

A STUDY OF THE PHENOMENON
OF WETTING FILMS

BY
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A THESIS

Presented to the Graduate School of Michigan State College
of Agriculture and Applied Science in Partial Fulfillment
of Requirements for the Degree of Doctor of Philosophy

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East Lansing, Michigan
1935

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Acknowledgement

I wish to express my sincere appreciation and gratitude to Dr. C.W. Chamberlain of the Physics Department of Michigan State College, whose helpful criticisms and suggestions were a constant source of inspiration in the experimental work as well as in the preparation of this thesis.

Herbert L. Warren

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A Study of the Phenomenon of Wetting Films

The wetting method of measuring the depth of a liquid in a container is extremely inaccurate; this is especially true in the case of gasoline, naphtha and alcohol. In attempting to solve the problem of measuring accurately the depth of gasoline in an underground tank a problem which is developing serious labor difficulties and enormous economic loss, a very curious phenomenon was observed. Gasoline was found to wet a vertical glass plate to a height much greater than could be accounted for by the phenomenon of capillarity.

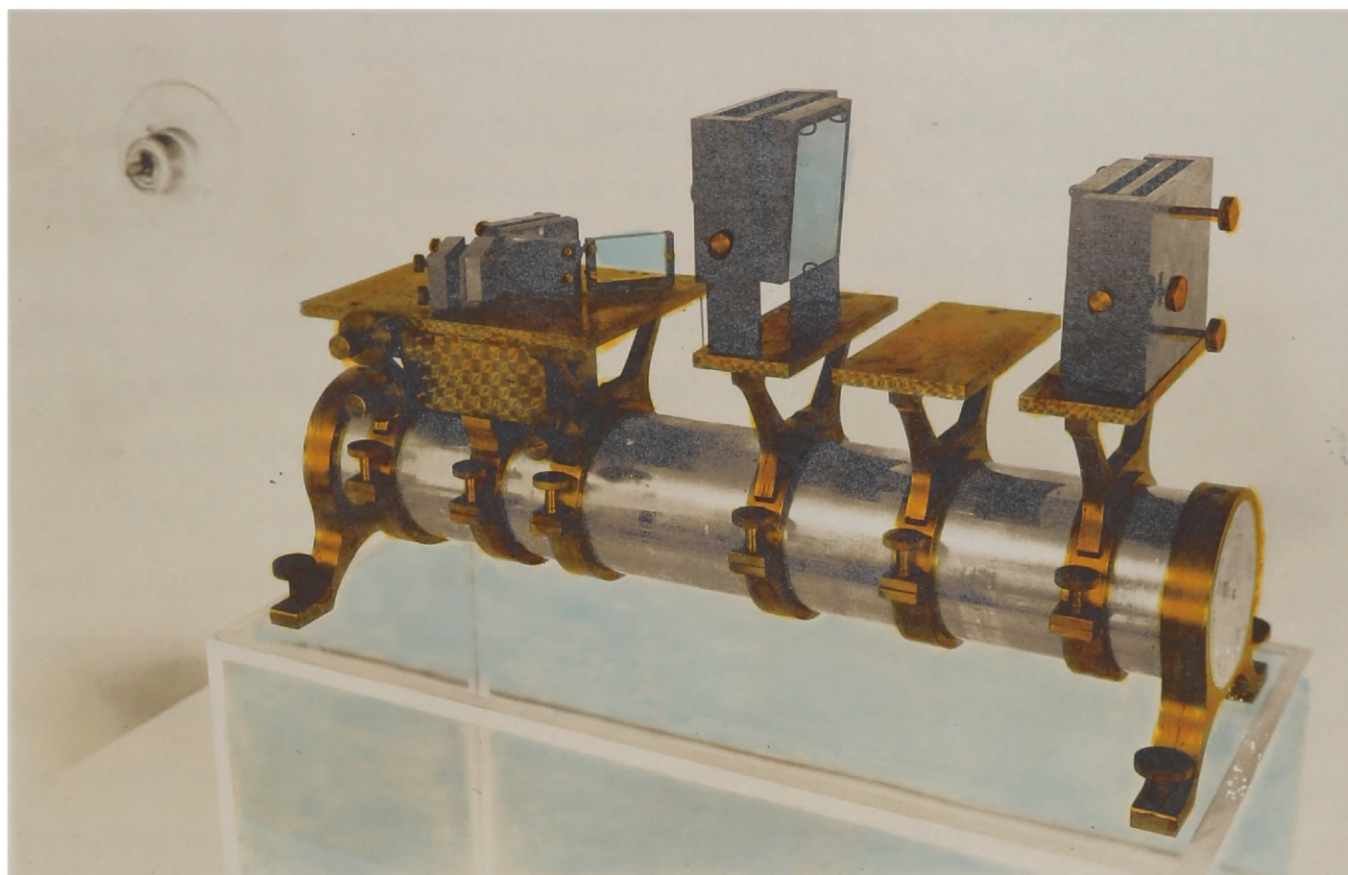
This phenomenon has been termed the wetting film, to distinguish it from the wringing film and the adsorbed film.

Wringing Film. Rolt (1) in speaking of the "Wringing" of Block Gauges says, "A most valuable feature of these gauges is the fact that it is possible to "wring" two or more gauges together, by first cleaning them and then bringing their faces into contact with a combined sliding and twisting motion.----- The adherence is due almost entirely to the presence of a liquid film between the faces.----- It is interesting to note that this minimum thickness found for

wringing films is roughly twice the accepted value of the radius of molecular attraction- a relationship which offers explanations for most of the properties associated with the phenomenon of wringing." The radius of molecular attraction was measured by Chamberlain (2) in 1910.

Quincke (3), in 1869, made an attempt to measure the Radius of Molecular Attraction, hereafter designated as R , and concluded that it was greater than 5×10^{-6} cm. It was generally agreed that a liquid film could not exist less than $3R$ thick. Reinhold and Rucker, in 1881 (4), 83 (5), and 93 (6) measured liquid films 1.2×10^{-6} cm. thick. Johonott and Chamberlain (7), in 1899, measured films 0.6×10^{-6} cm. thick, and observed the splitting of the Reinhold and Rucker film, and the reverse phenomenon of doubling. These results made it impossible to longer accept Quincke's determination of R .

As the value of R is far beyond the limit of the best compound microscope it was necessary to employ a new type of measuring instrument. Chamberlain designed the Compound Interferometer at Denison University and with the assistance of Ernst Keil, instrument maker of the Department of Physics in Barney Laboratory, constructed the instrument shown below.



The optical parts, possessing an accuracy greater than one twentieth of a light wave, were figured by O.L.Petitdidier. The value of R was found to be 1.5×10^{-7} cm., or one and a half millionths of a millimeter. Films one R thick are twenty times smaller than can be observed by the best compound microscope and, in the case of water, is approximately five molecules thick.

Adsorbed Film. An adsorbed film is a layer of a liquid or gas which has condensed on a solid surface. It is a manifestation of the force of adhesion.

Wetting Film. A wetting film is that film which spreads over a solid or liquid surface making contact at an angle with the liquid surface.

Liquids which Produce Wetting Films. While the present investigation was undertaken to determine the cause of the large wetting film on gasoline, and the varying character of this film, many liquids were examined to determine which ones possess the ability to form wetting films, and possibly throw light upon the cause of the phenomenon.

Ethyl alcohol (C_2H_5OH) has a wetting film which creeps very rapidly up the surfaces of silver and glass. Measurements on alcohol were not taken for two reasons: first, because of the work of Langmuir and second, because it seemed advisable to confine the experimental procedure to hydrocarbons. Results of this investigation show why alcohol creeps up the sides of a glass container. Langmuir (8) gives an explanation of the spreading of organic molecules, having the $-COOH$, $-CO$, and $-OH$ radicals, over liquid surfaces. While it is true that alcohol creeps up a vertical glass plate the glass plate must have on it a wetting film, as has been shown by Chamberlain.

Ether was found to creep producing a very thin wetting film.

Gasoline forms a wetting film in rather a violent manner. It was impossible to account for the wetting film by capillarity. In general new films can be produced by two methods; first, disturbing the surface, producing a small wavelet; second, by introducing a small amount of air near the surface of the gasoline. Different samples of gasoline were tried as well as treated and untreated gasoline and in each case a wetting film was formed.

A sample of ordinary cleaning naphtha was found to produce a wetting film, but not so great as that of gasoline.

Turpentine, which has as its main constituent pinene, was found to act very similar to naphtha, producing an appreciable wetting film.

Liquids which Produce no Wetting Films. Acetone and benzene form no wetting films.

Castor oil ($C_{17}H_{32}(OH)COO)_3C_3H_5$ does not creep up the sides of a vertical container but it does spread over the surface of water according to Langmuir's theory, if placed on the water in small quantities.

Distillate, a product formed during the distillation of crude oil, does not creep.

Fuel oil grade "A" which contains hydrocarbons of high molecular weight was found not to creep.

Treated and untreated kerosenes do not produce wetting

films. By a treated kerosene or gasoline is meant one which has been treated with sodium plumbite (Na_2PbO_2) to remove the sulfur.

The fact that kerosene does not creep is contrary to statements made by many authors. This can be explained by the conclusions reached in this investigation. The old kerosene, because of the commercial demand, was distilled between a wide range of temperature. The demand for modern gasolines has increased to such an extent that the range over which gasoline is distilled is increased; making it necessary to decrease the limits for the distillation of kerosene.

Hydrogen peroxide and dilute acetic acid (CH_3COOH) do not creep.

Xylene gave results which were very similar to benzene showing no wetting film.

Cenco pump oil, paraffin oil and a medium grade of motor oil were found to produce no wetting film.

Wetting Films from Mixtures of Liquids not Producing Wetting Films. In mixing different liquids in an attempt to stop the formation of the wetting film and also to see if the effect could be increased, a very interesting phenomenon was observed. It was found that certain hydrocarbons which in themselves would not produce a wetting film did have a wetting film when mixed. In Table I below are the percentages of liquids used, when the first observable wetting film was

noted.

Table I

Cenco Pump oil-----50%,	Xylene-----50%
Paraffin oil-----33 1/3%,	Xylene-----66 2/3%
Fuel oil Grade "A"-----50%,	Xylene-----50%
Kerosene-----50%,	Xylene-----50%
Xylene-----50%,	Benzene-----50%
Cenco Pump oil-----50%,	Benzene-----50%
Paraffin oil-----33 1/3%,	Benzene-----66 2/3%
Fuel oil Grade "A"-----50%,	Benzene-----50%
Kerosene-----50%,	Benzene-----50%
Benzene-----50%,	Ether-----50%
Xylene-----50%,	Ether-----50%
Paraffin oil 12½%, Cenco pump oil 12½%, Ether 12½%, and Benzene 62½%.	

In connection with the mixing of benzene and xylene with ether it must be remembered that it was previously stated that ether had a very thin wetting film.

The wetting film in some of the above cases is slight but it was found that if the proportion of xylene or benzene was increased the rapidity with which it rises increases as the amounts of xylene and benzene are increased.

It should also be noted that all mixtures containing

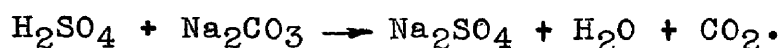
benzene and xylene contain equal amounts of each component.

Saturated and Unsaturated Hydrocarbons. The cracking process produces unsaturated hydrocarbons in the gasoline. To investigate their effect in producing the wetting film the unsaturated hydrocarbons were removed. This was done by two methods.

First method. Fifty cc. of concentrated sulfuric acid (H_2SO_4) were mixed with 500 cc. of gasoline and the resulting mixture placed in a mechanical shaker for two and a half hours. The mixture was then placed in a separator funnel and the oxidized gasoline and carbon compounds were poured out the bottom of the funnel. To the remaining gasoline another 50 cc. of concentrated sulfuric acid was added and the mixture again placed in the mechanical shaker for two hours. Again the oxidized gasoline and carbon compounds were separated out by the separator funnel.

With a small sample of gasoline the bromine test for unsaturated hydrocarbons was made. The testing liquid was a solution of water saturated with bromine. The disappearance of the bromine color indicated that all of the unsaturated hydrocarbons had not been saturated by the sulfuric acid. It was now necessary to add another 50 cc. of concentrated sulfuric acid to the gasoline and shake as before until

the gasoline was completely saturated. To this saturated gasoline a 10% solution of sodium carbonate (Na_2CO_3) (10 grams of Na_2CO_3 and 100 cc. of water) was added. This mixture was placed in the mechanical shaker for fifteen minutes. The precipitate thus formed was drained off. This precipitate contained the sulfate compounds according to the equation,



The resulting gasoline solution was washed twice and the water drained off through the separator funnel. Anhydrous calcium chloride (CaCl_2) was added to the gasoline and allowed to stand over night to remove the water. The saturated gasoline was then poured off and found to still produce a wetting film.

Second Method. Another method used to remove unsaturated hydrocarbons from gasoline was to mix with the gasoline an equal volume of a 5% solution of sodium carbonate (Na_2CO_3). To this was added a 2 to 5% solution of potassium permanganate (KMnO_4). This mixture was mixed by a mechanical shaker until the purple color changed to brown. This was continued until there was no further change in color. Distilled water was then added and the gasoline thoroughly washed, after which the water was drawn off by a separator funnel. The remaining water was removed by anhydrous

calcium chloride (CaCl_2) which was allowed to stand in the gasoline over night.

The liquids given in Table II below were tested for unsaturation of the hydrocarbons using the bromine test.

Table II

Treated gasoline	Wetting film	Saturated
Treated Kerosene	No wetting film	Saturated
Untreated gasoline	Wetting film	Saturated
Untreated Kerosene	No wetting film	Saturated in itself but unsaturated due to sulfur content
Untreated distillate	No wetting film	Unsaturated
Treated fuel oil Grade "A"	No wetting film	Unsaturated
Naphtha	Wetting film	Unsaturated
Alpha Phenyl Beta pentene	No wetting film	Unsaturated

The main component of turpentine is pinene which is unsaturated due to bending and double bond and the strain of bending is only partly neutralized by the double bond. It was found that turpentine has a wetting film. The structural formula for pinene is given in Fig. 1 Plate I.

Benzene on the other hand is unsaturated due to bending and double bond. One effect just neutralizing the other.

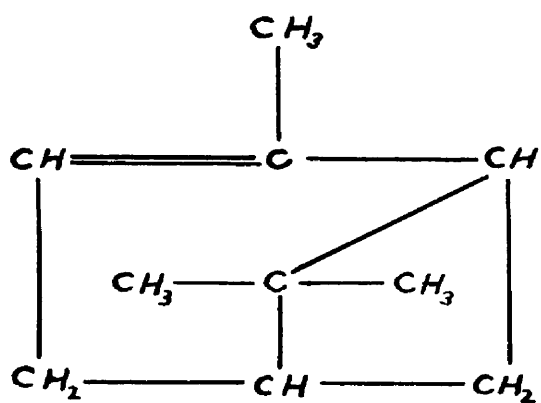


FIG 1

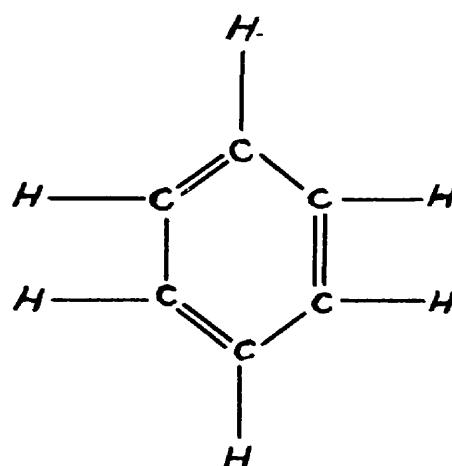


FIG 2

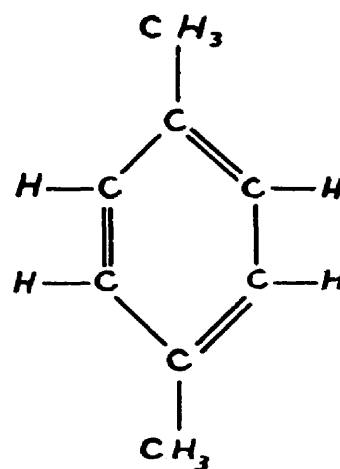
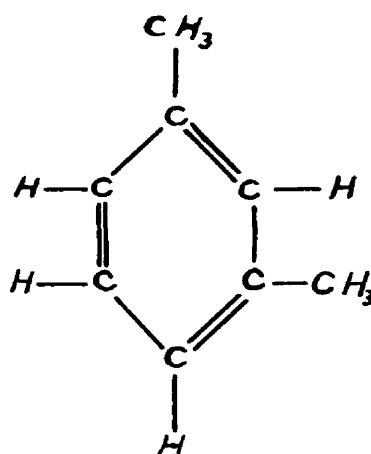
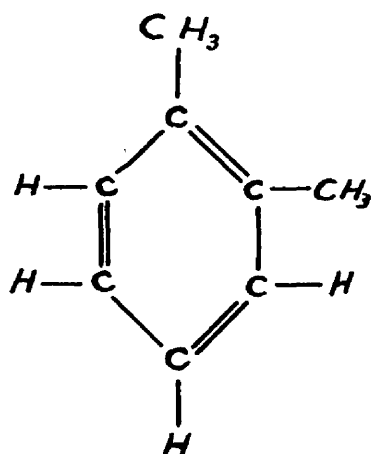


FIG 3

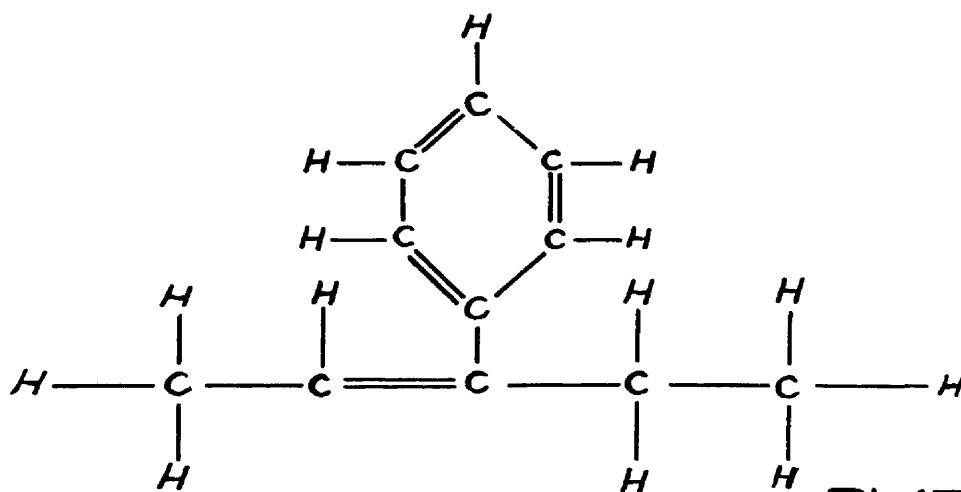


FIG 4

Benzene is therefore a very stable saturated compound. It was found in this investigation that benzene does not have a wetting film. Fig. 2 Plate I shows the benzene structural formula.

Xylene like benzene is a perfectly saturated compound. It is unsaturated due to bending and double bond. These two effects exactly neutralize each other forming a very stable saturated compound. There are three kinds of xylene, Ortho-, meta-, and para-, each having a formula $C_6H_4(CH_3)_2$ but a different structural formulae, Fig. 3 Plate I. In all probability the xylene used in this investigation was a mixture of the three different xylenes.

The compound alpha phenyl beta pentene is unsaturated and has the structural formula shown in Fig. 4 Plate I. Alpha phenyl beta pentene was found to have no wetting film.

From the above results it can be seen that the creeping or wetting film in the case of mixtures of Hydrocarbons does not depend upon the saturated or unsaturated condition of the hydrocarbons.

Low Temperature Combustion. Low temperature combustion was investigated as another possible source of the energy required to produce wetting films.

A jet of oxygen was passed into the vapor above liquid gasoline. It was found that the gasoline wetting film established a point of equilibrium about 2.5 cm. above the surface of the gasoline in the container. After equilibrium was established gasoline tears rolled down the wetting film. These tears did not readily pass into the surface of the gasoline but seemed to have a tendency to return up the wetting film. If the oxygen is turned off more tears will be formed. If oxygen is again admitted just as a tear gets near the gasoline surface it was found, that the tear did not enter the surface, but entered a new wetting film which has been formed by the admission of oxygen. This new wetting film crept up the surface of the old wetting film.

Workers in the field of low temperature combustion have concluded that all surfaces apparently have the power to produce the effects of confined, flameless combustion when at high temperatures. Large surfaces will ignite inflammable gas mixtures at a lower temperature than small ones.

It is known that ionization does not play a primary role in flame propagation and that it is manifest rather as a result than a cause. Ionization is one of the later steps of combustion.

Many tests were made to determine if low temperature

combustion was a factor in the production of wetting films. A type K, Leeds and Northrup potentiometer was used in conjunction with thermo junctions of copper and constantin. One junction was placed in the liquid gasoline while the other was so arranged that it could be placed anywhere inside the container, either in the wetting film or in the gasoline vapor. Another set of junctions was arranged in such a way that the difference in temperature between the atmosphere and the liquid gasoline could be determined. The liquid gasoline was used as the reference temperature. The container with its thermo junctions and liquid gasoline was placed in a constant temperature bath.

After equilibrium was established, with the exploring thermo junction five centimeters above the liquid gasoline, a small amount of air was admitted. It was found that the gasoline vapor was slightly heated. Upon admitting more air the exploring junction was cooled but quickly reestablished the condition of equilibrium. Measurements indicated that the gasoline vapor was slightly warmer than the liquid gasoline.

With the exploring thermo junction placed in the wetting film one centimeter above the liquid it was found upon admitting air near the top of the container that the junction in the wetting film was cooled. A similar result was

obtained when the exploring junction was placed in the wetting film two centimeters above the surface of the gasoline.

When oxygen is admitted to a tube containing gasoline a succession of wetting films rapidly followed one another notwithstanding the fact that the amount of disturbance transmitted to the surface is very small. Illuminating gas produced more rapid formation of wetting films than oxygen. The admission of air causes a wetting film to rise rapidly up the sides of a glass container.

Early Observers of Wetting Films. James Thomson(9) in 1855), explained "the curious motions commonly observed in the film of wine adhering to the inside of a wine-glass, when the glass, having been partially filled with wine, has been shaken so as to wet the inside above the general level of the surface of the liquid," by the "consideration that the thin film adhering to the inside of the glass must very quickly become more watery than the rest, on account of the evaporation of the alcohol contained in it being more rapid than the evaporation of the water,---- the watery portions having more tension than those which are more alcoholic, drag the latter briskly away."

Maxwell (10) accepted James Thomson's explanation and called attention to the reference to the phenomenon in

Proverbs xxiii, 31.

Hall (11), while trying to prove that the angle of contact of alcohol was zero, which was doubted by many observers at this time, proposed to check the angle of contact. "If there is a finite contact-angle for each plate, the values found for $T \cos \theta$ will be different. If these values are all alike, it is reasonably certain that the contact-angle is zero." Hall then gives the results in tabular form. He used plates of platinum, zinc, silver, tin, glass. To compensate for the observed discrepancy in zinc and silver, Hall says, "the zinc plate was slightly wedged shaped and not very regular on the edge. There was no such irregularity in the silver plate; but on watching closely I could see that the alcohol crept rapidly up the plate, wetting it to a height of several millimeters above the normal line of contact. Several other trials with a silver plate showed the same peculiarity. There may have been something similar happening on the zinc plate, but if so I failed to detect it."

Thomson and Maxwell assumed the solid walls to have been wet by mechanical shaking and did not observe a wetting film creeping up a dry surface. Hall apparently observed an alcohol film wetting a silver surface, and believed it

accounted for variations in his determinations of the angle of contact of alcohol with silver and zinc, although he observed no wetting film on the surface of zinc, mica, platinum, or glass. The single instance of spreading observed by Hall can be explained on Langmuir's theory, as alcohol contains an OH radical. It thus appears that true wetting films have not been given previous study.

Surface Tension. The relationship between wetting films and surface tension was next investigated. According to Laplace's Theory of Surface Tension (12) the contractile force of liquid surfaces is attributed to the attractions of the molecules immediately below the surface of the liquid for those on the surface, producing a tendency for the surface molecules to move into the interior. Foley (13) has offered the following objections to Laplace's theory. The magnitude of the force normal to the surface would depend on the curvature of the surface and would be greater at a convex surface than at a flat or concave surface. Consequently the rise of water in a capillary tube would be due to the fact that the downward pressure of the film outside the tube is greater than the downward pressure of the film inside the tube. Two simple experiments show the falsity of Laplace's theory.

Suppose a long capillary tube be taken and its lower end placed some distance into the water and the height of the capillary column noted. Now drop some soap solution on the water outside the tube and thus lower the tension outside. If the liquid is supported by the excess of pressure outside the tube, the height of the capillary column should be lessened. On the contrary the height remains constant for some time.

If the experiment be repeated but this time placing the soap solution in the capillary tube, the tension inside the tube is reduced (demanding a reduced pressure inside) and the outer pressure remaining constant, it would seem according to Laplace that the excess of the outside pressure would be increased and that the water should rise in the capillary. Instead of rising it immediately falls.

Randall, Williams, and Colby (14) give a very acceptable explanation of surface tension. Suppose in a container the molecules in the surface are considered. They will have an attraction for any molecular attraction. Likewise molecules within this distance from the walls of the container will exert a force of attraction for the walls. Suppose now that a molecule is slipped out of the surface layer by some means or other. When this happens the surface at that instant is

slightly smaller than it was previously. This diminution of the area of the free surface causes the phenomenon known as surface tension. This dynamic explanation of surface tension constitutes a more useful conception of the phenomenon.

The surface tensions of naphtha, turpentine, and gasoline were measured with a platinum ring on a torsion du Nouÿ tensiometer. The values of the surface tensions are given in the following table.

Table III

Temperature Degrees Centigrade	Surface Tension in Dynes / Centimeter		
	Naphtha	Turpentine	Gasoline
43			24.08
40		29.24	24.22
38		29.24	24.63
36			24.91
35		29.72	
34		29.86	25.04
32	25.11	29.93	25.18
30	25.18	30.27	25.32
28	25.46	30.62	25.46
26	25.73	30.82	25.46
24.5		30.89	
24	25.80		25.87
23	26.01		

Effect of Saturated Vapor above Gasoline Surfaces. If a container partly filled with gasoline and sealed is allowed

to stand the space above the gasoline becomes saturated with gasoline vapor providing some liquid gasoline remains in the container. When this condition of saturation is reached it is impossible to start a wetting film by means of a wavelet on the liquid surface.

Measurements of Pseudo Viscosity. Measurements of the pseudo viscosity were taken for gasoline, naphtha, and turpentine. The measurements were taken with a Tag-Saybolt Universal Thermostatic Viscosimeter. In this type of instrument the time in seconds is determined for the flow of a definite amount (60 cc.) of the material at the required temperature through a given opening. The temperatures and times of flow are given in the following table.

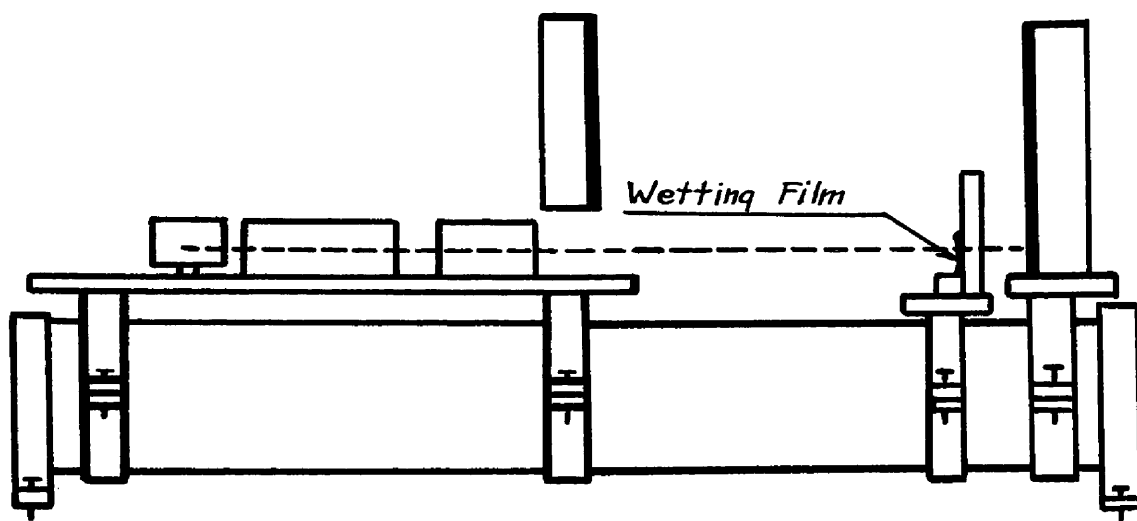
Table IV

Temperature Degrees Centigrade	Time of Flow in Seconds.		
	Naphtha	Turpentine	Gasoline
5			29.2
10	30.0	35.6	
20	30.0	36.0	29.4
30	30.0	34.1	29.6
40	33.1	33.0	30.0

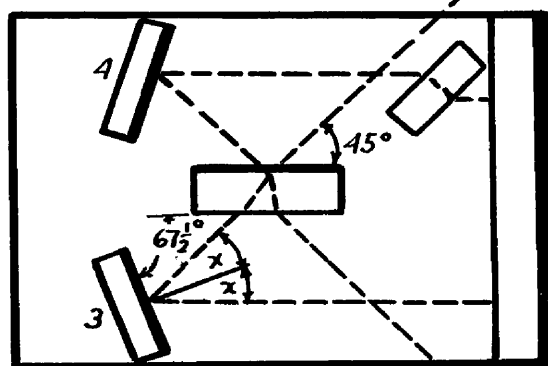
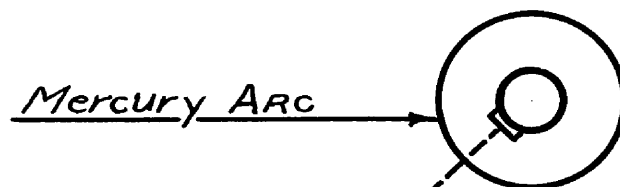
The pseudo viscosity measurements include all factors affecting resistance to shear as well as the true viscosity

of the liquids; the latter would increase, while the former would, in general, decrease with increased temperature. Table IV indicates a negliable change of pseudo viscosity with change of temperature in the case of the three liquids examined, and that wetting films are not caused by the small changes in temperature due to surface combustion.

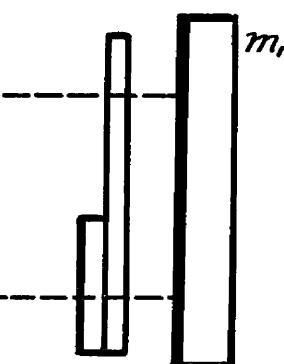
Method of Measurement. The source of the energy required to produce wetting films was found by means of the Universal Interferometer used in the measurement of the Radius of Molecular Attraction. It was designed and constructed in the Barney Laboratory at Denison University. Plate II shows a plan of the instrument. A beam of light from a mercury arc, made monochromatic by the use of filters, is incident upon a plate silvered with a 50% film on the side toward the source. In order to utilize the largest possible aperature the beam must have an angle of incidence of 45 degrees. At the 50% film the beam is divided into transmitted and reflected portions each meeting an end mirror (3 and 4) adjusted so as to reflect the light beams parallel to each other and to the dividing plate. Plate II shows the angles which the end mirrors make with the axis of the instrument. The beam transmitted by the plane parallel dividing plate is parallel to the incident beam



Side View



Cathetometer



Top View

and is reflected by the end mirror (3) in a direction parallel to the dividing plate and the axis of the interferometer. The angle $2x$, therefore, equals 45° . The angle between the end mirror and the axis of the instrument, or the dividing plate, is $90^\circ - x$ or $67\frac{1}{2}^\circ$. The transmitted and reflected rays are reflected by the end mirrors to a large mirror m' . If they meet this mirror at perpendicular incidence they are returned upon themselves to the dividing film where they undergo a second division. The reflected portion of the transmitted ray and the transmitted portion of the reflected ray are received in the telescope of a cathetometer, and Fizeau interference fringes observed in the plane of the mirror m' . If the instrument is to be used as a compound interferometer the mirror m' is tilted so that the beam is reflected to the mirror m_2 which is elevated just enough to allow the beam coming from the end mirrors to pass under to mirror m' . The angle between the mirrors m' and m_2 can be adjusted so as to produce any desired number of reflections between them, the interfering beams eventually meeting one of the mirrors at perpendicular incidence and returning upon themselves, producing interference bands of any desired order.

The wetting film to be measured was placed on an optical

plate placed between m' and m_2 in such a way that clear glass was in one of the two interfering paths and glass with the wetting film was in the other. The glass plate extended through both paths so that no correction for the increased optical path was necessary.

The bed plates carrying the dividing mirror, end mirrors, compensating plate, the mirror m_2 , and the mirror m' are clamped on a large bronze tube. They can therefore be moved to any desirable position on the tube. The end mirror (4) is fastened directly to the bed plate in such a way that it can be rotated about its center. The mirror (3) can also be rotated about its center and is connected through an opening in the bed plate to the movable carriage of a small but exceedingly accurate interferometer. This makes it possible to move mirror (3) forward and backward and in this way lengthen or shorten the optical path of this beam.

Because of the difficulty in producing a collimated beam of light the adjustment of the mirrors can best be made using a beam of sunlight. The successive images are seen on the mirrors m' and m_2 , and the order of the compounding can easily be determined.

The optical plate upon which the wetting film was allowed to creep was divided into two parts by a strip of

collodion. On the bottom of half of this plate was fitted a container coated with collodion.

The material under observation was placed in the container and the wetting film formed on half of the optical plate. This placed the wetting film in one optical path of the interferometer and at the same time provided a means of placing the same thickness of optical glass in both paths.

The formula used in calculating the thickness of the wetting film is $D = \frac{\delta \lambda}{N(n'-1)}$, where D is the thickness of the wetting film, δ the interference fringe displacement in terms of number of fringes, λ the wave length of light employed, N the number of times the light passes through the wetting film, and n' the index of refraction of the wetting liquid. The total change in optical path is $\delta \lambda$, $\delta \lambda / N$ the change in optical path due to one interfering ray passing once through the wetting film, $n'-1$ the difference between the index of refraction of the wetting film and the index of refraction of air which the wetting film displaces.

The fringe displacement was measured with a cathetometer fitted with a micrometer eyepiece. In every case many readings were taken and the average of the readings used in the calculations.

The index of refraction of the material was measured with an Abbé refractometer, and here again the value taken was the average of many readings. The following is a table of the indices of refraction of several liquids as measured by the Abbé refractometer, the temperature in each case being 22° centigrade.

Table V

Saturated Gasoline	1.4209
Unsaturated Gasoline	1.4302 to 1.4279
Naphtha	1.4191
Turpentine	1.4720
Benzene	1.4980
Xylene	1.4953
Ethyl Alcohol	1.3629
Acetone	1.3590

Thickness of Wetting Films. The thickness of the wetting films of naphtha are given in Table VI. The three groups of results are for the same naphtha but the values represent longer exposure to the atmosphere. The naphtha in group 2 had been exposed longer than the naphtha in group 1. Likewise the naphtha in group 3 had been exposed longer than the naphtha of group 2.

Table VI

Group 1			
Temperature Degrees Centigrade		Thickness of Wetting Film in Centimeters	
23.5		0.0000311	
24.0		0.0000356	
Group 2		Group 3	
Temperature Degrees Centigrade	Thickness of Wetting Film in Centimeters	Temperature Degrees Centigrade	Thickness of Wetting Film in Centimeters
18.0	0.0000335	16.0	0.0000427
19.0	0.0000392	18.0	0.0000478
20.0	0.0000443	19.0	0.0000494
21.0	0.0000472	25.0	0.0000536

In making the above measurements the green line of the mercury arc 0.0000546073 centimeters was used. The values of n' , the index of refraction of the various materials used, are given in Table V.

Table VI shows that the longer a given liquid is exposed to the atmosphere the thicker becomes the wetting film for any given temperature. There is also an increase in the thickness of the wetting film resulting from an increase in temperature.

The diagram, Fig. 1 Plate IV, shows a typical wetting film of naphtha. In the center of the diagram can be seen interference patterns which are irregular in nature. This is due to the debris which has been carried to the top of the wetting film and left there when the film drains, and also to tears which are formed at the top of the film. The narrow interference bands in this region show that the tears and debris are approximately ten times the thickness of the wetting films, which is determined by measuring the displacement of the Fizeau bands in the upper and lower portions of Fig. 1.

Upon observing the wetting films with a telescope they were seen to split at the top one or more times. It was also observed that new wetting films creep up over the old wetting films and these new films were extremely flat across the top and had a very sharp radius of curvature at the upper edge. This suggested that wetting films vary in thickness by some constant. This was found to be the case. Taking the values for the thicknesses of the wetting films with their corresponding temperatures from group 2 of Table VI and obtaining all of the possible combinations by subtracting the various thicknesses from each other, one obtains the thicknesses of film which correspond to the different degrees of temperature, as shown in Table VII.

Table VII

Temperature Difference in Degrees Centigrade	Difference in Thickness of Films	Difference in Thickness of Film per Degree Change in Temperature
1	0.0000057	0.0000057
1	0.0000051	0.0000051
1	0.0000036	0.0000036
2	0.0000108	0.0000054
2	0.0000087	0.00000435
3	0.0000144	0.0000048

If the difference in thickness of film per degree change in temperature are now divided by the radius of molecular attraction, 1.5×10^{-7} cm. it is found that they are exactly multiples of this value. The results are accordingly 38.00R, 34.00R, 24.00R, 36.00R, 29.00R, and 32.00R. It appears from this calculation that the wetting films split along planes of cleavage one R apart. Successive wetting films differ in thickness by R or multiples of R.

Flow of Liquid in Wetting Films. Wetting films have been observed 10 cm. above the liquid surface; the height depending on the solid surface, the nature, age, and temperature of the liquid, and the degree of saturation of

the vapor space. A study of the phenomena illustrated in Fig. 1 Plate IV showed the presence of vigorous motions in the wetting film. While under fixed conditions wetting films always rose to an equilibrium point there were many indications that this equilibrium was a dynamic one. Observations with the interferometer showed the formation of successive wetting films creeping up over the preceding film. The motion which was continuous as long as the vapor space was unsaturated, could be explained on the assumption that the liquid adjacent to the solid was descending while the outer portion was ascending. Attempts were made to observe the oppositely moving currents by means of suspended particles. As the thickest wetting films measured were only one wave length thick it is readily seen that a particle small enough to be suspended in the downward flowing liquid, contacting neither the solid wall nor the upward flowing liquid, would be beyond the limit of resolution of the best compound microscope. The continuous upward movements were readily observed, but the particles were caught by the solid wall when the liquid current turned downward.

The predicted phenomena was readily observed, however, when a creeping liquid, containing small suspended particles, was introduced into a receiver, the bottom of which was

concave upward. The plano-convex drop of liquid thus formed was surrounded by a wetting film. The microscope plainly showed the suspended particles rising in the center of the drop, flowing outward in the upper portions and toward the center in the lower portions of the drop. The vigorous motions were maintained as long as evaporation continued.

The Effect of Age and Temperature on the Surface Tension of Naphtha. Table VIII shows the effect of temperature on surface tension for fresh naphtha and for stale naphtha; that is naphtha which was exposed to the atmosphere in order that the more volatile fractions might evaporate.

Table VIII

Temperature Degrees Centigrade	Surface Tension in Dynes / Centimeter	
	Fresh Naphtha	Stale Naphtha
37.0		26.49
35.0		26.49
32.0	25.11	26.69
30.0	25.18	26.98
28.0	25.46	27.19
26.0	25.73	27.59
24.0	25.80	27.66
23.0	26.01	28.21
22.5		28.44

The curves representing these values are given in Fig. 2 Plate III.

Evaporation at Curved Surfaces. Surface tension,

according to Ewing (15), is the skin of a liquid at any surface which separates liquid from vapor and is the seat of a definite amount of potential energy. One of the results of surface tension is to make the conditions of equilibrium between liquid and vapor depend upon the curvature of the liquid surface. The normal conditions for equilibrium between vapor and liquid apply only to flat surfaces. In this condition the vapor, at the same temperature as the liquid, has what is called a saturated vapor pressure for that temperature. In consequence of surface tension a small drop will evaporate into an atmosphere that would be saturated or even supersaturated with respect to large drops or large quantities of the liquid, because the vapor pressure which is required to prevent evaporation from the curved surface of a small drop is greater than the vapor pressure which will prevent evaporation from a flat surface of the same liquid at the same temperature. The equilibrium vapor pressure for a small drop is higher than the normal saturation pressure.

Again as the result of surface tension, the energy contained in a drop of liquid is greater than the energy contained in an equal volume of liquid when it forms a part of a mass of the same liquid at the same temperature.

As, a small drop contains more energy, due to surface tension, per unit mass than a large drop of the same liquid at the same temperature, because the small drop has a relatively larger area. The area of the surface layer can be taken as a measure of the stored energy.

When the thickness of a vertical liquid film is reduced to eight times the radius of molecular attraction its surfaces are parallel. If such films are stretched, or allowed to evaporate, they split in the middle, and exist in stable form $4R$ thick. Such films, known as the first and second black, because of their low reflection power, are too thin to produce destructive interference between the light rays reflected from the front and back surfaces. Films of greater thickness than the first black show Newton's interference bands in colors but they store the same potential energy in their surfaces.

If a drop is evaporating under conditions which keep its temperature constant, energy must be supplied in proportion to its loss of mass to provide for its latent heat of vaporization. The drop will lose some of its surface energy because it is decreasing in size, and this supplies part of the latent heat, the remainder coming from the outside. A drop will evaporate into a space which is saturated for the

same liquid in large quantities. Thus it is seen that there can be no equilibrium between a drop and a surrounding atmosphere of saturated vapor. As the drop gets smaller a point is reached in which the loss of potential energy due to the contraction of the surface supplies all the latent heat of vaporization. After this point is reached the drop will continue to evaporate without any outside supply of heat.

The equilibrium between a liquid and vapor depends upon the curvature of the surface between them, if they are at the same temperature. Liquid with a flat surface is in equilibrium with the vapor above it when the vapor is at the pressure of saturation and there is no tendency on the whole for the liquid to evaporate or the vapor to condense.

A liquid having a convex curved surface is in equilibrium with the vapor only when the vapor pressure exceeds the normal saturation pressure by a definite amount, that is, only when the vapor is sufficiently supersaturated.

The degree of supersaturation necessary for equilibrium depends upon the curvature of the surface, in a manner first established by Kelvin (16). Kelvin's formula is

$$\log_e \frac{P'}{P_s} = \frac{2S}{RT} \text{ or}$$

where P' is the equilibrium vapor pressure over a curved surface and P_s is normal pressure of saturation, S is the surface tension in dynes per linear centi-

meter. By assuming a perfect gas RT was put equal to PV . The value of RT is for a gram molecule, and must be divided by the molecular weight of the liquid to reduce the value to cgs units, ρ is the density of the liquid and r the radius of a drop of liquid assumed to be spherical. This formula determines the pressure P' which must be maintained in the supersaturated vapor around the drop in relation to the normal pressure of saturation P_s for the same temperature, if the drop just escapes shrinking by evaporation. An increase in P' for which the value has been calculated would cause the drop to grow. A drop smaller than that for which the value was calculated would disappear by evaporation; likewise a drop having a value of r larger would grow.

It is only when the drop is exceedingly small that the excess of P' over P_s is considerable. Kelvin calculated that for water vapor at 10°C , RT (which is treated as equal to PV) is 1.30×10^9 cgs units. The surface tension of water at that temperature above 76 dynes per linear centimeter, and ρ is one gram per cubic centimeter. Then $\log_{10} \frac{P'}{P_s} = \frac{1.01}{D}$, where D is the diameter of the drop in millionths of a millimeter. The formula gives for drops of water the values given in the Table IX.

If Kelvin's formula is applied to naphtha drops at

10° centigrade it becomes $\log_{10} \frac{P'}{P_s} = \frac{1.2066}{D}$, where D is the diameter of the drop of naphtha in millionths of a millimeter.

When Kelvin's formula is rewritten to apply to the case of a thin vertical film, such as that produced in the capillary space between two parallel plates, it becomes $\log_e \frac{P'}{P_s} = \frac{2S}{RT \rho (2d)}$ where d is the distance between the parallel plates.

If d is given in millionths of a millimeter, we have in the case of naphtha at 10° C, that $RT = 0.273 \times 10^9$ cgs units. The surface tension of naphtha is $S = 28.3456$ and its density $\rho = 0.7466$. Therefore $\log_{10} \frac{P'}{P_s} = \frac{0.6033}{d}$. This formula expresses how large the pressure P' must be in the supersaturated vapor around the top of the wetting film, which has a radius of curvature d, in relation to the normal pressure of saturation P_s , for the same temperature, on the flat surface of the wetting film.

The ratio P'/P_s for different values of d given in Table IX below for naphtha are plotted along with Kelvin's value for water vapor in Fig. 1 Plate III.

Table IX

Diameter of Drop of Water in millionths of a millimeter		Ratio of P'/P_s for Water Vapor	
100		1.02	
50		1.05	
10		1.26	
5		1.59	
2		3.2	
1		10.2	

Diameter of Drop of Naphtha in Millionths of a Millimeter	Ratio of P'/P_s for Naphtha Vapor	Radius of Curvature of Wetting film of Naphtha against a Single Plate in Millionths of Millimeter	Ratio of P'/P_s for Naphtha Vapor at Top of Wetting Film
100	1.014	100	1.028
50	1.028	50	1.060
10	1.149	10	1.320
5	1.320	5	1.743
4	1.415	4	2.003
3	1.589	3	2.525
2	2.003	2	4.012
		1.5	6.370
1	4.012	1	16.094

For large radii of curvature the ratio P'/P_s for the three curves approaches unity, because then the surface is becoming flat. Chamberlain's value for the radius of molecular attraction, 1.5×10^{-7} cm., is now generally accepted. Chamberlain also determined the minimum thickness

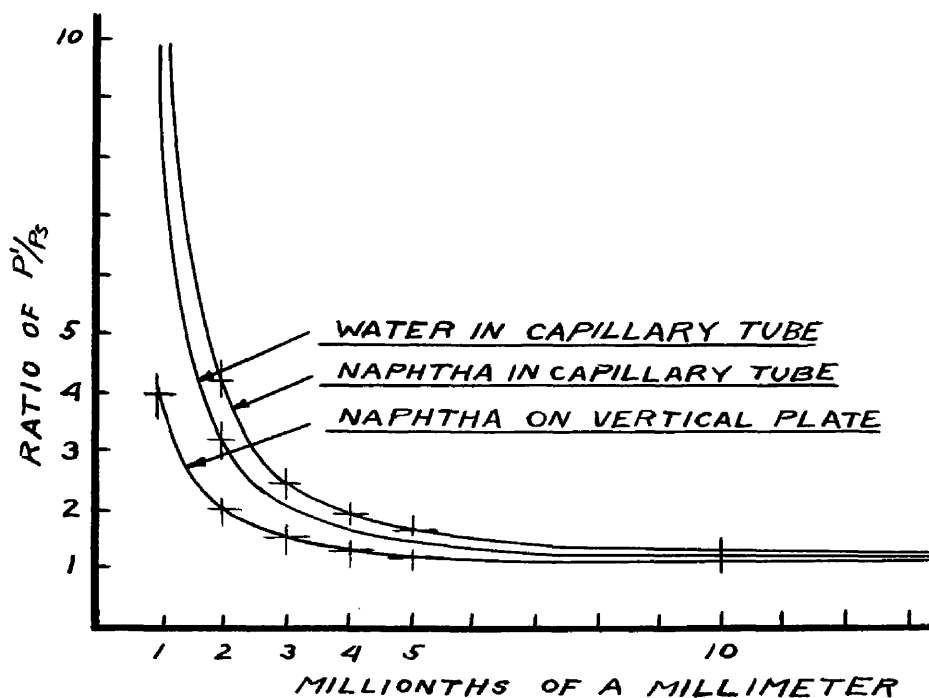


FIG 1

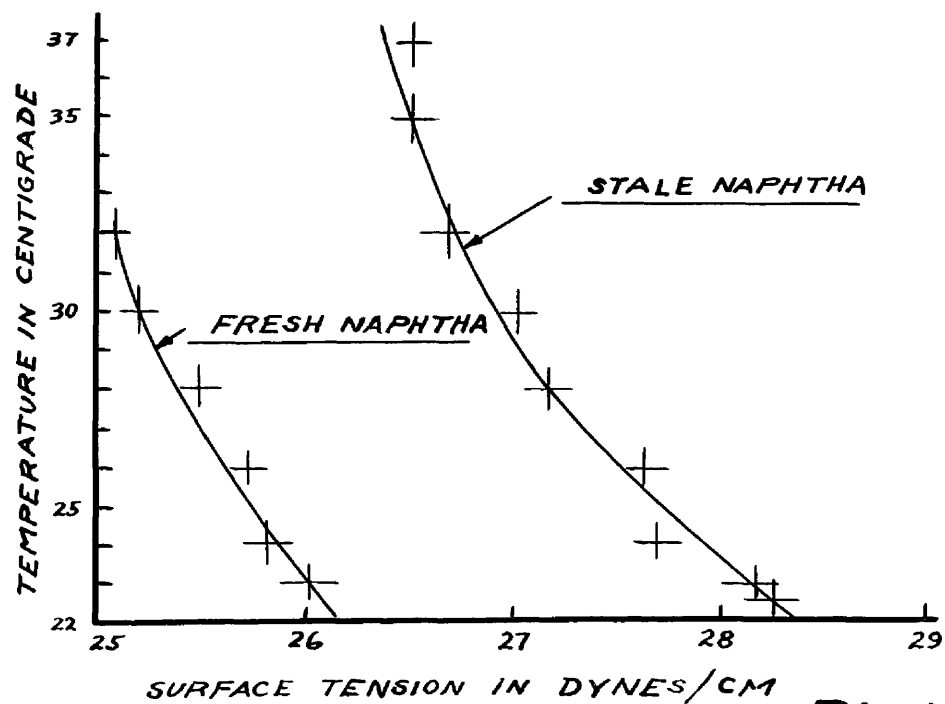


FIG 2

PLATE III

of a stable liquid film to be $4R$, or 6 millionths of a millimeter. At this value the curves begin to separate rapidly and turn upward. When the radius of curvature equals the radius of molecular attraction, that is at 1.5 millionths of a millimeter, P'/P_s is large, and for a value slightly less than this a drop would evaporate in an explosive manner. Surface tension exists in a film 1.5 millionths of a millimeter in thickness. If it were possible to form a film of less than this thickness its surface tension would be weakened. In other words it would explode and become vapor, since its energy content is equal to the latent heat of vaporization. That this is the case is shown by the rapid increase in the ratio of P'/P_s in the region of 1.5 to 1 millionths of a millimeter.

Notwithstanding the large differences in surface tension and density between water and naphtha the curves in Fig. 1 Plate III show similar characteristics.

A steel straight edge 11 cm. long and 0.02 cm. thick, the upper edge of which had been sharpened to a razor edge, was placed in one path and parallel to the axis of the interferometer. The lower edge was submerged in naphtha.

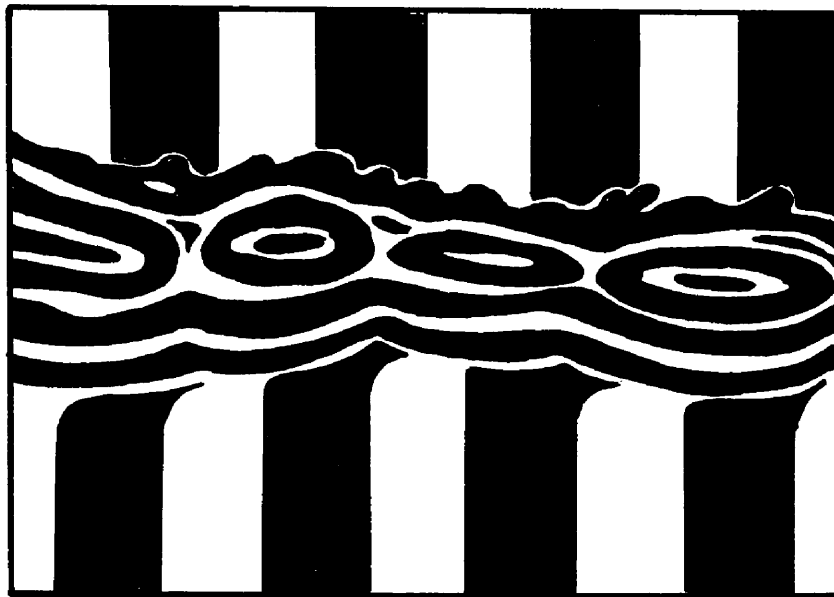


FIG. 1

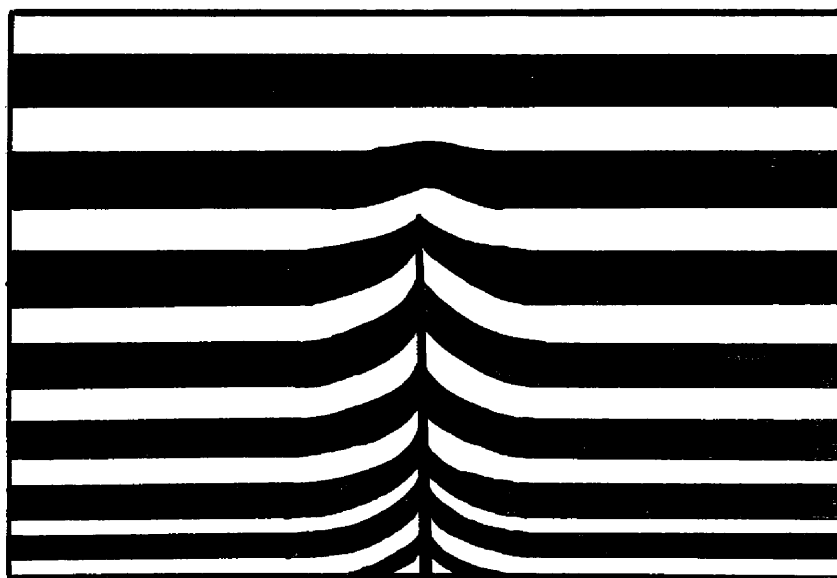


FIG 2

PLATE IV

The appearance of the Fizeau bands is shown in Fig. 2 Plate IV. The curvature of the Fizeau bands is due to the evaporation of naphtha. The increasing distance between bands from bottom to top is due to the vapor density gradient which existed above the naphtha surface. The curvature of the bands from the flat side of the straight edge outward indicates the evaporation from the flat surface of the wetting film. The band just above the straight edge shows a kink, due to the high rate of evaporation from this sharp edge.. The fact that the band is curved at all indicates very rapid evaporation, because the area of liquid at this curved surface is very small and a large amount of material would have to evaporate to show this curvature in a band above the sharp edge.

Summary. 1. Wetting films are formed by liquids containing two or more components of different vapor tensions.

2. Materials which produce no wetting film are found to be able to produce a wetting film when mixed if the liquids have different vapor tensions.

3. Saturation and unsaturation of the hydrocarbons play no part in the production of wetting films.

4. Low temperature combustion is not sufficient to contribute appreciably to the production of wetting films.

5. The variation of pseudo viscosity with temperature does not contribute appreciably to the production of wetting films.

6. The thickness of wetting films increases with rise in temperature; due to the increase in the true viscosity of the liquid mixture.

7. The thickness of wetting films increases with the age of the liquid mixture.

8. Wetting films have planes of cleavage which are exact multiples of the radius of molecular attraction.

9. Differences in surface tension due to localized evaporation play a primary role in the lifting of a wetting film.

10. The small radius of curvature at the top of a wetting film, resulting in a high rate of evaporation producing a region of high surface tension and supplies the energy necessary to move the superficial layer upward. This drags with it some of the body of the liquid. The thickness, of the upward moving layers, depends on the true viscosity of the liquid mixture. Debris collects at the top of a liquid film in much the same manner as drift material on a beach.

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