5460A) was isolated by a filter mounted so it could be moved out of the light path to permit observation of the film with polychromatic illumination. For the observation of films on vertical surfaces a metallographic microscope was mounted in a horizontal position on an optical bench. The metal specimens were supported vertically from the lower end of a rod adjustably

mounted on a separate carriage. Another carriage positioned beneath the specimen bore a table whose vertical location was alterable by a rack and pinion movement. This table carried a small beaker of the liquid under study. A draining film was formed by bringing the table and beaker up until the plate was about three-quarters wet by the liquid. The beaker was sufficiently wide so the plate could be kept away from the meniscus curvature near the beaker walls. The immersion was done slowly and smoothly so that the liquid surface formed a horizontal line across the face of the plate. Drainage was initiated by lowering the beaker with as smooth a movement as possible by squeezing the table and the supporting carriage between the thumb and forefinger in the manner of pulling the trigger of a gun. The film drainage was particularly sensitive to any jerky or hesitant movement in lowering the beaker. Unusual edge effects were not propagated into the central area of observation. The geometry of the liquid at the bottom edge of the plate had no detectable effect on the upper part of the film if the bottom edge was more than 2 cm from the section studied. The usual practice was to keep the lower end of the plate touching the surface of the liquid.

All spreading experiments were performed at 25°C in a constant temperature room. The metal plates and disks were allowed to come to thermal equilibrium before an experiment commenced. The steel disks on which horizontal spreading was studied were protected from airborne dust and aerosols by a covered glass cell through which the spreading liquid could be observed microscopically. The vertical steel plates and coated slides were not enclosed, but ellipsometric determination of the rate of contamination indicated that it required nearly a day for a layer 10A in thickness to accumulate, whereas observations on the vertical plates were limited for the most part to the first 4 or 5 hours. It was not always possible to determine the film profile unambiguously from a single interference photomicrograph when the film of liquid developed a ridge or a ridge and a trough. Progressive changes in band widths on a given photomicrograph were sometimes helpful in indicating the presence of a maximum or minimum, which could then be confirmed by viewing the film with polychromatic illumination and noting the sequence of interference colors.

TABLE 1
Surface Tensions and Viscosities of the Spreading Liquids

Liquid	Surface Tension (dynes/cm)	Kinematic Viscosity (centistokes)
Aliphatic Hydrocarbons		
Hexane	18.4	0.46
n-Hexadecane	27.6	4.0
Pristane (tetramethylpentadecane)	25.6	7.3
Squalane (hexamethyltetracosane)	27.6	26.8
Squalene (hexamethyltetracosahexene)	31.0	17.0
Aromatic Hydrocarbons		
Dodecylbenzene	31.5	21.7
Polyamyl-naphthalene	32.2	101.6
Amylbiphenyl	34.2	17.4
Liquid Polymers		
Polyisobutylene*	28.3	346.0
Polychlorotrifluoroethylene (Kel F)†	27.4	49.4
Polychlorobiphenyl (Arochlor 1221)‡	41.8	6.7
Methyl Silicone Oils§		
7 cs oil	19.2	6.9
7 cs oil, fraction	19.4	7.5

*Amoco Chemicals Corp.

†Minnesota Mining and Mfg. Co.

‡Monsanto Chemical Co.

§Dow Chemical Co.

The Ellipsometric Determination of Film Thickness

The principal use that was made of the ellipsometer was to study the upper edge of the films on vertical plates where the thickness became less than 1000Å and could not be observed with the interference microscope. The ellipsometric measurement of film thickness is described in the literature (8, 9). For the purposes to which the technique was applied here, the approximate equation given by Drude (9) relating the film thickness and refractive index with the optical parameters of the incident and reflected light was entirely adequate. In order to use the Drude approximations it was necessary to assume the refractive index of the liquid film to be the same as that of bulk liquid. These approximate equations are highly inaccurate for film thickness greater than 100Å.

The films studied with the ellipsometer were of uniform thickness in the horizontal direction but varied in thickness continuously in the vertical direction. It was therefore desirable that the area of film viewed by the instrument be as narrow as possible in the vertical direction so that the film thickness in the observed area would be nearly constant. The aperture of the instrument was therefore reduced to a narrow horizontal slit by cementing two pieces of razor blade edge across the 1-mm opening to leave a 0.2-mm space between them. Any further reduction in the slit width diminished the light intensity beyond the working sensitivity of the instrument.

When viewed through a relatively wide aperture (1 × 2 mm), regions of the film having thickness greater than $\lambda/4$ exhibited interference bands in nearly the same position as the interference bands observed with unpolarized, normal incident light. Although there is not an exact correspondence between the bands observed in the two different ways, the interference bands retained their identity and did not move significantly even with a complete change of setting of the quarter-wave plate and analyzer of the instrument. Therefore, an approximate film thickness was computed from these bands, taking account of the angle of incidence imposed by the ellipsometer.

RESULTS

The spreading of selected high molecular weight organic liquids was observed on both horizontal and vertical surfaces by interference microscopy. Liquids having low vapor pressures were taken so that evaporation of the spreading liquid would have a negligible effect on film thickness. This choice provided relatively viscous liquids whose spreading was slow and conveniently observed. As much as was possible the liquids were chosen to have comparable viscosities so that differences in their spreading behavior could be identified with other factors than viscosity. The choice of spreading liquids was limited to relatively non-polar materials because molecules having highly polar functional groups were generally adsorbed on metal surfaces to form monomolecular films over which the liquid cannot spread (3).

The behavior which was found characteristic of many liquids on horizontal surfaces is illustrated by the photomicrographs (Fig. 1A) of a drop of squalane on a polished, stainless steel disk. Measurements were made of interference band spacing and of band widths and from these measurements the film profiles for each photomicrograph were plotted as in Fig. 2. The dome shaped profile initially assumed by the drop had within an hour developed a plateau region and was advancing with the leading edge at a small angle to the solid surface. After three hours the drop still maintained an apparent angle with the solid and a ridge had developed behind the leading edge. The individual profiles could not be drawn to an experimental intercept of the horizontal axis because the first order interference band corresponds to a liquid layer about 1000Å thick.

Careful examination of these drops revealed that a thin film of liquid invisible with the interference microscope extended out ahead of the apparent edge of the spreading liquid. The actual angle of contact with the solid is therefore zero and not a finite angle as the interference photomicrographs might suggest. Breath patterns formed by breathing over the spreading drop indicated that the outer edge of the film was distinctly ahead of the first order interference band. These experiments also showed that the

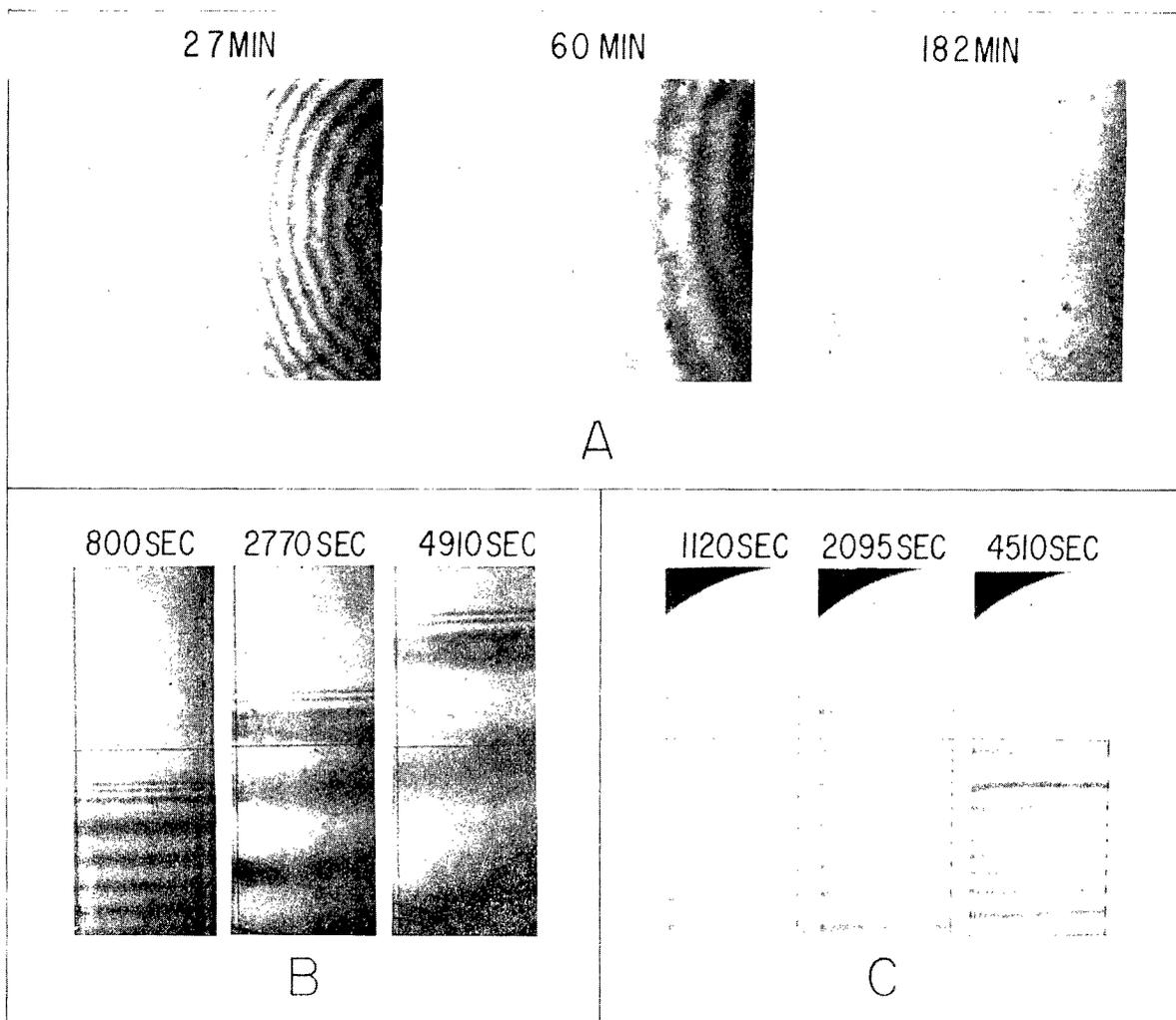


Fig. 1 - Interference photomicrographs: (A) Squalane drop spreading on a horizontal steel surface; (B) Squalane film spreading up a vertical steel plate; (C) A film of polyamyl-naphthalene receding down a vertical steel plate.

advancing edge of this invisible film was close to the visible edge during the initial stages of spreading but that the distance between them increased as the liquid spread. The presence of this very thin film was also demonstrated by placing ahead of the visible edge minute drops of another liquid, such as isopropyl 1,9-diphenylnonane, having a surface tension higher than that of squalane. When placed on the invisible film such drops would immediately retract from the spreading liquid but when placed on clean metal surface they would spread uniformly in all directions.

The upward spreading of liquid on vertical surfaces was in many respects similar to the be-

havior observed on horizontal surfaces. Photomicrographs for squalane on a polished stainless steel plate are presented in Fig. 1B; the upward spreading of the edge is evidenced by the progressive displacement of the first order interference fringe from the stationary reference line. The film profiles plotted in Fig. 3 were drawn from the corresponding interference photomicrographs. The dotted lines in this figure and in all the other figures represent the profile for purely hydrodynamic drainage calculated from an equation given by Jeffreys (10):

$$x = \frac{g}{v} h^2 t$$

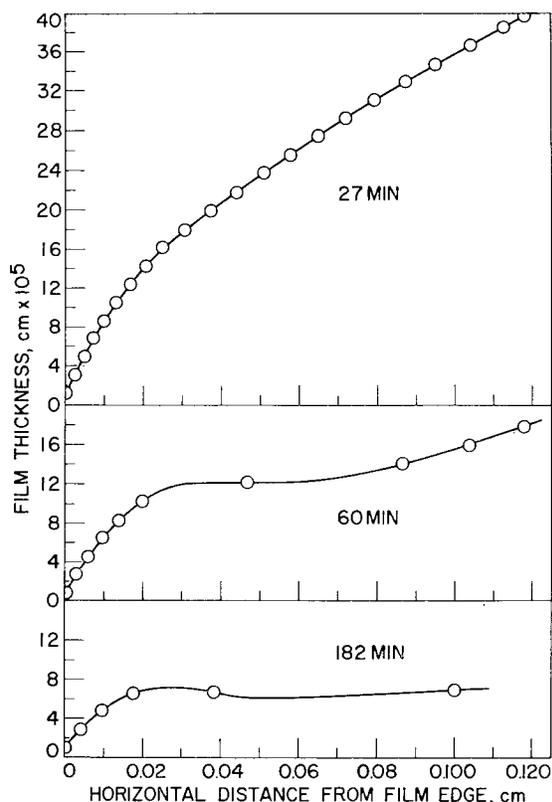


Fig. 2 - Profiles of the edge of a squalane drop spreading radially on a horizontal steel surface. Horizontal scale expanded 250 times vertical scale.

where x is the distance along the plate measured from the initial position of the liquid surface when drainage began, h is the film thickness, t the time of drainage, and ν is the kinematic viscosity of the liquid. This equation was derived for laminar flow from a vertical plate without including the effect of surface forces, and so by superimposing the calculated profiles on the experimental film profiles it is immediately evident to what extent surface forces have disturbed the hydrodynamic drainage of the liquid.

The position of the liquid surface when drainage began, which corresponds to the point on the plate from which the hydrodynamic profile is drawn ($x = 0$), was determined by plotting the displacement of the film edge from the reference line against the time of drainage. The displacement was a reasonably linear function of the time so that the data could be extrapolated to $t = 0$ and the intercept taken as the initial position of the liquid surface. It should be noted that the

horizontal scale of film thickness has been expanded 250 times the vertical distance scale. The actual slopes, therefore, lie much closer to the vertical than the figures suggest. The film profile, if plotted to equal scales in the two dimensions, would have been almost indistinguishable from the edge of the figure.

Inspection of the film profiles shows that the apparent angle of contact that the upper edge of the film makes with the plate and the progressive development of a ridge of liquid at the leading edge resemble the spreading phenomena observed on horizontal surfaces. For this particular experiment this geometry was maintained through the first 6000 sec, after which there was a gradual decline in the maximum height of the ridge and in the apparent angle of contact. As had been observed for drops of squalane on horizontal surfaces, breath patterns and indicator drops demonstrated the presence of liquid ahead of the first order interference band of squalane films on vertical plates.

The extent and thickness of the primary film, which was invisible with the interference microscope but detectable by breath patterns, were investigated directly with the ellipsometer. Quantitative ellipsometric measurements indicated that in the early stages of spreading the primary film was particularly thin and extended only a short distance ahead of the first order interference band. A region of the plate from the first order interference band to 8 mm above it was scanned with the ellipsometer after 1 and 5 hr of drainage. The settings for the instrument over this entire region were the same as for light reflected from the bare steel substrate. Evidently the primary film does not extend far enough beyond the first order interference band at these times to allow resolution of its width by the 0.2-mm slit of the ellipsometer.

Successful quantitative measurements of the thickness of the squalane primary film were possible after 18 and 42 hr of drainage. The film profiles determined from these measurements are shown in Fig. 4. The film thickness was measured at various distances from a reference line drawn on the metal plate. The points plotted at about 1200Å thickness correspond to the first order interference fringe. These measurements demonstrate a sharp change in the slope of the film and also a tendency for the primary film to thicken over the 24-hr period. Undoubtedly there

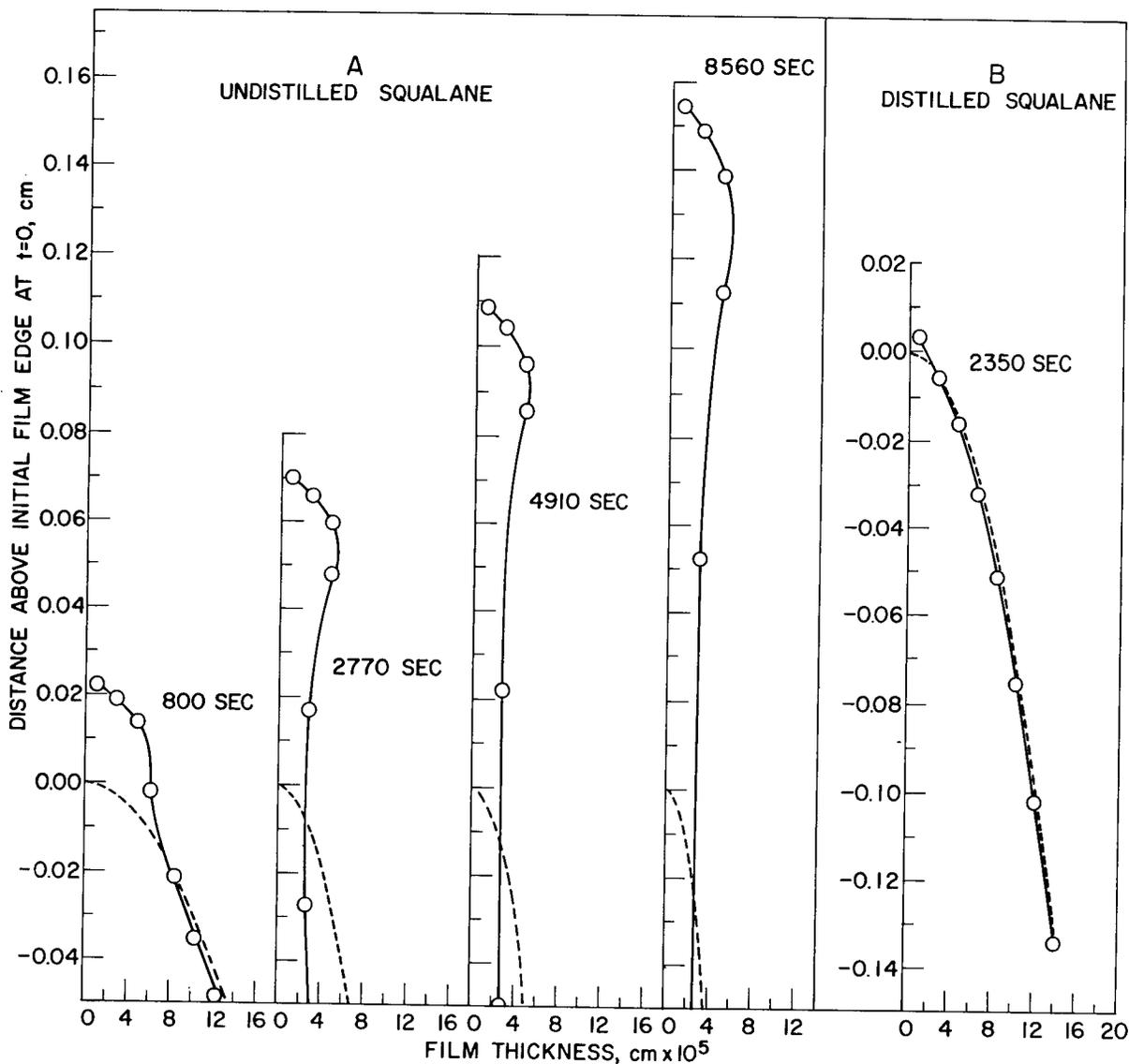


Fig. 3 - Film profiles for: (A) Undistilled squalane spreading up vertical steel plates, (B) Distilled squalane spreading up vertical steel plates. Horizontal scale expanded 250 times vertical scale.

is some error in the measurement of film thickness where the thickness is changing abruptly and also near 100A where the Drude calculations of film thickness are invalid. However, such errors would not alter substantially the inference of an abrupt change in film slope just outside the first order interference fringe.

The presence of a ridge near the leading edge of a spreading film conflicts with the equilibrium configuration required by surface tension and gravity, for liquid forming a zero contact angle

with a plane solid surface. To explain the presence of a ridge it is necessary to look for transient phenomena of a dynamic rather than a static character. However, a static experiment was found which proved particularly helpful in defining the conditions required for the formation of a ridge of liquid at the leading edge of spreading films. Specifically, a ridge was observed at the upper edge of films draining from vertical plates when upward spreading had been prevented by forcing the edge of the film to assume a finite

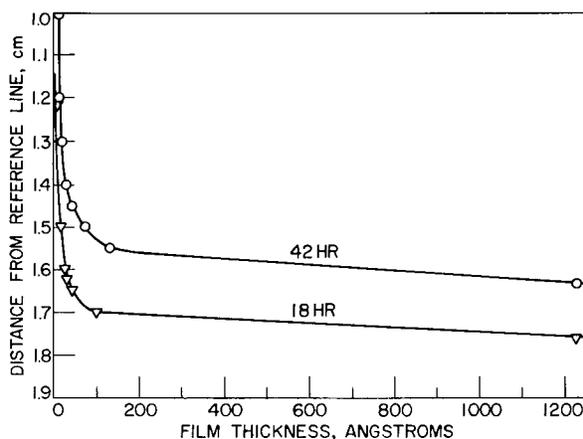


Fig. 4 - Ellipsometrically determined profile of the leading edge of a squalane film spreading up a vertical steel plate. Horizontal scale expanded 10^6 times vertical scale.

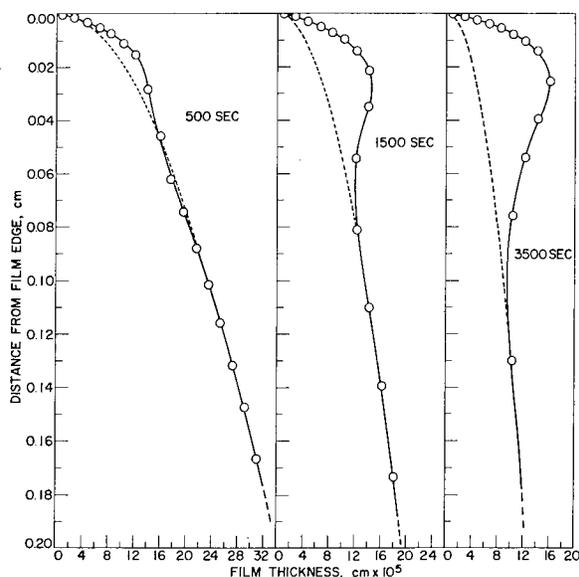


Fig. 5 - Film profiles of a squalane film draining from a perfluorodecanoate barrier on a vertical steel plate. Horizontal scale expanded 250 times vertical scale.

contact angle with the plate. To do this a narrow band of potassium perfluorodecanoate monolayer was deposited across a clean metal plate about three-quarters of the distance from the bottom edge by touching the plate with a silk string that had been wet with an aqueous solution of the soap. It was already known that squalane will not spread on a close-packed monolayer of these perfluorinated molecules. The plate was dipped

into a vessel of squalane until the barrier was in the liquid surface and drainage was initiated by lowering the vessel from this position.

The profiles of a squalane film draining from a perfluorodecanoate barrier are presented in Fig. 5. The film established itself some distance below the visible residue left by the aqueous soap solution, presumably at the edge of the perfluorodecanoate monolayer. The presence of the barrier entirely prevents spreading and imposes a contact angle of slightly over 1 degree on the upper edge of the film. A ridge of liquid developed at the upper edge of the film and this geometry was maintained for the 72 hr during which the film was observed. Below the ridge the drainage corresponds closely to that predicted for purely hydrodynamic flow.

In a second experiment drainage was initiated from about 1 mm below the region of the barrier. At first the upper edge of the squalane film spread in the same manner as the film shown in Fig. 3, but when the liquid reached the barrier the upward spreading of the film ceased. However, there was a sustained flow of liquid from the film below up to the stationary edge where the liquid formed into a ridge. The ridge formed in this manner reached the same dimensions as the ridge that had been observed at the upper edge of draining films that had been originated at the barrier. This experiment demonstrated the spontaneity of ridge formation whenever the surface of the liquid was forced to assume a finite contact angle with the plate. The explanation of ridge formation by spreading squalane then requires some dynamic mechanism which will maintain a nearly constant slope of the advancing edge of the secondary film in the face of the zero contact angle required for a spreading liquid.

The Effect of Volatile Constituents

A large part of the spontaneous spreading behavior observed for squalane and for other liquids was found to be due to the presence of materials which had a greater volatility than the main constituent but were otherwise chemically similar. This was first suspected when it was found that different batches of squalane had very different spreading behaviors even though each batch had been carefully cleaned of polar contaminants. When a batch of squalane was molecularly distilled, three fractions were obtained having slightly higher volatilities than the main

fraction (Table 2A). The result of removing these volatile materials was to reduce drastically the rate of upward spreading on a vertical plate and to eliminate any evidence of ridge formation at the advancing edge (Fig. 3B). In Fig. 6A the vertical distance spread is plotted as a function of time for a distilled and undistilled squalane. The rate of spreading, *i.e.*, the slope of the plot, was relatively large for the undistilled material, about 2.5×10^{-5} cm/sec. Over the same time interval the rate of spreading of the stripped material was nearly zero. The spreading rate for the undistilled squalane appears nearly constant in Fig. 6A but after 20 hours had decreased to 0.05×10^{-5} cm/sec.

Experiments were made to determine to what extent the original spreading behavior of the distilled squalane could be reinstated by adding to the

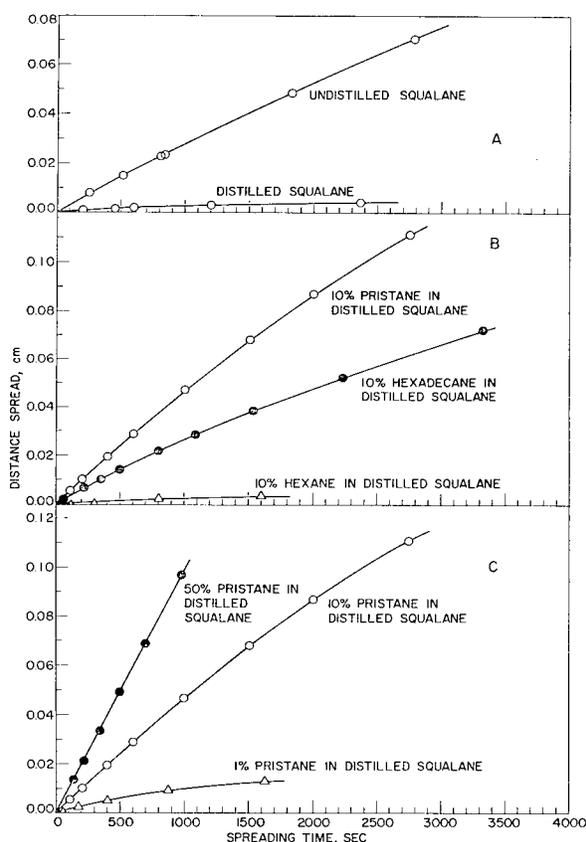


Fig. 6 - Comparison of distance spread vs time on vertical steel plates for: (A) Distilled and undistilled squalane, (B) 10% mixtures of hydrocarbons in squalane, (C) Various mixtures of pristane in squalane.

stripped material various amounts of saturated hydrocarbons more volatile than squalane itself. In Fig. 6B the spreading rate of distilled squalane is compared with the rates for 10% mixtures of distilled n-hexane, distilled n-hexadecane, and pristane in distilled squalane. These three hydrocarbons were chosen because they have volatilities greater than squalane, the difference being greatest for hexane. The hexadecane and pristane, a branched saturated hydrocarbon having a slightly higher molecular weight than hexadecane, have nearly the same boiling point, but the surface tension of pristane is 25.6 dynes/cm whereas hexadecane has a surface tension of 27.6 dynes/cm. Addition of lower molecular weight hydrocarbons did restore spontaneous spreading behavior to squalane but not in proportion to the volatility of the additive. Despite their comparable volatilities, the mixtures of pristane and hexadecane with squalane did not have identical spreading properties. The pristane mixtures spread nearly twice as fast as the hexadecane mixture. Evidently, the surface tension of the more volatile component is also of importance. The highly volatile hexane, on the other hand, did not have any noticeable effect on the spreading behavior of the distilled squalane. Figure 6C shows that increasing the concentration of pristane increased the spreading rates, but the rate of the 50% pristane mixture was not five times the rate of the 10% mixture.

The invisible or primary film that had been detected in advance of spreading squalane was not eliminated by distilling the liquid but was, at any given time, distinctly farther ahead of the apparent edge of a film of distilled liquid than it was for the undistilled liquid. After about an hour of draining and spreading on a vertical plate, breath patterns revealed liquid on the surface 3 or 4 mm in front of the stationary visible edge of distilled squalane whereas at this relatively early time no primary film was detectable by this technique ahead of the advancing edge of a film of undistilled squalane.

The radial spreading of squalane on horizontal surfaces also was markedly reduced after distillation. Figure 7 shows that, after an initial gravitational spreading, drops of distilled and undistilled squalane both reach nearly constant spreading rates which are less than half as great for the distilled as for the undistilled liquid. As on the vertical plates, the advancing edge of the stripped

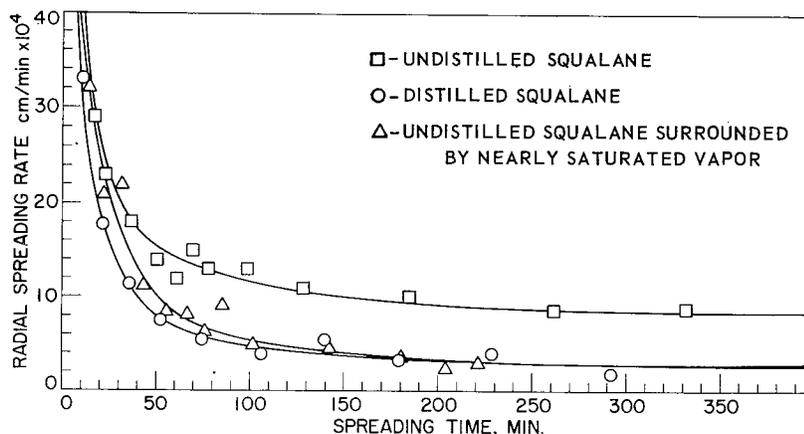


Fig. 7 - Radial spreading rates of squalane drops on horizontal steel surfaces.

squalane did not show any ridge formation. Breath patterns demonstrated a primary film considerably ahead of the drop of distilled squalane.

Further evidence that spontaneous spreading is associated with the evaporation of volatile components from the liquid appeared when it was found that the spreading tendency of undistilled squalane could be reduced to that of the distilled material by saturating the surrounding air with vapor from the liquid. This effect was demonstrated by applying a film of undistilled squalane to the inside of the glass cell enclosing the test specimen. Figure 7 shows that such a drop in an atmosphere nearly saturated with its own vapor spread at a rate almost identical with that of the distilled squalane.

In order to test the generality of the observations on the spreading of squalane, spreading tests were made with a variety of viscous nonpolar liquids, including a group of polymeric materials. To insure scratch-free and reproducible surfaces, these spreading experiments were made on Nichrome films vacuum deposited on microscope slides. The spreading behavior grouped these liquids into three classes.

Group I - Liquids which spread upward exhibiting a primary film and a secondary film with nearly constant slope at the leading edge (n-hexadecane, pristane, squalane, squalene, and the polymer liquids; polychlorobiphenyl, polymethylsiloxane, polyisobutylene, and polytrichloroethylene).

Group II - Liquids whose edge remains stationary except for the development of a zero contact angle and a primary film above the original boundary (dodecylbenzene and highly purified liquids containing only a single molecular species).

Group III - Liquids whose edge appears to recede from the original boundary, but leaves a primary film and shows a zero contact angle (amylbiphenyl and polyamyl-naphthalene).

In group I the rate of upward spreading and the volume of liquid lifted above the original boundary varied widely but showed no simple correlation with structure or viscosity. The film profiles for films of these liquids at about 1000 sec of drainage are given in Fig. 8 and the spreading rates for these liquids can be seen in Fig. 9. The polymeric liquids, which are known to consist of mixtures of macromolecules of differing molecular weight and volatility, showed some of the most spectacular upward spreadings; *e.g.*, polyisobutene, most viscous of the liquids examined, had one of the highest spreading rates. A 7-cs dimethylsiloxane isolated from a higher molecular weight oil as a narrow distillation fraction spread much less vigorously (Fig. 9A) than a commercial dimethyl silicone of the same viscosity.

Both group II and group III liquids were alkyl aromatic hydrocarbons known from their methods of preparation to be mixtures of molecules having different alkyl substitution and molecular weight. Liquids of group III had an unusual receding behavior (Figs. 1C and 10A). No true

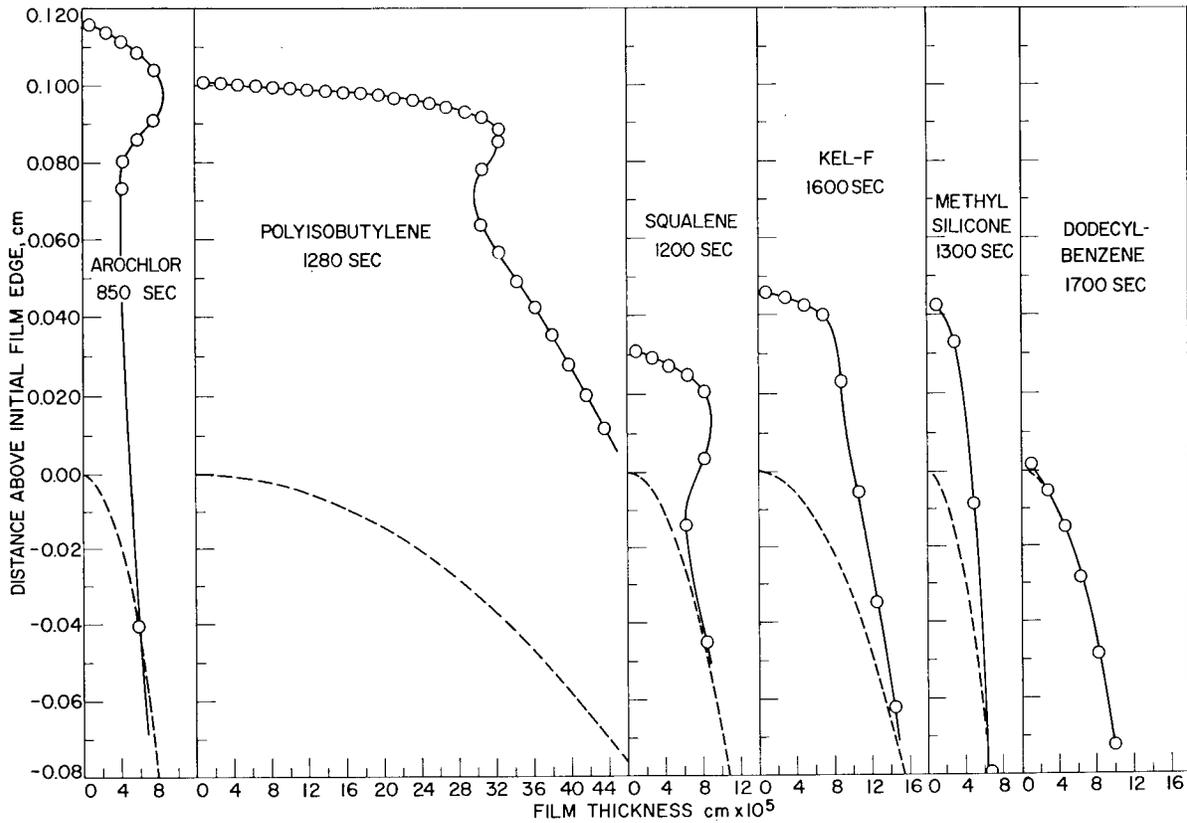


Fig. 8 - Film profiles for various liquids spreading upward on vertical Nichrome surfaces. Horizontal scale expanded 250 times vertical scale.

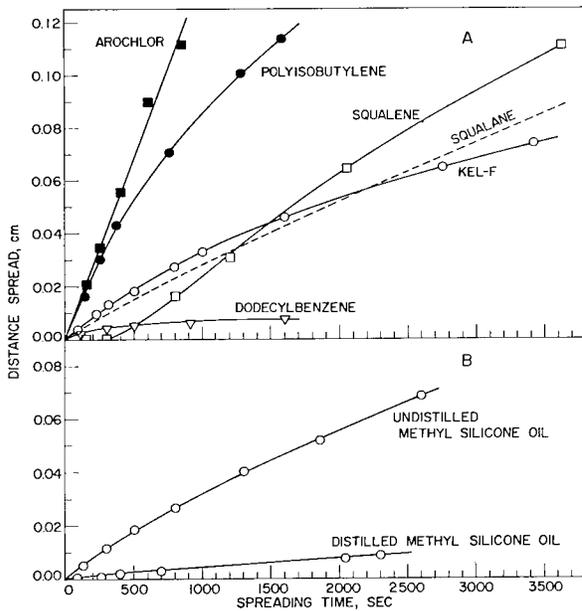


Fig. 9 - Comparison of distance spread vs time for various liquids: (A) Comparison of different structural types, (B) The effect of the degree of heterogeneity of a polydimethyl silicone liquid.

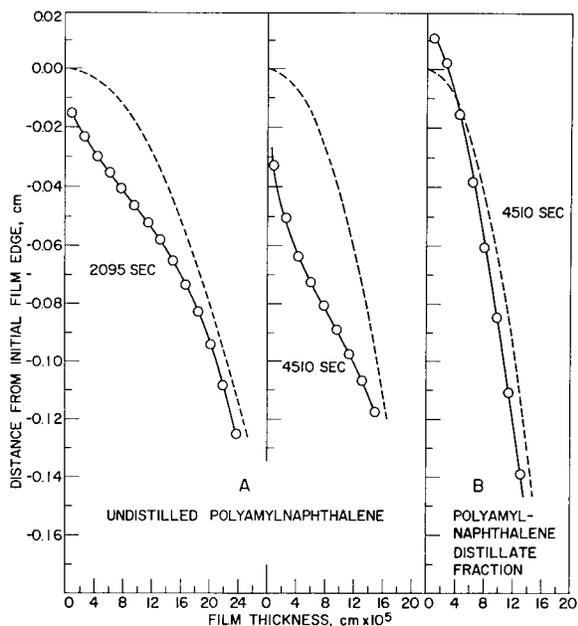


Fig. 10 - Film profiles on vertical steel plates for: (A) Undistilled polyamyl-naphthalene, (B) A fraction distilled from polyamyl-naphthalene. Horizontal scale expanded 250 times vertical scale.

contact angle greater than zero was formed; the broadening of the first interference band showed that the liquid surface approached the plane of the solid asymptotically. A drop of the polyamyl-naphthalene on a horizontal stainless steel surface spread initially under gravity but spreading stopped after a few minutes. The drop was dome

shaped but it showed no definite contact angle with the surface. The recession of the apparent boundary reported here is not to be confused with the much more common retraction of liquids which form definite contact angles. Fractional distillation of the polyamyl-naphthalene reduced its tendency to recede on a vertical surface, and one of the fore run fractions even spread upward slightly (Fig. 10B). Tables 2 and 3 show that the surface tensions of the main fractions remaining after stripping of volatiles from squalane and from polyamyl-naphthalene differed from those of the original fluids by only 0.4 dyne in each case. However, it is significant that the surface tension of the squalane was increased by stripping, while that of the polyamyl-naphthalene was lowered. Another significant fact about the group I and group III liquids was that the heat from a concentrated light source, when directed so as to strike one side only of the drop on a horizontal surface, accelerated the spreading of group I liquids and the recession of group III liquids.

The Effect of Surface Finish of the Solid on the Rate of Spreading

The stainless steel surfaces employed in this study were optically polished on a pitch lap. They appeared scratch-free at 50X magnification with bright field illumination, but micro-scratches could be detected with dark field

TABLE 2
Properties of the Distillation Fractions of Squalane

Fraction	Temperature Range (°C at 1-4 μ Hg)	Volume (ml)	Surface Tension (dynes/cm)	Refractive Index
Original	-	500	28.2	1.4523
1	30-50	1.5	26.5*	1.4451
2	50-60	7.5	27.5	1.4461
3	60-65	27	28.5	1.4510
4	65-70	55	28.6	1.4525
5	70-80	355	28.6	1.4525
Residue	-	43	28.6	1.4525

*Determined by maximum bubble pressure method.

TABLE 3
Properties of the Distillation Fractions of Polyamyl-naphthalene

Fraction	Temperature Range (°C at 8 mm Hg)	Volume (ml)	Surface Tension (dynes/cm)	Refractive Index
Original	-	250	32.2	1.5479
1	175	5	32.9	1.5590
2	175-178	15	32.2	1.5515
3	179-186	50	32.4	1.5530
4	187-190	15	32.9	1.5543
Residue	-	100	31.8	1.5460

lighting. The plates were cleaned between tests by polishing on metallurgical felt charged with fine alumina. Although their surfaces appeared highly polished to the unaided eye, microscopic investigation showed that both the number and the depth of the scratches increased by almost an order of magnitude with repeated cleaning. Differences noted in the spreading of a given liquid up new and repolished surfaces prompted the use of melt-drawn microscope slides, on which Nichrome had been vacuum deposited. These surfaces showed no microscratches in dark field illumination.

The effect of random surface scratches (ca. 1.0 micro-inch rms hill height in the worst specimens) was to increase by as much as 50% the spreading rate of liquids that spread, but rough-

ness did not cause spreading of the "nonspreading" squalane obtained by distillation. Increased spreading rates on rough surfaces were usually associated with smaller constant slopes at the edge of the secondary film. The effect of scratches was examined more specifically by comparing spreading rates on plates treated to obtain a strong pattern of unidirectional scratches parallel to or perpendicular to the direction of spreading. Figure 11 shows that scratches in the direction of spreading accelerate the rate, while those at right angles to the oil movement reduce the spreading rate slightly below that on the smooth Nichrome coated slide. When these experiments were repeated with distilled squalane, this liquid was not induced to spread by a favorable scratch configuration.

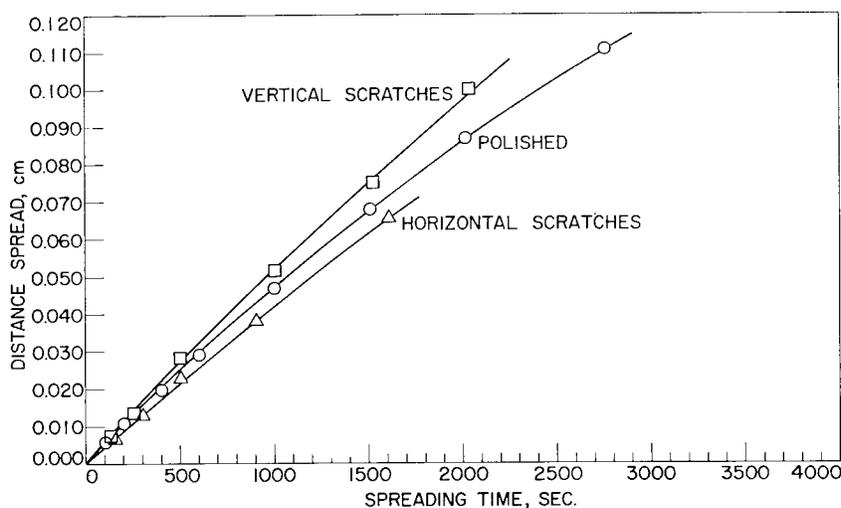


Fig. 11 - The effect of directional scratches on the distance spread vs time for 10% pristane in distilled squalane on vertical steel plates.

The Effect of the Surface Energy of the Solid on Spreading

It was to be expected that spreading rates and spreading geometries for a given liquid were essentially the same on the two metal surfaces, Nichrome and stainless steel. We were surprised to encounter essentially the same rate and spreading geometry on a stainless plate coated with a close-packed monolayer of barium dinonylnaphthalene sulfonate. Such a surface has been shown to have a critical surface tension for spreading of 29 dynes/cm, closely comparable with that for a polyethylene surface (7). This value of γ_c is only a minor fraction of the surface energy for a clean metal oxide surface. Tests with a 0.5% solution of barium dinonylnaphthalene in squalane ruled out the possibility that the monolayer was desorbed by the advancing oil. It appears that, given a liquid that wets a solid at a zero contact angle, the surface energy of the substrate is not an important factor in determining the rate of secondary spreading.

DISCUSSION

A systematic explanation of the spreading phenomena observed requires consideration of mechanisms which will account for the invariable advance of a primary film, relate the presence of volatile impurities to the spreading of secondary films, the frequent development of a ridge at their leading edge, and also account for the distinct recession of some liquids from a boundary at which they exhibit a zero contact angle. It should also explain the upward transport of significant amounts of liquid in films a micron or more thick.

In the case of the slightly volatile liquids studied, the primary film is considered to advance largely by surface diffusion. While evaporation does occur from squalane at 25°C, the rate is so low that the amount transferred across an 0.08-cm air gap between plane parallel surfaces of squalane and clean stainless steel during 72 hr is not great enough to be measurable with the ellipsometer. This instrument is capable of detecting the deposition of a monolayer or more of the hydrocarbon on clean steel. deBoer (11) has pointed out that the energy of activation for the lateral motion of a physically adsorbed molecule is significantly smaller than that required for desorption to the

vapor phase. The few surface diffusion constants of large organic molecules which have been measured appear to be of the same order of magnitude as the self-diffusion constants of similar molecules in the liquid phase (12). This magnitude appears adequate to account for the observed rates of advance of the primary film. These rates will vary with the concentration gradient between bulk film and clean metal and, more significantly, with the gradient resulting from differences in the energy of adsorption of the organic molecules on bare metal oxide and on a monolayer or more of the liquid species. Thus the crowding of the primary film by advancing bulk liquid sharpens the gradients and promotes faster diffusional advance. When the advance of bulk oil ceases, diffusion widens the primary film, reduces the gradient, and slows the diffusion rate.

Another factor which modifies the spreading rate of the primary film is the presence of microscratches or other microroughness on mechanically polished surfaces. These scratches are often 1000Å or less in width and have width-to-depth ratios of no more than ten (13). The radius of curvature of such a trough may be as small as 1×10^{-5} cm. The pressure difference across a concave squalane surface wetting such a scratch will be of the order of kilograms per square centimeter. It is sufficient to induce rapid flow of oil along the bottom of the scratch until the radius approaches infinity. Such open capillaries fill well ahead of the true diffusional advance of the primary film. Liquid spreads laterally from them by surface diffusion, so that a breath pattern reveals a network of squalane wetted strips ahead of the slow moving film boundary.

The secondary film advances over a primary film which is generally more than a monolayer in thickness. Both the experimental results and a consideration of the nature of the primary film indicate that differences between the surface energy of the clean solid and the surface tension of the liquid do not contribute materially to its upward movement against gravity. It is proposed that the movement of the secondary film results from a surface tension gradient produced in and near the advancing edge by differential exhaustion of a more volatile species, this exhaustion being greater the thinner the film. If the loss of volatile species raises the average surface tension of the liquid, surface tension will be highest in the primary film, decreasing to that of the original

liquid mixture as the film becomes thicker. As a result of this surface tension gradient the surface of the film will be drawn upward; the effect will extend as far as does the gradient itself. This movement of the surface layer will necessarily entrain some of the underlying liquid in accordance with hydrodynamic principles. As shown by the diagram of Fig. 12 the movement of liquid is greatest in the layer nearest the surface, which tends to increase the slope of the advancing edge of the secondary film. The process continues until this effect is balanced by gravity and the tendency of surface curvatures to be ironed out by surface contraction. This balance produces a steady state slope or false contact angle which decreases slowly over many hours as the more volatile component is exhausted from the bulk film. Such quasi-constant slopes are an invariable feature of rapid spreading.

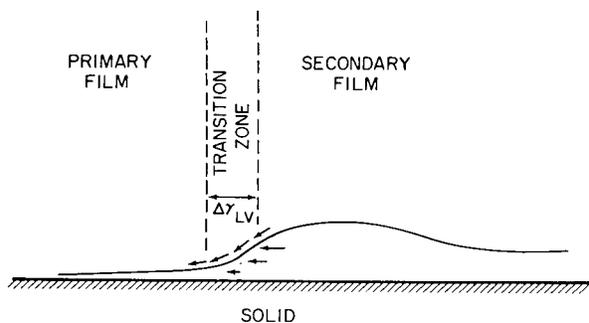


Fig. 12 - A schematic representation of the flow pattern responsible for secondary spreading.

This explanation for the upward migration of thick liquid films is not new; it was advanced over a hundred years ago by Thomson (14) to explain the "tears of strong wine" phenomenon. He suggested that the creep of liquor up the glass wall was due to a surface tension gradient maintained by progressive depletion of alcohol from the ascending film. We are not aware that this explanation has been extended before to the spreading of low volatile liquids.

This explanation of spreading is in agreement with the data reported. The spreading rate of squalane is dramatically reduced by removal of more volatile components in a molecular still. The fractions removed have lower surface tensions than either the original mixture or the undistilled residue. Spreading of the purified

squalane is enhanced by the addition of either hexadecane or pristane, which have higher and comparable volatilities and lower surface tensions than squalane. The increase in spreading rate is a function of the amount of volatile liquid added; for equal concentrations of either liquid the rate is increased more by pristane, which has a lower surface tension than hexadecane.

The complete failure of the 10% hexane in squalane mixture to spread is disconcerting until the rates of exhaustion of the various liquids from a thin film are examined quantitatively. Making reasonable assumptions about evaporation rates and diffusional transport of the volatile component through the solution, it can be shown that half of the hexane would be lost from a film 10 microns thick in one second.* Half exhaustion of hexadecane from an equally thick film would require several hours. Thus the surface tension gradients produced by the evaporation of hexane disappear before any detectable flow of the viscous squalane has occurred.

A more critical test of an evaporatively induced surface tension gradient as an explanation of spreading behavior is afforded by the alkyl aromatic liquids, which either do not spread or which actively recede from their original boundary while maintaining a zero contact angle. In the case of the alkyl biphenyls and alkyl naphthalenes, the fractions of lower molecular weight and higher volatility have higher surface tensions than the major high boiling component. This is because polyaromatic structures give higher surface tensions than aliphatic structures, and the proportion of polyaromatic component in the polyalkyl naphthalenes and biphenyls decreases as the size of the aliphatic substituent is increased. Figure 13 shows that the relation between molecular weight and surface tension for the alkyl polyaromatics is the inverse of that for aliphatic hydrocarbons. As a result of this inverse relation

*In calculating the depletion rates of hexane and hexadecane from films of their mixtures with squalane it was assumed that (a) the squalane is for all practical purposes nonvolatile, (b) that the mixture of hydrocarbons behaves ideally, and (c) that loss from a given film thickness is not replenished by lateral diffusion of solute from adjacent liquid. The calculated depletion times represent minimum values since the failure of any of the assumptions would lower the rate of loss. It was also calculated that a very slight concentration gradient between the surface and the base of the film would cause transport of solute to the surface as rapidly as it was removed by evaporation, so that the difference between the bulk and surface concentration is not an important factor in the spreading mechanism.

the surface tension of the primary film is reduced by evaporative loss of the more volatile component and the surface flow is from the primary film towards the bulk liquid. This flow pattern causes the film edge to recede on the vertical plate and opposes the normal radial flow under gravity of drops on horizontal surfaces. Figure 13 also reveals why the alkyl benzenes show little tendency to advance or recede; there is almost no variation in surface tension with the degree of alkyl substitution in this particular series, so that loss of lower homologs by evaporation does not produce significant surface tension gradients.

The formation of a ridge of thicker film is a common but not an invariable characteristic of rapid spreading; the cause of ridge formation is clarified by considering the case in which a ridge developed at the upper edge of a stationary vertical film. This occurred when a barrier to spreading was placed above a squalane film by depositing a band of potassium perfluorodecanoate monolayer. The squalane moved upward until it reached the edge of the barrier, where it developed a stable contact angle of about one degree.* Liquid continued to flow up the plate, however, until a distinct ridge developed. This ridge then persisted unchanged for many hours while the film below drained away in the manner required by the Jeffrey equation. Given a small but stable contact angle representing an equilibrium of surface forces, ridge formation can be seen to follow as a further consequence of this equilibrium. Because of the weight of liquid it must support, the upper surface of the film curves downward from the angle imposed at the barrier. The situation is crudely analogous to that of a flexible rod attached to a vertical wall at a fixed angle and progressively loaded at points away from the wall. A mechanical equilib-

*The equilibrium contact angle the squalane film formed at the barrier film edge requires explanation since it differs from the zero angle normally found on clean metal surface or the near 80° contact angle to be expected for squalane on a perfluorodecanoate monolayer (15). The small angle results because the edge of the barrier is not a straight line on the molecular scale but is a series of micropeninsulas and bays. The edge of the squalane is dragged against the peninsulas by the advance of liquid over clean steel at either side until a contact angle develops at the peninsula tip. The existence of the contact angle about the tip creates a local thickening of liquid film at this point. The action of surface tension to minimize the liquid surface thickens adjacent sections of the film, so that these also develop a finite angle at the film barrier. The apparent contact angle observed is the average of these effects when the angle developed becomes just sufficient to support the liquid retained in the resultant ridge.

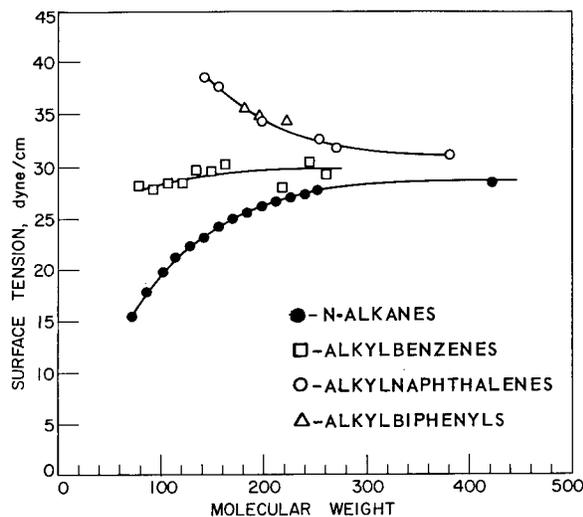


Fig. 13 - The change in surface tension with molecular weight for various groups of hydrocarbons.

rium must ultimately be reached at which surface forces balance the weight of liquid that is restrained from draining by the fixed slope at the upper edge of the film. In principle, the equilibrium shape of the ridge can be determined analytically from the general equation for the mechanical equilibrium of an interface in a gravitational field (16) but such a calculation is involved and has not been undertaken.

Once it is clear that ridge formation is a consequence of a slope at the film edge, the formation of a ridge at the leading edge of rapidly spreading liquids is readily understood. In the moving film, dynamic effects maintain the necessary fixed angle and a ridge forms unless the rate of upward liquid transport is great enough to maintain the spreading film at a thickness as great as that of the required ridge. In this exceptional case a shelf or plateau is formed, which may develop into a ridge as spreading continues.

When a drop of liquid is allowed to spread on a smooth horizontal surface, similar phenomena are observed, but the spreading pattern is modified because the gravitational forces are much smaller and operate to promote spreading rather than to oppose it. There is an initial gravity-driven spreading during the first few minutes, after which the hydrodynamic forces become negligible in comparison with the surface forces. The primary and secondary films then appear and ridges or plateaus form as in the case of upward spreading. Oils purified by removal of more

volatile components spread extremely slowly and maintain the characteristic domed profile of a static drop. A liquid containing volatile impurities of lower surface tension, on the other hand, usually takes the form of a plateau a few microns thick, which thins as spreading continues, but maintains uniform thickness within one or two wavelengths of light. This leveling is a logical consequence of the spreading mechanism proposed, since any variation in film thickness creates a surface tension gradient tending to pull liquid into the thinner portions.

The observation in this work and by Bangham (2) that in the presence of nearly saturated vapor the spontaneous spreading tendency of a drop is suppressed is entirely consistent with the proposed mechanism. The evaporative depletion of solute from the liquid edge is prevented by the presence of surrounding vapor.

The observed spreading behaviors were promoted by surprisingly small differences in surface tension between the primary and secondary films. The lot of undistilled squalane which spread most vigorously had a surface tension of 27.6 dynes/cm. The surface tension of purified squalane is 28.6 dynes/cm, which indicates that, at the advancing film edge of impure squalane, the maximum possible difference in surface tension between the primary and secondary films is 1 dyne/cm if all the more volatile components were lost from the primary film. Since the surface tension gradients are small, contaminants having comparable volatilities but minor differences in their surface tensions may produce significantly different spreading rates. A 10% solution of pristane in squalane has a surface tension of 28.3 dynes/cm, while a 10% solution of hexadecane in squalane has a surface tension of 28.5 dynes/cm. Since the surface tension of the purified squalane is 28.6 dynes/cm and pristane and hexadecane have comparable volatilities, the potential driving gradient for spreading of the pristane solution is approximately three times that for the hexadecane solution.

The similarity between the spreading behavior of impure squalane on clean stainless steel and on steel coated with a monolayer of barium dinonylnaphthalene sulfonate provides further support for the explanation of spreading offered here. The surface energy of the monolayer-coated steel is only a fraction of that for the clean oxide coated surface, but the monolayer's critical

surface tension for spreading (29 dynes/cm) is above the surface tension of the squalane. Consequently the latter gives a zero contact angle and forms a primary film on the monolayer. Since secondary spreading occurs over a primary film in both cases, the explanation proposed requires the spreading behavior on the two surfaces to be similar, and is in agreement with experiment.

Another support for the theory is furnished by the contrasting behaviors of the boundaries of drops of squalane and of polyaminonaphthalene when one side of each drop is warmed by a concentrated light beam. The heated boundary of the squalane drop spreads ahead of the unheated boundary on either side, while the heated edge of the drop of alkyl aromatic liquid recedes even more rapidly than the adjacent boundary. Evidently the heat, in each case, accelerates the process of evaporative depletion and thereby augments the surface tension gradient already present. If only the decrease in surface tension due to the increased temperature were operative, the heated squalane film should also have receded.*

The theory of spreading proposed makes it possible to select additives for almost any liquid in such a way as to either enhance or counteract its tendency to spread. Experiment verified that undistilled squalane could be made nonspreading for several days by the addition of 5% of isopropylbiphenyl. The latter has a surface tension 7 dynes/cm higher and a boiling point 50°C lower than squalane, so that evaporation at the edge of a film lowers the surface tension relative to the bulk liquid mixture instead of raising it. The polymethylsiloxane liquids are often troublesome because of their excessive spreading, but it was shown that the addition of small amounts of a more volatile methylphenyl silicone having a higher surface tension prevented spreading for two to three weeks.

*An interesting example of surface tension flow induced by temperature effects alone has been noted in thin films of silicone liquids on horizontal glass or metal plates heated to 400°C. Because of the great difference between the temperature of the plate and the air above it there is a sharp vertical temperature gradient in the liquid film. The surface of any thin spot in the film will be hotter and have a lower surface tension than thicker portions near it. Consequently the film is unstable and the liquid draws up into small droplets, distributed over a much thinner film against which they nevertheless show zero contact angles. The droplets spread as soon as the temperature is lowered.

PRACTICAL IMPLICATIONS

The spreading phenomena reported here have more than academic significance; they modify or control the performance of liquids in lubrication, in surface coating, and in the application of insecticides.

In the lubrication of ball bearings, oil is transported by surface creep from the grease supply to the raceway; this creep is favored by the molecular heterogeneity of ordinary petroleum oils, whose more volatile components have lower surface tensions than the total oil mixture. If one undertakes to lubricate with a radiation resistant alkyl aromatic oil, however, the situation may be reversed, and the deliberate inclusion of a minor amount of an oil of lower surface tension is indicated. The recession phenomena reported for silicone liquids on a 400°C surface remind us that at the high temperatures and temperature gradients existing in some military equipment oil films may be expected to migrate away from the hottest points on the surface, which may be where the lubricant is needed.

In the spray application of thin coatings it is important that the droplets spread quickly to cover bare islands on the surface; the results of this study point the way to formulations in which a high spreading rate is assured by the choice of solvents of suitable volatility and surface tension. Similar considerations apply to the spraying of disinfectants and insecticides.

The excessive creeping tendency that causes polymeric liquids such as polyisobutylene and the

methyl silicones to contaminate their surroundings can be counteracted by the addition of small amounts of a suitably chosen liquid.

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