[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, VACUUM OIL CO., INC.]

Spreading of Liquids on Solid Surfaces. The Anomalous Behavior of Fatty Oils and Fatty Acids with Experiments Leading to a Tentative Explanation

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Introduction

The accepted theories of spreading are supported by ample experimental evidence for the case of one liquid spreading upon the surface of another. For example, the known interfacial and surface tension relations lead to the expectation that fatty oils and fatty acids will possess a more marked spreading tendency on water than will hydrocarbons and well-refined mineral oils. This expectation is realized experimentally.

For the spreading of liquids on solids, however, the current theories are not well substantiated by experimental data. Indeed, for many liquid–solid systems there would appear to be a conspicuous, but heretofore overlooked, disagreement between theory and experiment. While the surface tension of solids and their interfacial tension against liquids cannot be measured, there is, nevertheless, considerable evidence to show that on metals as well as on water the fatty oils and fatty acids should possess a more pronounced spreading tendency than the mineral oils.

It is a matter of common observation that such is not the case. On smooth and clean metal surfaces a drop of olive oil or of oleic acid shows little tendency to flatten or spread, whereas liquid paraffin hydrocarbons and moderately viscous mineral oils spread readily and apparently without limit as long as any liquid substance remains.

It is the purpose of this paper to discuss some of the evidence for the genuine existence of the anomaly, and to suggest a tentative explanation based on experiments which will be described. The experiments are of further interest in that they show for the first time, as far as the authors are aware, the phenomenon of rupture of thin layers of liquid on a solid surface due to the instability created by an underlying adsorbed film of low surface energy. A similar effect for fatty and mixed oils on water is well known.

The Spreading Tendency

As early as 1805 Thomas Young[1] had considered the laws governing the spreading of liquids on solids, and had published his famous equation (1), describing the equilibrium of a drop of liquid on a solid surface.

$$T_m = T_{mo} + T_o \cos\theta \qquad (1)$$

Here the solid is represented by the subscript m, the liquid by o; T_m, T_{mo} and T_o are the surface tensions of the respective surfaces and interfaces, and θ is the angle of contact between the liquid and the solid.

(1) Young, *Phil. Trans.*, **95**, I, 65 (1805). See also "Works," i, p. 432.

In recent years Harkins and Feldman, Osterhof and Bartell and others[2] have formulated various spreading criteria which differ from each other in little except notation. If the tendency to spread be represented by S, then, ignoring the work of viscosity

$$S = T_m - T_{mo} - T_o \qquad (2)$$

for spreading on a solid surface.

The quantities T_m and T_{mo} cannot be measured, and it is consequently impossible to determine the numerical magnitude of the spreading tendency for any given instance of a liquid spreading on a solid surface. It is to be noted, however, that the common fatty oils and fatty acids differ but little in surface tension from mineral oils as a class. If there is any substantial difference, therefore, between the interfacial tensions of the fatty liquids against metals and the mineral oils against metals, that class of liquids which has the lower values of T_{mo} should possess the superior spreading tendency.

Evidence That the Interfacial Tension between Metals and Fatty Liquids Is Less than between Metals and Mineral Oils

(a) **Preferential Adsorption.**—In accordance with a well-known general principle, surfaces and interfaces tend spontaneously to assume a condition of minimum free surface energy. At an interface between a metal and a mineral oil containing fatty acid in solution, that constituent of the solution which lowers the interfacial tension by the greater amount should, therefore, become more concentrated than in the solution as a whole.

Fatty oils and fatty acids lower the static coefficient of friction between metal surfaces more than do mineral oils of the same viscosity. Moreover, a mineral oil containing only a small percentage of fatty acid lowers the friction almost as much as a straight fatty oil. The explanation generally accepted is that the fatty acids are preferentially adsorbed from their solutions in mineral oils by metallic surfaces. Other experimental evidence of a more direct nature will be presented later which leads to a similar conclusion, namely, that metal surfaces preferentially adsorb the fatty acids from solutions of the latter in mineral oil. On the principle stated above, the fatty acids must, therefore, reduce the surface tension of metals more than do mineral oils.

(b) **Interfacial Tension between Oils and Mercury.**—Harkins and Ewing, Wells and Southcombe, and Bhatnagar and Garner[3] have presented data showing that the interfacial tension between mercury and fatty liquids is considerably lower than between mercury and hydrocarbons or mineral oils. The differences reported are of the order of 20 to 50 dynes per cm. It is also shown that the addition of small percentages of fatty acid to a

(2) Harkins and Feldman, THIS JOURNAL, **44**, 2665 (1922); Osterhof and Bartell, *J. Phys. Chem.*, **34**, 1399 (1930).

(3) Harkins and Ewing, THIS JOURNAL, **42**, 2539 (1920); Wells and Southcombe, *J. Soc. Chem. Ind.*, **39**, 51T (1920); Bhatnagar and Garner, *ibid.*, **39**, 185T (1920).

mineral oil progressively lowers the interfacial tension between the oil and mercury.

Some rough preliminary measurements made during the course of the present investigation indicate that well-refined lubricating oils of a medium grade may have an interfacial tension against mercury 20 to 40 dynes per cm. higher than olive oil or than the same mineral oils containing 1 to 2% fatty acid.

The significance of these results to the question under discussion is obvious. Most solid metals probably have lower interfacial tensions against fatty oils and fatty acids than against mineral oils as is true for the case of the metal mercury. Moreover, the differences are not likely to be less than about 20 to 50 dynes per cm. As shown in Table I below, the difference between the surface tensions of the fatty liquids and the mineral oils is seldom greater than 2 or 3 dynes per cm. Clearly, on the basis of Equation (2) the fatty oils and fatty acids should manifest the more marked spreading tendency.

TABLE I

PREFERENTIAL WETTING OF POWDERS

o means powder wetted preferentially by oil; w means powder wetted preferentially by water

Test liquid	Viscosity, poises	Surface tension dynes/cm.	Zn	Cu	Fe	G
n-Tetradecane	...	..	w	w	w	..
Kerosene	...	26.2	w	w	w	w
Transformer oil	0.22	29.7	w	w	w	..
Light naphthene base oil	...	..	w	w	w	..
Turbine oil	0.53	30.0	w	w	w	w
Medium motor oil	1.33	31.0	w	w	w	..
Nujol	...	..	w	w	w	w
Turbine oil with 2% oleic acid	0.53	30.2	o	o	o	w
Turbine oil with 5% oleic acid	.52	30.0	o	o	o	..
Sperm oil	.28	31.8	..	..	..	..
Porpoise jaw oil	.32	29.1	o	o	o	..
Neat's-foot oil	...	..	o	o	o	..
Olive oil	.66	32.2	o	o	o	..
Lard oil	.90	32.0	o	o	o	..
Oleic acid	.37	31.5	o	o	o	w

(c) **Preferential Wetting of Powdered Materials.**—Davis and Curtis[4] have described a simple method of obtaining qualitative information on the relative interfacial tensions of powdered solids against water as compared to their interfacial tensions against organic liquids not miscible with water. The solid particles, completely immersed as a paste in one of the liquids, say liquid *o*, are brought into intimate contact with the second liquid, *w*, by stirring into the paste a quantity of the second liquid. The particles choose to remain in liquid *o* if, and only if $T_{mo} < T_{mw}$. If the reverse is

(4) Davis and Curtis, *Ind. Eng. Chem.*, **24**, 1137 (1932).

true, that is, if $T_{mw} < T_{mo}$, then, on the principle of minimum energy, the particles will be preferentially wetted by liquid w, into which they will pass and remain.

Davis and Curtis applied the test to 15 different powdered solids, and used on each solid eleven fatty oils, two mineral oils and several other organic liquids. They found, with few exceptions, that the fatty oils displaced water from the surface of all the solids and that water in turn always displaced the mineral oils. No powdered metals were tested by Davis and Curtis, but in the present investigation their procedure has been applied to tests on powdered zinc, copper and iron, using the liquids listed in Table I. A powdered glass, G, such as is used in baked enamel coatings was also tested with several of the liquids. The results are given in tabular form below, together with the values for viscosity and surface tension of the liquids used here and in the spreading tests to be described later. The surface tension and the viscosity were determined at room temperature; the former with the du Noüy tensiometer with the aid of the correction factors given by Harkins and Jordan;[5] the latter with the Michell viscometer.

It will be observed that in every instance the fatty oils and the liquids containing the fatty acid displace water from the metal powders, and that water, in turn, displaces the petroleum oils. In other words, the metals are preferentially wetted in the order fatty liquid–water–petroleum oil, or

$$T_{mf} < T_{mw} < T_{mp} \qquad (3)$$

where f, w and p represent, respectively, fatty liquid, water and petroleum oil. While the tests are only of a qualitative nature, yet, from the interfacial tension measurements of oils against mercury and from the very clean-cut manner in which the oils displace or are displaced by water in the present experiments, it seems safe to state that the difference between T_{mf} and T_{mp} must be considerably greater than the slight differences between the surface tensions of the fatty liquids and the petroleum oils.

It is not possible to say from these experiments which of the two classes of organic liquids shows the lower interfacial tension against glass. The experiments described below indicate, however, that against this solid, also, the fatty materials show a lower interfacial tension than the mineral oils.

(d) Deflocculation of Pastes.—An interesting experiment consists in mixing 10 or 20 g. of some very finely divided solid such as zinc oxide, powdered glass, powdered zinc, copper or iron into a paste with kerosene and then adding a drop of oleic acid. Only enough of the kerosene should at first be used as will wet the powder completely, yielding a paste so stiff that it can be molded into an upright prism. Considerably more kerosene can now be stirred in without changing the consistency noticeably, but if a single drop of oleic acid is added, the mixture, when stirred, becomes so thin that it will run far out over the plate.

(5) Harkins and Jordan, THIS JOURNAL, **52**, 1751 (1930).

For a similar experiment in which poppy seed oil took the place of oleic acid, Green[6] was able to show by photomicrographs that the pigment in the stiff paste was flocculated, whereas in the thin cream, which resulted from adding a drop of fatty material, the particles were evenly dispersed. The interpretation is that the fatty oil or fatty acid lowers the interfacial tension between solid and liquid to such an extent that no flocculating tendency remains. As long as a high interfacial tension prevails between solid and liquid the fine particles clump together to eliminate as much of the interface as possible.

The evidence of the experiments presented under (a), (b), (c) and (d), above, as well as others, such as heats of wetting, etc., which could be mentioned, is to the effect that the interfacial tension between metals and fatty oils and fatty acids is substantially less than between metals and petroleum oils. On the basis of the accepted theories of spreading, the spreading tendency of the fatty oils and fatty acids should then be correspondingly greater.

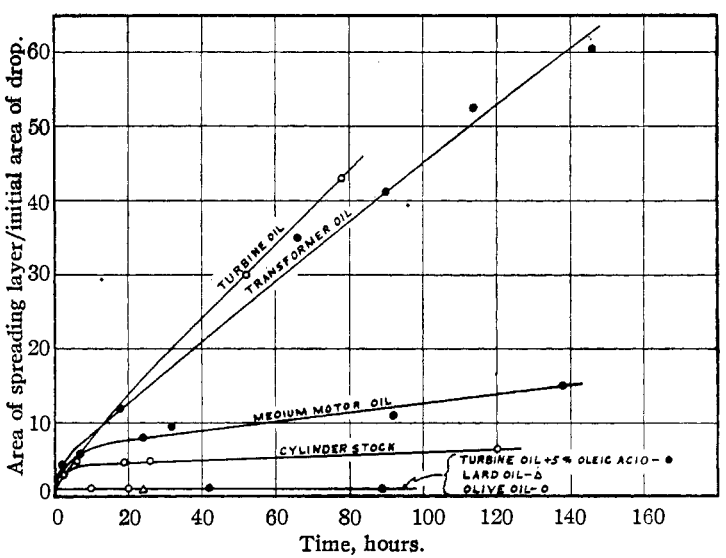

Fig. 1.—Spreading experiments on steel.

Spreading Experiments on Metal Plates

Figure 1 shows characteristic spreading graphs for droplets of various oils on brightly polished steel plates. In these graphs the ordinates represent the amount of spreading defined as the ratio of the area covered by the spreading layer at a chosen time to the initial area covered by the droplet. The initial area cannot be determined with precision, and a high degree of reproducibility is not obtained in duplicate experiments.

(6) Green, *Ind. Eng. Chem.*, **15**, 122 (1923).

The test plates were polished to a mirror finish on wet broadcloth using chromium oxide as abrasive. They were kept level during the experiments and were protected from dust by suitable covers. An ample supply of fresh air was provided in all cases.

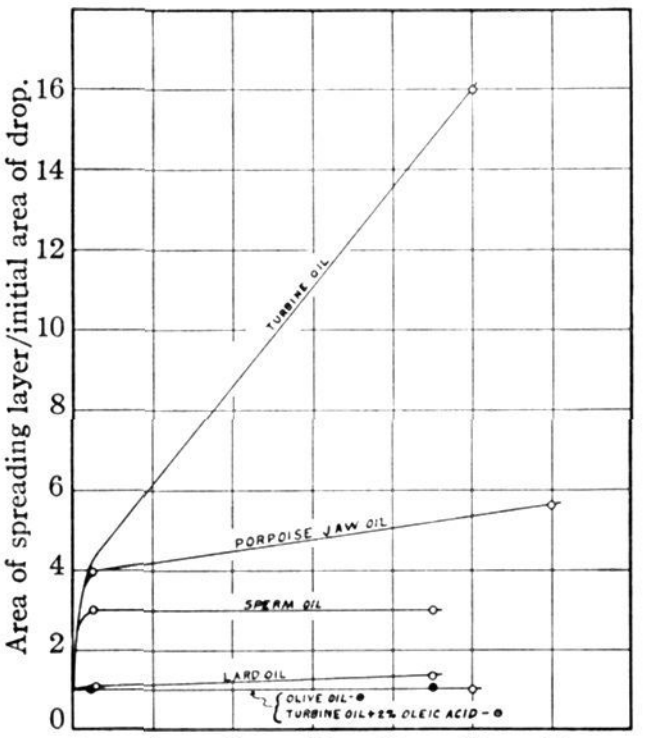

Fig. 2.—Spreading experiments on cadmium.

Figure 2 represents the behavior of several oils on polished surfaces of cadmium. It was not found possible to obtain as bright a polish on this metal as on steel, but, aside from this, the tests on cadmium and on steel were conducted under similar conditions. The shape of the curve for turbine oil is largely hypothetical as only the initial and final areas were measured.

In Fig. 3 the spreading liquid is a thin mineral oil. The non-spreading drop is olive oil. Both drops were initially of nearly the same size and both were put on the plate at the same time, about twenty hours before the picture was taken.

The behavior of mineral oils on a metal plate can be described by saying that each droplet flattens rapidly into a thin layer which seems to continue to spread indefinitely. In many instances the spreading has been observed to continue long after the layer has become so thin that several orders of color appear. With an oil as volatile as kerosene the area covered reaches a maximum in a few hours, after which the layer disappears due to evaporation.

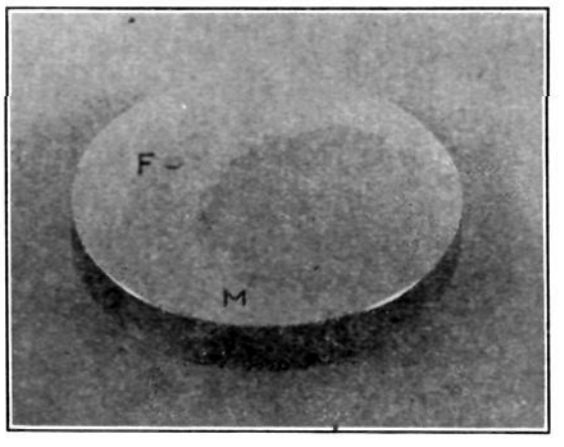

Fig. 3.—Relative spreading of fatty oil (F) and mineral oil (M) on steel plate.

Droplets of lard oil, olive oil and of mineral oils containing 5% or more of oleic acid spread only during the first few minutes after being placed on the plate. The lowest curves on Figs. 1 and 2 are representative. Porpoise jaw and sperm are exceedingly thin oils and have more marked spreading tendencies than other fatty oils. Mineral oils containing only 1 or 2% of fatty acid show

about the same behavior as fatty oils on cadmium, but on steel and several other metals their behavior is peculiar and striking, and will be described in a later section.

Cadmium was chosen as one of the test metals because of its close relationship to mercury in the Periodic Table. If cadmium is affected in the same manner and to a similar degree as mercury by fatty and mineral oils, then the interfacial tension between cadmium and the three oils whose curves are shown at the bottom of Fig. 2 must be about 20 to 40 dynes per cm. less than the interfacial tension between cadmium and the turbine oil. The greatest difference in the surface tensions of the oils is 2.2 dynes per cm. By Equation (2), the lard oil, the olive oil and the turbine oil containing fatty acid should thus possess the greater spreading tendency. Experimentally these oils are observed not to spread to an appreciable extent. The spreading of liquids on solids seems, therefore, to be determined in many cases by factors other than the energy requirements.

Behavior of Fatty Acids and of Oils Containing Fatty Acids on Flat Plates

When a drop of oleic acid is placed on a clean polished surface of steel it apparently does not wet the plate at all, but can be rolled about in much the same manner as a drop of mercury.[7] A film of mineral oil spreading on the plate is halted abuptly at the invisible path along which the oleic acid has passed, thus giving evidence of the deposition of an exceedingly thin film on that part of the plate with which the drop has been in contact. The path of the drop can also be brought out strikingly to the eye merely by breathing on the plate when it is cool. Gentle etching with fumes from inorganic acids will likewise make the path of the drop visible.

The above effects seem to occur for a fairly wide variety of materials. They have been observed in this investigation for oleic acid, for melted capric, palmitic and stearic acids and for melted cetyl alcohol on steel, brass, babbitt, glass and mica. Several of the common fatty oils such as castor, lard and olive manifest a somewhat similar behavior, but to a less marked degree. Cadmium and platinum seem to be wetted in the ordinary sense of the word by all of the liquids mentioned above. This may be due, in part, to the difficulty of getting a sufficiently smooth polish on the surfaces of these metals.

Mineral oils which spread rapidly on ordinary metal surfaces seem to have no spreading tendency when placed on a metal surface which is covered with the invisible fatty acid film. The film thus seems to be similar to the neutralizing surface layer (epilame) described by Woog,[8]

(7) This effect was first noticed by one of the authors (G. H. S. S.) in September, 1931.

(8) Paul Woog, *Compt. rend.*, **181**, 772 (1925). See also "Contribution à l'Étude du Graissage," Delagrave, Paris, 1926.

but its thickness is probably only a small fraction of the thickness of the layers of stearic acid deposited by Woog's patented process. Indeed, there is good reason to believe that the drop of fatty acid leaves behind it only an adsorbed film, which is, therefore, perhaps only a few molecules in thickness. For instance, the surface may be rinsed several times in benzol without removing the film.

The effect of the adsorbed film in reducing the wettability of the metal surface by mineral oils goes further. This was demonstrated by rolling several drops of fatty acid across a plate, and then dipping the lower half of the plate into a beaker of mineral oil. When the plate was withdrawn the clean metal retained a relatively thick layer of oil for an indefinite period, but all the oil ran off those portions which the fatty acid drops had touched.

Another detail of interest was observed when a drop of oleic acid was placed just on the edge of a very shallow pool or layer of motor oil on a polished plate. The plate was level so there was no tendency for the drop to roll by gravity. It moved, nevertheless, of its own accord into and through the layer of oil, mixing with the portion in its path, and leaving behind on the steel only the adsorbed film with no visible trace of liquid (Fig. 4). For experiments in which the layer of mineral oil was very thin, the drop of fatty acid was often observed to traverse the entire width of the pool and then to turn about and recross in the opposite direction, wiping out a continuous path all the way.

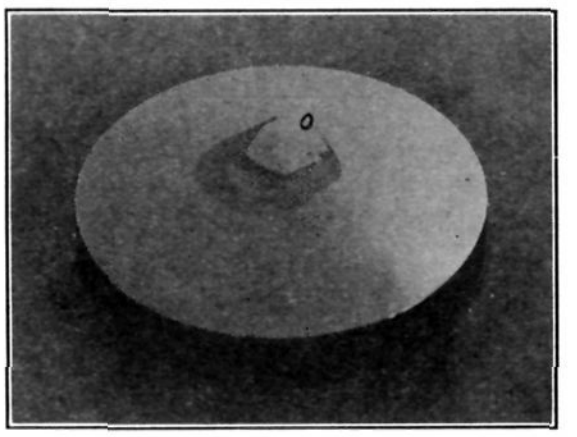

Fig. 4.—Action of a drop of oleic acid when placed at O on the edge of a spreading layer of mineral oil.

One additional group of observations may be described, after which an explanation of these phenomena will be attempted. When a drop of thin mineral oil containing 1 or 2% of oleic acid was placed on a polished steel plate it spread rapidly outward for a few minutes, at which time a hole appeared in the layer near its edge. This hole became elongated, expanding parallel to the circumference of the spreading layer. The main body of the oil pulled inward as the rupture progressed, until at last the oil was completely separated into two portions: a surrounding ring which continued to expand outward at a more rapid rate than the ordinary spreading, and an inner pool which contracted to a relatively small radius and then remained dormant (Figs. 5 and 6). On the metal surface between these two portions no liquid was visible. The surface was found to be

covered with an adsorbed film similar in all respects to the one obtained from the pure acid.

On steel and on several other solid surfaces, solutions of various fatty acids in oil were found to behave in a somewhat similar manner. Some combinations were more active than others. Solutions of capric acid and palmitic acid in oil seemed to be more energetic than oleic acid in oil.

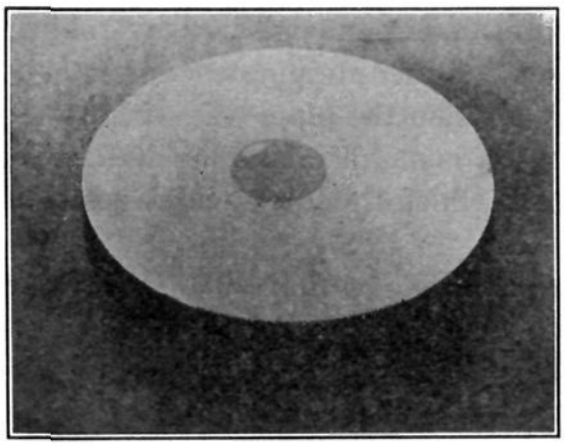

Fig. 5.—Ring commencing to break away (two per cent. of oleic acid in kerosene on steel).

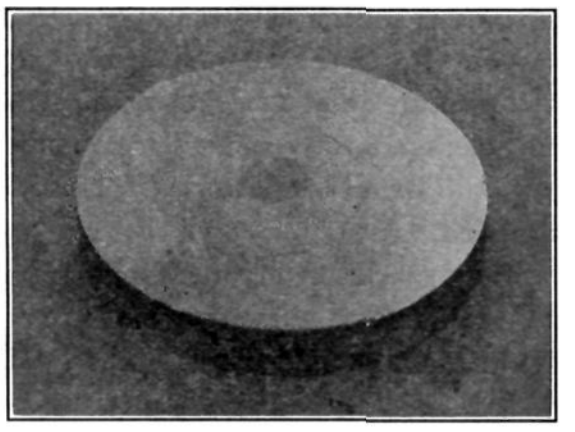

Fig. 6.—Later stage of ring mechanism (same view as Fig. 5 four minutes later).

Stearic acid solutions were almost inert. Fresh mica surfaces were somewhat more active than steel. For the more active combinations such as solutions of palmitic acid on steel or mica, the spreading layer sometimes appeared actually to fly to pieces on the surface, breaking up into numerous drops and droplets which moved rapidly about on the surface (Fig. 7). Each moving portion left in its wake a trail of adsorbed fatty acid on the metal surface.

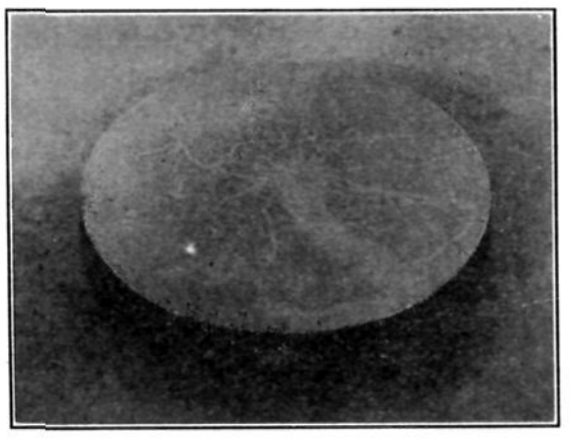

Fig. 7.—Configuration after explosive spreading (two per cent. of palmitic acid in kerosene on steel).

In some instances a drop as a whole was observed to move about. This behavior seems to be a characteristic of castor oil, the only non-compounded oil used, which was found to possess the type of activity mentioned here. On steel, drops of castor oil were observed to move slowly, leaving behind long thin arms of liquid. On fresh mica, the drop as a whole traveled about leaving no visible liquid behind.

The ability of a solid surface to produce the effects mentioned was found to be greatest immediately after the surface had been polished, and to

decline rapidly with time of exposure to the laboratory atmosphere. This was evidently due to moisture or oil vapors, for when the surface was kept in a clean dry atmosphere the activity was found to have suffered only slightly after a period of sixteen hours.

The effect of concentration of the fatty acid in the oil was tried. From 0.1% up to saturation—about 2%—solutions of palmitic and capric acid in kerosene showed little change in behavior, except that at the lower concentrations more time was required before rupture occurred and the break started farther in from the edge. With oleic acid, which is more soluble in oils, it was possible to go to higher concentrations, and the results are considered to be of significance in arriving at an explanation of the non-spreading of fatty oils and fatty acids in general.

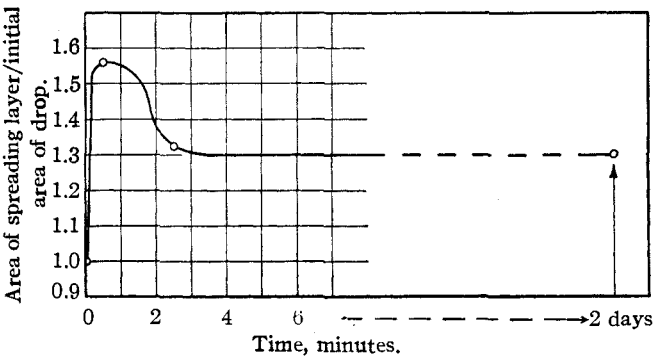

Fig. 8.—Spreading of a high viscosity compounded oil on steel.

At concentrations of oleic acid in kerosene less than one-half of 1% the initial rupture of the spreading layer was considerably delayed, and the ring which detached itself was wide. At 1% the rupture occurred sooner and closer to the edge of the spreading layer. At 2% the time before rupture was still less and the ring which detached itself was thinner than ever. At 5% the break often appeared to be just at the edge, and in several instances no visible ring could be observed to detach itself. In these cases a wave of contraction started at some point in the edge very shortly after the drop was placed, and spread around the periphery, the drop pulling itself inward as the wave progressed and then remaining completely dormant. At 10% no ring was ever seen, but the contraction of the drop immediately after placing was still visible. At higher concentrations this effect also disappeared, probably because it occurred too quickly to be observed.

For oils of higher viscosity, less fatty acid is required to make the rupture occur at or near the edge of the drop. For an oil of cylinder stock grade, 1% of oleic acid may be sufficient to produce a visible contraction of the drop after an initial period of spreading, without the appearance of any

visible fringe or ring. Figure 8 is plotted from measurements made on such a drop with a cathetometer.

Relation of the Experimental Results to the Non-Spreading of Fatty Oils and Fatty Acids

Certain similarities exist between the behavior of fatty acids and fatty oils on water and their behavior on metals as described above.

Oleic acid spreads rapidly on the surface of clean water to give a layer of visible thickness, which at once gathers itself back up into a drop. The water is left covered with an adsorbed film which reduces the surface tension to a low value. The regathering of the bulk of the material into a drop comes about as a consequence of the low surface tension of the water when covered with such a film. Oleic acid does not spread of its own accord on a polished plate, but if it is forced to spread into a thin layer by mechanical means it will at once gather itself back up into a drop when the applied force is removed. Moreover, the area with which it has been in contact will remain covered with an adsorbed film.

The surface energy of the metal so covered will be low, as in the case of water. The value will be considerably less than that of clean metal and substantially less than that of metal covered with mineral oil. This was demonstrated for the case of metal powders and mercury in a previous section; the experiments describing the behavior of fatty acids and of oils containing fatty acids on flat plates confirm the essential correctness of this view. For instance, mineral oils will not spread on or readily adhere to the surface of metal covered with the adsorbed film. The fatty acid itself will not wet such a surface as shown by the rolling effect and the gathering into a drop. Again, when a drop of oleic acid travels of its own accord through a thin layer of mineral oil on a polished plate, and removes the oil from the surface, it is believed that the driving power responsible for such behavior is the considerable lowering of the surface energy of the metal which occurs when the mineral oil is replaced by fatty acid.

When mineral oils containing a small amount of fatty acid spread and rupture on solid surfaces the behavior is similar, and the cause of rupture is the same as when the spreading of such liquids takes place on water. The phenomena are well known for spreading on water and mercury; they have been described often, and have been beautifully illustrated by Beilby and by Devaux.[9] Therefore, only a brief discussion of the main features as applied to spreading on solids will be given here.

When a drop of petroleum oil containing some fatty acid is placed on a polished plate, the petroleum portion spreads in its normal manner; the fatty acid is preferentially adsorbed on the solid surface, and lowers the interfacial tension between solid and liquid to such an extent that a condi-

(9) Sir George Beilby, "Aggregation and Flow of Solids," Macmillan and Co., London, 1921; Henri Devaux, *Kolloid-Z.*, **58**, 129 (1932).

tion of unstable equilibrium arises. The reason for this instability is comprised in the principles underlying Young's equation (1). It is perhaps sufficient merely to state in words that on an area of low surface energy the stable configuration for a small portion of liquid is not that of an extended film but that of a drop. At a certain minimum thickness of liquid layer, rupture therefore occurs. Any portion of oil in the midst of an area covered with the adsorbed film can only pull itself together into a drop; this is the situation for all the oil when the underlying substance is water or mercury. For spreading on solids, however, not all of the surface has been contaminated when rupture occurs, and the oil in contact with clean metal therefore continues to spread outward.[10]

A mechanism which may be responsible for the non-spreading of fatty oils and fatty acids is suggested by the experiments with kerosene containing varying percentages of oleic acid. For low concentrations the adsorbed film between the oil and metal seems to require more time to become organized completely than for high concentrations. It may be supposed that this film commences to form when the drop first touches the metal, and that it grows outward at a rate which is some direct function of the concentration of fatty acid. At low concentrations, therefore, not only will the rupture be delayed more than for high concentrations, but, when rupture is imminent, the advancing edge of the liquid layer will in general be farther away from the region in which the probability of rupture is the greatest. The break will occur closer and closer to the edge as the concentration is increased, until the ring which spreads outward becomes too thin to be seen. At very great concentrations it may be only of molecular dimensions. In all cases, however, the oil on the inward side of the rupture is pulled further inward by surface tension when rupture occurs, and is prevented from exhibiting any further spreading tendency by the surrounding area of metal of low surface energy.

This has been observed to be the mechanism of the non-spreading of mineral oils containing moderately high concentrations of oleic acid. The same explanation may be assumed for fatty oils and fatty acids if there exists in such liquids a small amount of a less active but spreading ingredient which permits the functioning of the mechanism described. Even for pure fatty acids a similar view can be held by considering the molecules as requiring at least a short time to become oriented on the surface. The ring which would be pictured as detaching itself in such a case would be a ring of unoriented molecules which would rapidly exhaust its substance in covering the metal surface to a very short distance beyond the edge of the drop.

(10) The ring or droplets which result from the rupture of the original layer move faster than the ordinary spreading rate, probably because the forces of surface tension roll the liquid up from the rear as fast as it spreads outward in the front. There is thus always maintained a hydrostatic head many times greater than that which is present in a normally spreading layer of oil.

The situation presented is somewhat curious. It might be said that mineral oils spread mainly because they reduce the surface tension of solids to a low value. With regard to fatty oils, fatty acids and mineral oils containing relatively large amounts of fatty acids, it becomes necessary to state that they fail to spread although they reduce the surface tension considerably more.

The paradox is adequately explained, for the case of the solutions of oil and fatty acid, by the ring mechanism which is easily and directly observed. For pure fatty oils and fatty acids the same mechanism suggests itself as a possible and reasonable explanation, although here other factors may have to be considered, especially for such materials as possess an appreciable vapor pressure. A high concentration of oleic acid vapor effectually prevents the spreading of mineral oils on a steel plate initially clean, presumably by condensing as an adsorbed film and lowering the surface tension of the metal. It seems likely that the condensation of vapor from a drop of oleic acid or fatty oil onto the immediately adjacent surface might similarly prevent the spreading which would be predicted for such a drop from energy considerations alone.

Adam[11] has suggested that the mechanism of spreading of a liquid layer on solids is the evaporation of the spreading material near its edge, followed by recondensation on the solid surface. The question might reasonably be asked as to how one and the same mechanism could produce spreading in the case of mineral oils, and prevent it in the case of fatty liquids. The probability that this situation actually prevails seems not to be great, but its possible existence may be admitted for the time being.

The answer to the above question would then seem to be that in the case of the fatty liquids the surface tension of the metal is reduced to such a low value by the condensed film as to make a liquid layer thereon unstable. If a layer thick enough to have the properties of a liquid should build up for a short distance beyond the drop, this layer would at once contract inward by reason of its own surface tension, and because of the low surface energy of the adjacent metal which, in the meantime, would have become covered with an adsorbed film.

An equally acceptable and perhaps simpler view is that when a liquid spreads, the liquid flows outward as liquid at the margin of the spreading layer, under the strong attractive influence of the solid surface molecules. If this point of view is adopted, the question discussed above does not present itself.

Regardless of what may be the mechanism of spreading, there can be little doubt that, in the case of fatty oils and fatty acids where the expected spreading fails to occur, the reason for the non-spreading is to be found in the fact that the surface energy of the metal surrounding the drop is re-

(11) Adam, "The Physics and Chemistry of Surfaces," Oxford, 1930.

duced to such a low level as to make a liquid layer on the metal unstable. This reduction in surface energy is brought about either by the ring mechanism described in this paper, by the condensation of vapors in advance of the spreading layer or, perhaps, by a combination of both. Mineral oils and mineral oil vapors also reduce the surface energy, but not to a sufficient extent to make a thin liquid layer on the metal unstable.

Other Suggested Explanations.—The literature seems to contain no previous mention of the anomaly of the non-spreading of the fatty oils and fatty acids, and there are consequently to be found but few suggestions of a helpful nature as to its cause. Harkins and Feldman[2] are of the opinion that practically all organic liquids should spread readily on all clean metal surfaces because many such liquids spread readily on water, and "since the free surface energy of solids is in general much higher than of liquids, and since in general the interfacial tension is less than that of the surface tension by a greater amount." These authors suggest that cases of non-spreading of liquids on solids are to be explained by the presence of impurities on the surface which lower the free surface energy.

The arguments set forth in the present paper constitute further substantiation of the view of Harkins and Feldman that, on the basis of energy considerations alone, organic liquids should spread on clean solid surfaces. The presence of impurities on the surface, however, seems inadequate to explain the non-spreading of fatty oils and fatty acids. It is difficult to understand, for instance, what the nature of the contaminant could be which would interfere so slightly with the spreading of mineral oils on metal plates and at the same time entirely prevent the spreading of the fatty liquids which are possessed of the superior spreading tendency.

Moreover, platinum can be cleansed of organic contaminants very thoroughly by heating to incandescence, and glass can be brought to a comparable condition of cleanliness with the aid of strong acids. The spreading behavior of mineral oils and of fatty oils and fatty acids on surfaces so cleansed is, nevertheless, qualitatively the same as on the metal surfaces used throughout this investigation. In general the behavior is the same also on surfaces of mica freshly exposed by cleavage.

A test which is generally recognized as a delicate one for detecting minute amounts of contaminants on a solid surface is to see how well the surface retains a film of water. All the experiments described in the present papers were made on surfaces which were clean in the sense that they were capable of being wetted perfectly by water.

Woog's[8] suggestion as to the reason for the non-spreading of fatty oils is more in keeping with the experiments described in this paper, although it seems to have been made on the strength of meager evidence. No consideration is given to the energy relations involved, and there is no mention of the fact of an anomaly. His description of the manner in which drops of

mineral oil containing fatty acid spread at first and then contract into drops is similar to some of the effects described in this paper (Fig. 8). If any rings separated from the drops in his experiments he apparently did not observe them. This may account for his failure to suggest any suitable mechanism for the formation of the zone of oriented molecules which he postulates as surrounding the drops.

Trillat and Cuypers[12] have quoted Woog's explanation without substantial modification.

Summary

Several lines of experimental evidence are described in support of the view that the interfacial tension between metals and petroleum oils is substantially greater than between metals and fatty oils or between metals and fatty acids.

The energy requirements for spreading on solids being the same as for spreading on liquids, the fatty oils and fatty acids should spread more readily than mineral oils on metal surfaces.

Experimentally, fatty oils and fatty acids spread little or not at all while mineral oils spread apparently without limit. The non-spreading of the fatty liquids must, therefore, be regarded as anomalous.

The higher fatty acids do not wet polished metal surfaces in the ordinary sense, but roll about freely. They deposit an adsorbed film on the surface which reduces the surface energy to a low value.

Thin layers of mineral oil containing fatty acids rupture spontaneously on metal surfaces. The explanation is the same as when a similiar phenomenon occurs on water, namely, the formation of an underlying film of low surface energy. Thin layers are unstable on areas of low surface energy.

Fatty oils and fatty acids are prevented from spreading on metal surfaces by the great reduction in the surface energy of the metal which is brought about to some distance in advance of the spreading layer by the breaking away of an expanding ring or by the condensation of vapors.

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(12) J. J. Trillat, *Metallwirtschaft*, **4**, 101 (1928); Paul Cuypers, *Deut. Uhrmacher Z.*, Nos. 35, 36, 37 (1927).