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Built-Up Films of Barium Stearate and Their Optical Properties

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The technique of depositing successive single layers of molecules of various stearates on a solid surface is described. Films containing 3001 layers have been built of barium-copper stearate. A photograph shows films built in a series of steps having intervals of 2 molecular layers. The contrast of the steps is plainly visible when the slide is illuminated by polarized light at angles near grazing incidence. By measuring the angles at which films containing known numbers of layers reflect minimum intensity of monochromatic light for the first five interference fringes, the thickness per layer and refractive index can be calculated with great accuracy. The thickness per layer of barium stearate was found to be 24.40A. The presence of traces of foreign substances in the water affect the spacing by 1 to 3 percent. The films are uniaxial crystals, the optic axis being perpendicular to the surface on which the films are built. The refractive index of the ordinary ray, n_1, and of the extraordinary ray in a direction perpendicular to the axis, n_3, are $n_1=1.491$, $n_3=1.551$. Equations are given which describe the refraction of the extraordinary ray, the intensity of the rays reflected from the upper surface and from the film solid boundary, the phase change at the boundaries, Brewster's angle, and other special properties of birefringent films. The intensity of the light and dark fringes reflected by films built on a series of glasses of known refractive indices is used as a measure of n_1. *Skeleton films.* Barium stearate films built at $p\mathrm{H}<7.0$ are composed of a mixture of stearic acid and neutral stearate. The stearic acid can be dissolved by benzene leaving a skeleton of stearate which is birefringent and has refractive indices much lower than those of the normal film. Measurements are given of a skeleton for which $n_1=1.30$, others for which $n_1=1.32$, $n_3=1.39$. Skeletons have been built having $n_1=1.25$ and 1.22. The skeleton for which $n_1=1.30$ had 99.2 percent of the thickness of the original film, although only 63.7 percent of its density.

A METHOD for depositing many successive single layers of molecules on glass or metal has been described in a previous paper.[1] A monolayer of stearic acid was spread on the surface of water containing barium salts, or salts of other bivalent metals, and was transferred to the solid by a process of dipping, the stearic acid film being kept under suitable 2-dimensional pressure.

Stearic acid spreads on a water surface with the carboxyl group of each stearic acid molecule in contact with the water while the hydrocarbon chain is nearly vertical.[2] The monolayer therefore consists of a sheet having carboxyl groups on the under surface and CH_3 groups on the upper surface, the thickness of the sheet being determined by the length of the molecular chain and the tilt of the chain with respect to the surface. In the dipping process the first layer attaches itself by its carboxyl groups to a clean solid surface when the solid is raised out of the water, causing the surface to be dry when it emerges. The second layer attaches itself as the solid is lowered into the water, the third layer as it is raised again, and so on. Thus the dipping process serves to fold the monolayer back and forth on itself so that the molecules in successive layers are oriented in opposite directions.

When the water on which the stearic acid spreads contains barium salts, the barium combines with the carboxyl groups of the molecules forming barium stearate. X-ray diffraction studies[3] of built-up films of this type have confirmed the evidence that the $(-COO)_2Ba$ groups lie in planes having a spacing which is twice the length of the molecular chain.

Three methods have been used for measuring the spacing of the molecular layers. (a) An optical method based upon the interference of light from the upper and lower surfaces of the film. This was described in the previous paper and will be further described in this paper. This method employs films having less than 500 layers, and requires a knowledge of the refractive index of the film. (b) A second optical method which has been used by Professor A. H. Compton and C. Holley to measure films built by Dr. Blodgett. A film containing a known number of layers, in the range 1000 to 3000 layers, was built on an optical

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[1] K. B. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935).
[2] I. Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).
[3] Clark, Sterrett and Leppla, J. Am. Chem. Soc. **57**, 330 (1935); Holley and Bernstein, Phys. Rev. **49**, 403 (1936).

flat adjacent to a film containing 100 layers, and the difference in thickness of the two films was measured with an interferometer. The method is independent of the refractive index of the film. (c) The methods of x-ray diffraction spectra.

Films containing 100 layers may be built of the stearates of Ba, Ca, Mg, Pb, Zn and other metals, or of stearic acid. Barium-copper stearate is the only substance with which it has been possible to build 1000 layers successfully; films have been built containing 3000 layers of this substance. Success in building large numbers of layers depends on properties of the film which are determined by the nature and concentration of salts dissolved in the water, the temperature of the water and the hydrogen ion concentration as determined by *p*H. Formulae of solutions used in film-building are given in a later section. The following properties of films affect the processes of building.

(1) INITIAL LAYER

The problem of depositing the initial layer on a clean metal or glass surface is distinct from the problem of building successive layers. The first problem requires a molecular sheet having an under surface which will adhere well to the solid; the second requires a sheet which adheres to a similar sheet.

In the case of a glass surface the initial layer is deposited more readily from alkaline water, $p\text{H} \geqq 8.5$ than from acid or neutral water. In the case of metal the best initial layers are usually obtained at $p\text{H}=6$ to 7.5. The glasses of high refractive index which we have used take up initial layers at $p\text{H}=7.0$ far more readily than ordinary glass (microscope slides).

In many experiments it is not essential that the initial layer be of the same material as succeeding layers, and in these cases the following method has proved very useful. The solid surface is coated with molten paraffin wax, or preferably with molten ferric stearate, and is rubbed vigorously with a cloth until every visible trace of the coating has disappeared. This treatment leaves the slide covered with a monomolecular layer of wax to which layers of barium stearate will attach themselves in the same way as to an initial layer of stearate. Built-up films of barium stearate can also be rubbed down and provide a very good foundation on which new films can be built.

When the experiments require that the initial layer be built in the same manner as the rest of the layers, the glass or metal can be cleaned by using the metallographic polish Shamva. The surface is scoured with Shamva, rinsed and swabbed under running water, and plunged wet into the water bath used for film building. Glass can also be cleaned with a hot concentrated solution of $K_2Cr_2O_7$ and H_2SO_4, but the acid is apt to attack glass of high refractive index, and affects the surface of certain kinds of glass microscope slides in such a way that a layer will not adhere to the glass. Metal can be cleaned by being made cathode in an electrolytic bath of caustic soda, water and alcohol, but the treatment usually etches the metal slightly.

When an initial layer of wax or other substance is used to coat the slide this is called a "1st layer," meaning that the barium stearate which attaches itself to the wax has the molecular orientation characteristic of the 2nd layer of barium stearate built on a clean surface. Only layers of odd number exist out of water, layers of even number exist under water. The numbers 100, 200, etc. which are given in the text are round numbers.

(2) SPEED

After an odd number of layers have been deposited, the surface consists of close packed CH_3 groups and so sheds water. When this slide is dipped into water covered by a barium stearate monolayer under pressure the next layer is transferred to the slide even if the slide is lowered very rapidly. To form the next odd layer by withdrawing the slide it is important not to raise the slide faster than the rate at which the water peels back from the slide. This peeling back is not caused by gravity but by a strong adhesion (between the hydrophilic sides of the two outer layers) which acts along the line of contact and so drives out the water film. When the slide is slowly withdrawn a large contact angle is observed between the water surface and the slide. The rate at which films can be built is thus limited by the rate at which the ascending slide sheds water, and the term "speed" refers to this limiting rate, not to the actual rate of building. A "fast film" is one which can be built in successive layers at a rate 20 or more layers per minute.

Speed is commonly the greatest for the first layers which are deposited, and gradually slackens as more layers are added. Films of magnesium stearate begin to lose speed after about 50 layers have been deposited and at about 200 layers the process is virtually brought to a halt; films of barium-copper-stearate retain their initial speed up to more than 1000 layers. Loss of speed is due to disorder in the molecular orientation of successive layers. Several different causes may contribute to produce a disordered arrangement, the chief cause being severe mechanical strains to which the films are subjected during the building process which many types of film are unable to withstand without sustaining injury. Traces of some impurities in the water may also greatly affect the speed.

(3) MECHANICAL PROPERTIES

A monolayer of a stearate on a water surface may be liquid or solid. Most of the factors which determine the state originate in the water on which the film lies. Langmuir and Schaefer[4] have shown that when the water contains barium carbonate in a concentration 10^{-4} molar, and the pH is adjusted by adding either ammonium hydroxide or hydrochloric acid, 21 percent of the stearic acid is converted to barium stearate at $p\text{H}=5.0$, 88 percent at $p\text{H}=9.0$. For purposes of film building a barium stearate film built with a solution 3×10^{-5} M barium carbonate at $p\text{H}\eqsim 6.5$ is slow, and becomes progressively slower at 20°C; the initial speed is maintained for a much greater number of layers at 15°C than at 20°C. A barium stearate film at $p\text{H}=7.0$ is fast. These results show that an increase in rigidity of structure obtained by lowering the temperature or increasing the pH results in a more ordered arrangement of the CH_3 groups in the successive layers laid down on the solid.

Barium stearate films are faster at $p\text{H}=7.5$ than at $p\text{H}=7.0$, but the greater rigidity at $p\text{H}=7.5$ is not desirable. Very rigid films give unsatisfactory results for the following reason. A slide commonly picks up many specks of dust or tiny crystals of stearic acid, and the manner in which succeeding layers are affected by these specks is very important. The trough used in the present experiments was covered by glass as a necessary protection from dust falling from the air upon the water surface; extreme precautions to obtain dust-free air were not attempted. After a particle of dust has attached itself to a slide, a series of layers of a tough viscous film will coat the particle so successfully that after four or six layers have been added the particle sheds water as readily as does the rest of the slide. This occurs although a particle 0.2 mm in thickness has 80,000 times the thickness of a monolayer. A weak film coats the particle so unsuccessfully that a small mound of soft barium stearate soon piles up on the particle and serves as a center from which disorder in successive layers spreads out over the slide, and water recedes more and more slowly from that area. Layers of rigid film tend to be broken by a projecting particle so that hundreds of minute bits of broken film collect around the particle, and although these areas shed water rapidly they spoil the uniformity of the film. Observation of the water meniscus, as water is shed by an ascending slide, shows that the meniscus travels over dust particles with a "chattering" motion in the case of a rigid film, a lagging motion in the case of a weak film.

Monolayers can be formed on a water surface which are so rigid that they cannot be used to build films. When a slide is raised and lowered through a surface of this type the layer of stearate does not attach itself to the slide, i.e., the layer "slips" instead of adhering at the boundary edge where the layer meets the slide. In many cases of slipping a few initial layers can be built up, then subsequent layers fail to adhere to the slide and the slipping of these layers is recognized by a characteristic very noticeable chattering motion of the water meniscus. In other cases no initial layers adhere. Films having this great rigidity are obtained with barium solutions at $p\text{H}=7.0$ which contain copper salts in a concentration 10^{-5} M, or aluminum salts in a concentration 10^{-6} M.

(4) FOGGING

After a number of layers have been built the film begins to have a fogged appearance. This occurs at 50 to 500 layers, depending on the type

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[4] I. Langmuir and V. J. Schaefer, J. Am. Chem. Soc. **58**, 284 (1936).

of stearate which is used. Examination under a microscope shows that a myriad of tiny specks of approximately uniform size are built into the film. Nearly always the number per unit area is uniformly graded from top to bottom of the slide (the slide is held in a vertical position during dipping), and is greatest at the bottom of the slide. As more layers are deposited the specks increase in size and density until they cause the water to recede so slowly that the progress of film building is halted. The only substance which thus far has successfully prevented fogging is copper, a copper salt being added in a concentration 2 to 3×10^{-6} M to water containing barium salts.

(5) CRACKING

A film of barium stearate built at pH = 7.0 and having a large number of layers invariably cracks in hundreds of fine lines. The tendency to crack increases with increasing thickness, cracking usually commencing at 300–500 layers. Films built on chromium crack more readily than films built on glass. At lower values of pH a greater number of layers can be deposited before the film commences to crack. Usually a cracked film curls upward slightly along the edges of the cracks. Water often works its way under a cracked film and loosens the film from the slide. Copper dissolved in the water is the only substance which has been found which will prevent cracking.

Good films can be built with the following two solutions:

Solution (a)
0.3×10^{-4} M $BaCl_2$ (or other soluble barium salt)
4.0×10^{-4} M $KHCO_3$
pH = 7.0 to 7.2. Temp $\leqq$ 22°C.

The water used in making the solution should be conductivity water having a specific resistance of 700,000 to 1,000,000 ohms-cm. If a brass or aluminum trough is used it should be lined with paraffin wax, and the floor of the trough should be covered with glass. Many solutions dissolve sufficient copper from a brass trough to affect the experimental results to a marked degree when the brass is coated with paraffin but is not covered with glass.

Films built with solution (a) are fast, reliable, and easily built. The solution is recommended for building films having less than 200 layers. A larger number of layers will become fogged or cracked, even 100 layers sometimes crack.

Solution (b)
0.3×10^{-4} M $BaCl_2$
2.0×10^{-4} M $KHCO_3$
0.02×10^{-4} M $CuCl_2$ (or other soluble copper salt)
pH = 6.8, temp < 22°C (temp < 20°C preferred).

The stearate should be left on the water surface for 5 min. before it is used for building, to allow time for copper to diffuse to the surface. Films built with solution (b) do not fog or crack at 1000 layers and can be built with fair success to 3000 layers. At thicknesses of 500 or more layers they have a faint green color, showing that the film contains copper stearate.

The problem of holding the copper concentration constant will be apparent from the following considerations. The trough used in the experiments contained 5000 cc of water and the area of water covered by a surface film was 3300 cm^2. Therefore the number of copper ions in the water, in a concentration 2×10^{-6} M was 7.36 times the number of pairs of stearate molecules on the surface, the molecules having an area per molecule 20×10^{-16} cm^2. The built-up films were not analyzed for copper content, but the results of analyses of similar films make it appear probable that not more than 25–50 percent of the stearic acid placed on the water surface was converted to copper stearate. Therefore each time a film was spread the concentration of copper ions in the water was reduced by 3 to 6 percent of the initial concentration.

In some experiments copper was introduced by covering the bottom of the trough with a clean sheet of copper. Under these conditions the rate at which copper was removed from the bath by surface films when new films were spread every 20 minutes was balanced fairly satisfactorily by the rate at which copper went into solution. Whenever the sheet was left in the trough for more than about 10 hrs. and no copper was removed, the resulting concentration of copper was much too high. It was pointed out in Section (2) that a concentration of copper 10^{-5} M causes films to slip completely; they frequently slip at 5×10^{-6} M.

Good results were obtained for 1000-layer films by scattering 100 small lumps of copper sulfide in the bottom of the trough. The copper sulfide contained 70.3 percent of copper. This method gave a concentration of copper which was never too high, even after standing in a solution for two weeks. The concentration was a little lower than was needed to build 3000 layers.

The amount of copper in water can be roughly estimated if one spreads a surface film on the water, then shoves all the film to one end of the trough, where it can be easily skimmed off the surface and dried on a porcelain slab in an oven at 95°–100°C. The green color of the film can be compared with the color of films skimmed from baths containing known concentrations of a copper salt. The film should be left on the water for at least 5 min. before it is skimmed. The method readily shows the presence of 10^{-6} M copper and can show less than this amount.

OPTICAL PROPERTIES OF FILMS

Built-up films of barium stearate are uniaxial crystals. The optic axis of the film is perpendicular to the surface on which the film is built. The birefringence is readily demonstrated by placing a 1000-layer film, built on glass, between crossed Nicol prisms or crossed Polaroid screens, the film being placed at azimuthal angle 45°. The film restores the light when the angle of incidence i of the light on the film is large; at $i=0$ it restores no light. The intensity of the restored light increases with increasing angle i.

Dr. L. Navias has investigated for us the birefringence of a 1000-layer film of barium stearate, employing a I red gypsum plate in the usual way and found that the film behaves as a positive uniaxial crystal.

REFRACTIVE INDEX

The previous paper described a method of determining the refractive index n of the films[5] by measuring Brewster's angle i_B for monochromatic light reflected from films of Ba stearate, Ca stearate, and stearic acid. Values of n were given which were derived from the relationship

$$n=\tan i_B. \qquad (1)$$

For barium stearate films the refractive index was found to be $n=1.462$. This method was employed before the experiments were made which showed that the films were birefringent and that the ray used to measure i_B was the extraordinary ray for which Eq. (1) is not applicable. The film thickness measurements of the previous paper were made by optical methods which employed the ordinary ray. These should be corrected by using the proper refractive index for the ordinary ray.

In any uniaxial crystal two of the three principal refractive indices, n_1, n_2 and n_3 are equal, so we may put $n_2=n_1$. Since the film is a positive uniaxial crystal, n_3 must be greater than n_1. For rays parallel to the optic axis the crystal behaves as an isotropic medium of refractive index n_1.

Since the barium stearate film lies in a plane perpendicular to the optic axis, the plane of incidence of oblique rays is parallel to the optic axis. The plane of the electric vector of the ordinary ray R_s is perpendicular to the plane of incidence while that of the extraordinary ray R_p is parallel to the axis. For ordinary rays at any angle the film behaves as an isotropic body having the refractive index n_1, but for extraordinary rays the refractive index, n, varies with the angle of refraction r, according to the equation

$$1/n^2=\cos^2 r/(n_1)^2+\sin^2 r/(n_3)^2. \qquad (2)$$

According to the Fresnel theory, the amplitude of the light reflected at normal incidence from an interface between two isotropic media of refractive indices n_a and n_b is given by

$$\rho=(n_a-n_b)/(n_a+n_b), \qquad (3)$$

the amplitude of the incident light being unity. If ρ is negative; i.e., when $n_b>n_a$, the phase of the light waves is reversed by reflection, but it is not reversed if ρ is positive.

Let us consider the interference of light reflected from the top and bottom surfaces of a film (on glass) consisting of N monolayers each of which has a thickness t. Let λ be the wave-length of the light, r the angle of refraction corresponding to the wave normal of the light (direction of ray in case of ordinary ray) and n be the refractive index for these waves. Interference occurs as a result of a phase difference between the ray which is reflected from the upper surface, and the

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[5] The symbol n for refractive index is used in the present paper in place of μ in the previous paper.

ray which travels from the upper to the lower surface and is reflected at the lower surface and travels back to the upper surface. The condition that the two rays shall differ in phase by an integral multiple of 180° is given by

$$nNt \cos r = m\lambda/4 \tag{4}$$

where m is an integer.

Since the refractive index of the film is greater than that of air the light reflected from the upper surface of the film always suffers a phase reversal. If the light reflected from the interface between the film and the glass also undergoes a phase reversal, the interference fringes produced by the film have minimum intensity for odd values of m, maximum intensity for even values of m. If, however, the light reflected from the lower surface is not reversed in phase the intensity minima correspond to even values of m.[6]

If films are built on glass in a series of steps having thicknesses equal to $m\lambda/4n$, where m represents successive integers, they will give at normal incidence a series of interference fringes of maximum contrast. These may be classified as belonging to series A or B defined by Table I.

Series A occurs when there is a phase reversal in the reflection of light at the interface, while for series B there is no reversal. For light at normal incidence this means that if the fringes correspond to series A the refractive index of the film must be less than that of the glass.

Let B be the value of ρ as given for example by Eq. (3), for the light reflected from the upper surface of the film, and let C be the value of ρ for the reflection from the interface. Let us now consider films forming steps whose thicknesses have been chosen by Eq. (4) to give a series of fringes of maximum contrast. The theory of interference, allowing for multiple reflections within the film, then gives for the amplitude ρ_M of the total light reflected from the film

$$\rho_M = (B \pm C)/(1 \pm BC). \tag{5}$$

The two extreme values of ρ_M are thus found by taking the + and the − signs in Eq. (5).

If we calculate the values of B and C by Eq. (3) and introduce them into Eq. (5), taking the positive sign in the numerator and denominator, we find

$$\rho_+ = (n_0 - n_g)/(n_0 + n_g) \tag{6}$$

where n_g and n_0 refer to the glass and to air. With the negative sign we get

$$\rho_- = (n_0 n_g - n_1^2)/(n_0 n_g + n_1^2). \tag{7}$$

The contrast between the steps of maximum and minimum brightness may be conveniently measured in terms of a quantity K, defined by

$$K = (\rho_+^2 - \rho_-^2)/(\rho_+^2 + \rho_-^2). \tag{8}$$

The ratio of the intensities I_+ and I_- of the light from the successive steps is thus

$$I_+/I_- = (1+K)/(1-K). \tag{9}$$

Let us put

$$n_1 = n_g - \Delta n. \tag{10}$$

Then if Δn is so small that we can neglect terms of higher order than the first we find by combining Eqs. (6), (7), (8) and (10) that

$$K = 4n_0 \Delta n/(n_g^2 - n_0^2). \tag{11}$$

The refractive index n_1 of the film was determined by the relative intensities of the interference fringes produced on glasses having nearly the same refractive index as the film. All observations were made with the light from a 6000-lumen sodium vapor lamp ($\lambda = 5893$A). Preliminary experiments had shown that 162 layers of barium stearate had a thickness equal to λ/n. Therefore a series of steps having 41, 81, 121 and 161 layers were built on three types of glass. Glass (1) (fused quartz) had a refractive index[7] 1.459 and glass (2) and glass (3), according to the manufacturer (Jena Glassworks, Schott and Gen. Jena), had indices of 1.4937 and 1.7854. To prevent reflection from the back of the glass the back was coated with black paint.

The films built on glass (2) when viewed by light at normal incidence were found to belong

TABLE I. *Sequence of interference fringes. Step films of thicknesses* $= m\lambda/4n$; $\lambda = 5893A$.

$m=$	1	2	3	4
$N=$	41	81	121	161 layers
Series A ($n_g > n_1$)	dark	bright	dark	bright
Series B ($n_g < n_1$)	bright	dark	bright	dark

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[6] R. W. Wood, *Physical Optics*, second edition, p. 155.

[7] *International Critical Tables*, Vol. 6, p. 342.

TABLE II. *Effect of underlying glass on interference fringes seen with the extraordinary ray R_p at various angles of incidence i. Measured for films of barium stearate built by using solution* (*a*).

i	(1) Series seen on glass (1) $n_g=1.459$	(2) Series seen on glass (2) $n_g=1.4937$	(3) Series seen on glass (3) $n_g=1.7854$	Contrast of bright and dark fringes (1), (2) and (3) refer to the 3 glasses
0	*B*	*A*	*A*	(1) Moderately strong contrast (2) Barely visible contrast (3) Strong contrast
45°±3	*B*	*A*	*A*	(1) Less than at $i=0$ (2) Greater “ “ “ “ (1) and (2) about equal
53° 20′	*B*	*A*	*A*	(1) Barely visible
55° 20′±1	—	—	—	Brewster's Angle ob-observed best with (3). No fringes with any glass
56° 50′	*B*	*B*	*B*	(1) Just begin to be visible
70°	*B*	*B*	*B*	(2) Greater than (1)

to series A, the contrast between the bright and dark fringes being 1.5 to 2 percent. The films built on glass (1) belonged to series B and at normal incidence much more contrast was seen than with glass (2). The refractive index n_1 of the film is therefore slightly lower than that of glass (2). Taking $K=0.0090$ corresponding to 1.8 percent contrast, we then find from Eq. (11) that $\Delta n=0.0028$ and the refractive index of the film for rays at normal incidence is thus

$$n_1=1.491. \tag{12}$$

For the films on glass (1) we should then have $\Delta n=-0.032$ and by Eq. (11) $K=-0.113$. The ratio of intensities of the bright and dark fringes should thus be 1.26 in agreement with a rough estimate of intensity.

Experiments with barium stearate films on glasses (1) and (2) using the ordinary ray at all angles of incidence gave fringes that indicated that n was constant and equal to n_1 in agreement with theory. Thus with glass (2) the faint fringes at all angles i belonged to series A while with glass (1) the fringes were of much greater contrast and belonged to series B.

With the extraordinary ray, however, very different results were obtained as shown in Table II.

The intensity of the light reflected from the upper surface of the film passes through zero and reverses in phase when i increases through Brewster's angle 55° 20′. The sequence of fringes should thus change from the A to B series (or *vice versa*) as i increases through Brewster's angle. The observations with glasses (2) and (3) are in accord with this theory. With glass (1), however, series B was obtained both at high and low angles. This must mean that at some angle of incidence between the limits of 53° 20′ and 56° 50′ the reflection from the interface between the film and glass (1) falls to zero and reverses in phase.

Analogy with the behavior of isotropic substances suggests that the disappearance of reflection from the interface on glass (1) should occur at an angle at which the refractive index n falls below 1.459. When this value of n is compared with the value $n_1=1.491$ it would indicate that the film is a crystal of negative character (a crystal is negative when $n<n_1$) whereas the direct optical tests have shown that it is positive. In a later section we shall show that these data are not inconsistent with values of n and n_3 which are greater than n_1.

Brewster's angle i_B was measured by a method which was described in a previous paper,[1] p. 1016. The films used for the measurements were built on glass (3) in steps which had maximum contrast at the angle i_B. These steps were 47, 95, 143 layers for films of barium stearate. At angles $i<i_B$ these steps form an A series for both R_p and R_s, at angles $i>i_B$ they form a B series for R_p (Table II) and an A series for R_s. The angle i_B at which the contrast between two neighboring steps reverses in intensity when the steps reflect the ray R_p of monochromatic light can be very accurately measured. It is essential that the Nicol prism which is used to furnish R_p should be turned so as to extinguish R_s completely, for if only a very small component of R_s be transmitted the angle at which the contrast reverses is greater than Brewster's angle. Under these conditions the contrast does not reverse until i increases to a value at which the B contrast supplied by R_p becomes greater than the A contrast supplied by the small component of R_s. The correct setting of the Nicol prism is found by determining the minimum angle at which the contrast reverses, this angle being i_B. The values $i_B=55°\,35'$ and $55°\,40'$ given in the previous paper were determined before the need for extinguishing R_s was fully appreciated. Recent measurements have given the result $i_B=55°\,20'\pm 1'$.

MEASUREMENTS OF THE SPACING t OF MOLECULAR LAYERS ON CHROMIUM

By determining the values of N which correspond to the interference minima in light reflected from the film, it should be possible by Eq. (4) to calculate nt/λ and then from the known values of n and λ to obtain t.

Eq. (4), however, is based on the simple Fresnel theory according to which the reflection from a surface produces a phase change of 0° or 180°. The observed slight elliptic polarization of light reflected from transparent media and the much stronger elliptic polarization from metals shows that in general the phase change is not exactly 0° or 180°. This effect can be taken into account by making the following modification of Eq. (4).

$$N(n/n_1)\cos r-N_0=m\lambda/4n_1t, \tag{13}$$

where N_0 in general varies with r and is different for the ordinary and the extraordinary ray but otherwise does not depend upon m.

It will be convenient to represent the first term of this equation by a special symbol which may be defined by

$$N_N=N(n/n_1)\cos r. \tag{14}$$

This is the value that N would have for normal incidence ($\cos r=1$ and $n=n_1$) on the assumption that N_0 does not change with i. If it is found that N_0 does vary with i no error, however, will be introduced into our calculations; it merely changes our interpretation of the physical meaning of N_N. Eq. (13) thus becomes

$$N_N-N_0=m\lambda/4n_1t. \tag{15}$$

The uncertainties in the value of N_0 may be eliminated by determining N for the successive minima which correspond to a series of odd or of even values of m. If the measurements of the successive minima are made at approximately the same angles of incidence the values of N_0 are the same for the various minima and thus by Eq. (15) the increment in N_N in passing from any minimum to the next should be

$$\Delta N_N=\lambda/2n_1t. \tag{16}$$

Since the thickness which a film must have in order to reflect minimum intensity of light depends on the angle i, values of N corresponding to various values of i were determined by the following method.

A slide was prepared with an initial series of several steps, a, b, c, $\cdots$, having 1, 3, 5 $\cdots$ layers or any other chosen sequence; the process of building films requires that the films contain an odd number of layers. With such thin films no interference colors are seen. Additional layers were then applied to the whole of the slide covered by the initial layer until colors began to appear.

Let N_a, N_b, etc. represent the number of layers on the a, b, c steps at any stage of this process. When the number of layers is sufficiently increased, if the film is viewed by an ordinary ray using light from a sodium lamp a minimum appears at one of the steps at small angles of incidence. Further increases in layers permit this minimum to be observed at larger angles. On chromium the minima become sufficiently sharp for useful measurements only when i is greater than 68° while on glass of high refractive index much smaller angles can be used.

The angle of incidence is measured at which two adjacent steps, say a and b, are equally bright. The value of N which corresponds to the minimum is then halfway between N_a and N_b. The first line in Table III gives data for the first minimum obtained with films on chromium using the ordinary ray. The minimum is given as occurring at $N=48$ when $i=79°\,7'$. This means that two adjacent steps $N=47$ and 49 were found to match in intensity when viewed at that angle.

Additional layers were then applied until a minimum corresponding to $m=2$ was observed with the extraordinary ray at a suitable angle of incidence. The data for this ray are given in the first three columns of Table IV. In this way by building N up to 518 all the minima up to $m=10$ were studied. Only one pair of steps, a and b, were used for every determination of N given in Tables III and IV. By this procedure all the data in these tables referred to films built up from the same film chromium boundary. It was found useful to have steps c, d, e, on the same slide having 2, 4, 6 more layers than b, because as progressive layers were applied to the entire slide the approaching minimum appeared first at the higher steps, and its position showed the precise number of layers which must then be added to the slide in order that the minimum should occur between *a* and *b*.

The procedure for measuring *i* consisted in mounting the slide on a spectrometer table with the film boundary between *a* and *b* situated in the axis of the table. The process of matching two steps was similar to the photometric matching of two fields of illumination. At angles greater than *i*, *a* was brighter than *b*, at angles less than *i* the contrast was reversed. There was no difficulty in measuring *i* with an accuracy which determined the thicknesses corresponding to successive light minima with a probable error of 0.1 molecular layer. With the ordinary ray satisfactory measurements could be made between 68 and 85°, but with the extraordinary ray because of the lower intensity and contrast the range was only from 77° to 85°.

Experiments were also carried out with films built on glass of very high refractive index, $n_g = 1.78$. Steps built on this glass showed great contrast when viewed by perpendicular light, the contrast diminishing with increasing *i*. The intensity of successive maxima and minima varied with the film thickness in accordance with a cosine curve.

TABLE III. *Intensity minima with ordinary ray, R_s of wave-length $\lambda = 5893A$ at various angles of incidence i. Film of barium stearate $pH = 7.0$; $\Delta N_N = 81.00$; $N_0 = -4.30$; $n_1 = 1.491$.*

m	N	i	$\cos r$	N_N obs.	N_N calc.
1	48	79° 7′	0.7525	36.13	36.20
3	150	68° 48′	.7804	117.06	117.21
	152	71 35	.7714	117.25	
	154	74 59	.7618	117.32	
	156	79 12	.7523	117.36	
5	254	68° 50′	.7803	198.20	198.21
	258	72 50	.7676	198.04	
	262	77 29	.7559	198.05	
	266	84 17	.7448	198.12	
7	356	67° 42′	.7842	279.18	279.21
	362	71 39	.7712	279.17	
	368	76 8	.7589	279.28	
	374	82 37	.7467	279.27	
9	460	67° 59′	.7831	360.23	360.22
	468	71 59	.7702	360.45	
	476	77 0	.7569	360.28	
	484	84 32	.7444	360.29	

In the case of films built on chromium the intensity distribution curve had very sharp minima, when the films were viewed at $i = 75° - 85°$, due to multiple reflections of light in the film. Fig. 1 is a photograph of a chromium slide 1×3 inches in size, on which 15 steps were built having 35, 37, 39, $\cdots$ 63 layers. The photograph was made by Mr. V. J. Schaefer using the ordinary ray R_s of sodium light. The upper photograph shows the appearance of the steps at an angle $i = 82°$. The intensity minimum which lay at $N = 49$ was sharply differentiated from the neighboring steps $N = 47$ and 51. The rest of the steps were all bright and had too little contrast to be visible in the photograph, most of them were not visible to the eye. In the lower photograph the same slide is shown illuminated at an angle $i = 75°$. The minimum then lay between $N = 47$ and $N = 49$ and was not so sharply defined. At $i = 80°$ there were 108 layers between successive minima, so that the series seen in the photograph would need to be extended for 54 steps before it would reach the next minimum. Therefore even in the lower photograph the minimum lay in a fairly narrow region, since the drop in intensity occurred in about 8 steps on either side of the minimum.

The data of Tables III and IV were obtained with barium stearate films on a slide of highly polished chromium plated brass which had

TABLE IV. *Intensity minima with extraordinary ray, R_p of wave-length $\lambda = 5893A$ at various angles of incidence i. Same film as Table III. $\Delta N_N = 81.00$; $N_0 = -7.01$ (at $i = 80°$); $n_1 = 1.491$; $n_3 = 1.551$.*

m	N	i	N_N obs.	N_N calc.
2	96	82° 54′	73.78	73.90
4	200	78° 12′	155.14	155.04
	202	83 49	155.05	154.90
6	304	77° 58′	235.94	236.05
	306	81 11	235.85	235.95
8	408	77° 28′	317.06	317.07
	410	79 41	316.96	317.00
	412	82 23	316.89	316.93
10	512	77° 8′	398.22	398.08
	514	78 56	398.02	398.02
	516	80 51	397.96	397.96
	518	83 16	397.89	397.88

previously been ground to a plane surface. The chromium was cleaned by being made cathode in an electrolytic bath of NaOH, water and alcohol. The initial steps transferred to the plate had a 2-layer step rise similar to the steps of Fig. 1.

The stearic acid films were spread upon doubly distilled water of specific resistance greater than 10^6 ohms-cm, the second distillation having been made in Pyrex glass. Barium bicarbonate was added to this water in a concentration 5×10^{-5} M. The barium bicarbonate was prepared in more concentrated solution by dissolving 0.3 g $BaCO_3$ in 1000 cc of water saturated with CO_2 at a pressure of 1 atmosphere. After a suitable amount of the barium bicarbonate solution was added to the water bath, air was bubbled through the bath to remove excess CO_2 and bring the *p*H to the value 6.7 which corresponded to equilibrium with the CO_2 contained in ordinary air. Measurements of *p*H were made by using La Motte standard indicators. The data of Tables III and IV were taken prior to the use of the solutions (a) and (b) recommended in this paper. The barium bicarbonate solution gave the same type of film as solution (a) but was more troublesome to prepare. The stearic acid which was used in all the measurements described in this paper was prepared by Dr. R. E. Burnett. Tests showed that this stearic acid had a very high degree of purity. The test for purity was described in a previous paper,[1] p. 1010.

MEASUREMENTS WITH ORDINARY RAY R_s

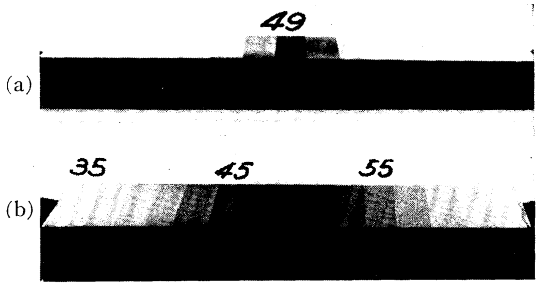
In Table III the values of cos r in column 4 were calculated from i by means of the equation

$$\sin i = n \sin r, \tag{17}$$

placing $n=n_1=1.491$, as given by Eq. (12). The value of N_N in the 5th column is the product N cos r in accord with Eq. (14).

It is seen that for any value of m, N_N is constant. This proves by Eq. (13) that within the range from $i=67$ to 85° (or r from 38 to 42°) there is no appreciable variation in N_0. The values of N_N are found to vary linearly with m, as they should by Eq. (13) and are accurately represented by the equation

$$\text{For } R_s\text{: } N_N = 40.502m - 4.30. \tag{18}$$



(a) $i=82°$. (b) $i=75°$.

FIG. 1. Interference fringe seen with 15 steps having 35, 37, . . . 63 layers of barium stearate built on polished chromium. Photographed with R_s ray of light $\lambda=5893$A.

The values of N_N in the last column of Table III have been calculated by this equation. A comparison of the observed values with the calculated (columns 5 and 6) shows that the probable error of the individual values of N_N is about ±0.07 layer. A comparison of Eqs. (18) and (13) gives

$$\text{For } R_s \text{ at } r=40°\text{: } N_0 = -4.30. \tag{19}$$

By Eqs. (12), (13), (16) and (18) we find taking $\lambda=5893$A.

$$\Delta N_N = 81.00 \text{ and } t=\lambda/2n_1\Delta N_N = 24.40\text{A}. \tag{20}$$

MEASUREMENTS WITH EXTRAORDINARY RAY R_p

For R_p, n is a function of r according to Eq. (2). Since r is not directly observed it is convenient to eliminate r from this equation by using Eq. (17) and so obtain

$$(n/n_1)^2 = 1 + (1/n_1^2 - 1/n_3^2)\sin^2 i. \tag{21}$$

Similarly r can be eliminated from Eq. (14) and then n can be eliminated by Eq. (21), so that

$$N_N^2 = N^2(1-\sin^2 i/n_3^2). \tag{22}$$

To calculate N_N from the data in columns 2 and 3 of Table IV we need to know n_3. To determine n_3 we make use of the fact that ΔN_N according to Eq. (16) must be the same whether R_s or R_p is used. Let ΔN_s and ΔN_p represent the increments in N between successive minima ($\Delta m=2$) which correspond to a particular value i (say i_M) for R_s and R_p, respectively. By interpolation in Tables III and IV for each value of m we obtain the value of N that corresponds to

$i_M=80°$ and by finding the successive intervals for $\Delta m=2$ we obtain:

$$\text{at } i_M=80° \quad \Delta N_s=107.89\pm0.05;\quad \Delta N_p=104.85\pm0.05.$$

From Eq. (22) we obtain

$$(\Delta N_N)^2=(\Delta N_s)^2[1-(\sin^2 i_M)/n_1^2] = (\Delta N_p)^2[1-(\sin^2 i_M)/n_3^2]. \quad (23)$$

Introducing the values of ΔN_s, ΔN_p and $i_M=80$ we find

$$n_3^2=n_1^2/(1.0589-0.06073n_1^2). \quad (24)$$

If we take $n_1=1.491$ as in Table III we thus obtain

$$n_3=1.551\pm0.002. \quad (25)$$

The values of N_N obtained by Eq. (22) are given in column 4 of Table IV. There is a slight decrease in N_N as i increases. The values of N_N (calc.) in the last column were calculated by the empirical equation

$$\text{For } R_p\text{: } N_N=40.50m-7.01-0.03(i°-80), \quad (26)$$

where $i°$ is i expressed in degrees. The differences between the observed and calculated values of N_N correspond to a probable error of ±0.06 layer. The coefficient of m agrees with that of Eq. (18) because n_3 was chosen to make it do so. The other terms indicate that

$$\text{For } R_p \text{ at } i=80°\text{: } N_0=-7.01 \text{ layers.} \quad (27)$$

The difference between N_0 given by Eqs. (19) and (27) is associated with the marked elliptic polarization of the light reflected from films on chromium.

BIREFRINGENCE MEASURED WITH OPTICAL COMPENSATOR

The birefringence of films of barium stearate having a total thickness of 5752 layers built on glass (made by placing two slides face to face, coated with 2751 and 3001 layers) was studied with the aid of a quartz wedge compensator. The relative phase retardation of the two rays transmitted by the film was found to be 180° at $i=56°$ for sodium light.

The retardation in path of the extraordinary ray R_p with respect to the ordinary ray R_s was

$$\Delta l=5752t[(n/\cos r_p-n_1/\cos r_s) +(\tan r_s-\tan r_p)\sin i] \quad (28)$$
$$=2947\text{A}.$$

The terms in the first pair of brackets give the difference in optical path of the two rays in the film, and the terms in the second brackets the path difference in air after the rays leave the film. Values of n were calculated by means of Eq. (21) using $n_1=1.491$ from Eq. (12) and a series of values of n_3. Then r_s and $\cos r_p$ were calculated from n_1 and n and the value $i=56°$ by Eq. (17), and $t=24.40$A was substituted from Eq. (20). It was found that if n_3 was assumed to be greater than n_1 in accordance with the results given in the preceding section, the value which satisfied Eq. (28) was $n_3=1.5514$. This is in close agreement with the value obtained in Eq. (25).

OPTICAL PROPERTIES OF CHROMIUM

Chromium has advantages as a surface on which to build films not only because it is non-tarnishable but also particularly because it has a low reflectivity and so gives strong interference fringes. We see by Eq. (5) that a perfectly reflecting metal ($C=1$) would give no fringes. With silver the fringes are very faint except at nearly grazing incidence.

The reflection coefficients ρ_s and ρ_p for the rays R_s and R_p and the corresponding phase changes δ_s and δ_p can be calculated by the electromagnetic theory from the index of refraction n_m and the index of absorption k of the metal.

The dashed line curves given in Fig. 2 for bare chromium have been calculated using[8]

$$n_m=3.59;\quad k=1.26 \text{ for } \lambda=5893\text{A}$$

by the complicated equations given in convenient form by W. König.[9]

The full line curves have been calculated for the interface between chromium and an isotropic medium of refractive index $n_1=1.491$ and therefore should give accurate values of C_s and approximate values of C_p for the interface

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[8] *International Critical Tables*, Vol. 5 (1929), p. 249. The equations for calculating ρ_s, ρ_p and Δ are also given.

[9] W. König, *Handbuch der Physik*, Vol. 20 (Julius Springer, 1928), p. 242.

between the chromium and the barium stearate films. These calculations gave the quantities δ_s and δ_p in terms of the angle of refraction r, but the data given in Fig. 2 have been expressed in terms of i, the angle of incidence in the air above the film. Thus with $i=90°$, $r=42°$ and the large changes in ρ_p and δ_p observed with bare chromium do not occur when the chromium is covered by the film.

The phase changes δ_s and δ_p are related to the quantities N_0 which we have found in our studies of films. Some part of N_0 may have its origin in a phase change at the upper surface of the film, but the extreme smallness of the elliptic polarization produced by reflection from transparent bodies would indicate that the larger part of N_0 should be due to the interface between the film and the metal. The addition of ΔN_s or ΔN_p layers, as given by Eq. (23) causes a phase retardation of 360° in the ray that traverses the film (down and back). Thus by proportion we find that

$$\text{For } R_s\text{:}\quad N_0=(\delta_s/360°)\Delta N_N/\cos r; \tag{29}$$
$$\text{For } R_p\text{:}\quad N_0^2=(\delta_p/360°)^2(\Delta N_N)^2/(1-\sin^2 i/n_3^2).$$

The values of N_0 have been calculated by these equations from the corresponding values of δ_s and δ_p in Fig. 2, using ΔN_N as given in Eq. (20). The results are shown in the two curves $(N_0)_s$ and $(N_0)_p$ in Fig. 3.

It is seen that $(N_0)_s$ is independent of i in agreement with the constancy of the calculated values of N_N in Table III for each value of m. The absolute value of $(N_0)_s$ is -5.28 which differs by one unit from the value -4.30 given in Eq. (18).

With the R_p ray, $-(N_0)_p$ increases with i and at $i=80°$ the rate of increase is 0.041 per degree, in reasonable agreement with the value 0.03 given by Eq. (26) as found from the variation of N_N with i in Table IV. The absolute value of $(N_0)_p$ at 80° in Fig. 3 is -9.10 which differs by 2 units from -7.01 given by Eq. (27).

In view of the fact that the values of n_m and k given for chromium in the I. C. T. are based on measurements of 1910, prior to the time that chromium plated surfaces were available, we should probably not expect better agreement. Perhaps the neglect of the anisotropic nature of the film for the R_p ray in the calculation of δ_p may account for the greater discrepancy in $(N_0)_p$.

The method that we have used to determine N_0 from molecular layers on metal makes it possible to find δ_s and δ_p separately, whereas the measurement of the ellipticity of the reflected light gives only Δ, the difference between δ_s and δ_p.

Films built on chromium in 2-layer steps show little contrast when seen by the R_s ray or the R_p ray at $i=45°$. If, however, the chromium slide is placed between crossed Polaroid screens and the plane of vibration of the incident light makes an angle of 45° with the chromium surface, great contrast in intensity is seen between the steps. Under these conditions the light reflected by the film is in general elliptically polarized, and the phase retardation of the resultant of the two R_s rays (reflected from the upper and lower surfaces of the film) with respect to the resultant of the two R_p rays is a function of the thickness of the film. If a quartz wedge compensator is introduced in the path of the light between the two Polaroid screens, the wedge being turned so that the dark band exhibited by the wedge traverses all the steps in the series, the variation of phase retardation with the thickness of the steps is beautifully demonstrated. The band of the wedge is seen as a sinusoidal wave having its steepest slopes at steps whose thicknesses correspond to intensity minima for the ray R_s or the ray R_p. The complete theory of the factors involved in the reflection of light by transparent films deposited on metal has been worked out by Hauschild.[10]

The Reflection of Light From the Upper and Lower Surfaces of Films on Glass

The general equations for the reflection of light from an interface between any crystal and an isotropic medium (both perfectly transparent) are very complicated but are given in convenient form by G. Szivessy[11] in the *Handbuch der Physik*.

For the case of a plane parallel plate of a uniaxial crystal (cut with surfaces perpendicular to the optic axis) lying between two isotropic media of refractive indices n_0 and n_g the equations

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[10] H. Hauschild, Ann. d. Physik **63**, 816 (1920).

[11] Szivessy, *Handbuch d. Physik*, Vol. 20 (1928), pp. 635–726.

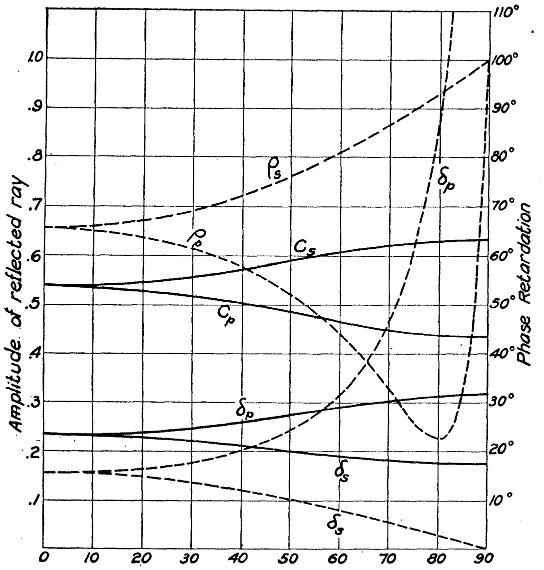

FIG. 2. Optical properties of bare chromium (dashed lines) and of the interface between chromium and a stearate film (solid lines). ρ_s and ρ_p are the amplitudes reflected from bare chromium for the R_s and R_p rays; C_s and C_p are the amplitudes reflected from the chromium-stearate interface. δ_s and δ_p are the phase retardations in degrees (beyond the normal 180° phase shift).

take the much simpler form:[12]

$$B_s=\frac{n_0\cos i-(n_1^2-n_0^2\sin^2 i)^{\frac{1}{2}}}{n_0\cos i+(n_1^2-n_0^2\sin^2 i)^{\frac{1}{2}}}, \tag{30}$$

$$B_p=\frac{n_0(n_3^2-n_0^2\sin^2 i)^{\frac{1}{2}}-n_1n_3\cos i}{n_0(n_3^2-n_0^2\sin^2 i)^{\frac{1}{2}}+n_1n_3\cos i}, \tag{31}$$

$$C_s=\frac{(n_1^2-n_0^2\sin^2 i)^{\frac{1}{2}}-(n_g^2-n_0^2\sin^2 i)^{\frac{1}{2}}}{(n_1^2-n_0^2\sin^2 i)^{\frac{1}{2}}+(n_g^2-n_0^2\sin^2 i)^{\frac{1}{2}}}, \tag{32}$$

$$C_p=\frac{n_1n_3(n_g^2-n_0^2\sin^2 i)^{\frac{1}{2}}-n_g^2(n_3^2-n_0^2\sin^2 i)^{\frac{1}{2}}}{n_1n_3(n_g^2-n_0^2\sin^2 i)^{\frac{1}{2}}+n_g^2(n_3^2-n_0^2\sin^2 i)^{\frac{1}{2}}}. \tag{33}$$

In these equations i is the angle of incidence in the medium of refractive index n_0; n_1 and n_3 are the refractive indices characteristic of the uniaxial crystal and n_g is that of the underlying glass. The quantities B and C are the amplitudes of the electric vectors of the reflected rays from the upper and lower surfaces, respectively, taking the amplitude of the light incident *upon that surface* as being unity.

It is evident from Eq. (5) that the interference fringes vanish if either B or C becomes zero. We see from Eqs. (30) and (32) that $B_s=0$ only when $n_1=n_0$, and $C_s=0$ only when $n_1=n_g$. There are, however, certain angles i_B and i_C at which B_p and C_p can vanish. These are given by:

$$\sin^2 i_B=n_3^2(n_1^2-n_0^2)/(n_1^2n_3^2-n_0^4) \tag{34}$$

and $\sin^2 i_C=n_3^2n_g^2(n_1^2-n_g^2)/n_0^2(n_1^2n_3^2-n_g^4)$. (35)

If n_3 and n_g differ only slightly from n_1, we may place

$$n_3^2=n_1^2+\Delta_3 \quad \text{and} \quad n_g^2=n_1^2+\Delta_g. \tag{36}$$

Then, neglecting terms involving Δ^2, we obtain (for $n_0=1$)

$$\tan i_B=n_1-\Delta_3/2n_1(n_1^2-1) \tag{37}$$

and $$\sin^2 i_C=n_1^2\Delta_g/(2\Delta_g-\Delta_3). \tag{38}$$

Thus Brewster's angle i_B decreases as n_3 increases above n_1, whereas with an isotropic substance the change with n is in the opposite direction. We can now understand the low value of i_B given in

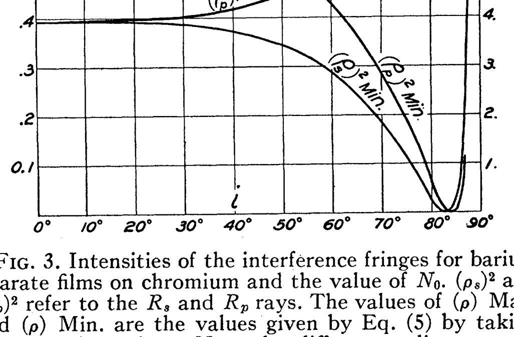

FIG. 3. Intensities of the interference fringes for barium stearate films on chromium and the value of N_0. $(\rho_s)^2$ and $(\rho_p)^2$ refer to the R_s and R_p rays. The values of (ρ) Max. and (ρ) Min. are the values given by Eq. (5) by taking the $+$ and $-$ signs. Note the different ordinate scales for $(\rho)^2$ and N_0.

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[12] To obtain these equations from those given in the *Handbuch der Physik* many variables must be eliminated. Eqs. (189) to (192) on p. 718 give expressions for B_s and B_p in terms of i, r and ζ (the angle between the wave normal and the ray). Similar equations for C_s and C_p must be derived from Eqs. (181) to (184) and are then expressed in terms of ζ, r and r_g, the angle of the ray transmitted into the glass. The angle ζ can be eliminated by Eq. (147) on p. 689. Then r and r_g can be eliminated by using $n_0\sin i=n\sin r=n_g\sin r_g$ together with the value of n given by Eq. (145).

Table II. Taking $n_1=1.491$ and $i_B=55°\,20'$ we calculate by Eqs. (37) or (34) that $n_3=1.552$, while Eq. (1) gives $n=1.446$. The value $n_3=1.552$ is in agreement with the result given in Eq. (25).

Real values of i_C occur only when n_g lies within the range for which the 2nd member of Eq. (38) is between 0 and 1. When $n_3>n_1$ and $n_1>1.42$, n_g must be less than n_1 in order that there shall be any angle i_C at which C_p vanishes. This explains the fact that for films on quartz, Table II, column 3, series B was observed at large as well as at small angles.

If for a film on quartz we take $n_g=1.459$, $n_1=1.491$ and $n_3=1.551$ from Eq. (25) we find by Eq. (35) $i_C=50°\,18'$. The data shown in Table II give the result that for films built on quartz i_C had a value between 53° 20′ and 56° 50′. A mean of these angles, $i_C=55°\,5'$ corresponds to the values $n_1=1.491$, $n_3=1.535$. The discrepancy of about 4 degrees between the calculated and observed values of i_C suggests that conditions obtain at the boundary between the film and quartz which are not fully described by Eq. (35).

Intensity of Interference Fringes Produced by Films on Chromium and on Glass

The data for C_s and C_p in Fig. 2, together with B_s and B_p given by Eqs. (30) and (31) enable us to calculate the intensities ρ^2 of the maxima and minima of the interference fringes on chromium by Eq. (5). The results of such calculations using $n_1=1.491$ and $n_3=1.551$ are given in Fig. 3.

It is seen that at $i=0$ the ratio of the intensities of the maxima and minima is 1.68. With the R_s ray this contrast steadily increases until at about 82° 30′ the minima become completely black, while the maxima reflect about 95 percent of the incident light. With the R_p ray as i increases the contrast decreases until it disappears at Brewster's angle 55° 20′. The contrast then reverses and increases very rapidly, becoming infinite at about 84°. These results agree with the observations.

The upper part of Fig. 4 gives the maximum and minimum values of ρ calculated by Eq. (5) from the values of B_s, B_p, C_s and C_p given by Eqs. (30) to (33), using $n_1=1.491$ and $n_3=1.534$, which are the values of n_1 and n_3 which correspond to the observed value of i_C for films on quartz. The curves shown are for glass (1) (quartz, $n_g=1.459$) and for glass (3) ($n_g=1.7854$). The separation of the curves for ρ_s and ρ_p for glass (2) $n_g=1.4937$ is too small to be shown in Fig. 3. The mean value of ρ for this glass lies approximately midway between the two values shown for glass (1). The index of contrast, K, defined by Eq. (8), is shown for glasses (1) and (2) in the lower part of Fig. 4. We see that for glass (1) the contrast decreases slowly, while for glass (2) it increases rapidly when i increases and at 43° the contrasts are equal. These results are in complete agreement with the observations given in Table II. The observed points of disappearance and reappearance of fringes with glass (1) occur at $i=53°\,20'$ and 56° 50′. The contrast is about 1 : 1.15 at these points, so the fringes become invisible between these limits because of the low intensity of the reflected light (less than 0.04 percent). With glass (3), on the other hand, the intensity of the reflected light at Brewster's angle is 0.4 percent and in this neighborhood a relative change in intensity of 2 percent is caused by a change in i of a little less than 2′. Thus, the observed accuracy of measuring i_B on glass (3) and the inaccuracy with glass (1) is explained quantitatively.

The optical properties of the built-up films on chromium and on the several glasses are thus in accord with the theories given for uniaxial crystals with their optic axis perpendicular to the plane of the film. The analysis that we have made furnishes several independent methods by which n_1 and n_3 can be determined accurately. Thus with measurements of ΔN_N we have the possibility of precise measurements of t, the spacing of the layers. If then films are also used for x-ray diffraction measurements a direct comparison of optical and x-ray wave-lengths can be made.

Spacing Measurements for Films Built on Glass

When spacing measurements were made with films built on glass, the films had to be built with a greater step-rise than in the case of films on chromium since the minima were not so sharply defined. A step-rise of 10 layers was sufficient when the films were built on glass of refractive index $n=1.78$, when glass of lower refractive index was used the step-rise had to be 16–20 layers.

The results which were obtained showed that measurements made with films on glass, $n_g = 1.78$ and a 10-layer step-rise, had the same probable error as with films on chromium having a 2-layer step-rise. The films on glass had the advantage that they could be measured at small angles of incidence and when i is small the calculated values of cos r are less affected by an error in the value of the refractive index than when i is large. With R_s accurate measurements could be made at angles up to about 50°, which was a greater range than for the case of chromium. The values of $n_s \cos r$ calculated from $n = 1.491$ were independent of the angle, as in the case of the data in Table III. When the glass was thoroughly cleaned by being scoured with Shamva the values of $-N_0$ obtained in accordance with Eq. (2) were $-N_0 = 0.2$ to 1.0 layer, the value commonly obtained being 0.7 layer. These relatively small values are in accord with the known small degree of elliptic polarization from transparent media.

Small variations in N_0 were attributed to the manner in which the glass was cleaned in successive runs. The glass $n_g = 1.78$ was visibly stained by dilute acid, also long exposure to the air produced a film on the surface which had a thickness of many stearate layers. Scouring the surface with Shamva removed films of stain and grease very satisfactorily, but the Shamva itself adhered to both glass and metal and could not be removed merely by rinsing the surface with a stream of running water. Even after thorough swabbing with cotton under water some traces of Shamva were frequently detected which were sufficient to account for small variations in N_0 of the magnitude which were observed. The values of N_0 obtained for chromium cleaned with Shamva were subject to similar variations within a range of approximately ±0.2 layer. Chromium cleaned by being made cathode in an electrolytic bath showed an increase in $-N_0$ of 1 layer as a result of becoming slightly etched by being cleaned about 10 times.

EFFECT OF FOREIGN SUBSTANCES DISSOLVED IN BENZENE

The solution of stearic acid in benzene which was used to spread the monolayer on water in these experiments contained stearic acid in a concentration which was commonly 3×10^{-4} by weight. The benzene was "Benzene Merck" which was redistilled in this laboratory.

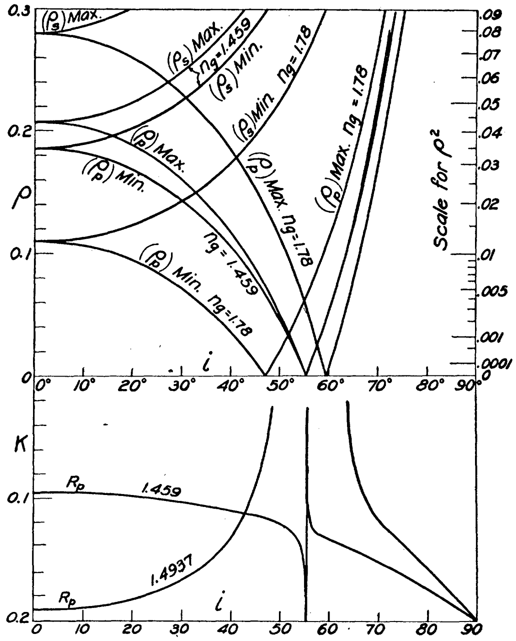

FIG. 4. Upper figure: intensities of interference fringes for films on three glasses. Ordinates with scale on left are the absolute values of ρ and with scale on right are intensities ρ^2. Lower figure: absolute values of index of contrast for films on two glasses. (0.2 on ordinate scale should be 0.)

The effect of the presence of a small amount of a dissolved oil in the benzene was demonstrated by adding mineral oil in a concentration 3×10^{-4} by weight to redistilled benzene containing a concentration 3×10^{-4} stearic acid. Films containing 200 layers were readily built on chromium with this mixture. They had a spacing approximately 80 percent greater than the normal spacing for barium stearate and were much less transparent, a large part of the light which fell on the film being reflected as scattered light. The appearance when seen in a microscope indicated that much of the oil had gathered into a myriad of droplets. When "Benzene Merck" was used without being redistilled a spacing 6 percent greater than normal was obtained, and films having more than 100 layers on chromium showed marked scattering of light.

Effect of Substances Dissolved in Water on Spacing of Layers and on the Refractive Indices

A large number of measurements have been made to determine the number of layers between successive minima, ΔN_N, for films of barium stearate built from many different solutions. The values were found to range from $\Delta N_N=79$ to 82 for films which could be built in a satisfactory manner. Most of the values lay between $\Delta N_N=81.2$ and 81.8. The values were independent of pH, temperature, and barium concentration, within the range in which these variables were commonly used for film building. This range was $p\mathrm{H}=6.5$–7.2, temperature 15°C–25°C, barium concentration 0.3×10^{-4} to 10^{-4} M. The presence of Cu in a concentration 2×10^{-6} did not affect the spacing. The differences obtained in values of ΔN_N were attributed to small amounts of foreign substances present in the water on which the films were spread. The belief that foreign substances were responsible for the variations was derived from data of the type shown in Table V. Water obtained from a still lined with tin was used to make up solutions on successive days, all the solutions being 0.3×10^{-4} M $BaCl_2$, 2×10^{-4} M $KHCO_3$, $p\mathrm{H}=6.8$. Some of these solutions produced films which gave data of the type shown in columns (*a*), Table V, whereas others gave data of the type in columns (*b*). In the type (*a*) ΔN_N increased steadily for each successive interval from the 1st to the 6th minimum. In every case when data of this type were obtained and a second series of measurements was made with films built from the same solution, the initial values obtained in the second measurements were similar to the final values of the first measurements. This made it appear very probable that the water used for the solution (specific resistance = 900,000 ohms-cm) contained a trace of some substance which was used up by the successive films. The series in columns (*b*) did not have this regular trend, the greatest departure from the mean value 81.6 being 0.2 layer.

TABLE V. *Films built on glass. Initial layer formed by rubbing down 50 layers of barium stearate.*

	(*a*)		(*b*)	
m	N_N	ΔN_N	N_N	ΔN_N
1	39.0		38.8	
3	118.6	79.6	120.4	81.6
5	199.2	80.6	201.9	81.5
7	280.0	80.8	283.7	81.8
9	361.1	81.1	365.1	81.4
11	442.3	81.2	446.8	81.7
13	523.5	81.2	528.4	81.6
				Mean 81.6

Mr. Schaefer has been conducting experiments which have shown that minute traces of tin, lead and silica in concentrations as low as 10^{-8} parts by weight in the water can produce effects of this kind. The effect on the 2-dimensional viscosity of the films[13] is a particularly sensitive indication of the presence of these impurities. The measurements given so far in this paper were made at a time when we had no knowledge of the nature of the foreign substances which may be responsible for changes in n and ΔN_N. Recently we have made a few observations with distilled water from various sources and have sometimes added small amounts of salts of divalent elements.

Using a laboratory supply of distilled water of specific resistance about 300,000 ohms-cm which had passed through tin lined lead pipe, we find with barium stearate films built up on quartz that with the extraordinary ray (compare with Table II) the B series is observed up to $i=56°\,0'$ that there is then a range between 56° 0′ and 62° 30′ at which the A series is seen and at still larger angles the B series again appears. Thus for these films we may take $i_B=56°\,0'$ and $i_C=62°\,30'$. These values would indicate by Eqs. (34) and (35) that n_1 is about 1.515 and that n_3 is at least 1.56. These effects are probably due to traces of lead.

To investigate the effects produced by lead, $PbCl_2$ was added, sufficient to make the solution 3×10^{-6} molar with respect to Pb, the solution being 3×10^{-5} molar with respect to Ba. Films built from this solution on glass having a refractive index of 1.5106 showed at $i=0$ a fairly strong B series, so that n_1 for this film must have been at least 1.52. Films built from this solution on quartz gave with R_p the B series for $i<56°\,35'$ followed by the A series at $i>56°\,35'$ with no return to the B series. The value of i_B for films

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[13] I. Langmuir, Science **84**, 379 (1936).

built on glass $n = 1.78$ was 56° 10′. With $n_1 = 1.52$ and $i_B = 56° \ 10'$ we find by Eq. (34) $n_3 = 1.559$.

On doubling the amount of lead the films were more difficult to build, but a value of n_1 was found which was slightly less than 1.5106.

Films of pure stearic acid spread on distilled water $p\mathrm{H} = 5.8$ without any added salts at $i = 0°$ gave no observable fringes on glass of $n_g = 1.5106$, so that we may take $n_1 = 1.510$.

SKELETON FILMS

When a slide coated with a film of barium stearate which has been built at $p\mathrm{H} = 6.5$ is soaked for 1 to 10 sec. in benzene and is then withdrawn from the benzene, a striking change is observed in the interference color reflected by the film. The color of the soaked film corresponds to an optical thickness much less than that of the new film. Further soaking produces little or no change of color. The change is due to a large decrease in the refractive index of the film, the actual thickness being practically unaltered. Before the film is soaked it consists of a mixture of barium stearate and stearic acid,[4] the proportion of each component being determined by the barium concentration and pH of the water solution used in building the film. The benzene dissolves the stearic acid and leaves the barium stearate as a skeleton with air filling the spaces previously occupied by the stearic acid.

The data in Tables VI and VII refer to a film which had an initial refractive index $n_1 = 1.499$ and after soaking in benzene the refractive index of the skeleton was $n_W = 1.30$. Several skeleton films have been built which had the value $n_W = 1.25$, and in one case $n_W = 1.22$. From the law of Clausius and Mosotti

$$(n^2 - 1)/(n^2 + 2) = k \times \text{density} \qquad (39)$$

we have the result that $n_W = 1.30$ corresponds to a skeleton structure containing 63.7 percent of the material in the initial film. The values $n_W = 1.25$ and $n_W = 1.22$ correspond to 53.8 percent and 47.7 percent, respectively.

The removal of 35 to 40 percent of the material can be accomplished with practically no shrinkage in thickness of the film. Due to the decrease in refractive index vivid colors are obtained with skeleton films built on ordinary glass microscope slides, $n_g = 1.51$ to 1.52, whereas normal films are barely visible on this glass. The air spaces in the film may be filled with oil by allowing a drop of mineral oil to travel across the film. The oil does not wet the film permanently but withdraws from the path which it has traveled, and this path is then seen to have the same color as that of the film before it was soaked. If a moderately volatile oil such as tetradecane or kerosene is used, the color gradually returns to that of the skeleton film as the oil evaporates.

When more than about 50 percent of the material of the film is removed, the skeleton commonly shows partial collapse and has a fogged appearance. Films which have collapsed completely, due to the removal of more than about 60 percent, are no longer transparent. The best skeleton films are obtained when the films contain less than 100 layers, for the reason that the water solutions which must be used to build films containing a large proportion of stearic acid are at $p\mathrm{H} = 6.5$ which is a range of pH in which films are slower than at $p\mathrm{H} = 7.0$ and become progressively slower as every successive 100 layers are added. A series of steps can be built in 50-layer intervals which appear perfectly transparent before the series is soaked, but when withdrawn from the benzene the higher skeleton steps are fogged in a manner which shows that the tendency to collapse is greatest for the films which are built at the lowest speed. A study of the skeleton of a film thus affords an important test of the building qualities of the material of which the film is composed.

A large part of the stearic acid is usually removed from the film by benzene in 10 to 60 sec., often it is removed in 1 sec. Prolonged soaking in

TABLE VI. *Intensity minimum $m = 3$ with ordinary ray of wave-length $\lambda = 5893A$ for normal and skeleton films of barium stearate built on glass.*

FILM	N	i	cos r calc. for $n = 1.499$	N cos r	cos r calc. for $n = 1.30$	N cos r
Normal	124	17°57′	0.9786	121.35		
	134	38 55	.9079	121.66		
	144	53 40	.8433	121.44		
			Mean	121.48		
Skeleton	144	14°47′	0.9854	141.90	0.9805	141.19
	154	30 52	.9396	144.70	.9189	141.51
	164	41 20	.8977	147.22	.8613	141.25
	174	49 22	.8623	150.04	.8119	141.27
	184	57 0	.8288	152.50	.7640	140.58
Skeleton filled with Nujol	124	17°55′	.9787	121.36		
	134	38 32	.9096	121.89		

benzene frequently results in a gradual slow decrease in optical thickness, but this is usually accompanied by a slow collapse of the skeleton. In order to build a skeleton which will have a desired value of n_W the proportion of the film that is to be dissolved is fixed by the stearic acid content of the film. For example, the data in Table VI refer to a film built at $p\mathrm{H}=6.4$ which lost 36.3 percent of its initial material. Films built from a solution having the same barium content and $p\mathrm{H}=7.0$ lose practically no material when soaked in benzene for 1 min.

The amount of material which can be removed at a given pH value, and the amount which can be removed without causing collapse are both affected to a great extent by the presence of traces of foreign substances in the water. In recent experiments the skeleton films which have been built when using barium acetate have shown less tendency to collapse than those built with barium chloride. The presence of copper in the water usually causes the films to crack when skeletonized. A wide variety of effects produced by foreign substances in the water when building skeleton films is being studied by Mr. Schaefer.

The measurements given in Table VI were made with a film built on glass $n_g=1.78$ in steps having 119, 129, $\cdots$ 229 layers. The water solution was 10^{-4} M barium acetate, 0.2×10^{-4} M $\mathrm{KHCO_3}$, 10^{-5} M KCN. The KCN was added in order to remove traces of copper from the solution. The temperature was 19°–20°C, $p\mathrm{H}=6.4$. The initial layer was built from a solution containing the same concentration of barium, $p\mathrm{H}=8.5$.

The refractive index of the normal film was found by building steps on the standard glasses. Steps built on glass $n_g=1.4937$ formed a B series which had a contrast about one-half as great as the A series exhibited by the steps on $n_g=1.5106$. The refractive index was therefore $n=1.499$. This value is higher than the usual value $n=1.491$ obtained for films built at $p\mathrm{H}=7.0$ to 7.2 because of the greater percentage of stearic acid at $p\mathrm{H}=6.4$, the refractive index of pure stearic acid films being 1.51.

TABLE VII. *Skeleton and normal films on chromium compared with R_s ray of white light.*

COLOR	N (NORMAL)	N_W (SKELETON)	N/N_W
2nd-order yellow	127	169	0.7515
2nd-order red	145	189	.7672
2nd-order blue	163	219	.7443
			Mean .7510

The data in column 5 for the normal film were calculated using $n=1.499$. The resulting values of $N\cos r$ are in good agreement. After these measurements were made the film was soaked in benzene for 1 min. The values of $N\cos r$ in column 5 for the skeleton were calculated using $n=1.499$, in column 7 using $n=1.30$. The results in column 7 are reasonably constant whereas in column 5 they show a steep upward trend with increasing i. The refractive index of the skeleton was therefore 1.30.

All films which reflect minimum intensity corresponding to a particular value of m have a constant value of $nNt\cos r$ (by Eq. 4), if one neglects N_0 (Eq. (13)) which is a very small term in the case of films on glass. Therefore

$$t_W/t=nN\cos r/n_WN_W\cos r_W, \qquad (40)$$

where the subscript W refers to the skeleton film. Substituting $n=1.499$, $n_W=1.30$, $N\cos r=121.48$, $N_W\cos r_W=141.2$ (from Table VI) we have the result $t_W=0.992t$. That is, the removal of 36.3 percent of the bulk of the film was accompanied by a shrinkage of only 0.8 percent in thickness.

When the skeleton was filled with Nujol the optical properties were nearly identical with those of the original film. Table VI gives the results of measurements of the oil-filled film. The refractive index of Nujol is 1.480 and of stearic acid is 1.51. The increase in the value of $N\cos r$ at $N=134$ from 121.66 for the normal film to 121.89 for the oil-filled film is in accord with the lower mean value of refractive index.

During the process of building these films on glass a chromium slide was attached to the back of the glass slide. The films on the chromium were also skeletonized by being soaked for 1 min. in benzene. The colors of the steps were then compared with a standard color-scale made of normal films built on chromium in 18-layer intervals. The skeleton and the standard were viewed by the R_s ray of white light at $i=80°$. The steps which matched most nearly in color are listed in Table VII. Eq. (40) was applied to these data with the assumption that N_0 for skeleton films on chromium was the same as for normal films. The value of n_W which was required to satisfy Eq. (40) when $N/N_W=0.7510$ and $i=80°$ was $n_W=1.295$. Thus the method of building films simultaneously on glass and chromium affords a useful means of making two independent determinations of n_W which cover a range of i from 14° to 80°.

After the data given in Tables VI and VII were obtained, films were built on seven microscope slides, each film having steps of 333, 343, 353 layers. All were soaked in benzene for 1 min. Measurement of the angles i at which these films reflected the minimum $m=7$ gave the result $n_W=1.32$. It frequently happens that after a water solution has stood in a trough for several hours the values of n_W which are then obtained are slightly higher than the initial values. This is probably due to a gradual accumulation in the solution of substances dissolved from the trough or taken up from the air.

The slides were stacked in a pile and the birefringence of the total of the seven films was measured by means of a quartz wedge compensator using transmitted light. The relative phase retardation of the R_s and R_p rays corresponded to $\lambda/4$ for sodium light at $i=48°$ and $\lambda/3$ at $i=54°$. The total thickness Nt_W of the 2471 layers was 59,800A, taking $t_W=24.2$A. Therefore the factor $5752t$ in Eq. (28) was replaced by 59,800. For $\Delta l=1473$A at $i=48°$ it was found that when $n_1=1.32$ the value of n_3 which gave terms which satisfied Eq. (28) was $n_3=1.390$. For $\Delta l=1964$A at $i=54°$ the calculated value was $n_3=1.391$.

A measurement of Brewster's angle made after these films were built gave the result $i_B=51°\ 17'$. Substituting $i_B=51°\ 17'$ and $n=1.32$ in Eq. (34) we obtain $n_3=1.383$. The refractive indices of the normal films built at pH$=7.0$ were $n_1=1.491$, $n_3=1.551$ from Eqs. (12) and (25). The skeleton films having $n_1=1.32$ and $n_3=1.390$ or 1.383 have therefore approximately the same value of n_3-n_1 as the normal films.

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Properties of the Surface Magnetization in Ferromagnetic Crystals

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The magnetic powder patterns found on polished iron crystals (which may contain a few percent of silicon) have been studied more carefully by using a macroscopic model and by investigating the forces on the powder particles. Reasons are given for preferring one of two simple models to explain the patterns; some interesting implications of the proposed model are then considered. Experiments are described which indicate that the structures under discussion originate during the polishing operation, but that other than magnetic causes must be responsible for the remarkable regularity of the patterns.

A SMALL magnetic field applied normal to the *polished* surface of a silicon-iron single crystal will cause magnetic powder in a colloid suspension placed on it to collect into regular patterns related to the crystal symmetry. To explain these patterns, which resemble mazes with paths about 4 microns wide on a (100) surface but consist of lines parallel to a [110] axis on a $(1\bar{1}0)$ surface, McKeehan and Elmore[1] assumed the surface to contain blocks about 2 microns on a side spontaneously magnetized along <100> or <110> axes in the surface, with opposing magnetizations at about one-half

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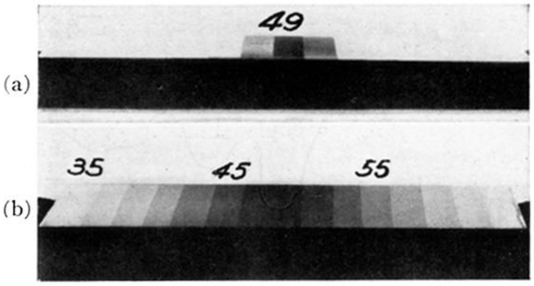
[1] L. W. McKeehan and W. C. Elmore Phys. Rev. **46**, 226 (1934) W. C. Elmore and L. W. McKeehan, Trans. A. I. M. E. **120**, 236 (1936).



(a) $i=82°$. (b) $i=75°$.

FIG. 1. Interference fringe seen with 15 steps having 35, 37, . . . 63 layers of barium stearate built on polished chromium. Photographed with R_s ray of light $\lambda=5893\text{A}$.