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NAVY DEPARTMENT

Report

on

The Spreading Characteristics of Lubricating Oils

Part II

The Effects Due to the Presence of Alcohols, Phenols, Acids, Ketones, and Esters.

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ABSTRACT

The work described in Part I of this report concerned the spreading upon water of aliphatic fatty acids dissolved in mineral oil and the work herein presented concerns the same mineral oils containing in solution either the alcohols, phenols, ketones or esters. Some additional related work on acids is also described.

Whereas acids in oil can be detected when as little as one part in 100,000 by weight is present, all alcohols, phenols, ketones and esters containing only one polar group caused spreading only when more than one part in 1000 by weight was present.

The essential characteristics of the oil spreading manifested by the various series of compounds studied are described.

The causes of the observed phenomena involved in the spreading of oil drops have been systematically sought and can now be considered well understood.

Finally, recommendations are made for the application of these results to various Naval oil problems.

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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Engineering letter JJ14/L5-(5-31-Ds) of 8 June 1938.

(b) Statement of Problem

2. The experimental work presented here forms Part II of a report on the investigation of the phenomena involved in the spreading of oil drops on water. Broadly speaking, this research was initiated in order to ascertain the potentialities and limitations of using such phenomena as a means of detecting the presence of thermal break-down products or constituents of the oil which cause varnish and sludge formation and corrosion in internal combustion engines, and also of detecting the presence of any additive agents in lubricating oils. Because the results described in Part I were considered so promising, the following experimental studies were made on spreading phenomena in oils due to the presence of the fatty alcohols, phenols, ketones and esters. These organic chemicals are triply interesting since they are likely break-down products of oils, are commonly used additive agents, and often are powerful emulsifying agents.

(c) Known Facts Bearing on the Problem

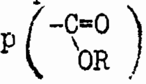
3. No work has ever been published on the effects on oil spreading of any organic compounds other than fatty acids(1,2,3,4). Furthermore, even these early studies of fatty acids were so limited and incomplete as to be useless, as reference to Part I will show.

4. In Part I the general phenomena involved in the spreading of oil drops on water were described. All the phenomena reported were explained satisfactorily with the exception of the non-spreading of the long-chain acids on acid water free from metallic ions. In this report the mechanism involved has also been completely unraveled, largely due to the useful and simple results obtained in connection with the study of the aliphatic alcohols.

5. The only previous reference to the spreading effects of non-acids was made by Stenstrom and Vigness(1) who simply remarked that cetyl alcohol and capro-aldehyde do not cause oil spreading on water (work reported here shows those results to be incorrect). However, the early work of Langmuir(3,4) on the spreading of stearic acid upon acidified water has proved to be most helpful, although extremely sketchy and incomplete.

(d) Theoretical Considerations

6. If molecules of a fatty acid are present in solution in a mineral oil, ionization of the polar end of the molecule, the carboxyl group, can happen when in the course of its diffusion through the oil it reaches the oil-water interface. The electrical forces arising from

that ionization process would be expected to add their effect to the forces tending to hold the molecule at the interface. On the other hand, molecules having a non-ionizable polar group like the alcohol group (OH), the ketone group (C=O), or the ester group  $\left(\begin{array}{l}-C=O \\ \quad\backslash OR\end{array}\right)$ would be less firmly held at the interface and might leave it after a certain average duration or "life-time" and disappear within the volume of the oil drop.

7. Stated in another way, long-chain molecules with ionizable polar groups will have long average life-times at the oil-water interface, while those with non-ionizable polar groups will have much shorter average life-times. In fact, the results of Part I prove that the ionized acid molecules all remain indefinitely at the interface. On the other hand, all non-ionizable molecules will not remain at the interface but will be taking part in a dynamic equilibrium which will involve a steady flow of molecules to the interface from the interior of the oil drop, the temporary adsorption of a certain proportion, and the subsequent loss from the interface of adsorbed molecules due to the combined defects of thermal agitation and molecular collisions. At equilibrium a certain average number of the molecules will be adsorbed at the interface and the remainder will be in solution in the oil drop.

8. Obviously oil containing non-ionizable polar molecules will spread equally well on acid or on alkaline water or on water containing dissolved metallic ions, while oil containing ionizable molecules will spread most when placed on water arranged to have that acidity (or pH) most effective in causing ionization.

9. If these theoretical considerations are correct, oil spreading phenomena will permit one to experimentally distinguish between ionizable and non-ionizable molecules, since obviously the former would show more spreading for very small concentrations of the polar molecules than the latter.

10. The equilibrium of the surface tension forces acting on a thin oil disc is graphically shown in Plate 6. Since the angle θ is small, the following relation of the three surface tension forces acting at point P must hold for static equilibrium, i.e., non-spreading of disc:

$$F_{OW} + F_{OA} \geq F_{WA} \qquad (A)$$

For a pure mineral oil on clean water at 20° C. the following surface tension data are correct to a sufficient degree of accuracy:

F_{WA} = 73 dynes/cm.

F_{OW} = 31 " "

F_{OA} = 55 " "

Hence, (A) holds since $31 + 55 > 73$.

11. Now polar molecules adsorbed at the oil-water interface, PQ, will exert, by virtue of their thermal agitation and mutual collisions (and also because they are constrained to move only in the interfacial area), a surface pressure, F . Therefore, in equation (A) to the force, F_{OA} , must be added the pressure, F , hence introducing numerical values,

$$31 - F + 55 \geq 73 \qquad (B)$$

and this relation will be fulfilled so long as F is less than or equal to 13.

12. Thus, when F exceeds 13 dynes per centimeter disc spreading will begin and the more F exceeds 13, the more rapid the spreading will be. In other words, such an oil drop containing polar molecules can spread only when the interfacial film pressure, F , due to the adsorbed molecules exceeds a certain definite value which for most mineral oils is somewhere between 10 and 14 dynes per centimeter at room temperature. Consequently, if the area per molecule, A_O, in the adsorbed film can be found by measuring the spreading of oil drops, it will be that value of A_O corresponding to the packing together of the molecules under the equilibrium pressure, F .

(e) Narrative of Original Work Done at this Laboratory on the Problem

13. The fatty alcohols have been added to either light or heavy mineral oil and the effects of the alcohol concentration and temperature have been investigated in considerable detail. The effects of varying the pH of the water and also of the presence in the water of metallic ions have been studied. The area, A_O, occupied at the oil-water interface by the molecules of the various alcohols has been measured.

14. Because the behavior of these alcohols furnished a valuable clue as to the cause of the earlier non-spreading of fatty acids in oil when placed on acidified water, a further study of all the fatty acids described in Part I was made in order to complete our knowledge of their behavior under these circumstances. In addition, undecenoic acid has also been studied.

15. A considerable number of aromatic and naphthenic alcohols were studied.

16. A series of ketones both aliphatic and aromatic have been studied.

17. A series of esters of a monohydric and of a trihydric alcohol and two esters containing two polar groups each were studied.

18. A new method has been developed as an incidental result of this work which has proved a sensitive means of measuring the solubilities in oil of long-chain compounds, and with which a number of approximate solubility measurements of interest have been obtained.

DESCRIPTION OF MATERIAL AND DATA OBTAINED

(a) Aliphatic Alcohols

19. Each of the members of the homologous series of fatty alcohols listed in Table VIII were dissolved in Crystal Company petrolatum (light mineral oil) and drops of each solution were spread on the clean surface of distilled water at 25°C. It was found that the addition of an alcohol to pure mineral oil will not cause an oil drop to spread unless the weight concentration, w , exceeds a certain definite concentration, w_0 . The more w exceeds w_0 the more rapid the rate of spreading of the drop and the greater the maximum area attained in spreading. If $w-w_0$ is sufficiently great, the film shows uniform interference colors, in which case it breaks up into a number of smaller oil discs soon after attaining its maximum diameter. The lower the molecular weight of the alcohol, the more rapid the spreading, and the more violent the break-up of the oil disc after maximum extension. In fact, the low molecular weight alcohol, hexanol, spreads and bursts violently into thousands of tiny droplets in the space of a few seconds, while the high molecular weight alcohol, hexadecanol, spreads much more slowly and after reaching its maximum diameter the disc merely gradually contracts. In all cases, tests with talc (see Part I, paragraph 27) show there is edge loss occurring which is much less pronounced for high molecular weight molecules than for those of low molecular weight.

20. If the maximum spreading area per gram of the oil drop ($\pi R^2/m$) be plotted against $w-w_0$ a good straight line graph is obtained for each substance studied. This result, which has proved quite general for non-ionized molecules, is precisely the same as that found by Langmuir(3,4) in his study of the spreading of stearic acid on acid water. The results for hexadecanol, tetradecanol, dodecanol and decanol when dissolved in light mineral oil and spread at 25°C. are given in Table I-A and also in Plate 1.

Table I-A

Spreading of Aliphatic Alcohols in Light Mineral Oil.
(Temperature of 25°C.)

Alcohol	N	w_0 in gm/gm	W_0 moles/1000 gm	a_0
Octadecanol	18	Too insoluble	–	–
Hexadecanol	16	1.940×10^{-3}	0.802×10^{-2}	57.2 A^2
Tetradecanol	14	1.660×10^{-3}	0.776×10^{-2}	65.7 A^2
Dodecanol	12	1.393×10^{-3}	0.749×10^{-2}	56.2 A^2
Decanol	10	1.140×10^{-3}	0.722×10^{-2}	55.4 A^2

Table I-B

Spreading of Aliphatic Alcohols in Heavy Mineral Oil.
(Temperature of 25°C.)

Alcohol	N	w_0 in gm/gm	W_0 in moles/1000 gm	a_0
Octadecanol	18	Too insoluble	-	-
Hexadecanol	16	2.10×10^{-3}	0.868×10^{-2}	38.2 A^2
Tetradecanol	14	1.84×10^{-3}	0.861×10^{-2}	61.5 A^2
Dodecanol	12	1.41×10^{-3}	0.759×10^{-2}	48.7 A^2
Decanol	10	1.285×10^{-3}	0.814×10^{-2}	54.3 A^2

21. The explanation of these results is quite readily given along the lines laid down in paragraphs 6 to 12, for they are manifestations of short life-time adsorption at the oil-water interface. Every molecule of alcohol which reaches the interface does not remain there indefinitely, but due to the effects of the oil solubility of the hydrocarbon chain of the molecule and to the effects of the collisions of the interfacial molecules with one another and with the neighboring water and oil molecules, after a brief stay each polar molecule leaves the interface and disappears into the volume of the oil drop. At any instant, however, the interfacial area will be occupied by adsorbed molecules and their thermal agitation and mutual repulsive forces will result in the creation of a two-dimensional interfacial film pressure which will always act to increase the interfacial area, or in other words, to cause the oil drop to spread on the water as much as external forces permit. However, the spreading cannot commence until the film pressure F exerted by the adsorbed molecules is at least a little greater than the resultant of the surface tension forces acting on the thin disc, as has been shown in paragraphs 11 and 12. This force has been shown to be between 10 and 14 dynes per centimeter.

22. No spreading occurs when w is less than w_0 because the film pressure F is too small. As spreading takes place the alcohol molecules adsorb as fast as new interfacial area is made available. The newly arrived adsorbed molecules must come from the alcohol distributed within the volume of the oil drop in the neighborhood of the interface, and the volume concentration in the drop decreases accordingly. Evidently, the spreading will cease when the volume concentration of the alcohol in the drop has decreased to the value w_0, and static equilibrium will result. As evidence of the correctness of this description, if a multiple piston (see Part I, page 12) be employed to exert an external pressure on the oil drop, the disc contracts completely when the external pressure is around 15 dynes - quite unlike the behavior under the same conditions of adsorbed films of ionized molecules; for they merely contract until the closest possible packing of the adsorbed molecules results.

23. Consequently, the difference in concentration $w-w_0$ represents the amount of alcohol which had to flow to the interface in order to permit the disc to expand to its maximum spreading area, A . Hence if m is the mass of the oil drop, the number of the alcohol molecules given up by the solution to form the film will be:

$$(w-w_0)\,\frac{m}{M}\,6.06 \times 10^{23} \qquad \text{(C)}$$

where M is the gram molecular weight of the alcohol. If a_o is the area occupied by a polar molecule in the interface and R is the maximum radius attained by the spreading oil disc, then $A = \pi R^2$, and the number of molecules in the interface must be:

$$\frac{\pi R^2}{a_o} \qquad \text{(D)}$$

Since expressions (C) and (D) must be equal:

$$\frac{\pi R}{a_o} = (w-w_0)\;\frac{m}{M}\;(6.06 \times 10^{23}) \qquad \text{(E)}$$

24. Differentiating equation (E) with respect to w gives the relation:

$$\frac{d}{dw}\left(\frac{R^2}{m}\right) = \frac{a_o}{M}\;(6.06 \times 10^{23}) \qquad \text{(F)}$$

The left hand side of F is the slope, tangent θ, of the straight line whose equation is given by (E), and it can be obtained by plotting $\pi R^2/m$ on the axis of ordinates against w on the axis of abscissae. Hence the useful relation is obtained:

$$a_o = (6.06 \times 10^{23})\; M \tan \theta \qquad \text{(G)}$$

which permits the calculation of a_o from a measurement of $\tan \theta$ provided the gram molecular weight, M , of the adsorbed polar molecules is known.

25. It was found that whereas a_o was not temperature-sensitive, w_0 was very much so. Since w_0 is the concentration at which F equals the net surface tension forces acting on a flat disc of oil, and since the surface tensions of oil and water are affected markedly by temperature changes, w_0 would be expected to prove temperature sensitive. It was found for aliphatic alcohol that raising the temperature 1°C. increased the value of w_0 by 10 per cent roughly. It is worth noting that this temperature increase may also be in part due to the increase in solubility with temperature.

26. The results obtained with the aliphatic alcohols dissolved in mineral oil are given in Tables I-A and I-B and in Plate 1. In the third column w_0 is the intercept on the w axis (see paragraph 20) expressed in grams of alcohol per gram of oil. In the fifth column will be found the area per adsorbed molecule a_0 expressed in the unit of 10^{-16} square centimeters which is denoted by A^2.

27. One regularity shown by these data has been brought out in Plate 2 by plotting w_0 against N, the number of carbon atoms in each molecule. It is worth remembering that N is nearly proportional to the molecular weight, M. From the straight line of Plate 2 one concludes that a more significant quantity than w_0 is the intercept on the w axis expressed in gram moles per thousand grams of oil, and this value, denoted by W_0, is presented in the fourth column of the preceding tables. It is evident that W_0 is very nearly the same for all alcohols dissolved in the same mineral oil, and the values for the two different mineral oils used are not far apart.

28. As stated in paragraph 19, edge loss, or the edge diffusion phenomena described in Part I, page 9, also occurs here. And it also becomes more pronounced the shorter the chain length of the molecule. Shortly after the spreading drop has reached its maximum diameter, a series of phenomena occur which are quite characteristic of the molecule chain length of the adsorbed molecules. The differences are quite qualitative but useful. If there are 16 carbon atoms in the chain, as in hexadecanol, the process consists of a gradual contraction of the disc accompanied by weak edge loss; if there are 12 carbon atoms, as in dodecanol, the disc slowly breaks up by the splitting off from the periphery to form a half dozen or so flat discs which in turn gradually contract as considerable edge loss is manifested; if there are 10 carbon atoms in a chain, as in decanol, the discs breaking off are smaller, far more numerous, and the process occurs in the space of a few seconds, while the edge loss is much stronger; finally, if there are only 8 or 6 carbon atoms in a chain, as in octanol or hexanol respectively, the disc seems to literally explode in a two-dimensional sense, and hundreds of tiny, almost hemispherical, drops are left skating about on the water for 15 seconds or less.

29. From the linear relation between $\frac{\pi R^2}{m}$ and w, a value of a_0 can be computed readily; however, the existence of edge loss obviously causes the calculated value of a_0 to be too small, the error being greater the more pronounced the edge loss, or in other words, the lower the molecular weight. Hence a_0 is nearly correct for values of N of 14 or more, while for lower values it is too small. One can safely say from an inspection of the last column of Table I-A, for example, that a_0 for hexadecanol is actually not far from 57 A^2, but that it must be greater for all the alcohols of shorter chain length than 16. These conclusions are illustrated by the curve P_2 of Plate 5 which was constructed by plotting the value of a_0 of Table I-A against the number of carbon atoms per chain, N. The dotted tangent line P_2Q_2 was drawn in order to

give a rough indication of the course the curve P_2 would have run if no edge loss had been present. The actual curve is nearly parabolic due to the very rapid increase in edge loss with decreasing values of N .

30. It might be thought that the low value of a_0 for values of N less than 14 is due to the dissolving into the water of the adsorbed molecules. Although N.K. Adams' rule(5) that monolayers at the air-water interface of alcohols and acids are insoluble only if N is greater than 12, it is not true for monolayers at the oil-water interface. This is logical since in the latter case the molecule is attracted both by the water and by the oil, while in the former case is attracted by the water only. Much experimental evidence that Adams' rule does not apply can be cited from work carried on at this Laboratory; however, it is sufficient to describe one experiment with octanol dissolved in oil at a concentration which does not cause much disc spreading but does not show strong edge loss. If the boundary of the disc is compressed externally with a talc film on water to prevent edge loss and an hour later the pressure is released, the edge loss commences practically undiminished. If the adsorbed octanol molecules had been appreciably water soluble, all of them would be dissolved in that time since an hour is enormously greater than the time needed for all the octanol molecules to diffuse from out of the oil drop, adsorb, and finally dissolve in the water.

(b) New Solubility Phenomena

31. Experiments were made with light mineral oil to which progressively larger amounts of hexadecanol were added until w exceeded the solubility limit as shown by subsequent precipitation of crystals. It was found that as long as the solubility limit was not exceeded uniformly, colored films were obtained and the graph of $\pi R^2/m$ versus w was a good straight line. When w exceeded the solubility limit of

$$w_m = 2.5 \times 10^{-3} \text{ gm/gm}$$

the graph of $\pi R^2/m$ versus w still was a straight line, but the spreading oil disc developed numerous colored spots which were evident because they spread faster than the rest of the disc. When w was less than w_m no spots appeared during spreading. Experiments with tetradecanol showed similar results when w exceeded the value of $w_m = 6.1 \times 10^{-3}$, and the colored spots which appeared spread very rapidly relative to the rest of the film. Similarly, experiments with dodecanol showed that when w exceeded $w_m = 10.2 \times 10^{-3}$, the colored spots appeared but the incidence of the phenomena was not so well defined a function of w as in the case of hexadecanol and tetradecanol.

32. Since experiment showed that precipitation occurred only when the hexadecanol concentration w exceeded 2.5×10^{-3}, it was decided that this appearance of spots was due to exceeding the solubility limit. Consequently, the other two experiments furnished the solubility limits for tetradecanol and dodecanol. The resultant solubilities are in agreement with the well known fact that the solubility of alcohols

in oil increases as the number of carbon atoms, N , decreases.

33. The appearance of these spots is due to the more rapid spreading of the oil disc in the vicinity of an undissolved crystal or an undissolved droplet of the alcohol. This change in the character of the spreading of oil drops in passing through the solubility limit can be used as a sort of two-dimensional titrating technique to measure the solubility of any slightly soluble substance which by itself is above to spread on water as a monolayer. However, it cannot be employed with much success if the solubility limit w_M is great, since the rate of disc spreading increases with the difference $w-w_0$, and so before w has reached the value w_M the speed of spreading will have become so great that it will be impossible to differentiate with the naked eye between the spreading in the locality of the undissolved crystal and that of the surrounding film.

34. In Table II are listed the solubilities in grams of alcohol per gram of oil of the three alcohols studied. These measurements are correct to within 5 per cent. Such accuracy was considered sufficient for the purpose of this work.

Table II

Solubilities of Alcohols in Mineral Oil
(Temperature of 25°C.)

Alcohol	N	Solubility in Grams per Gram In Light Mineral Oil	Solubility in Grams per Gram In Heavy Mineral Oil
Octadecanol	18	Less than 2×10^{-3}	Less than 2×10^{-3}
Hexadecanol	16	2.5×10^{-3}	2.6×10^{-3}
Tetradecanol	14	6.1×10^{-3}	4.4×10^{-3}
Dodecanol	12	10.2×10^{-3}	8.8×10^{-3}

(c) Application of Solubility Data to Theory of Adsorption

35. The solubility data of the preceding paragraph permit an important experimental conclusion with regard to the mechanism involved in the spreading of non-ionized molecules. Referring to Table I, or Plate 1, it is seen that w_0 decreases as N decreases. If the linear increase in the area of the spreading disc with increasing w were due to the fact that w_0 were actually the solubility limit and $w-w_0$ the excess undissolved alcohol which in that way was made available to be adsorbed and cause spreading, then necessarily w_0 would have to be greater for hexadecanol than for dodecanol. But the solubility measurements of the preceding paragraph show that the reverse is actually the case. Hence w_0 is not the solubility limit, but is less than that; in fact, the difference becomes rapidly greater as N decreases, as a

comparison of Tables I and II will show. The only conclusion left is that the spreading of oil discs containing non-ionized molecules is a manifestation of interfacial adsorption - in agreement with the general theory advanced in paragraph 7 and further described for alcohols in paragraph 21.

36. The lack of disc spreading found at 25°C. for octadecanol dissolved in mineral oil has a simple explanation. From Table I it is evident that w_0 increases as N increases, while from Table II the solubility w_M decreases as N increases. In the case of octadecanol, or of alcohols of still greater molecular weight, w_M is less than w_0 ; that is, the low solubility does not permit dissolving enough alcohol for the adsorbed molecules to exert a large enough surface pressure to cause disc spreading.

(d) Spreading of Non-Ionized Aliphatic Acids

37. The preceding investigation of the spreading of alcohols has furnished, free from doubt, the clue as to the cause of the non-spreading of long-chain fatty acids on acid water as described in Part I, pages 15-16; for on acid water the fatty acids are not ionized, hence they should adsorb like any other polar but unionized molecule, and hence should show oil disc spreading only when w exceeds some value w_0 of an order of magnitude of around one part in 1000 by weight.

38. The spreading on acid water of each of the saturated aliphatic acids studied in Part I and the unsaturated acids, octadecenoic and undecenoic acid, were also studied where dissolved in light mineral oil, and it was found in each case that precisely the same type of spreading occurred as in alcohols. In Plates 3 and 4 will be found graphs of the results of plotting $\frac{\pi R^2}{m}$ against w for each of these acids, while in Tables III-A and III-B are presented the results in a form suitable for comparison with Table I for the corresponding alcohols.

Table III-A

Saturated Acids in Light Mineral Oil - Temperature 25°C.
(Spread on 0.01 N HCl)

Acid	N	w_0 in gm/gm	W_0 moles/1000 gm	a_0
Octadecanoic	18	Too insoluble	-	-
Heptadecanoic	17	2.050×10^{-3}	0.752×10^{-2}	63.8×10^{-16}
Hexadecanoic	16	1.708×10^{-3}	0.667×10^{-2}	72.0×10^{-16}
Tetradecanoic	14	1.370×10^{-3}	0.601×10^{-2}	70.5×10^{-16}
Tridecanoic	13	1.300×10^{-3}	0.607×10^{-2}	68.9×10^{-16}
Dodecanoic	12	1.113×10^{-3}	0.556×10^{-2}	69.8×10^{-16}
Undecanoic	11	0.920×10^{-3}	0.494×10^{-2}	57.4×10^{-16}

Table III-B

Unsaturated Acids in Light Mineral Oil - Temperature 25°C.
(Spread on 0.01 N HCl).

Acid	N	w_0 gm/gm	W_0 moles/1000 gm	a_0
Octadecenoic	18	0.710×10^{-3}	0.252×10^{-2}	46.0×10^{-16}
Undecenoic	11	0.650×10^{-3}	0.353×10^{-2}	61.1×10^{-16}

39. A graph of w_0 against N (see Plate 2) furnishes similar results to those for alcohols, from which can be inferred again that W_0 (expressed in gram molecules per thousand grams of oil) is roughly constant for a homologous series. However, the variation in W_0 from the mean is greater than with the alcohols.

40. Upon comparing each alcohol and acid of the same chain length, N, it is evident that a_0 is greater for acids than alcohols; in fact, the mean value of a_0 for acids in light mineral oil is 67.1 A^2, while for alcohols it is 58.6 A^2. Also the value of W_0 for acids (0.613×10^{-2}) is less than the corresponding value (0.762×10^{-2}) for alcohols.

41. The higher values of a_0 found for the fatty acids are not due to the effect of traces of ionization of the acids since the same results were found on acid water varying from 0.01 normal to 0.05 normal. The lower value of W_0 for acids can be considered either as a manifestation of the smaller solubility of oil for acids than for alcohols, or as evidence of greater adhesion of the carboxyl group for the water interface than that of the hydroxyl group. The lower value of W_0 for the unsaturated acids octadecenoic and undecenoic than the corresponding saturated acids octadecanoic and undecanoic is noteworthy and must mean that the presence of double bonds increases the average life-time of the adsorbed molecules. The evident parallelism between the graph $\frac{\pi R^2}{m}$ versus W for undecanoic and undecenoic acids, and for octadecenoic acid and heptadecanol, is also noteworthy and means that a_0 is independent of the presence of double bonds in the hydrocarbon chain.

42. Just as in the case of alcohols, the saturated fatty acids show an increasing value of w_0 as the number of carbon atoms per chain, N, increases, and similarly it was found that the solubility in the light mineral oil decreased as N increased. Thus hexacosanoic acid (N = 26) has a solubility less than 10^{-4}, eicosanoic acid (N = 20), has a solubility somewhere between 0.4×10^{-3} and 1.0×10^{-3}, octadecenoic acid (N = 18) has a value of around 1.0×10^{-3}, and finally for tetradecanoic acid it is definitely greater than 3.0×10^{-3}.

43. It was found that oil drops containing octadecanoic acid (N = 18) would not spread on acid water at 25°C. This behavior is similar to that of octadecanol as described in paragraph 35, and has the same cause, i.e., w_0 , for octadecanoic acid would, by Table III-A, of necessity be greater than for heptadecanoic acid. Therefore w_0 is greater than 2.05×10^{-3}; but the solubility of octadecanoic acid is less than 1.0×10^{-3}, as has been mentioned in the preceding paragraph. Hence disc spreading is impossible.

(e) Aromatic and Naphthenic Alcohols and Phenols

44. A group of non-aliphatic alcohols were studied by the same technique previously described for the aliphatic alcohols and the same general phenomena were encountered. The solutions studied were all in light mineral oil and only approximate measurements of w_0 were made, primarily because it was considered only necessary for present purposes to find out the orders of magnitude. The results are listed in Tables IV and V and the compounds used are described in Table VIII, appended.

Table IV

Spreading of Aromatic or Naphthenic Alcohols in Light Mineral Oil.
(Temperature of 25°C.)

Alcohol	N	w_0 in gm/gm	W_0 in moles/1000 gm
α -Naphthol	12	1.0×10^{-3}	0.6×10^{-2}
β -Naphthol	12	1.0×10^{-3}	0.6×10^{-2}
Benzyl alcohol	7	3.4×10^{-3}	3.2×10^{-2}
Diphenyl carbinol	13	0.9×10^{-3}	0.55×10^{-2}
Phenyl benzyl carbinol	14	1.0×10^{-3}	0.51×10^{-2}
Cyclohexanol	6	2.4×10^{-3}	2.4×10^{-2}
1-Ethyl cyclohexanol	8	2.7×10^{-3}	2.1×10^{-2}

Table V

Spreading of Phenols in Light Mineral Oil.
(Temperature of 25°C.)

Phenol	N	w_0 in gm/gm	W_0 in moles/1000 gm
p-tert-amyl phenol	11	0.5×10^{-3}	0.3×10^{-2}
p-cyclohexyl phenol	12	0.5×10^{-3}	0.3×10^{-2}

45. The interesting alcohols 4,4'-dihydroxy diphenyl, 3,4-dihydroxy diphenyl, p-hydroxy diphenyl, and tri-phenyl carbinol were all found to be far too insoluble in mineral oil to be capable of causing spreading effects at room temperature.

46. These alcohols in oil all spread equally well on water with or without dissolved metallic salts and regardless of the pH. The phenols showed a slightly greater spreading at high pH than the low, but the difference was not sufficient to permit any reliable use of the effect. The study of phenols of greater chain length might give more interesting results, however. These observations are in good agreement with the well known weakly acidic properties of phenols.

47. Molecules having the same number of carbon atoms, N, differ greatly in their solubility in oil and in water. The greater the oil solubility the greater must be the value of W_0. This is illustrated by a comparison of W_0 for hexanol (1.45×10^{-2}) and cyclohexanol (2.4×10^{-2}), the latter compound being by far the more soluble. Similarly a comparison of heptanol with benzyl alcohol ($N = 7$) shows that W_0 equals 0.81×10^{-2} for the former and 3.2×10^{-2} for the latter (which is also the more soluble).

48. All of the alcohols and phenols studied were extremely soluble. For the least soluble some approximate measurements of the solubility, w_M, were made. Thus, the solubility at 25°C. for α-naphthol was between 1.8 and 2.6×10^{-3}, for diphenyl carbinol it was 9.8×10^{-3}, while for phenyl benzy-carbinol it was between 12.0 and 19.0×10^{-3}.

49. Results on the aromatic and naphthenic alcohols and phenols can be summarized briefly as follows: No disc spreading occurs unless W_0 is between 0.3×10^{-2} and 3.0×10^{-2}; and for all values of W greater than W_0 spreading area increases linearly with W. In general for compounds of the same N the greater the solubility in mineral oil the greater the value of W_0.

(f) Aromatic and Aliphatic Ketones

50. Solutions in light mineral oil of various aliphatic and aromatic ketones were tested for disc spreading on water. No effect on spreading of the pH or the presence of metallic salts was found. The results are given in Table VI.

Table VI

Spreading Data for Ketones in Light Mineral Oil.
(Temperature of 25.0°C.)

Ketone	N	w_0 in gm/gm	W_0 in moles/1000 gm
Methyl nonyl ketone	10	12.2×10^{-3}	7.2×10^{-2}
Di-n-amyl ketone	10	15.1×10^{-3}	8.9×10^{-2}
Di-undecyl ketone	23	12.0×10^{-3}	3.6×10^{-2}
Di-heptadecyl ketone	35	Too insoluble	-
Di-phenyl ketone	13	13.4×10^{-3}	7.3×10^{-2}
Di-benzyl ketone	15	6.0×10^{-3}	2.9×10^{-2}
Phenyl undecyl ketone	18	41.7×10^{-3}	16.0×10^{-2}

Spreading commenced only when w exceeded w_0 and as in the case of alcohols no spreading occurred if w_M was less than w_0. The ketones because of their high solubility in oil would not spread until W_0 was higher than was the case for acids, alcohols or phenols of corresponding values of N.

51. The solubilities were not measured except for the least soluble which were di-undecyl ketone ($w_M = 15 \times 10^{-3}$) and di-heptadecyl ketone ($w_M = 1.5 \times 10^{-3}$). In the case of the di-heptadecyl ketone it was not possible to dissolve enough ketone in the oil to reach w_0; hence no disc spreading could be obtained.

(g) Aliphatic Esters

52. The spreading of light mineral oil solutions of a group of aliphatic esters of monohydric and tri-hydric alcohols were investigated and the results are presented in Table VII.

Table VII

Spreading Data for Esters in Light Mineral Oil.
(Temperature of 25.0°C.)

Ester	N	w_0 in gm/gm	W_0 moles/1000 gm
Ethyl myristate	16	15.0×10^{-3}	5.9×10^{-2}
Methyl stearate	19	6.0×10^{-3}	2.0×10^{-2}
Ethyl stearate	20	6.1×10^{-3}	2.0×10^{-2}
Methyl sebacate	10	1.9×10^{-3}	0.94×10^{-2}
Ethyl ricinoleate	20	7.8×10^{-5}	0.0024×10^{-2}
Tricaproin	21	1.3×10^{-3}	3.3×10^{-2}
Triheptylin	24	0.87×10^{-3}	0.20×10^{-2}
Tricaprylin	27	5.3×10^{-3}	1.1×10^{-2}
Trilaurin	39	6.2×10^{-3}	0.98×10^{-2}
Tripalmitin	51	Too insoluble	-
Tristearin	57	" "	-

53. The spreading discs containing esters behaved like the alcohols, acids and ketones as regards the effect of varying w. No effect of the pH of the water was found except in a few cases where the greater and instantaneous increase in spreading on alkaline water was unquestionably due to the presence of impurities in the compound used of the organic acid from which the esters had been prepared. As usual, when the solubility w_M was less than w_0 no spreading occurred. Such was the case for tristearin and also for tripalmitin, whose solubilities in light mineral oil at 25°C. were less than 0.9×10^{-3} gram per gram. The triesters show clearly that W_0 is the least for the least soluble members of a homologous series in agreement with the results found with all the other homologous series.

54. As would be expected from the results given in Part I, page 13, on ricinoleic acid, ethyl ricinoleate should show similar unique spreading effects. The small value of w_0 (7.8×10^{-5}) given in Table VII is certainly unique among the esters studied. This is due to the existence in this particular ester of two polar groups, a hydroxyl group near the middle of the molecule and an ester group at the end of the molecule.

This gives the molecule two possible places of attachment to the oil-water interface, and from the experimental results obtained here one must conclude that practically every ethyl ricinoleate molecule reaching its adsorptive behavior is quite similar to that of ricinoleic acid.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

55. The work of Part I on the spreading of mineral oil on water due to the solution in the oil of fatty acids has been extended to cover alcohols, phenols, ketones, and esters and a point has been reached where some definite conclusions may be made which are of considerable technical value in the analysis of oils, oil break-down products, and emulsions.

I. The spreading of oils on water occurs only when polar molecules are present in solution in oil.

II. The amount of such polar molecules necessary to initiate spreading is remarkably dependent on whether or not the molecule contains an atomic grouping which will ionize in contact with water; if so, one part in 100,000 by weight causes measurable spreading, and if not, approximately one part in 1000 or even more is necessary.

III. When no ionization of a polar molecule is permitted or it is impossible because of the structure of the molecule, the oil spreading is the more noticeable the lower the solubility of the polar molecules in the oil. Therefore, spreading increases as the molecular weight decreases, as the number of double bonds decreases, and as the melting point decreases.

IV. When more than one polar group is present in the molecule and the configuration is such as to permit both groups to adsorb simultaneously at the water-oil interface, a much increased oil spreading for the molecular concentration involved results. If the adsorption of both groups is strong enough, spreading due to around one part in 100,000 by weight will be found, and it will be independent of the pH of the water.

56. The results of Part I showed that the spreading oil drop technique was a remarkably sensitive method of detecting acid in oils. The results of this report increase enormously the reliability of the tests for acids since conclusions II and III above prove that no other organic substances with one polar group in the molecule will spread one-hundredth as much as will the acids on alkaline water.

57. The mechanism of the spreading process for ionizable molecules was unraveled in Part I. In this report the mechanism of the spreading of non-ionizable molecules has been found.

58. It has been shown that whereas at the water-air interface acid or alcohol molecules are insoluble when N is less than 12 (Adams' rule), the results of this work demonstrate that at the oil-water

interface such molecules are insoluble even if N is as low as 6. This result has important applications in the study of additive oiliness agents, of emulsifying agents, and of wetting agents.

59. As an incidental result of the experimental work described here, a new and often useful method of measuring the solubilities in oil of definitely soluble polar organic compounds has been developed.

(b) Recommendations

60. A study of amines and amides and also of a number of compounds whose molecules contain more than one polar group is underway and a report will be probably submitted around July 1 as Part III of this series. After that it is recommended that a number of investigations be made of the applicability of this new technique and the information now already obtained with it to certain Naval problems. More specifically these recommended investigations are:

(1) The analysis of lubricating oils, especially for their thermal stability and for the catalytic effects of metals on their stability.

(2) A study of the emulsifying tendencies of oil, especially Naval fuel oils.

(3) The preparation of oils most suitable for use in combating malaria by their spreading on stagnant water.

(4) The preparation of the most suitable oils for calming waves in the vicinity of a ship.

(5) The preparation of most suitable oils for minimizing the evaporation of water from storage tanks in tropical climates.

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Table VIII

Names and Structural Formulae of Organic Compounds Used and Not Described in Part I.

Name	Common Name	Structural Formula
n-octadecanol	stearyl alcohol	$CH_3(CH_2)_{16}\ CH_2(OH)$
n-hexadecanol	cetyl alcohol	$CH_3(CH_2)_{14}\ CH_2(OH)$
n-tetradecanol	myristyl alcohol	$CH_3(CH_2)_{12}\ CH_2(OH)$
n-dodecanol	lauryl alcohol	$CH_3(CH_2)_{10}\ CH_2(OH)$
n-decanol	decyl alcohol	$CH_3(CH_2)_8\ CH_2(OH)$
n-octanol	octyl alcohol	$CH_3(CH_2)_6\ CH_2(OH)$
n-hexanol	hexyl alcohol	$CH_3(CH_2)_4\ CH_2(OH)$
9-undecenoic acid	undecylenic acid	$CH_3CH{:}CH(CH_2)_7COOH$
1-hydroxy naphthalene	α -naphthol	$C_{10}H_{17}\cdot(OH)$
2-hydroxy naphthalene	β -naphthol	$C_{10}H_{17}\cdot(OH)$
phenyl carbinol	benzyl alcohol	$C_6H_5\cdot(CH_2)(OH)$
diphenyl carbinol	benzhydrol	$(C_6H_5)_2\cdot CH(OH)$
phenyl benzyl carbinol	-	$(C_6H_5)\cdot CH_2\cdot CH(OH)\cdot(C_6H_5)$
cyclohexanol	-	$C_6H_{11}(OH)$
1-ethyl cyclohexanol	-	$C_2H_5\cdot(C_6H_{10})\cdot OH$
p-tert-amyl phenol	-	$C_5H_{11}\cdot(C_6H_4)\cdot OH$
p-cyclohexyl phenol	-	$(C_6H_{11})\cdot(C_6H_4)\cdot OH$
methyl nonyl ketone	-	$CH_3(C{=}O)\cdot C_9H_{19}$
di-n-amyl ketone	-	$C_5H_{11}(C{=}O)\cdot C_5H_{11}$
di-n-undecyl ketone	laurone	$CH_3(CH_2)_{10}\cdot(C{=}O)\cdot(CH_2)_{10}\cdot CH_3$
di-n-heptadecyl ketone	stearone	$CH_3(CH_2)_{16}\cdot(C{=}O)\cdot(CH_2)_{16}\cdot CH_3$
diphenyl ketone	benzophenone	$(C_6H_5)\cdot(C{=}O)\cdot(C_6H_5)$
dibenzyl ketone	-	$(C_6H_5)\cdot CH_2\cdot(C{=}O)CH_2\cdot(C_6H_5)$

(Continued)

Table VIII (Continued)

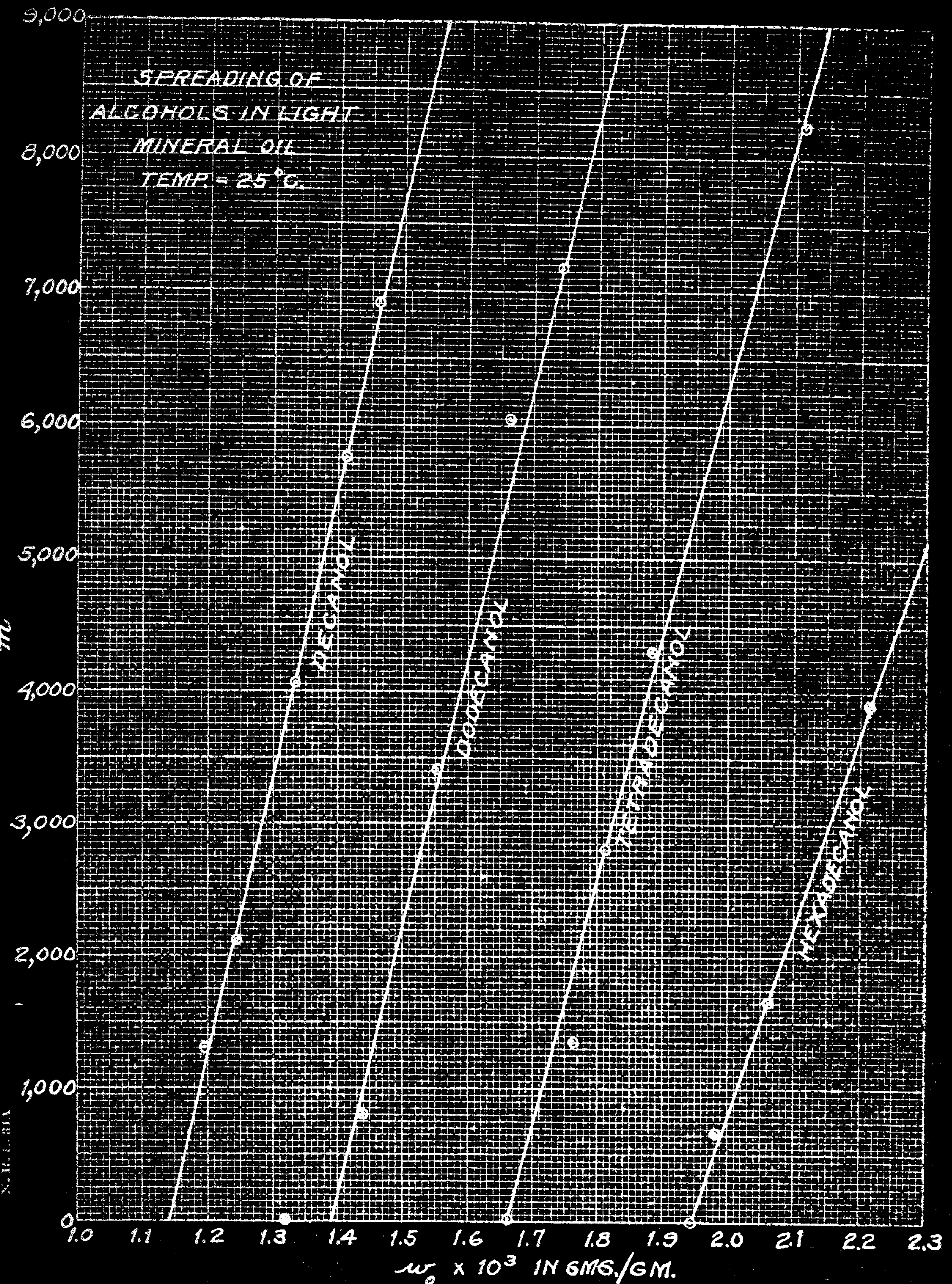
Name	Common Name	Structural Formula
phenyl undecyl ketone	-	$(C_6H_5)\cdot(C{=}O)\cdot C_{11}H_{23}$
ethyl myristate	-	$CH_3(CH_2)_{12}\cdot COO(CH_2)CH_3$
methyl stearate	-	$CH_3(CH_2)_{16}\cdot COOCH_3$
ethyl stearate	-	$CH_3(CH_2)_{16}\cdot COO(CH_2)CH_3$
methyl sebacate	-	$CH_3OOC\cdot(CH_2)_8\cdot COOCH_3$
ethyl ricinoleate	-	$CH_3(CH_2)_5(CH\cdot OH)CH_2(HC{=}CH)(CH_2)_7$ $COO(CH_2)CH_3$
tricaproin		triglyceride of hexanoic acid
triheptylin		triglyceride of heptanoic acid
tricaprylin		triglyceride of octanoic acid
trilaurin		triglyceride of dodecanoic acid
tripalmitin		triglyceride of hexadecanoic acid
tristearin		triglyceride of octadecanoic acid

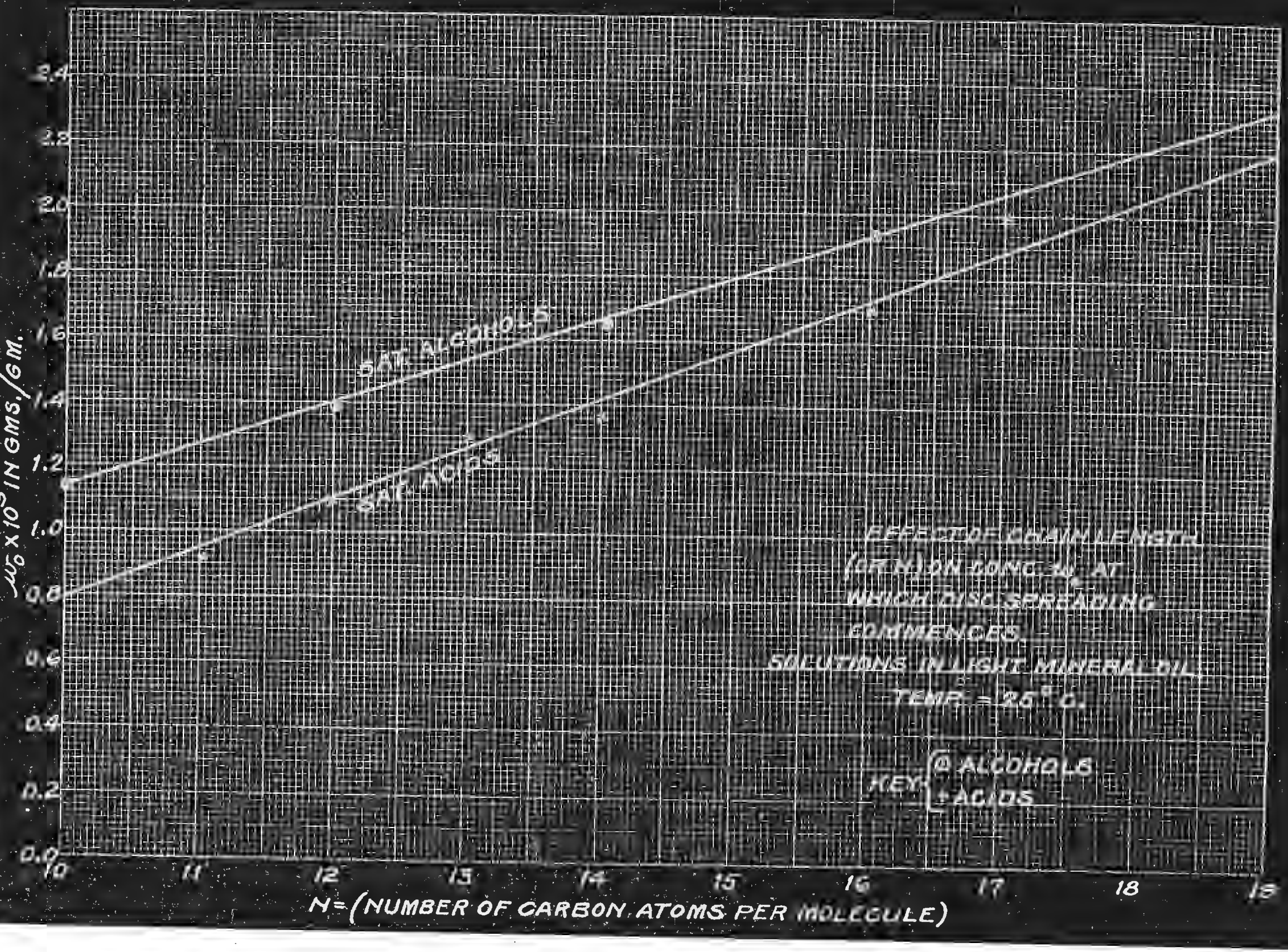
NAVAL RESEARCH LABORATORY

DATE

IF SHEET IS READ THIS WAY (HORIZONTALLY) THIS MUST BE TOP   IF SHEET IS READ THE OTHER WAY (VERTICALLY) THIS MUST BE

N. R. L. 81A

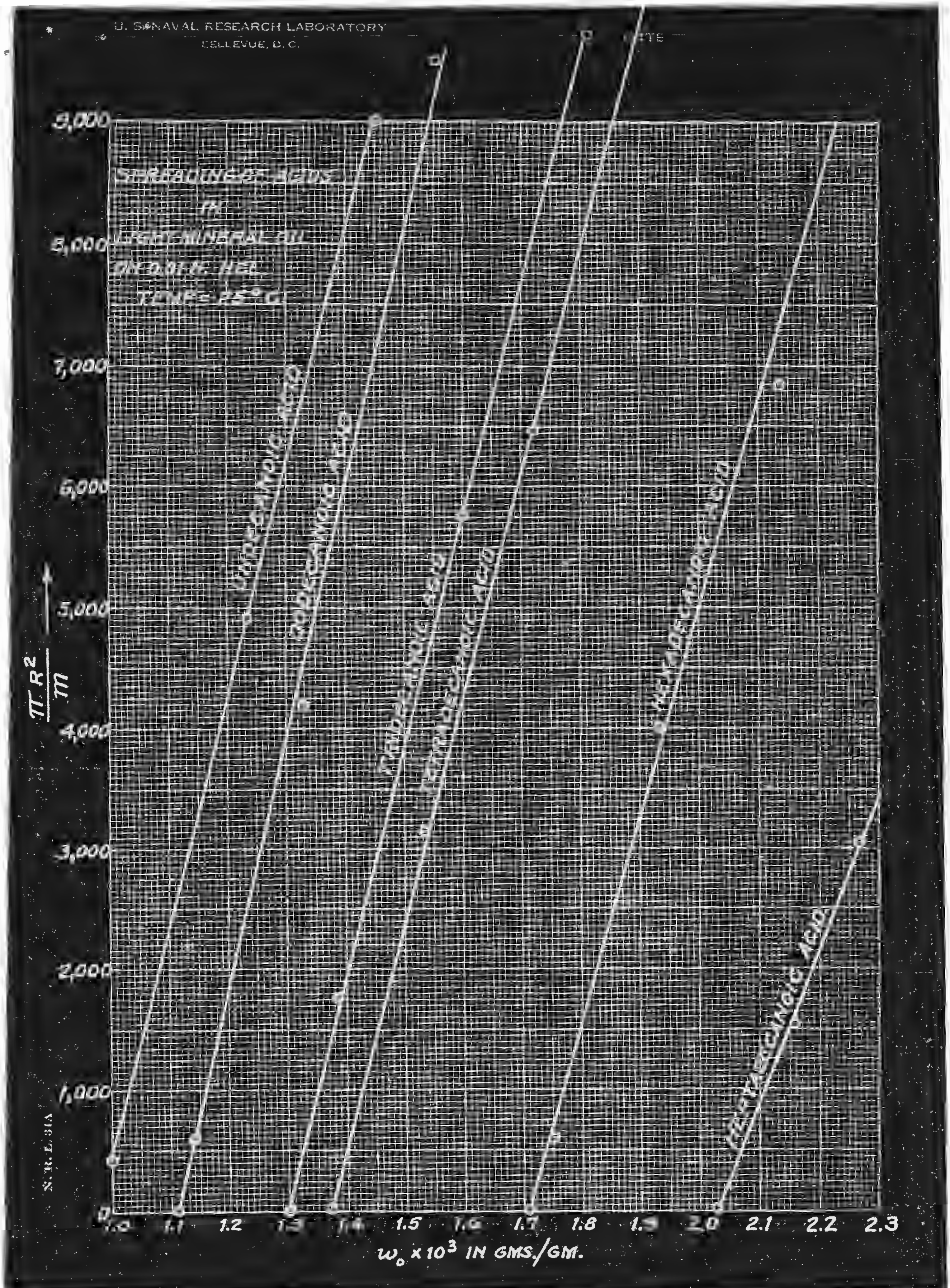




EFFECT OF CHAIN LENGTH (OR N) ON CONC. μ_0 AT WHICH DISC SPREADING COMMENCES.

SOLUTIONS IN LIGHT MINERAL OIL

TEMP. = 25° C.


U. S. NAVAL RESEARCH LABORATORY
BELLEVUE, D. C.
DATE
SPREADING OF ACIDS
IN
LIGHT MINERAL OIL
ON 0.01 N. HCL
TEMP = 25°C
UNDECANOIC ACID
DODECANOIC ACID
TRIDECANOIC ACID
TETRADECANOIC ACID
HEXADECANOIC ACID
HEPTADECANOIC ACID
$\frac{\pi R^2}{m}$ →
0
1,000
2,000
3,000
4,000
5,000
6,000
7,000
8,000
9,000
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
$w_0 \times 10^3$ IN GMS./GM.
N. R. L. 31A

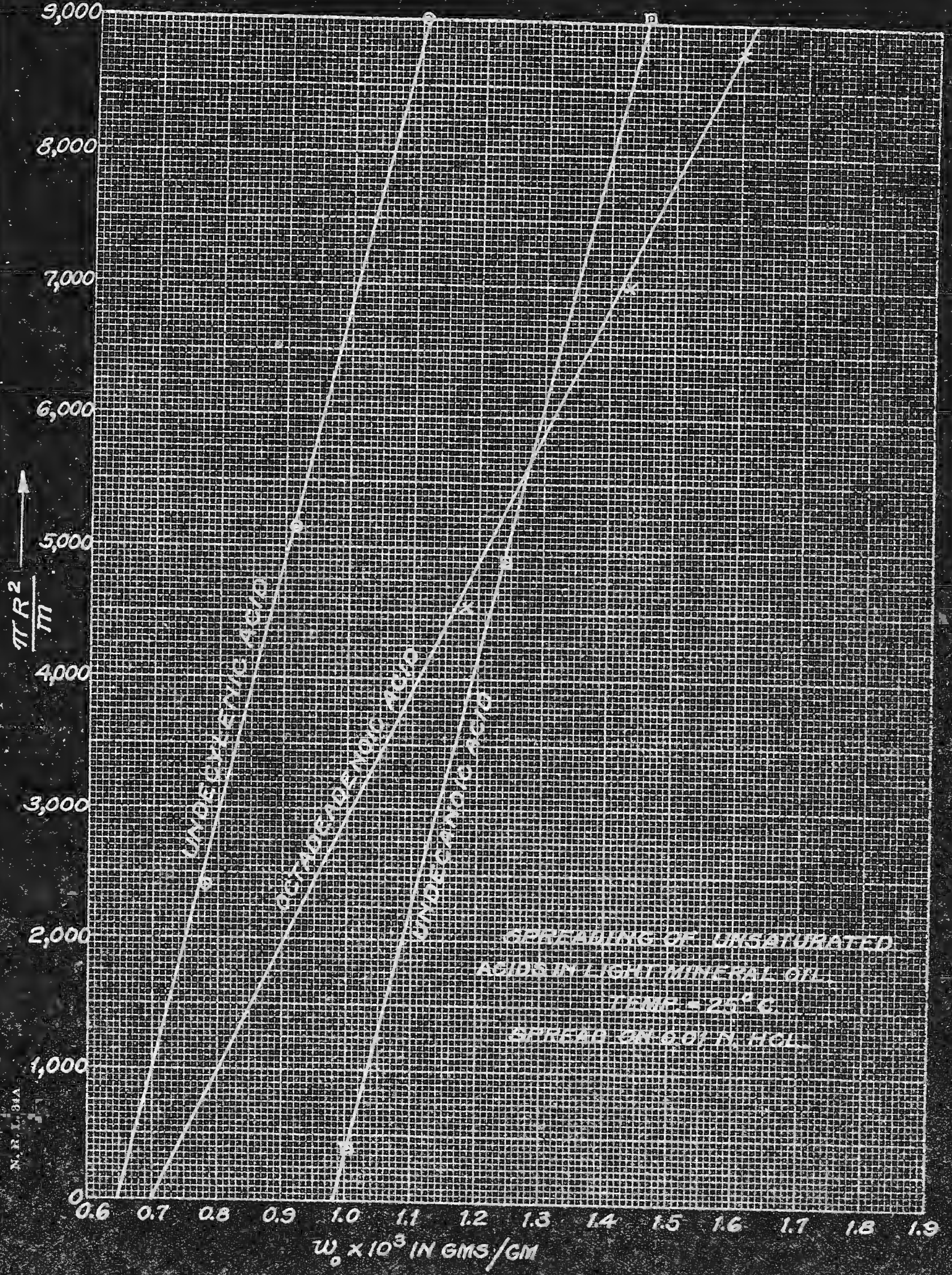

9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
$\frac{\pi R^2}{m}$
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
$w_o \times 10^3$ IN GMS./GM
UNDECYLENIC ACID
OCTADECADENOIC ACID
UNDECANOIC ACID
SPREADING OF UNSATURATED
ACIDS IN LIGHT MINERAL OIL
TEMP. = 25° C.
SPREAD ON 0.01 N. HCL
N. R. L. 84A

PLATE 4

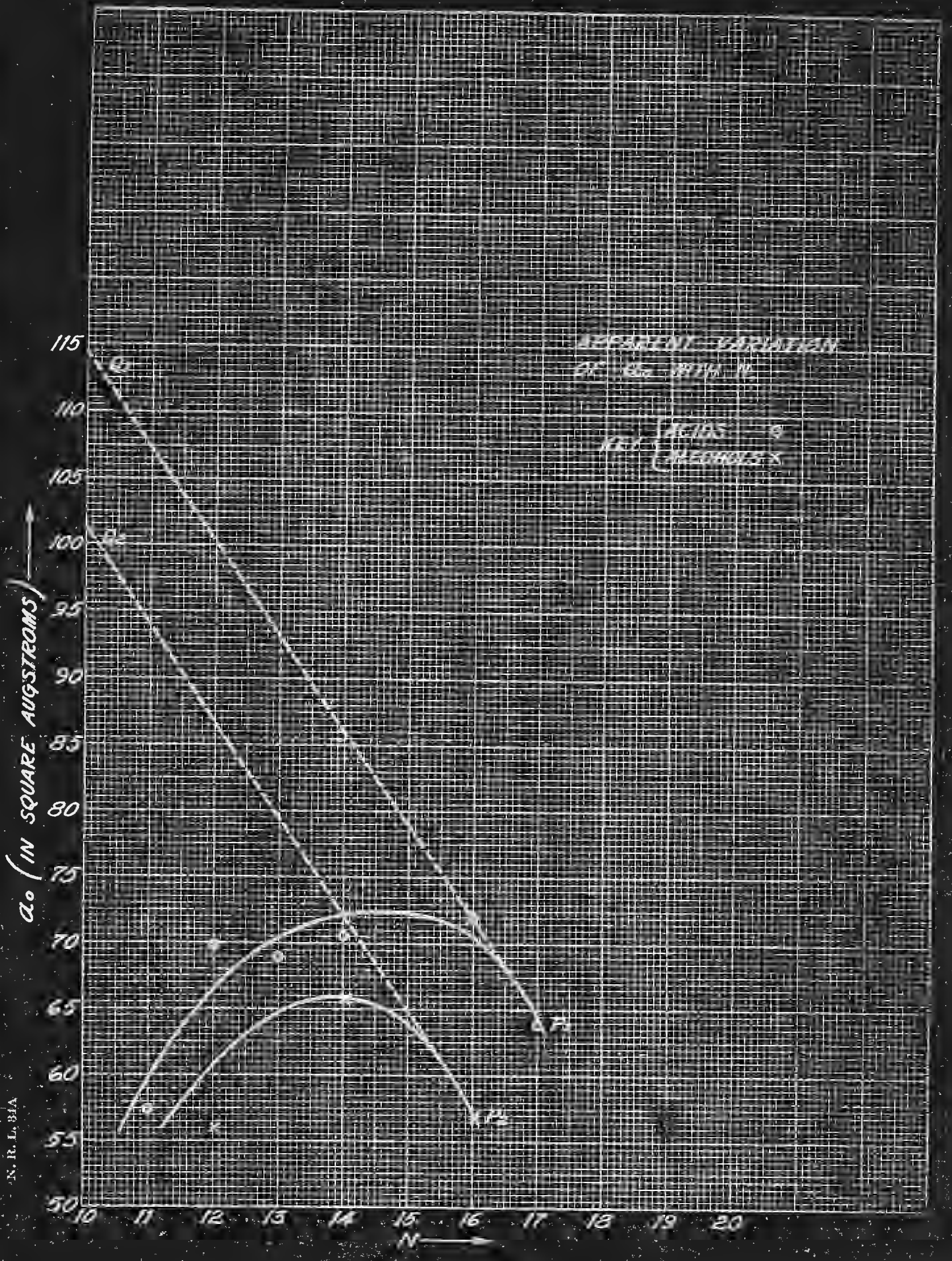
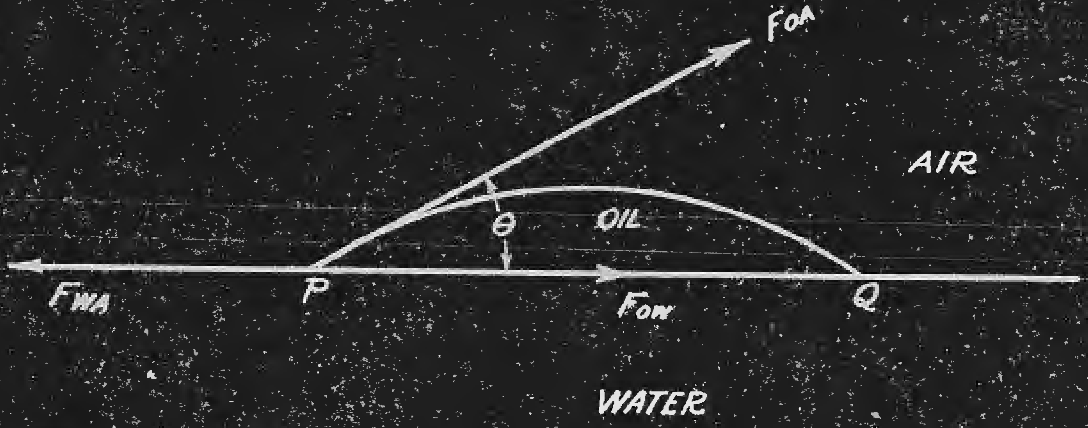

BELLEVUE D.C.
DATE
APPARENT VARIATION
OF a₀ WITH N
KEY { ACIDS ⊙
ALCOHOLS ×
a₀ (IN SQUARE AUGSTROMS) →
115
110
105
100
95
90
85
80
75
70
65
60
55
50
10
11
12
13
14
15
16
17
18
19
20
N →
P₁
P₂
N. R. L. 31A

PLATE 5



SURFACE TENSION FORCES
ACTING ON A THIN OIL DISC

PLATE 6