2. In addition to showing the above change, xanthone and fluorenone possess new bands in sulfuric acid solutions which are believed to be associated with the stabilization of the quinonoid structure for these compounds. Solutions of stannic chloride produce the same changes on the absorption spectrum of xanthone that sulfuric acid does.

3. The production of color with xanthone and sulfuric acid or stannic chloride is not due to the ether oxygen.

4. The color of ketone chlorides and sulfuric acid or stannic chloride is of a different nature from that of ketones and resembles that of triarylcarbinols and salts of these carbinols. It is postulated that in such solutions the ketone chlorides exist in a quinonoid modification.

ANN ARBOR, MICH. RECEIVED MARCH 28, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Films Built by Depositing Successive Monomolecular Layers on a Solid Surface

BY KATHARINE B. BLODGETT[1]

A previous paper[2] has described briefly a method of depositing successive monomolecular layers of "stearic acid" on glass. Subsequent experiments,[3] which will be discussed in this paper, have shown that the substance deposited on the glass was calcium stearate and not stearic acid. The layers were deposited one at a time; thus a film could be built having a thickness of 1, 2, 3 or more layers of molecules. Further development of the method has made it possible to deposit more than 200 layers on glass and on various metals.

This paper will describe experiments in which the thickness of films containing many layers was measured by means of the interference of monochromatic light reflected by the films. These measurements were made with films of calcium or barium soaps of long-chain fatty acids deposited on glass having a high refractive index. Films can be built with fatty acids[4] when deposited on a metal, but fatty acids do not adhere readily to glass.

A monomolecular calcium stearate film is formed on water by placing a small amount of stearic acid, dissolved in benzene, on a clean surface of water containing calcium salts. The stearic acid spreads rapidly in a monomolecular film.[5] If the *p*H of the water-bath is greater than 5.0, approximately, the Ca ions in the water combine with the carboxyl group of the adsorbed molecules, converting the film to calcium stearate. The film may be neutral soap or an acid soap, depending on the *p*H of the water. The term "acid soap" is used here in the sense in which it is used by McBain[6] and other writers to refer to compounds of the fatty acid and the neutral soap. Both types of soap will be called "calcium stearate" in this paper.

The film is transferred from water to glass[7] by raising a clean glass slide slowly out of the water on which the film is spread. A constant surface pressure is maintained on the film as the glass is raised through the surface. If the water-bath is alkaline (*p*H > 7.5), the stearate molecules show a ready tendency to attach themselves to glass, so that the surface pressure causes them to be shoved off the water and onto the glass. Langmuir, Adam and others have demonstrated that the fatty acids tend to orient themselves on a water surface with the —COOH "head" of each molecule in contact with the water and the chain tilted at a more or less steep angle with the plane of the water surface. In the present experiments the monomolecular layer of calcium stearate is similarly oriented and the layer is transferred to glass with the $(\text{—COO})_2\text{Ca}$ heads attached to the glass, and the paired chains perpendicular to the plane of the glass. The exposed upper surface of the film is composed of closely packed CH_3 groups.

---

(1) The experiments described in this paper were commenced in collaboration with Dr. Irving Langmuir and were continued while he was traveling in the Orient. The writer is indebted to Dr. Langmuir for urging her to develop further the method described in the previous paper, and for contributing many important suggestions which have been included in this paper.

(2) K. B. Blodgett, THIS JOURNAL, **56**, 495 (1934).

(3) I. Langmuir, *J. Franklin Inst.*, **218**, 153 (1934).

(4) G. L. Clark, R. R. Sterrett and P. W. Leppla, THIS JOURNAL, **57**, 330 (1935).

(5) (a) I. Langmuir, *ibid.*, **39**, 1848 (1917); (b) N. K. Adam, *Proc. Roy. Soc.* (London), **A99**, 336 (1921), and succeeding papers.

(6) J. W. McBain, M. Taylor and M. E. Laing, *J. Chem. Soc.*, **121**, 621 (1922), and other papers.

(7) I. Langmuir, *Trans. Faraday Soc.*, **15**, 62 (1920); reprinted in *G. E. Rev.*, **24**, 1025 (1921).

A film in which all the molecules are oriented with the CH_3 groups at the upper surface possesses the exceptional property that neither water nor oil will wet the surface. The property of shedding water is an important factor in the present experiments. As a glass slide is slowly raised out of the water on which a film is spread, the water recedes from the glass wherever the film attaches itself to the solid surface, and if the slide be withdrawn from the water fairly slowly (5 to 10 cm. per minute), it will emerge completely dry. This enables the experimenter to regulate the speed at which he lifts the slide so that the stearate film may be deposited uniformly over the entire surface.

The speed with which a film attaches itself to glass is governed by three factors, *p*H, calcium concentration, and temperature of the water-bath. The speed increases with increasing values of one or more of these variables. Thus at 20° a solution nearly saturated with calcium carbonate, 5×10^{-4} molar, gives films which coat glass with fair speed at *p*H 7.5, and with greater speed at *p*H 8.0; whereas a solution 1×10^{-4} molar calcium carbonate needs to have a value of *p*H about 0.5 higher in order to give the same results. The speed in every case is greater at 35 than at 20°.

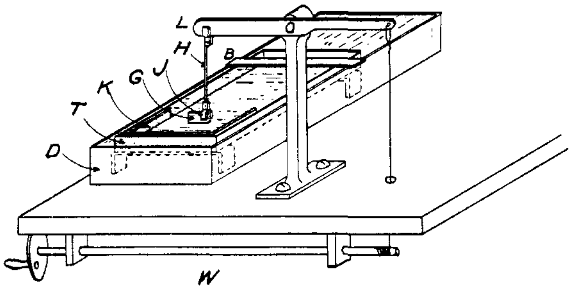

Fig. 1.—Apparatus for transferring a monomolecular film from a water surface to a solid surface.

When the *p*H of the water is less than *p*H 7.5, approximately, the film shows less tendency to detach itself from the water and attach itself to the glass, and at *p*H < 7.0 it has very little tendency to coat the glass in this manner. However, excellent films can be deposited from water at *p*H 6.0 to 7.0 by withdrawing the glass from the bath completely wet, the surface of the water on the glass being covered with calcium stearate, and then removing the water from beneath the film by drying the slide slowly at a low heat.

In each of these methods it is important that the film be held under constant pressure while the glass is being raised. Dr. Langmuir pointed out that pressure could be most conveniently applied by placing a tiny drop of castor oil or oleic acid, or some other hydrophilic oil, at one end of the trough. A hydrophilic oil has the property that the molecules of the oil spread on water until they have covered all the available area with a monomolecular layer, crowding together into this layer until they have established an equilibrium surface pressure.[8] The equilibrium pressure exerted by an oil is a characteristic property of each individual pure oil; for example, oleic acid exerts approximately twice as much pressure as castor oil. After the surface is covered with a monomolecular layer, the surplus oil remains gathered in many small lenses. If, however, new space becomes available on the water surface, oil spreads instantaneously from these lenses and covers the new area also with a monomolecular layer. Thus a drop of oil placed at one end of a trough on which a calcium stearate film has been spread, acts as a surface piston to hold the stearate film under constant pressure at every instant. Oil used for this purpose is called "piston-oil" and its use is illustrated in Fig. 2.

After glass has been coated with one layer, additional layers can be added one at a time by dipping the glass in and out of the water-bath on which a monomolecular layer of calcium stearate is spread. The successive operations will be described in the following section.

Apparatus and Technique

The process of depositing the layers is carried out in a trough of the kind developed by Langmuir and by Adam for studying films on water. The trough T, shown in Fig. 1, is filled with water to the brim. It stands in a water-bath D, the temperature of which is controlled. The edges and inner surface of the trough and the metal barrier B are coated with paraffin wax. Three detachable strips of glass K serve as a pen within which the benzene solution of stearic acid is placed on the water surface, to prevent the benzene from reaching the waxed edges.

The glass slide G is raised and lowered by means of a lever L operated by a hand windlass W. A simple mechanical device of this sort is needed for the reason that it is difficult to lift the slide slowly by forceps held in the hand without an occasional backward "hitching" motion. Hitching must be positively avoided since a film is deposited each time the slide is raised and lowered. A pinch-clamp at L holds the rod H and a similar clamp J at the lower end of H holds the slide. The slide and the clamp which hold it are both thoroughly cleaned in a hot solution of concentrated sulfuric acid and potassium di-

---

(8) A. Cary and E. K. Rideal, *Proc. Roy. Soc.* (London), **109A**, 301 (1925).

chromate, washed in running water, rinsed in distilled water and lowered at once beneath the surface of the water in the trough. The clamp holds the slide faced in such a direction that the surface on which the films are to be deposited is perpendicular to the water surface and to the length of the trough.

Figure 2 illustrates the method used to keep the area occupied by piston-oil fenced off from the area occupied by calcium stearate, by means of the waxed silk thread S_1. This precaution is necessary for the reason that if piston-oil is permitted to reach the slide G, and if one layer of this oil is accidentally deposited on the slide, it will usually prevent the slide from taking up any more layers of calcium stearate.

The surface of water in the trough T is first cleaned by sweeping the metal barrier B over the surface. When much oil is present on the surface, the oil that is swept against the waxed edges of the trough tends to adhere to the wax in spots and causes subsequent trouble. This may be avoided by placing a strip of paper underneath B. The strip is made wider than B so that it extends 6.3 mm. in front of B and takes up oil as it advances. The grade of paper commonly used for scratch-pads works well. A waxed edge which has become oily may be cleaned tolerably well by wiping the wax with clean wet filter paper.

In order to test the water surface for the presence of oily films after it has been swept by B, lay a silk thread in a large circular loop on the surface at one end of the trough (not shown in Fig. 2) and blow on the thread. If the surface is clean the thread can be easily blown from one end of the trough to the opposite end. The amount of oily film remaining after a surface has been cleaned should cover not more than 10% of the total area. The extreme precautions which are required to reduce this contamination to one per cent. are impractical in a trough in which piston-oil is used constantly. Therefore the following procedure has been devised whereby the residual film is prevented from contaminating the calcium stearate film.

A small metal clip is tied to each end of a waxed silk thread S_1. The thread is waxed by being soaked in a benzene solution of paraffin wax, and dried; it must not take up so much wax that it becomes stiff. After the water surface has been cleaned and the slide G has been lowered into the water near one end of the trough, these clips are attached to opposite edges of the trough at C and the thread is laid on the surface in the position shown in Fig. 2(a). Stearic acid dissolved in benzene is placed on the surface near G, and as the stearic acid spreads it pushes the fence before it, as shown in Fig. 2(b). After spreading has ceased, the thread is fastened to the edge at points midway along the film by two small copper hairpins F (Fig. 2(c)).

A tiny drop of piston-oil is now placed on the surface at P which breaks up into many tiny lenses surrounded by a monomolecular film that presses against the thread-fence and causes the calcium stearate film to contract slightly in area (Fig. 2(d)). Calcium stearate forms the type of film known as a "condensed" film, that is, it contracts only slightly as the external surface pressure is increased from zero pressure to 30 dynes/cm. As soon as the calcium stearate has contracted to an area at which the pressure within the thread-fence equals the pressure exerted by the piston-oil outside the fence, the spreading of piston-oil ceases. A thread S_2 is then laid in the position shown in the diagram as a double safeguard, so that if piston-oil accidentally passes S_1 it will remain in the area between S_1 and S_2. The process of depositing layers of calcium stearate on the slide G is then begun; the details of this process are described in the section entitled "Successive Layers." Each time one layer is deposited the film is depleted by an amount equal to the total area of the slide, front and back, and the thread is pushed forward a corresponding amount by the piston-oil until nearly all of the calcium stearate is transferred to the glass (Fig. 2(e)). Since any dust or fuzz particles which fall from the air upon the water are transferred with the film to the slide, a glass cover is laid over the trough after the threads are in position, the cover being supported by two movable metal bridges not shown in Fig. 1.

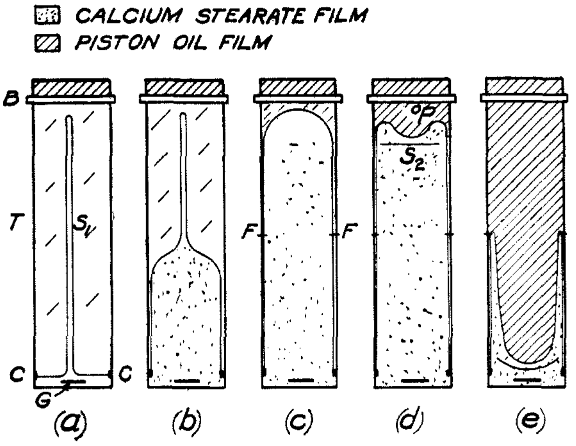

Fig. 2.—Use of a waxed thread to mark the boundary of a monomolecular surface film.

The oleic acid that was used as piston oil was purified by fuller's earth which was mixed with the oleic acid for thirty minutes at the temperature of boiling water and was then separated in a centrifuge. The oleic acid exerted a surface pressure of 29.5 dynes/cm. at 20°. Cary and Rideal[8] found that the pressure of oleic acid (spread on $^1/_{100}$ N HCl) was nearly constant over moderate ranges of temperature. Their measurements show a linear decrease in pressure with increasing temperature, of an amount 0.07 dyne/cm. per degree C. The pressure of castor oil was found to vary considerably among various samples of the oil; the sample that was used exerted 16.5 dynes/cm. at 20°. These pressures were measured by means of a surface pressure balance.

The determinations of pH values were made by means of indicators, the colors being matched to La Motte color standards. Small samples of water taken from the trough were used for making these determinations.

In the case of alkaline solutions, sodium bicarbonate was used as a buffer in a concn. $^1/_{1000}$ molar, and sodium hydroxide was added when necessary to obtain the desired pH. Tests made at pH 9.0 showed that when sodium bicarbonate and sodium hydroxide were added to a solution $^1/_{10,000}$ molar in calcium carbonate in an amount which made the concentration of Na ions $^1/_{200}$ normal, the presence of the Na ions in this concentration did not interfere with the processes of depositing layers of calcium stearate from the surface of the solution. When the Na concentration was increased to $^1/_{100}$ normal, a first layer was found to be somewhat reluctant to adhere to glass; at $^1/_{50}$ normal the reluctance was very marked. The reluctance was probably due to the fact that sodium stearate does not attach itself to glass, *i. e.*, films cannot be deposited from alkaline solutions containing Na but no Ca.

Samples of stearic and palmitic acid from various sources were tested for purity by a very sensitive method described in a previous paper.[2] The stearic acid that was used for the measurements given in Table I was prepared by Dr. R. E. Burnett in this Laboratory, the palmitic acid was given by Dr. E. Emmet Reid. The arachidic acid that was used was not pure; the melting point was 70°.

The test for purity of stearic or palmitic acid consisted in determining the temperature at which mineral oil saturated with the fatty acid in question would spread on $^1/_{100}$ N hydrochloric acid. Cary and Rideal[8] have shown that a pure fatty acid lowers the surface tension of acid water only if the temperature of the water is above a critical value, the critical temperature increasing with the length of chain of the fatty acid. In the present method one per cent. of fatty acid was dissolved in Squibb's Liquid Petrolatum wax by warming the Petrolatum slightly. The solution was then cooled to 25° in the case of stearic acid and to 10° in the case of palmitic acid at which temperatures the greater part of the fatty acid crystallized. The solubility of stearic acid in Petrolatum is 0.16 per cent. at 25°.

A drop of the mixture of oil and stearic acid crystals was placed on a clean surface of $^1/_{100}$ N hydrochloric acid at 25°, and if the drop remained in a lens having a diameter less than 1 cm. the temperature of the acid water was raised and new drops were tested at successive temperatures until the critical temperature was reached at which drops commenced to spread to disks of diameter much greater than 1 cm. If the temperature was raised 1° above this critical temperature, the increase in spreading was very great, a single drop spreading out to cover many hundred square centimeters. If stearic acid contained a trace of palmitic or other lower fatty acid, the critical spreading temperature was lowered, usually by several degrees. The purest stearic acid that has been tested commenced to spread between 28 and 29°, the purest palmitic acid between 12 and 13°. The method has the advantage that several samples of a given fatty acid may be tested simultaneously on the same water surface: the sample which spreads the least contains the least amount of impurity consisting of lower fatty acids. The test does not reveal the presence of higher acids.

Caution.—The theory on which the preceding test is based requires that the Petrolatum solution shall be saturated, and shall ***not*** be supersaturated. If the solution be supersaturated, it will spread at a temperature lower than the critical temperature, and the observations will be deceiving. The crystallization of fatty acids from Petrolatum takes place slowly; therefore the oil should always be cooled to a temperature at least 3° lower than the critical temperature. Since the oil mixture is full of tiny crystals, it becomes saturated rapidly when a drop of the mixture is placed on water that is slightly warmer than the oil. One should allow about one minute's time before judging the spreading of a small lens in order to allow the lens to become saturated at the water temperature.

Successive Layers

Two distinct series, Y and X, of successive layers of calcium stearate can be deposited, their occurrence depending mainly on the *p*H and temperature of the water.

Y-Films Built of "Alternating Layers."—A layer of a Y-film is deposited each time glass is raised through a surface layer, and also each time it is lowered through the surface layer. The *first* layer must be deposited on the first *up*-journey, as previously described; the second layer is deposited on the next down-journey; the third on the next up-journey, and so on. After a slide has been coated with an initial layer, which must usually be deposited rather slowly, the succeeding layers may be deposited at a rate ten to fifteen per minute on a slide 2.5 cm. in height.

The layers of odd number, Y′, are oriented in the opposite direction from layers of even number, Y″, for the following reason. The first layer is oriented with the $(\text{—COO})_2\text{Ca}$ "heads" next the glass and the CH_3 groups away from the glass. As stated in the earlier paper, when glass coated with a first layer is next lowered into the water, the film on the water surface attaches itself to the slide, but, since water makes a contact angle of approximately 90° with a CH_3-surface, the film is turned upside down as the slide carries it down into the water. The phenomenon is striking when the motion of the film is observed by means of scattered talc particles. This film remains attached upside down to the underlying layer, that is, with the CH_3-groups toward the glass and the heads away from the glass, and forms the second layer of the series. As the glass is raised from the water the third layer attaches itself with the heads adjoining the heads of the second layer and the CH_3-groups away from the glass. All layers of odd number are oriented similarly to the first, with the heads toward the glass, and all layers of even number similarly to the second with the heads away from the glass. This type of alternate orientation of successive layers is usual in fatty acids. Müller[9,10] and others have shown by x-ray analysis that the molecules in crystals of fatty acids are oriented end to end, in opposite directions.

(9) A. Müller, *J. Chem. Soc.*, **123**, 2043 (1923).

(10) A. Müller and G. Shearer, *ibid.*, **123**, 3156 (1923).

Since the molecules in the Y″-layers, deposited as the glass travels downward into the water, are oriented with the heads away from the glass, these layers adhere tightly to water. This property can be demonstrated by the following test. An even number of layers, such as four layers, are deposited on a slide and after the down-journey on which the fourth layer is deposited the slide is kept under water while the water surface is swept clean. The slide is then raised through the clean surface. If the calcium content and *p*H of the water are high, glass coated with two or four layers emerges from the water completely wet. If the number of layers is an even number higher than four, say 10 layers, the glass emerges dry, shedding water as it rises. Close examination shows, however, that the 10th layer does not remain attached to the glass in this case, but is ripped off the glass by the adhering water and returns to the surface of the water-bath, leaving the slide coated with 9 layers. This is readily shown by sprinkling the clean water surface with talc or with sulfur before the slide is withdrawn. As the slide rises the particles recede from the slide, whereas if perfectly clean glass be withdrawn through a clean water surface, the particles do not recede. If the calcium content and *p*H of the water are not high, but have the values commonly used for depositing Y-films which will be given in this paper, the layers of even number almost always return to the surface of the water-bath when this surface is not covered with a surface film under pressure. When, however, the water is covered with a surface film under pressure, the even-numbered layer remains on the glass and the next odd-numbered layer is deposited on top of it as the glass is raised. Therefore films built of Y-layers are considered to exist out of water only in odd numbers of layers.

Y-Layers are the type of layers which are commonly deposited and are most easily investigated. They are the only type that have been observed in the case of barium and magnesium stearates. With calcium stearate they occur on water at *p*H < 7.0, and often occur at *p*H $= 7.0$ to 8.5.

The solution which was used for depositing the layers from which the data of Table I were obtained was $^1/_{10,000}$ molar calcium carbonate. It was made from a more concentrated solution of $Ca(HCO_3)_2$ obtained by bubbling carbon dioxide through a mixture of 0.5 g. of calcium carbonate per liter of water. The $^1/_{10,000}$ molar solution was prepared in the trough and air was bubbled through it to remove the excess carbon dioxide until the *p*H rose to the value of 6.4. The bath was maintained at *p*H 6.4 to 6.6, at 22 to 23°. When this solution is in equilibrium with the pressure of carbon dioxide contained in ordinary air the *p*H is 6.9, approximately; therefore, a small amount of carbon dioxide was passed through the bath about every forty-five minutes to maintain the desired value. The reason for preferring the lower value was that at *p*H 6.9 the film on the water surface crumpled wherever it was rudely broken, so that as the glass slide rose and fell through the surface broken bits of the film gradually gathered on the glass, giving it a fogged, soapy appearance. At *p*H 6.4 this did not occur when castor oil was used as piston oil. When oleic acid was used, which exerted a higher pressure and had therefore, a greater tendency to produce a crumpled film, it was found advisable to lower the *p*H to 6.2 or 6.0.

When this solution is used the first layer must be "dried on" the glass in the manner previously described. Subsequent layers, however, are deposited very readily, so that on the second ascent, as the third layer is deposited, the glass emerges from the surface shedding water nearly as rapidly as though the glass were coated with paraffin wax. There is plainly a marked difference between the forces which attach a film to underlying layers of calcium stearate and those which attach it to clean glass, since a film will not detach itself from water at *p*H 6.4 in order to attach itself to glass (unless the water be removed by drying), but attaches itself readily to glass coated with one or more layers of calcium stearate.

X-Films Built of "Non-Alternating" Layers.—These layers have the property of being transferred to the glass slide only as the slide travels downward into the water. As the glass is raised out of the water no layer is deposited. The question of whether a layer is deposited or is not deposited is decided by watching the motion of the thread which encloses the calcium stearate film on the water surface (Fig. 2). The slide sheds water perfectly in either case as it rises through the water surface, but if the slide receives a layer of calcium stearate as it travels upward, the thread moves toward the slide, if it receives no layer the thread does not move.

X-Layers are obtained from films spread on alkaline water containing calcium or strontium.

A solution of $^1/_{10,000}$ molar calcium carbonate, pH 9.0, gives layers of this type at room temperature. Other values of pH and temperature at which these layers have been investigated will be discussed in a later section of this paper.

Layers of this type are not deposited next to the glass, for the first 5 or 10 or more layers occur as alternating layers even on alkaline water. After these first layers are deposited the film commences to "slip" on the ascent of the glass, that is, it fails to attach itself to the glass as the glass rises through the surface. When this occurs the water receding from the slide commences to form a noticeably steeper contact angle with the glass than when the water recedes depositing a film as it goes.

Under suitable conditions X-layers may be deposited as regularly as Y-layers, a hundred or more consecutive layers being deposited on descents and none on ascents. This means that each layer deposited on a descent acquires the property of shedding water before the glass rises from the water. Therefore, the molecules in these layers must acquire end-groups which have a very different composition or packing from the molecules deposited in the case of the Y series, for it was shown previously that each Y″-layer adheres tightly to water until the Y″-layer takes up a Y′-layer which sheds water. Some experiments will be described in a later section which afford evidence that the molecules in an X-layer undergo a change after the layer has become attached to the slide.

A slide coated with Y-layers taken from a solution $^1/_{10,000}$ molar in calcium carbonate at $pH < 7.0$ will immediately take up X-layers if the pH be changed to 9.0, and will resume the Y-series if the pH be restored to $pH < 7.0$. At intermediate values of pH, particularly at pH 7.0 to 7.5, either type of film may be deposited. For example, in this range one may deposit 40 or more alternating layers, and then for no apparent reason the films commence to slip on one part of the slide and one obtains non-alternating films over that area for the next 10 or 20 layers, and then the alternating process may be resumed; in the meantime the remainder of the slide will have continued taking up alternating films without interruption, so that one obtains a slide coated with a greater number of layers in one place than in another place. This difficulty may be avoided in the case of Y-films by working at $pH < 7.0$, or better at $pH < 6.8$. It may usually be avoided with X-films by working at $pH > 8.5$, and by using fresh solutions; but the conditions which govern the X-series are less clearly defined than those which govern the Y-series. For example, water which has been in an open trough for two or three days has frequently ceased to give X-films at any pH, but when the trough was cleaned and filled with a fresh solution, X-films were obtained at once. On the other hand, three-day-old solutions have often given perfect X-films. Presumably certain substances present in the air or in the walls of the trough enter the water and affect its properties with regard to X-films.

Measurement of Film Thickness

Films composed of several layers of molecules exhibit interference colors when deposited on glass, provided that the refractive index of the glass is sufficiently different from the refractive index of the film so that light is plentifully reflected from the optical boundary between the film and the glass. The glass used in the present experiments had a refractive index 1.64 and films on this glass showed vivid color. A film containing only 9 layers can be seen to show a faint yellow-brown color, due to the diminished intensity of blue light. As the number of layers is increased the color of the film changes, corresponding to the change of the absent color to the successive longer wave lengths green, yellow, red. As still more layers are added the spectrum is repeated.

A method has been developed for recording the successive stages by depositing on a single slide "steps" of 21, 41, 61, etc., layers, or any other chosen sequence. The steps are deposited by covering all of a clean wet slide (I), except 0.5 cm. length, with another clean wet slide (II) having the same dimensions. After 20 layers are deposited the covering slide (II) is moved 0.5 cm. while the slides are under water, so that it then covers all but 1.0 cm. of (I), and the next 20 layers are deposited on both the first and the second areas. The colors of the steps are made to appear much more vivid by pressing a slide of wet cobalt glass against the back of (I) while the films are being deposited on the front of (I). The slide (I) then forms the center of a sandwich, between the cobalt glass and the cover glass (II), all three being held together by the clamp J (Fig. 1). The sandwich should be assembled under water, and the covering slide should be moved only when the slides are under water, to prevent contaminating oily films from reaching the glass.

A slide coated in steps shows bands of vivid color when viewed by white light. When the films are built of calcium stearate the first eight bands have the following colors when viewed by light of perpendicular incidence: 21 layers yellow-brown, 41 dark blue, 61 light blue, 81 yellow, 101 red, 121 blue, 141 green, 161 red-yellow. When monochromatic light is used the steps appear as a series of dark and bright bands, the intensity of the reflected light varying from step to step. The series of intensities ranges between a maximum and a minimum value, varying with the thickness of the step in the manner illustrated by the curve in Fig. 3. The abscissa scale of the diagram in Fig. 3 has been drawn for the case of calcium stearate steps illuminated by sodium light at perpendicular incidence. For this case the first three intensity minima were found to occur at steps having the thicknesses 39, 121, 203 layers (Table I). The light source was a 6000-lumen sodium vapor lamp.

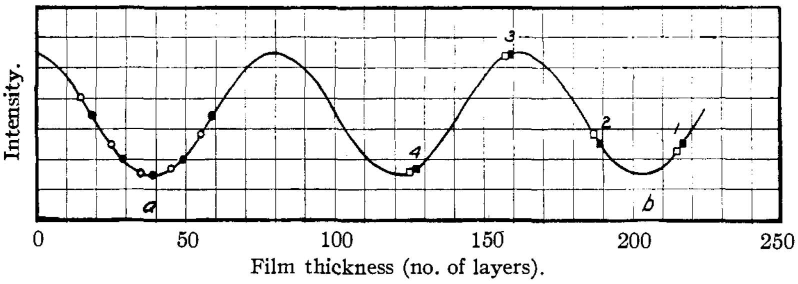

Fig. 3.—Two methods (a) and (b) of determining the thickness of a film which reflects minimum intensity of monochromatic light. The curve is drawn for the case of calcium stearate illuminated by sodium light at perpendicular incidence.

The number of layers corresponding to an intensity minimum may be determined by either of two methods (a) or (b).

(a) **Symmetrical Intensities.**—Alternating films are deposited in a series of five steps having a uniform step-rise for the series. A step-rise of ten layers is convenient for this purpose. When the number of layers reaches 15, 25, 35, 45, 55 the steps reflect light with intensities corresponding to the open circles in Fig. 3(a). The 35 step is seen to be the darkest of the five steps, but the intensity of 35 is not symmetrical with respect to 25 and 45, the 45 step appearing considerably darker than the 25 step. When four more layers are added to the entire slide, bringing the steps to 19, 29, 39, 49, 59, the 39 step is found to be symmetrical with respect to 29 and 49. The thickness of 39 layers therefore corresponds to minimum intensity for sodium light. As more layers are added to the slide, the steps are seen to pass through a maximum of intensity at 80 layers, a second minimum at 121, and so on.

(b) **Matched Intensities.**—The second method consists in bringing two neighboring steps to exactly equal intensity. A series of steps Nos. 1, 2, 3, 4 are built (Fig. 3(b)) in which the step-rise between consecutive steps may be any known even number of layers and is preferably not uniform for the series. In the diagram step No. 1 and step No. 2 are 28 layers apart, No. 2 and No. 3 are 30 layers apart, No. 3 and No. 4 are 32 layers apart. When any two neighboring steps match exactly, a maximum or minimum lies at a thickness half-way between the two. Thus since No. 1 and No. 2 match when they have thicknesses 217 and 189 layers, respectively, the minimum lies at 203. When No. 1 and No. 2 have thicknesses slightly less than these, such as 215 and 187, the diagram shows that the intensity of No. 1 is less whereas that of No. 2 is greater than the matching intensity. Due to this "seesaw" of intensities about a maximum or minimum, the contrast observed between two neighboring steps changes so rapidly with changes in thickness that an addition of two molecular layers to both steps is plainly visible to the eye, and under good conditions the addition of one layer can be detected.

After No. 1 and No. 2 have been matched, more layers are added to all four steps until No. 2 and No. 3 are brought to matching positions on opposite sides of the minimum, and then No. 3 and No. 4 are matched; thus three independent determinations of the location of the minimum are obtained. These three determinations usually agree exactly; when the values disagree they differ by not more than one layer. The interval between successive steps should be chosen in such a way as to cause the intensity of the steps to lie on a steep part of the intensity curve when the steps are being matched. Widely different intervals may be used if desired, but it has been found most practical to choose three which are not very different, such as the intervals 28, 30 and 32 illustrated in the diagram, for the observer soon learns to gage intensity differences in terms of thickness differences if the intensities that are used lie always on about the same part of the curve.

Films of calcium palmitate, calcium stearate and calcium arachidate have been measured by method (b). Table I gives the results of these measurements for alternating films. The quality of these substances as "building material" for films is markedly affected by the length of the chain. Calcium palmitate, having 16 carbon atoms in the chain, is troublesome to work with and seldom gives satisfactory films after about 100 layers have been deposited, the small imperfections in many of the first 100 layers causing a cumulative roughening of the surface. Calcium stearate (C_{18}) works well, and calcium arachidate (C_{20}) works the best of the three. Subsequent experiments have shown that for a given length of chain one obtains the best results by using the soap of a heavy metal. Barium stearate films are more easily built than films of calcium stearate, whereas magnesium stearate films are very troublesome.

TABLE I

MEASUREMENTS OF "ALTERNATING" (Y) FILMS OF CALCIUM SOAPS

Water-bath 1/10,000 molar calcium carbonate, *p*H 6.4, temp. 22°. Piston oil: castor oil. Refractive index of films $\mu = 1.471$.

(1) n	(2) μt, Å.	(3) Å.	(4) Calcium palmitate (C_{16}) N_P	 ΔN_P	(5) Calcium stearate (C_{18}) N_S	 ΔN_S	(6) Calcium arachidate (C_{20}) N_A	 ΔN_A
0	1473	1001	45		39		35	
1	4420	3005	138	93	121	82	108	73
2	7367	5008			203	82	181	73
3	10313	7011					255	74
							Mean	73.3

(7) $\frac{\Delta t}{\Delta N_P}$ Å.	(8) $\frac{\Delta t}{\Delta N_S}$ Å.	(9) $\frac{\Delta t}{\Delta N_A}$ Å.	(10) $\frac{\Delta t}{16\Delta N_P}$ Å.	(11) $\frac{\Delta t}{18\Delta N_S}$ Å.	(12) $\frac{\Delta t}{20\Delta N_A}$ Å.
21.5	24.4	27.4	1.35	1.36	1.37
	24.4	27.4		1.36	1.37
		27.0			1.35
	Mean	27.3		Mean	1.36

The thickness t of a film which shows minimum intensity when illuminated by light of wave length λ at perpendicular incidence is $t = (2n + 1)\lambda/(4\mu)$ where n has the values 0, 1, 2, . . ., and μ is the refractive index of the substance of which the film is composed.[11] Column (2) in Table I gives the values of μt which correspond to the values of n in Col. (1) when sodium light was used, taking as the value of λ a mean of the sodium D lines, $\lambda = 5893$ Å. The refractive index of the films was determined by a method which will be described; it was found to be $\mu = 1.471$ (Table II). Column (3) gives the values of t calculated for this value of μ.

Columns (4), (5), (6) give the number of layers N at which minima occur for the three substances, and the values of the difference ΔN between minima. The values of ΔN are estimated to have a probable error of ±0.5 layer for the C_{20} and C_{18} chains, and ±1 layer for the C_{16} chain. Columns (7), (8), (9) give the values of $\Delta t/\Delta N$ calculated from these data for the three substances. Columns (10), (11), (12) give $\Delta t/\Delta N$ divided by the number of carbon atoms in the chain of the substance. The results in the last three columns are seen to be closely similar for the three substances, having an average value 1.36 Å.

Müller[12] found by x-ray measurement of stearic acid crystals that the length of a pair of molecules arranged end to end was $c = 48.84$ Å. He found that the axis of the chains was inclined at an angle $\beta = 63°38'$ with the plane in which the carboxyl groups lay, so that the spacing between consecutive carboxyl planes was $c \sin \beta = 43.76$ Å. The value $\Delta t/\Delta N_S = 24.4$ in Col. (8) gives the thickness of a single layer of calcium stearate. The agreement between this value and $c/2$ of Müller's measurements implies that $\beta = 90°$ for the calcium stearate films. That is, the surface pressure exerted on the molecules as the films are deposited causes the molecules to assume positions perpendicular to the plane of the glass surface.

Piper[13] measured by x-ray diffraction the long spacings of potassium soaps of the fatty acids. His results for acid soaps are given below, for comparison with the corresponding measurements made by the present method (Cols. (7), (8), (9)). The data are given in terms of the spacing corresponding to a single layer.

	C_{16}, Å.	C_{18}, Å.	C_{20}, Å.
Piper	22.64	25.23	27.82
Cols. (7), (8), (9)	21.5	24.4	27.3

Piper found that the spacings for neutral potassium soaps were approximately 20% less than the spacings for acid soaps. In the case of calcium stearate films no change was found in the spacing of Y-films when the *p*H of the water was changed within the range of *p*H in which Y-films could be deposited. Barium stearate Y-films can be deposited over a wider range of *p*H than calcium stearate Y-films. No difference in thickness was found between barium stearate films formed at *p*H 6.9 and at *p*H 8.5.

When the data for film thickness, given above, are plotted against the number of carbon atoms in the chain, Piper's data lie on a straight line having a slope $t_C = 1.275$ Å. per C atom. The complete range of Piper's data extends from the C_4 chain to the C_{24} chain. The writer's data give a slope 1.45 Å.; however, if the estimated prob-

---

(11) This equation applies only to cases, such as the present case, where μ has a value less than the refractive index of the substance on which the film is deposited.

(12) A. Müller, *Proc. Roy. Soc.* (London), **A114**, 546 (1927).

(13) S. H. Piper, *J. Chem. Soc.*, 236 (1929).

able error is taken into consideration, it is found that the possible slopes range from 1.34 to 1.55. That is, the range of data from C_{16} to C_{20} is too short to afford an exact determination of t_C.

The lowest value $t_C = 1.34$ is higher than most of the values previously determined by other workers from x-ray measurements of fatty acids and of soaps. The highest value obtained from the measurements made by Slagle and Ott[14] is approximately 1.2 Å. The value of the length which each CH_2 group contributes to the chain, calculated on the theory[10] that the chain is a zigzag in which the lines joining the centers of successive carbon atoms are inclined at the tetrahedral angle 109°28′, is 1.257 Å., the diameter of the carbon atom being 1.54 Å. The higher value obtained in the present experiments seems to indicate that the molecules, being held under much constraint from the pressure applied by the piston oil, assume orientations and lengths which have a greater "long spacing" than when films are formed by other methods. Piper[15] and others have shown that the long spacing is affected by the degree of constraint imposed on the molecules of a fatty acid while crystallization is taking place.

The surface pressure exerted by oleic acid, 29.5 dynes/cm., on a molecular wall 25 Å. in thickness, is 118 atmospheres. In the case of castor oil, 16.5 dynes/cm., the pressure is 66 atmospheres. Castor oil was used for the series of measurements given in Table I for the reason that calcium palmitate tends to collapse slowly on the water surface when subjected to the pressure of oleic acid. Only a very slight difference was found between series of films obtained when castor oil was used and those obtained with oleic acid. In the case of calcium stearate, for example, the number of layers between successive minima for sodium light was $\Delta N_S = 82$ in the case of castor oil (Table I), and $\Delta N_S = 80$ to 81 in the case of oleic acid. This observed increase in thickness of approximately 2% for a change in pressure of 13 dynes/cm. is in accord with Adam's[6] measurements of the compressibility of monomolecular films of palmitic acid on pure water. He found that the force required for 1% decrease in area (corresponding to 1% increase in thickness in the present experiments) was 5.9 dynes/cm.

Clark, Sterrett and Leppla[4] have used the method of the present experiments to deposit films which they have measured by means of x-ray diffraction. They obtained the value 47.55 Å. for the long spacing of built-up layers of calcium stearate, and 47.53 Å. for the long spacing of pure synthesized calcium stearate studied by the older methods. These long spacings correspond to the thickness of two monomolecular films turned in opposite directions. They found for calcium palmitate a long spacing 43.50 Å. and for myristate 39.55 Å. A plot of their values for the three chains against the number of carbon atoms in the chain has a slope $t_C = 1.0$ Å.

Films of barium stearate deposited from a solution $^1/_{10,000}$ molar in barium carbonate gave the same value of ΔN_S as films of calcium stearate. Barium stearate films were found to have a refractive index $\mu = 1.46$ (Table II). Piper[13] observed, when he compared the long spacing of thallium stearate with that of potassium stearate, that "a very small change in spacing is produced by the addition of a very heavy metallic atom." The change which he observed was 2.3% for the normal palmitate, 0.5% for the normal stearate. Films of magnesium stearate in the present experiments were also the same as calcium stearate within the limits of error of the measurements; it was found difficult to produce homogeneous films of magnesium stearate when the number of layers exceeded about 50.

Clark has pointed out that films of stearic acid may be deposited from the surface of purest distilled water. He obtained for these films a long spacing 46.05 Å. The writer has deposited films of stearic acid on polished chromium (*i. e.*, chromium-plated brass) from distilled water, *p*H 5.2 to 5.4, and from the same water to which sufficient hydrochloric acid was added to lower the *p*H to 4.2. These films were found to have a value of μt_1 approximately 8% less than the calcium or barium stearate layers, where t_1 is the thickness per layer. The films at *p*H 4.2 gave the same result as films at *p*H 5.2. The value of μt_1 was estimated in the following manner.

Two color scales were made on separate slides, to serve as gages. On the first slide there was built a series of ten "20-layer" steps of barium stearate, *i. e.*, the steps had 21, 41, . . ., 201 layers. On the second slide ten "18-layer" steps of barium stearate were built, *i. e.*, the steps had 19, 37, . . ., 181 layers. When the slides were viewed side by side, by white light at normal incidence, they formed two different color series. A series of ten

---

[14] F. B. Slagle and E. Ott, THIS JOURNAL, **55**, 4399 (1933).

[15] S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, 2313 (1926).

20-layer steps of stearic acid was then built using oleic acid as piston-oil, and it was found that this series nearly matched the 18-layer series of barium stearate which was also built at oleic acid pressure ($\Delta N_S = 80$ for oleic acid pressure). The difference in μt_1 between stearic acid and barium stearate was estimated as being 8% of μt_1 for barium stearate. The refractive index of stearic acid was found to be $\mu = 1.48$. From the measurement $\Delta N = 80/0.92$ and the refractive index one obtains the result $\Delta t/\Delta N = 22.9$ Å. for the thickness per layer of stearic acid.

Determination of Refractive Index.—The refractive index μ of the calcium stearate films was determined by measuring the "polarizing angle" of the films. The method was based on certain laws of optics which will be stated briefly.

When light is reflected from a surface, the component of vibration parallel to the plane of incidence is reflected with an amplitude different from that of the component perpendicular to the plane of incidence. The component parallel to the plane of incidence has the following properties.

(i) The intensity is zero when $(\varphi + \chi) = 90°$, where φ is the angle of incidence of the light illuminating the reflecting surface, and χ is the angle of refraction. The angle of incidence at which $(\varphi + \chi) = 90°$ is the "polarizing angle" φ_P. At this angle $\sin \chi_P = \cos \varphi_P$, hence $\mu = \tan \varphi_P$, since by definition $\mu = \sin \varphi / \sin \chi$.

(ii) When $\varphi < \varphi_P$, the amplitude of the reflected light is in phase with that of the incident light.

(iii) When $\varphi > \varphi_P$, the amplitude of the reflected light has a difference of phase of 180° from that of the incident light.

In the present measurements the reflected light was polarized by means of a Nicol prism which transmitted the component parallel to the plane of incidence. The polarizing angle φ_P was determined by measuring the angle at which the change of phase of 180° between Case (ii) and Case (iii) occurred. This was done by viewing two neighboring steps, one of which was built with a thickness which reflected minimum intensity when illuminated by sodium light at an angle of incidence $\varphi = 55°$, and the other with a thickness which reflected maximum intensity at the same angle. The angle $\varphi = 55°$ is less than the polarizing angle of calcium stearate and corresponds to Case (ii).

When φ was made greater than the polarizing angle, the light reflected from the surface of the film changed 180° in phase; but the light reflected from the film–glass boundary did not change phase because refraction of the light as it entered the film caused the light to arrive at this boundary at an angle of incidence far less than the polarizing angle characteristic of a glass–film boundary. Therefore when the difference of path length between the ray reflected from the surface of the film and the ray reflected from the film–glass boundary was such that the two rays produced minimum intensity at an angle slightly less than φ_P, the relative phase change of 180° at φ_P caused these rays to produce maximum intensity at an angle slightly greater than φ_P. *Vice versa*, a maximum for $\varphi < \varphi_P$ changed to a minimum for $\varphi > \varphi_P$. Thus two neighboring steps which were seen as a minimum and a maximum for $\varphi < \varphi_P$ exchanged brightness as φ passed through the polarizing angle; and at the polarizing angle the steps matched exactly. The angle at which the steps matched was found to be very critical, and could therefore be measured with a probable error less than 0.1 degree.

In order to obtain the greatest sensitiveness it was desirable that the steps be built so that the thicknesses would correspond exactly to maximum intensity. The theory of the method is the same for steps having any difference in intensity, but obviously the method is most sensitive when the difference in intensity is as great as possible. The number of layers which were needed to build the steps was calculated from the data of Table I by means of the formula for the path difference l between the rays reflected from the upper and from the lower surface of a film of thickness T, which is $l = 2 \mu T \cos \chi$. For the data of Table I, $\cos \chi = 1$. When $\varphi = 55°$, $\chi = 33°50'$, $\cos \chi = 0.83$. The steps were therefore built as follows: minimum at $\varphi = 55°$, 47 layers; maximum, 97 layers; minimum 147 layers. The steps were deposited on glass having a refractive index 1.64, from a solution $^1/_{10,000}$ molar in calcium carbonate, *p*H 6.4, temp. 22°. The slide was mounted at the center of a spectrometer table in such a position that the boundary line between two steps lay in the axis of the table. A horizontal beam of unpolarized light illuminated the slide. The observer viewed the slide by looking through the slit in the end of a collimator tube, a Nicol prism being mounted in the axis of the tube. The plane of the light transmitted by the prism was parallel to the plane of incidence, that is, the plane was horizontal. The angle φ_P was determined by measuring the difference $2\varphi_P$ between two positions of the slide in which a maximum and a minimum were seen to exchange brightness, one position occurring when the observer viewed the slide at the angle of reflection φ_P and the other position at $-\varphi_P$.

The results of these measurements are given in Table II. The measurements were not made for the C_{16} and C_{20} soaps. The refractive indices of molten palmitic and stearic acids are nearly equal, the values[16] being $\mu = 1.4273$ for molten palmitic acid at 79.8° and $\mu = 1.4299$ for molten stearic acid at 80.2°. It seems probable, therefore, that variations in μ with the chain length of the soaps are negligible for the purposes of the present measurements.

TABLE II

REFRACTIVE INDEX μ OF FILMS

Substance	No. of layers of two neighboring steps	Θ_P	$\tan \Theta_P = \mu$
Calcium stearate	47 and 97	55°45′	1.469
Y-Films	97 and 147	55°50′	1.473
(pH 6.4)		Mean	1.471
Calcium stearate approx.	42 and 87	55°47′	1.471
X-Films approx.	87 and 132	55°45′	1.469
(pH 8.8)		Mean	1.470
Barium stearate	47 and 97	55°35′	1.460
Y-Films	97 and 147	55°40′	1.464
(pH 6.9)		Mean	1.462
Stearic acid	51 and 103	55°55′	1.478
Y-Films	103 and 155	56°5′	1.487
(pH 5.2)		Mean	1.482

In order to measure the refractive index of stearic acid by the method used for calcium stearate it was necessary to deposit the stearic acid on glass rather than on chromium. The component of the light reflected from the surface of a film which is used for making these measurements has such low intensity at angles of incidence near the polarizing angle that if the intensity of the light reflected from the film–solid boundary be great, the very weak ray has little effect in modifying the intensity of the strong ray. Therefore in order to obtain as much contrast as possible between steps of minimum and maximum intensity, the ray from the film–solid boundary must be weak, and glass serves this purpose far better than chromium.

Stearic acid does not attach itself readily to glass, and no method was found of depositing a first layer which would adhere to the glass satisfactorily while 50–100 layers were built on top of it. Imperfections in the first layer always allowed water to work its way underneath this layer and gradually to rip sections of the film off the glass. The difficulty was obviated by depositing a first layer of barium stearate on the glass from a barium carbonate solution, pH = 8.6, and then building on top of this first layer successive stearic acid layers taken from distilled water.

Decrease in Thickness Produced by Heat.—Significant changes occur in the thickness of Y-films when the films are heated. The record of four tests will indicate the nature of the results recently obtained; a systematic investigation of the effects of heating has not yet been made. The films were baked in an oven the temperature of which was held constant with an accuracy of 1° by thermostat control.

(1) Calcium stearate, Y-films. Water pH 6.6, T 22°, $^1/_{10,000}$ molar calcium carbonate. Pressure: castor oil. Films deposited on polished chromium in seven 20-layer steps. The slide was baked for fifteen minutes at 100° and during baking the thickness of each step decreased 20%. The decrease was measured by using as a gage the colors of an unbaked slide on which seven 16-layer steps had been built. Further prolonged baking at 100° produced no further change in thickness. A change took place, however, in the structure of the film, for when viewed by transverse light each step scattered light of a color complementary to the color of the same step when viewed by reflected light. Baking at 150° produced a gradual transition from a transparent film to a white, opaque film, which caused the colors to appear to be "fading out," the transition taking place in an uneven, spotty manner over the surface.

(2) Barium stearate, Y-films. Water pH 8.5, T 22°, $^1/_{10,000}$ molar barium carbonate, $^1/_{1000}$ molar sodium bicarbonate, plus a very small amount of sodium hydroxide. Pressure: oleic acid. Surface: polished chromium. The slide was baked for ten minutes at 100° and showed a 10% decrease in thickness. Further baking at 100° for two hours produced no further change in color. Complementary colors seen by scattered light. Baking at 150° caused gradual change to opaque film.

---

(16) "International Critical Tables."

(3) Barium stearate, Y-films. Water *p*H 6.9, T 22°, $^1/_{10,000}$ molar barium carbonate. Pressure: oleic acid. Surface: polished chromium. Baking at 65° for ten minutes caused no change in thickness. Steps viewed by scattered light showed not complementary colors but colors which would be seen by reflected light from steps having approximately 20% less thickness. After twenty minutes at 65° the difference in color between scattered and reflected light was less marked, after thirty minutes at 65° the difference had disappeared. After ninety minutes at 65° the steps continued to retain the same thickness which they had had originally. The slide was then baked at 70° and after ten minutes much of the film was opaque, after 20 minutes every step except the 21 and 41 layer steps was completely white. It was observed in three separate tests that the two thinnest steps were the last to lose color and become opaque.

The transition temperature 70° in this test is the melting point of stearic acid. It is higher, however, than the transition temperature observed for films of stearic acid (see Case 4). The films in Case (3) had the same thickness as the films in Case (2), and did not have the thickness of stearic acid films. It seems probable, therefore, that in Case (3) the films were an acid barium stearate composed of neutral barium stearate and stearic acid combined in a proportion which is not known, and that in Case (2) the films were neutral stearate. Barium stearate which was made from sodium stearate by precipitation with barium chloride showed no sharp melting point, but became sticky at about 140°.

(4) Stearic acid, Y-films. Water *p*H 5.2 to 5.4, T 22°. These films gradually deteriorated at 65°. The transition temperature was somewhat less sharp than in Case (3).

The marked decrease in thickness which occurred in Cases (1) and (2) seems to indicate that in these cases the molecules were able to re-orient themselves as a result of molecular agitation at the higher temperature, and that they then departed from the constrained positions in which they were deposited and assumed orientations more nearly characteristic of the substance in its normal state. Piper[14] found from his studies of potassium palmitate, stearate and eicosoate that "in contrast with the acids, which possess a number of crystalline forms, only one form appears to exist for these pure anhydrous salts at the ordinary temperature."

Dr. Langmuir has pointed out that a decrease in thickness of 20% in a film which remains transparent must be accompanied by an accumulation of about 20% of the material in small mounds or ridges on the surface, these excrescences occupying a comparatively small fraction of the area of the surface. The strong forces exerted by the molecules in their constrained upright positions become sufficient to expand the film in a lateral direction when the forces are increased and the rigidity of the film is diminished by heat. The expansion produces breaks and ridges in the films analogous to the pressure ridges which are commonly seen in the ice of a large frozen lake. The following brief study was made of the structure as seen with the aid of a microscope.

A barium stearate film of the type described in Case (2) was baked at 100° for ten minutes, after which it showed a decrease in thickness of 10%, the color of the light scattered by the surface being then complementary to the color of the reflected light. The film was viewed through a microscope by dark-field illumination, at a magnification 270:1. The steps having a thickness of 81 or more layers were seen to be crossed by a series of parallel ridges. The direction of the ridges was parallel to the line of intersection which the plane of the water surface made with the plane of the slide when the film was being built. Mr. L. L. Wyman has measured the spacing of the ridges on a film of 141 layers, thickness $T = 3.4 \times 10^{-6}$ cm. He found an average spacing of 6.56×10^{-4} cm., which is 19 T.

The spacing of the ridges was nearly the same for all the steps which were thick enough to show any ridges, but on the thickest step (141 layers) additional ridges were seen which were more pronounced than the first set. The second set ran parallel to the first but with much wider spacing, and had occasional cross ridges at right angles. These preliminary observations have shown that the growth of the ridges may be studied as a function of film thickness and conditions of baking, and further experiments will continue this study.

The phenomenon of films which scatter light having a color complementary to the color of reflected light has been observed by Wood[17] in the case of "frilled" transparent films on metallic surfaces. The phenomenon is attributed by him

---

[17] R. W. Wood, "Physical Optics," 2d ed., p. 172; 3d ed., p. 206; R. W. Wood, *Phil. Mag.*, **7**, 385 (1904).

to the effect of a mesh structure which is "so small that it can be detected only with the highest powers of the microscope." In the present case it is due to the ridges on the surface, and a further study of these ridges should lead to an explanation of the phenomenon.

It can be argued that water is held by the films as they are deposited, and that the presence of layers of water accounts for the high value of t_C and loss of water accounts for the shrinkage at high temperature. Films of barium stearate placed in a desiccator for three days at room temperature showed no change whatsoever in color. Further tests are needed to decide this question.

Optical Properties of the Film–Glass Boundary.—If the values of N in Cols. (3), (4), (5) of Table I are plotted against the values of μt in Col. (2), the result is a linear plot which does not pass precisely through the origin. At $t = 0$, the plot shows $N_P = -1.5$, $N_S = -2$, $N_A = -1.7$. Intercepts $N = -1$ to -2 layers were obtained from every set of data that was taken in the course of making these measurements. That is, the mechanism by which reflection of light takes place at the glass–film boundary is of such a nature that the reflection appears to take place at an average distance approximately 20 to 40 Å. beneath the surface of the glass.

Films deposited on glass may be loosened from the glass by acid and the entire film floated off on a water surface. This is accomplished by placing a few drops of acid (20 to 50% hydrochloric acid) on one end of the slide from which the film has been wiped off so that the acid comes in direct contact with the glass. The slide is tipped slightly so as to bring the acid up to the edge of the film, and the acid then creeps slowly under the film, disrupting the bond which attaches the film to the glass but not dissolving the film. A film which exhibits a given interference color on glass exhibits the complementary color when floating on acid or water, since the index of refraction of glass is greater and the index of refraction of water is less than that of the stearate.

Measurement of X-Films.—These films occur on alkaline water containing calcium or strontium. They have not been observed in the case of magnesium or barium. The latter substances have not been so thoroughly investigated as calcium, so it cannot be said with certainty that X-films never occur with these substances, but they have not appeared in the range *p*H 7.0 to 11.0, at temperatures 20 to 30°.

Layers in an X-series are deposited only as the slide descends into the water, as previously described. Let n be the number of journeys which the slide must make in order that a thickness $\Delta t = 2947/\mu$ Å. may be added to the film on the slide, counting each ascent as one journey and each descent as one. Then in the case of Y-films $n = N$ where N is the number of layers corresponding to this value of Δt. In the case of X-films $n = 2N$ provided that no films whatsoever are collected on ascents.

If N' films are collected on ascents, $n = 2(N - N')$.

The question of whether a slide collects a small amount of calcium stearate on some of its ascents is not easy to decide, for the following reason. Experiments have shown that under certain conditions n may range nearly all the way from $n = 2N$ to $n = N$. That is, a slide may take up an amount of calcium stearate on successive ascents which corresponds to the thickness of N' layers N' having any value from 0 to $N/2$. This occurs for the reason that the amount taken up by an ascending slide depends on the length of time which the slide has spent under water since the preceding descent. If the time under water is short, the glass collects a film on the ascent; if the time is long it collects little or no film.

This property of X-films was first observed in cases of "graded" films. In these films the upper edge of the slide (the edge which emerges first from the water) takes up more calcium stearate than the lower edge, for the reason that the upper part of the slide always spends less time under water than the lower part. The result is a film having a thickness which slopes continuously from the upper to the lower edge of the slide. The continuous grading of thickness is made apparent by the continuous grading of color. The following experiment tested this property of X-films more exactly.

A fresh solution was used, $^5/_{10,000}$ molar calcium carbonate, *p*H = 7.4. Pressure: oleic acid. Values of $n/2$ were measured at various temperatures. That is, journeys of the slide were counted while thicknesses of two "matched layers" (method (b) Fig. 3) were changed from values on each side of the first minimum for sodium light to values on each side of the next maximum. The results are given in Table III.

The seven sets of measurements were made consecutively with the same solution. The comment "Dipped at usual rate" means that the slide was allowed to descend rapidly and was raised as rapidly as it would shed water, the two operations requiring about ten seconds for completion.

TABLE III

MEASUREMENTS OF "NON-ALTERNATING" (X) FILMS OF CALCIUM STEARATE

Solution $^5/_{10,000}$ molar calcium carbonate, *p*H 7.4. Piston-oil: oleic acid.

Temp., °C.	$n/2$	
	Piston-oil: oleic acid	
33	68	Dipped at usual rate
26	66	Dipped at usual rate
20	Graded thickness: 42 top, 62 bottom	Dipped at usual rate
15	44	Dipped at usual rate
17.5	72	Held under water 30 sec. after each descent
17.5	42	Dipped at usual rate
17.5	66	Held under water 30 sec. after each descent

Those values of $n/2$ in Table III which are high correspond to cases in which comparatively little stearate was collected on ascents. High values were obtained consistently with this solution at $T \geqq 24°$. At $T \leqq 17.5°$ high values were obtained only when the slide was left under water for an exceptionally long period of time. When the slide was withdrawn at the usual rate at 17.5°, the count $n/2 = 42$ was obtained. This is almost exactly the value for Y-films, $n = 80$ for oleic acid pressure. These results are interpreted as meaning that a change takes place in the molecules which form the layer collected on a descent, the rate of change depending on the temperature of the water. As a result of this change the layer which would ordinarily adhere on an ascent (as it does adhere in the case of Y-films) does not adhere, or adheres only at various spots on the surface.

At the higher temperatures the change occurs in a time which is short compared with the time of dipping; at 20° the time is approximately the same as the time of dipping so the change occurs more completely on the lower portion of the slide which spends the longer time under water; at 17.5° the time is more than ten seconds less than thirty seconds.

The maximum values of $n/2$ which have been obtained for X-films were obtained with solutions $^1/_{10,000}$ molar in calcium carbonate, *p*H 8.8 to 9.0, T 25°, pressure castor oil. The slide was dipped at the usual rate. The alkalinity was secured by adding sodium hydroxide, and a concentration of $^1/_{1000}$ molar sodium bicarbonate to serve as buffer. The values of $n/2$ obtained for this solution were 74 to 76. If these values represent perfect X-films, the difference between $N_X = n/2 = 74$ to 76 and $N_Y = n = 80$ represents the difference in packing between the layers of molecules in the two cases, the thickness of the layers being 5 to 8% greater for X-films than for Y-films.

A slide coated with steps of X-films was baked in the oven at 100° at the same time as the slide of Y-films described in Case (1) of the section dealing with baked films. The X-films showed no decrease in thickness due to baking. They deteriorated at 150° in the same manner as the Y-films.

Miscellaneous Films

Mr. V. J. Schaefer has assisted the writer in studying several different varieties of films.

Films can be built on a metal surface as readily as on glass, provided the metal has a mirror polish. If the metal is not highly polished, a first layer is reluctant to adhere to the surface. Films have been built on chromium, nickel, brass, steel, cast iron, silver, platinum. Films on polished chromium exhibit remarkably fine colors and this metal was used for building the step-gages previously described.

The colors of films on chromium are especially brilliant when the slide is illuminated at angles of incidence greater than about 65° by polarized light, the colors of the steps when the light is polarized in the plane of incidence being in most cases complementary to the colors when the light is polarized perpendicular to the plane of incidence. A greater variety of color effects is obtained when the slide is illuminated at these angles of incidence by light polarized in a plane at azimuth 45° and is viewed through a Nicol prism. The colors of the light transmitted by the analyzing Nicol change as the Nicol is rotated.

When steps of barium stearate having 1, 3, 5,..., layers are built on polished chromium, and the slide is illuminated at angles near grazing incidence by light polarized in the plane of incidence, the difference in intensity of light reflected from the successive steps is easily seen, and the difference between a single layer and clean chromium is plainly visible.

Before the films are deposited the metal is cleaned electrolytically by being made cathode in a solution 2.5% in sodium hydroxide and in water and alcohol, with a current 1.5 amp. for about ten seconds. Only a small concentration of water is used to dissolve the sodium hydroxide.

In the case of glass the first layer is deposited most readily from alkaline water, in the case of metal most readily from water that is neutral or slightly acid. The solution used for making the step-gages on chromium was $^1/_{10,000}$ barium carbonate in equilibrium with the pressure of carbon dioxide present in ordinary air (*p*H 6.9 approximately, at *T* 22°). If the metal has a high polish and is thoroughly clean, the first layer attaches itself readily and water recedes rapidly as the slide is raised on the first ascent. The first layer is reluctant to attach itself to glass under the same conditions and must usually be dried on.

A number of different kinds of glass were used in these experiments. Every kind of glass that was used took up a first layer readily from alkaline water. Small differences were observed in the case of films deposited from acid water, the differences being very small, however, compared with the great difference between glass and metal in this respect. The glass used for all the measurements of film thickness, $\mu = 1.64$, took up a first layer from acid water more satisfactorily than any other glass, the first layer being deposited by drying the slide in an oven. This glass contained about 50% of lead. Bausch and Lomb microscope slides, $\mu = 1.52$, took up a first layer under these conditions which was slightly less perfect than a first layer deposited on the glass containing a high percentage of lead. The layer was apparently attached less firmly to the microscope slide than to the lead glass. A sample of plate glass of thickness 0.7 cm. was very troublesome, the first layer being usually not at all uniform. The composition of this glass was not known to the writer.

Stearic acid is taken up by chromium very readily from acid water. Step-films of this substance have been built at *p*H 4.2 using the pressure of oleic acid. High pressure must be used with stearic acid, for at low pressure fatty acids form expanded films on acid water and the expansion apparently interferes seriously with the building of successive layers. Adam[6] gives the value *p*H 5.5 approximately, as being the hydrion concentration at which palmitic acid commences to form expanded films. At *p*H 3.6 the film on a water surface collapsed so rapidly under oleic acid pressure that films could not be built at room temperature. Probably by lowering the water temperature films could be obtained at lower values of *p*H. Both Langmuir and Adam have found fatty acid films less stable under pressure on acid water than on neutral water.

Mr. Schaefer has deposited films of stearic acid on glass from distilled water (*p*H 5.2) by drying the slide in an oven at 50°. The slide was held in a horizontal position in the oven. After a first film is dried by this method, a few successive films of stearic acid can be deposited on top of it in the usual manner. If the slide is dried at temperatures higher than about 60°, successive films cannot be deposited satisfactorily. He found it necessary to use oleic acid for he could not form a first film at the pressure of castor oil which would take up successive films. At *p*H 5.2, *T* 22°, the film on the water surface contracted at a rate which was initially very slow but became quite rapid after about five minutes at oleic acid pressure. This difficulty was avoided by working at 15°, at which temperature there was almost no contraction.

The experiments on the effect of raising films to a high temperature, described in a previous section, demonstrated that films taken up from neutral or alkaline water were not composed of free fatty acid, but of acid soap or neutral soap. The substance of which the film on the water surface is composed may be studied very simply by skimming it off the water. The entire length of a trough is covered with a monomolecular film and then a barrier is used to shove all the film to one end of the trough. As the film is jammed by the barrier it breaks and wrinkles, and much water is enclosed in the wrinkles. Thus the very small amount of stearic acid required to cover a large surface, 0.3 mg. for 1300 sq. cm., assumes an appreciable volume when the jammed mass is collected at one end of the trough. It may then be readily skimmed off the water by a strip of metal, and heated over a flame to observe the melting point. When the films are calcium stearate, the soap remains white and solid while the water held by the soap boils away. When the films are stearic acid, the acid is seen to melt before the water commences to boil.

It has not been found possible to build films of sodium stearate by any of the ordinary methods using solutions containing Na but no Ca. Since sodium stearate is soluble in water, the strong affinity for water presumably prevents it from leaving the water to attach itself to a solid. A solution $^1/_{1000}$ molar in sodium hydroxide gave films which showed no tendency to adhere to a solid, but when a concentration of 3×10^{-6} molar calcium carbonate was added to this solution, moderately good films were obtained at once. Calcium may be added to a solution in the form of calcium chloride instead of calcium bicarbonate and gives the same results for corresponding values of *p*H. The carbonate is more satisfactory in most cases since it serves as an alkali.

The soaps which have given satisfactory films have all been the soaps of bivalent metals. In addition to the soaps of Mg, Ca, Sr, Ba, good films have been built using Zn and Pb. The films of Sr, Zn and Pb have not been measured. Films from solutions containing aluminum chloride have the property that these films will not adhere to a solid either on an ascent or on a descent of the slide. If a slide coated with stearic acid or with the soap of another metal be lowered into a solution containing aluminum chloride in a concentration $^1/_{100,000}$ molar (*p*H 5.4) on which a surface film is spread, no layer adheres on the descent. This property of an aluminum soap is markedly different from the properties of soaps of the alkaline earth metals, which always adhere to a descending slide.

Composite films can be built by depositing one substance on top of another. A palmitate can be deposited on top of a stearate, or *vice versa.* Stearic acid can be deposited on top of barium stearate, etc. Dr. Langmuir has suggested that films could be built for use as diffraction gratings for soft x-rays by depositing $(2n + 1)$ layers of barium stearate, then $2n$ layers of stearic acid, then $2n$ layers of barium stearate, and so on in alternating succession. The stearic acid would be more transparent to radiations of short wave length than the barium stearate and would therefore serve to space the series of layers of barium stearate at known intervals apart.

Summary

Films were built by transferring monomolecular layers from a water surface to a solid at a rate ten to fifteen per minute. The films were made of calcium soaps of palmitic, stearic and arachidic acids. The Mg, Sr, Ba, Pb and Zn soaps and the fatty acids were also used. Two different types of layers of calcium stearate were observed, their occurrence depending on the *p*H and temperature of the water from which the films were transferred.

Films were deposited on glass, chromium, nickel, brass, steel, cast iron, silver and platinum surfaces. They were built in steps having 21, 41, 61, . . ., 201 layers, and in other chosen sequences of odd-numbered layers. These steps showed vivid interference colors when viewed by white light. A single layer could be seen on polished chromium by means of polarized light.

The thickness of step-films was measured by means of the interference of reflected monochromatic light. The refractive index was determined by measuring the polarizing angle by a new and sensitive method. The results gave values of film thickness a little greater than the long spacings of the corresponding fatty acids determined by other workers by means of x-ray diffraction. They were 2 to 4% lower than Piper's measurements of the potassium acid soaps of fatty acids. The melting point of barium stearate films indicated that films taken from water, *p*H 8.5, were probably neutral stearate; from water, *p*H 6.9, acid stearate.

SCHENECTADY, NEW YORK RECEIVED APRIL 1, 1935