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## Prevention of Liquid Spreading or Creeping

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The spreading of liquids over solid surfaces can be prevented by three different approaches: (a) the liquid may be inherently nonspreading in its pure state, (b) the liquid can be made nonspreading by the addition of carefully selected solutes, or (c) the solid surface can be modified by coating it with substances of low surface energy.

The present-day requirements for nonspreading oils for watches, fuses, and various types of indicating instruments are very stringent. Methods for fulfilling these requirements were examined in terms of the basic mechanism of spreading and wetting, the effect of chemical composition on spreading, and the use of oleophobic additives. The difficulties in obtaining appropriate liquids can be avoided by the alternative approach of modifying the solid surface. Monolayer coatings of some selected substances, although effective in the prevention of oil spreading, are sometimes too readily removed. Coatings of some fluorinated polymers however are easy to apply and remain effective when laid down in the form of a circular ring surrounding the oil drop. Thus, it becomes possible to employ any one of the many available spreading-type lubricating oils.

### INTRODUCTION

In the lubrication of large machinery the whole bearing is usually surrounded by a viscous lubricant which is continually renewed at determined intervals of time. The present-day conditions for the lubrication of watches, clocks, and many indicating meters, however, are quite different since the oil in the watch must be left in the bearing for months or even years. During this long interval the lubricant must remain in the form of a drop without spreading away. Thus, the most important requirement for a good watch oil is for it to remain in a small, nongumming drop at the lubricating point for long periods of time.

By the seventeenth century, certain bearings of watches and clocks consisted of a steel pivot rotating on a ruby or sapphire surface. Each bearing was lubricated with a tiny drop of a nonspreading oil. Practice today is not much different except that synthetic corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) has replaced the natural gems.

Until about 30 years ago, nonspreading clock oils had been obtained mainly by various refining procedures from porpoise jaw oil, black fish oil, olive oil, neat's foot oil, and bone oils by procedures which were more or less considered as trade secrets. The principal difficulties with these products were their tendencies to evaporate, to thicken,

and to deposit gums. Batches of oil from the same source were often too variable in nonspreading and stability properties, effective product control was rare, and oil specifications were inadequate. During the twentieth century, Woog (1,2) and Bulkley and Snyder (3) found that by the addition of small concentrations of oleic or stearic acid, as well as olive, castor, and lard oil, the spreading tendency of refined oils on polished steel, brass, and jewel bearing material was decreased. They concluded that this reduced spreading tendency was due to a very thin coating deposited on the bearing surface. Woog (1,2) developed and patented a process in which a dilute solution of the fatty acid in a volatile solvent was used to coat the bearing surfaces with a thin film or "epilame" of fatty acid. Some refined oils suitable for watch lubrication did not spread on such a film-coated surface. Since the film, however, was removed whenever the bearing was cleaned with a solvent, a new film treatment was necessary after every cleaning. In mass production, therefore, the process did not justify itself, especially since this process also promoted increased oxidation.

As the supply of effective, high-quality clock oils became increasingly meager and the cost mounted accordingly, several clock manufacturers started research on clock oils and their synthesis. The best-known American investigation, supported first by the Elgin National Watch Company and later during World War II by the Navy Bureau of Aeronautics, was conducted by Barker and co-workers (4,5) of the Mellon Institute. During an extensive

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search among organic liquids with the requisite physical and chemical properties for clock lubricants, including nonspreading at subzero temperatures, they prepared several hundred synthetic compounds and 185 blends (5). From this they developed a useful synthetic clock oil (N-28) which was acceptable to the military late in World War II and has been the basis for military clock oils used since (see Mil. Spec. MIL-L-3918 of 29 Aug. 1955). Despite this success, it was still desired to improve the lubricant as regards lower vapor pressure, better oxidation stability, lower freezing point, and lower cost. In addition, at the end of World War II there still was no theory offered to explain the nonspreading of either these synthetic oils or of the formerly used natural products.

In the decade after the War, Zisman and co-workers at the U.S. Naval Research Laboratory investigated the surface chemistry of the spreading of oils and other liquids on solids, and by 1958 they had published an essentially complete picture of the various mechanisms involved. At a recent symposium, Zisman (6) reviewed our present knowledge of the molecular mechanisms and theory relating to the wetting of solid surfaces.

### PURE NONSPREADING LIQUIDS

It has been established that the spreading tendency of a liquid decreases with an increase of its contact angle  $\theta$  on the respective solid surface and that the cosine of the contact angle bears a linear relationship to the surface tension of the liquid  $\gamma_{LV}$ . The relation between contact angle  $\theta$ , surface tension  $\gamma_{LV}$ , and work of adhesion  $W_A$  is given by the classic Dupré equation

$$W_A = \gamma_{LV} (1 + \cos \theta) + f_{SV}$$

where  $f_{SV}$  stands for the specific free energy decrease on immersion of the solid in the saturated vapor of the liquid (7). Nonvolatile liquids exhibiting nonzero contact angles (liquids useful for clock oils) have negligible values of the term  $f_{SV}$  (8). The Dupré equation demonstrates that maximum adhesion of the droplet of oil can be expected when  $\gamma_{LV}$  is as large, and  $\theta$  as small, as possible. In quantitative agreement with this expectation, it has been found that all of the useful clock oils have values of  $\gamma_{LV}$  above 35 dynes/cm at 20°C and values of  $\theta$  smaller than 15 degrees.

Pure liquids exist which are inherently nonspreading on high-energy surfaces. The back-

ground on the wettability of low-energy surfaces (6) has proved essential in explaining the spreading properties of these liquids on high-energy surfaces. The pure nonspreading liquids can be grouped into three classes. The first class, the autophobic liquids (9), is exemplified by molten stearic acid, octyl alcohol, tricresyl phosphate, and trichlorodiphenyl (10). The first molecules of these liquids to come in contact with the solid adsorb instantly to form a monomolecular film whose critical surface tension of wetting is less than the surface tension of the liquid, thus preventing it from spreading upon its own adsorbed film. The second class of nonspreading pure liquids is comprised of numerous esters which, although able to spread completely on metal surfaces, are unable to spread on glass, silica, and sapphire. The ester hydrolyzes immediately upon adsorption on these hydrated solid surfaces (11); of the two products of the hydrolytic reaction, the one having the greater average lifetime of adsorption remains to coat the surface with a close-packed monolayer, thereby blocking further progress of the hydrolysis reaction. If this protective monolayer has a critical surface tension of wetting which is less than the surface tension of the liquid ester, nonspreading results, *i.e.*, the ester is unable to spread upon the adsorbed film of one of its own hydrolyzed products. It can now be understood why many of the early clock oils could be made from such raw materials as porpoise jaw oil, black fish oil, bone oil, and olive oil. Such substances are rich in fatty acid esters whose hydrolysis, though slight, releases fatty acids and alcohols capable of serving as effective oleophobic film-forming solutes. A third class of nonspreading liquids which may exist is comprised of those liquids whose surface tensions are so high and adhesional energies so low that the energy of adhesion is smaller than that of cohesion and, thus, spreading is thermodynamically impossible, *i.e.*, the Harkins spreading coefficient is negative. If such liquids exist, they differ from autophobic liquids in not leaving a film behind them when rolled over a horizontal polished solid surface (10).

### PREVENTION OF SPREADING BY OLEOPHOBIC ADDITIVES

By utilizing the principles responsible for the nonspreading qualities of pure liquids, methods can be devised to impart those same qualities to

spreading liquids. This result can be achieved by the addition of selected solutes which act in either of two manners. The first approach is based on the ability of the solute to adsorb on a high-energy surface and form a monolayer with a critical surface tension of wetting less than the surface tension of the original liquid. Having modified the higher energy surface, this monolayer then prevents the liquid from spreading on that surface. When the liquid involved is an oil, the solute is said to make the oil oleophobic to the solid surface, and the solute is called an oleophobic additive (12-16). If the liquid surface tension is below 24 dynes/cm, the oleophobic additive must be a fluorocarbon or silicone derivative; if it is above 24 dynes/cm, a fatty acid or other paraffinic polar compound will be effective. When the liquid surface tension is above 30-32 dynes/cm, a branched-chain or cyclic hydrocarbon derivative can be used as the polar solute. The second approach is based on the addition of a more volatile solute which creates a surface tension gradient at the edge of an oil drop that opposes the spontaneous spreading of the oil. This method was reported at a recent symposium by Bascom *et al.* (17). The use of oleophobic additives as a means to obtain nonspreading properties presents a number of problems such as the limited solubility of these additives in many oils or the necessity of using very low concentrations of the additive so that  $\theta$  will not become so large as to cause inadequate adhesion. When  $\theta$  is kept small enough to be below 15 degrees, the additive concentrations necessary are often so low that any careless handling of the lubricant during storage or in pouring it from one container to another may cause a significant decrease in the oleophobic property because of the adsorption by the active ingredient on the walls of the container.

Synthetic clock oils have been and can readily be found from among the aromatic esters of aliphatic alcohols or acids (4,11,18); some have high enough surface tensions to be autophobic, and many are nonspreading because their hydrolytic products adsorb to form low-energy surface films. The introduction of aromatic rings in the molecular structure always increases the slope of the viscosity-vs-temperature curve and, hence, decreases the temperature range over which the oil can be used, a difficulty evident in the work of Barker *et al.* (4), O'Rear (19), and Portnay *et al.* (20). Recent results of Cottington *et al.* (21) on the control of oil spread-

ing by the use of certain silicone additives capable of adsorbing as monolayers on high-energy surfaces have shown a new route to making nonspreading oils. Their results have already led to the development of a useful clock oil from an ester containing only one aromatic ring (22).

One of the unexpected results of the long-term NRL study of spreading and wetting was to dispel an old, widely-held belief that a good lubricating liquid has better wetting and adhering qualities to a bearing surface than a poor lubricant. It was shown that the ability of liquids to spread on metals has no necessary relation to their lubricating properties (16,23-25). On the one hand, some liquids such as tricresyl phosphate have exceptionally good boundary lubricating properties but do not spread on clean metals. For this reason, clock oils containing tricresyl phosphate are in use, but they have steep viscosity-vs-temperature graphs and the fault that even the slightest decomposition will liberate corrosive phosphoric acid. On the other hand, liquids like the dimethyl silicones have inadequate boundary lubricating properties, yet spread freely on all clean metals. In general, it can be shown that the molecular structural requirements for good spreading ability are very different from those for good boundary lubrication properties.

### CONTROL OF SPREADING THROUGH MODIFICATION OF THE SURFACE

The previously reviewed investigations of spreading and wetting make it possible to give a simple and fundamental explanation of the epilame treatment of Woog (1,2). Essentially the epilame is a modification of the substrate surface. A close-packed adsorbed monolayer of a higher fatty acid, such as stearic acid, has a  $\gamma_c$  value of 24 dynes/cm. Any oil or other liquid having a surface tension  $\gamma_{LV}$  greater than 24 dynes/cm at 20°C would therefore be nonspreading on such a monolayer, and the equilibrium contact angle would be greater the larger the difference from liquid surface tension to critical surface tension. The epilame treatment can be improved greatly by applying our present knowledge of the constitutional laws of wetting. Since a silicone resin coating on a solid surface can be prepared having a value of  $\gamma_c$  as low as 23 dynes/cm (8,21), such a coating can be used in place of the fatty acid as

the epilame. It is possible to lay down such a silicone coating on a metal or gem from an air-drying lacquer or dilute benzene solution; thus, it is apparent that an effective and more durable epilame treatment can be made using such a silicone air-drying varnish. An immediate advantage would be the less destructive action of many solvents used in cleaning watches and clocks to the silicone coating than to Woog's epilame of stearic acid.

Another way to prevent spreading of the instrument oil is to use one of several commercially available fluorinated polymers whose low values of  $\gamma_c$  render them especially attractive for such application. Suitable coatings can be made from Teflon (polytetrafluoroethylene), FEP Teflon (a commercial copolymer of tetrafluoroethylene and hexafluoropropylene), and fluorinated esters of polyacrylic or polymethacrylic acid, with  $\gamma_c$  values of 18.5 (26), 17.0 (27,28), 11.1, and 10.6 dynes/cm (29), respectively. Such coatings will prevent the spreading of any lubricating liquid known. However, one essential precaution must be observed in using such coatings. Since these liquids have such low values of  $\gamma_c$ , the drop of oil placed on top of the coating will have a contact angle so large that the adhesion of the liquid to the coating will be inadequate, and any slight jar of the instrument might be able to detach the oil drop. This difficulty can readily be avoided, however, by applying the fluorocarbon resin coating in the form of a circular ring surrounding the oil drop. If the oil in the middle portion does not rest on the coating, there will be adequate adhesion to the bearing surface.

A few points deserve mention concerning techniques for depositing the above coatings. Teflon coatings are normally applied from a dispersion in water (18), and in applying them there is usually difficulty with the requirement of a brief bake at temperatures around 700°F in order to sinter the Teflon particles, to obtain good film adhesion, and to eliminate the water and additives. This treatment is often impractical in the manufacture of many instruments. The coating procedure is more advantageous with FEP Teflon (30) since its melting point of 545°F is lower; in addition, small bearings may be coated by immersing each in a fluidized bed of the hot polymer powder (31).

A more generally applicable and simpler method, which does not require any heat treatment, can be used with either of the fluorinated polymers prepared as research products by the Min-

nesota Mining and Manufacturing Company. The chemical formulae of the respective homopolymers investigated at NRL are  $C_7F_{15}CH_2OCOC(CH_3)=CH_2$ , 1H,1H-pentadecafluorooctyl methacrylate (polymer A), and  $C_8F_{17}SO_2N(C_3N_7)C_2H_4OCOCCH=CH_2$ , 2-(N-propylperfluorooctane sulfonamido)ethyl acrylate (polymer S) whose properties had been described previously (29). These low-surface-energy films can be readily laid down from a solution in an appropriate solvent such as xylene hexafluoride or benzotrifluoride which, after slow evaporation, leaves a suitable coating. A fine camel's hair brush can be used to paint bands of any desired width (such as from 1 to 3 mm) around a circular area surrounding the bearing and of sufficient size to contain the oil drop. These fluorinated materials have the additional advantage of not being readily dissolved by any of the cleaning solvents commonly used in the instrument field. Organic solvents such as xylene, petroleum ether, or AMSCO 140 solvent (140°F Flashpoint Aliphatic Solvent manufactured by American Mineral Spirits Co.) had no adverse effect on polymer A coatings on stainless steel, brass, and aluminum disks when totally immersed for three weeks at ambient temperature. Ammonia-containing aqueous watch cleaning solutions are capable of detaching the coating after prolonged immersion without dissolving it. (Extra Fine Solution by L and R Manufacturing Co. started to loosen the film edges on a stainless steel disk after two days' immersion and completely detached the film after two weeks; Concentrate Cleaning Solution by Zenith Cleaning Fluid Co. had the same effect, but after an immersion period of four weeks.) Fluorinated solvents, such as Freon TF (b.p. 117.6°F), understandably act as good solvents on the polymer.

To determine the applicability of these coatings as instrument-oil barriers for drops of either spreading or nonspreading watch oils, spreading tests were made on three freshly cleaned smooth surfaces of 18/8 stainless steel, on fused Pyrex glass, and on synthetic sapphire. Small rings of the fluorocarbon coating had been deposited on each surface by the above-mentioned techniques. Three drops of each of the five chemically diverse spreading oils and of the one synthetic nonspreading oil (Table 1) were placed in the uncoated centers of the rings, one drop to a ring. These oils were then observed periodically while stored in a dust-free, closely confined chamber at 20°C. Each oil drop

TABLE 1  
Oils Observed for Spreading in Uncoated Center of Fluorinated Polymer Rings

Spreading Oil	Surface Tension $\gamma_{LV}$ <sup>o</sup> at 25°C (dynes/cm)	Source
Bis(2 ethyl hexyl) sebacate	30.1 (20°C)	Rohm and Haas
Bis(1H,1H,7H dodecafluoroheptyl) 3-methyl glutarate	24.6	Naval Research Laboratory
Silicone DC 200 (20 cs at 25°C)	20.6	Dow Corning
Petroleum lubricating oil MS 3042	28.9	Esso Standard Oil
Ucon Fluid DLB-140E	29.1	Union Carbide Chemical Co.
Nonspreading clock oil 14-L-16	32.3	Lehigh Chemical Products Co.

spread initially over the uncoated surface within each circle, and it did this for each of the three different surfaces used, until it came in contact with the inner rim of the ring-shaped coating of the fluorinated polymers. Figure 1 shows the results of 100-day tests for the stainless steel substrate. All oil drops, with the exception of one system, still remained confined within the rings after 100 days. The one exception was observed with the fluorinated ester drops, bis(1H,1H,7H dodecafluoroheptyl)3-methyl glutarate, which spread over the coating of polymer S only (Fig. 1, upper left, series marked "2"), regardless of the nature of the substrate surface. After three to four days this oil began to creep over the inside rim of the coating, and then it slowly continued over the whole width of the band and remained there for the 100-day observation period. On stainless steel the oil drop never passed the outer rim of the fluoropolymer S; on glass the oil reached the outer rim of about half the band, but never did on the opposite half; on sapphire, one of the three drops of the fluorinated ester oil spread beyond the outer circumference onto the clean surface after 90 days.

The reason why the fluorinated ester drops spread over one of the fluorinated coatings (polymer S) can be explained by mutual attraction promoted by the structural and chemical affinity of the two fluorine-containing organic compounds. It had been established (29) that the fluorinated side chains of polymer S are sterically less closely packed and have more freedom of rotation than those of polymer A, so they may permit some

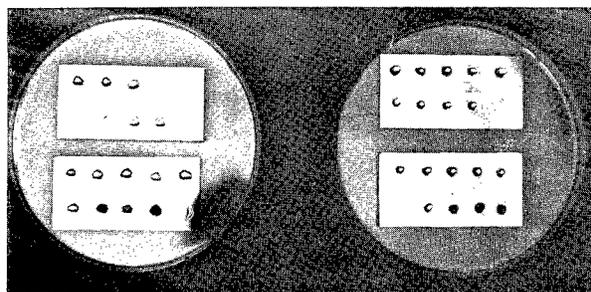


Fig. 1 - Oil drops after 100 days at 20°C on stainless steel substrate. The drops are confined by circular rings of polymer S (left) and polymer A (right). Three drops each of six oils were used in the test; each series of three drops is numbered on the substrate. One circular ring on each substrate was not coated with oil.

lateral penetration of the closely related fluoro-chains of the glutarate ester, whereas polymer A with its tight array of sidechains is impervious to such penetration. The fluorinated ester exerts a slight solvent action on polymer S, but not on polymer A, when the polymer is totally immersed in the ester for periods longer than ten days at ambient temperature, or two days at 50°C.

Requirements of lubricants to remain non-spreading at subzero as well as high temperatures are increasingly common in modern instruments. After 100 days at 20°C, the above-mentioned specimens were therefore subjected to cycling between +50°C and -20°C for 24 hours at each temperature to observe if spreading could be induced or whether the adhesion of the coatings remain acceptable. After twenty full cycles (40 days), all

liquids with the exception of the fluoroester were still contained within the rings of polymer S. On sapphire and glass some of the liquid drops, especially nonspreading clock-oil 14-L-16, were slightly flattened out, whereas on stainless steel the drop shape remained unaltered. Most of the liquids began to creep over the containing bands of polymer A after two full cycles but did not go beyond them even after the 20 full cycles. Again the drops on stainless steel showed the least effect. These observations may indicate that the coefficient of expansion of polymer S is not so different from those of steel, glass, and sapphire as to adversely affect its adhesion to these materials. Coatings of polymer A, however, are more susceptible to temperature changes; this is evidenced by the spreading of almost all oils to the rim of the polymer ring on sapphire and glass. The adhesion relative to stainless steel is much greater, as shown by the almost unchanged shape of the oil drops after full cycling.

### CONCLUSIONS

It has been shown that the prevention of liquid spreading can be accomplished by three different approaches:

1. The use of a pure nonspreading liquid.
2. The modification of a spreading oil through additive agents. Selected solutes can be added which act by either of two methods: (a) their low surface tension makes them capable of adsorbing as monolayers having a critical surface tension lower than the surface tension of the liquid; (b) their higher volatility creates a surface tension gradient.
3. The modification of the solid surface. The surface can be (a) completely coated by monolayers of low-surface-energy compounds on which oil drops having higher surface tension will not spread, or (b) covered with narrow ring coatings of insoluble polymers of low surface energy, such as fluorocarbon derivatives, which surround the oil drop.

Since the nonspreading oil feature can be obtained by the surrounding ring-shaped coating of a fluorocarbon resin, the nonspreading requirement of the oil is not essential. Hence, it becomes possible to employ any one of the many available spreading-type lubricating oils (such as petroleum, polyethers, or aliphatic diesters) which fulfill to a

higher degree than present clock oils all of the other important requirements of such oils, *i.e.*, small temperature coefficient of viscosity, low pour point, lowest possible evaporation rate, and low cost, as well as excellent boundary lubricating properties, rust inhibition, and oxidation stability.

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