Use of Interference to Extinguish Reflection of Light from Glass

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The phenomena of interference of light rays reflected from the two boundaries of a thin film cause the intensity I_R of the resultant light to be greater or less than the intensity of the individual rays. The value of I_R is determined by (a) the refractive index of the film, n_1, and the substance on which the film is deposited, n_g, (b) the thickness of the film, (c) the angle of incidence at which light strikes the film, (d) the wave-length of the light. The conditions necessary to obtain extinction of reflected light are described. In the case of monochromatic perpendicular light $I_R=0$ when $n_1=n_g^{\frac{1}{2}}$ and the thickness t is given by $t=0.25\lambda(2a+1)/2$ where a is zero or an integer. The technique of building films which have the required values of n_1 and t is described. The films are made by building up monomolecular layers, each layer consisting of 50 percent cadmium arachidate and 50 percent arachidic acid. The film is then soaked in alcohol which dissolves the arachidic acid and leaves a skeleton of cadmium arachidate. The refractive index of the skeleton is determined by the amount of arachidic acid which has been removed from the film. Since the interstices are of molecular size there is no appreciable scattering of the reflected light.

THE reflection of light from glass surfaces has created many difficult problems. It is well known that the design of optical instruments, and the methods of illuminating objects by means of light shining through a glass window, are much hampered by this characteristic feature of glass.

When light of intensity E falls on a transparent plate, the light T transmitted by the plate is given by $T=E(1-I_R)^2(1-\alpha t)$ where I_R is the fraction of the light which is reflected by a single face of the plate, t is the distance which the light travels in the plate which is assumed to be large compared with a wave-length of light, and α is the absorption per unit distance. Therefore a plate which is treated in such a way as to diminish I_R shows a corresponding increase in light transmission T.

In 1892 Harold Dennis Taylor,[1] the English lens expert, discovered that a badly tarnished photographic lens transmitted more light than a new lens. He found that he could develop this tarnish chemically by immersing the lens in an aqueous solution of ammonia and sulphureted hydrogen.

In 1916 F. Kollmorgen[2] found means of treating most of the glasses used in optical work with different chemicals so as to diminish the light reflected from their surfaces. He prepared disks of a barium crown glass of refractive index 1.6 and showed that an untreated disk transmitted 89 percent of light, whereas the transmission of a similar disk was increased by suitable treatment to a maximum value of 96 percent. Kollmorgen calculated that the light transmitted by a gunsight containing seven untreated lenses and two prisms was reduced by reflection at the several surfaces to 36.2 percent of the incident light. He showed that in a periscope the loss by reflection reduced the light received by the observer to 25 percent of the light received by the periscope. He also pointed out that multiple reflections in a lens system gave rise to a veil of stray light which caused a loss of brilliancy and contrast in the image.

Kollmorgen believed that the chemical treatment "formed at the surface a vitreous compound having a refractive index considerably lighter than that of the glass itself." Wright[3] also experimented with various chemical treatments to produce a surface layer of this type. Neither experimenter was aware that the effects which he observed were due to interference between the light rays reflected from the upper and lower surfaces of the layer.

In 1935 Strong[4] coated plate glass ($n_g=1.52$) with evaporated films of fluorite for the purpose of using interference to decrease reflection. One of these films caused a decrease of 54 percent in

[1] Harold Dennis Taylor, *The Adjustment and Testing of Telescope Objectives* (T. Cook, York, England, 1896).
[2] F. Kollmorgen, Trans. Soc. Ill. Eng. **11**, 220 (1916).
[3] F. E. Wright, Ordnance Department Document No. 2037, p. 76.
[4] J. Strong, J. Opt. Soc. Am. **26**, 73 (1936).

the light reflected at normal incidence, and another a decrease of 85 percent.

Recent developments in experimental work with built-up films[5,6] have provided a means of coating glass with a type of film which extinguishes the reflection of monochromatic light. When a plate of glass, coated on both sides with a film which is built so as to extinguish sodium light at perpendicular reflection, is held a few inches from a 6000-lumen sodium vapor lamp and the glass is seen against a black background, the image of the lamp is almost completely imperceptible and the glass has the appearance of black velvet. When a stripe of the same type of film is built on soda-lime glass and one looks through the glass at a sheet of white paper or at the sky, the effect of the increased transmission is very striking. The stripe has the appearance of clean glass and the clean glass on either side of the stripe appears to be slightly smoked. The contrast is plainly visible since the transmission of the stripe is 99.2 percent for white light, and of clean glass is 92 percent.

In order that a film shall extinguish monochromatic light the properties of the film must be suited to the refractive index of the glass, the wave-length of the light, and the angle at which the light is to be extinguished. This paper will describe the methods by which skeleton films of cadmium arachidate are built so as to meet these requirements.

Cadmium arachidate is a soft substance which is completely removed from glass if the glass is wiped with a cloth. The film is permanent, however, if it is not touched and is not exposed to bright sunlight for long periods of time. The writer has a film which has been kept for four months in an unstoppered tube in a desk drawer, and has shown no perceptible change during that time. These films therefore supply an exceedingly useful tool for the exact study of interference.

Cartwright and Turner[7] have shown that evaporated films of LiF, MgF_2, CaF_2, NaF and chiolite will reduce the reflection of visible light from two glass surfaces to about 0.4 percent. This results in a transmission of about 99.6 percent, as recorded by the Hardy color analyzer.

[5] K. B. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935).
[6] K. B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).
[7] C. H. Cartwright, and A. F. Turner, Bull. Am. Phys. Soc. **13**, 10 (1938).

Conditions for Extinguishing Reflection of Monochromatic Light

When a glass surface is covered with a thin transparent film the light reflected by the glass is governed by the laws of interference. The ray reflected from the air-film boundary interacts with the ray reflected from the film-glass boundary to form a resultant ray of intensity I_R. The value of I_R is given by

$$I_R = B^2 + C^2 + 2BC \cos (2\pi D/\lambda), \tag{1}$$

where B and C are the amplitudes of the rays reflected from the air-film and film-glass boundaries, respectively. These rays will be called the B ray and the C ray. The symbol D denotes the difference in optical path between the path traveled by the B ray and that traveled by the C ray. The value of D is given by

$$D = 2n_1 t \cos r_1, \tag{2}$$

where t is the thickness and n_1 is the refractive index of the film, and r_1 is the angle of refraction of light in the film when light is incident at an angle i. In the case where the film is an isotropic substance, or where it is a uniaxial crystal and the measurements deal with the ordinary ray, the value of $\cos r$ can be calculated from i and n_1 since $n_1 = \sin i/\sin r_1$.

The Fresnel formulae for the amplitudes B and C reflected at perpendicular incidence are

$$B = (n_0 - n_1)/(n_0 + n_1), \tag{3}$$

$$C = (n_1 - n_g)/(n_1 + n_g), \tag{4}$$

where n_g, n_1 and n_0 denote the refractive indices of the glass, the film, and the medium in which the glass is viewed which is commonly air. When n_0 refers to air we have $n_1 > n_0$ and the value of B is negative, the negative value indicating that the ray undergoes a phase reversal at the boundary. In Eqs. (3) and (4) the amplitude of the ray incident on a boundary is taken as unity.

The formula of Eq. (1) neglects multiple reflections in the film. The effect of multiple reflections is slight in the case of transparent films built on glass, since the number of these reflections is very small, the intensity of a single

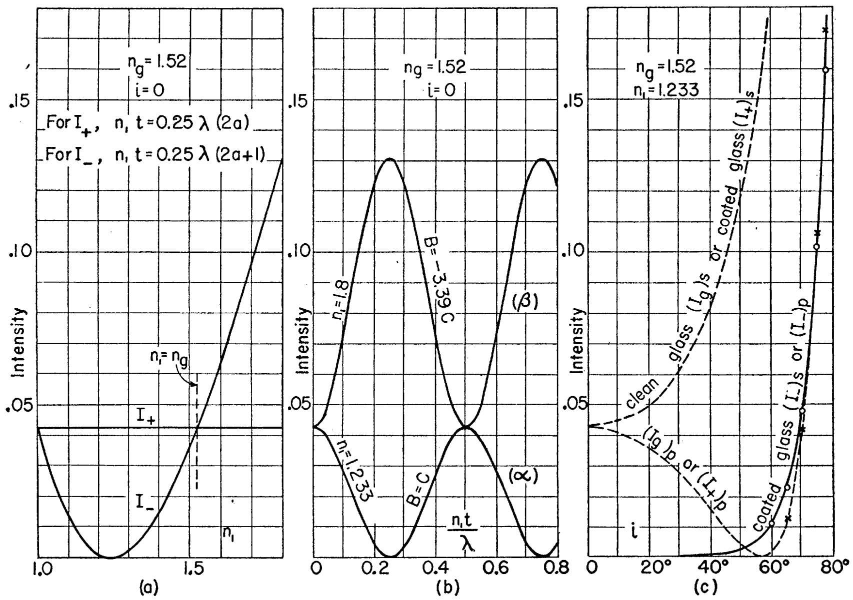

FIG. 1. Reflection of light from films built on glass $n_g = 1.52$. Intensity as a function of: (a) refractive index n_1 of films; (b) optical thickness of film, measured in terms of wave-length λ; (c) angle of incidence i. Incident intensity was 1.0.

reflection being usually about 1 percent. The correction which can be applied to Eq. (1) for multiple reflections has been derived[6] for the cases $D = a\lambda$ and $D = \lambda(2a+1)/2$ where a is zero or an integer.

For $D = a\lambda$, $$I_+ = [(B+C)/(1+BC)]^2, \quad (5)$$

For $D = \lambda(2a+1)/2$, $$I_- = [(B-C)/(1-BC)]^2, \quad (6)$$

where I_+ and I_- are corrected values of I_R. The calculation of the correction for other values of D is complicated. The theory of the problem is similar to that of the reflection of light by a Fabry and Perot interferometer, but in the present case the reflection at the boundaries is so small that the correction becomes negligible.

Effect of refractive index

The curves in Fig. 1 represent the reflection of light from films built on glass $n_g = 1.52$. Fig. 1(a) shows the maximum and minimum values of the intensity, plotted as a function of n_1, for the case of perpendicular light ($i = 0$). These intensities I_+ and I_- were calculated by means of Eqs. (3), (4), (5) and (6). The curves show that I_- is the minimum value when $n_1 < n_g$, but becomes the maximum value when $n_1 > n_g$.

Strong[4] pointed out in his paper that the intensity was zero when n_1 was given by

$$n_1^2 = n_g n_0. \quad (7)$$

In the present case the value of n_1 given by Eq. (7) was $n_1 = 1.233$.

Effect of film thickness

Equation (1) shows that the intensity of reflected monochromatic light varies as a function of $\cos(2\pi D/\lambda)$ where D is proportional to $n_1 t$ in accordance with Eq. (2). The curves in Fig. 1(b) represent the variation of intensity of perpendicular light, plotted as a function of $n_1 t/\lambda$.

The values of B and C which were used to calculate the curves of Fig. 1(b) were obtained by means of Eq. (3) and Eq. (4), for the cases $n_1 = 1.233$ and $n_1 = 1.80$. For curve (α), $n_1 = 1.233$, $B = C = -0.1043$; for curve (β), $B = -0.2857$, $C = 0.0843$. The maximum and minimum values of the intensity were calculated from Eq. (5) and Eq. (6) and correspond to points on the curves in Fig. 1(a) for the given values of n_1. The curves of Fig. 1(b) are cosine curves drawn through these values of I_+ and I_-. Curves drawn in this way represent a close approximation to the actual variation of intensity with film thickness, since the correction which is applied by substituting $I_{\pm}=[(B\pm C)/(1\pm BC)]^2$ for $(I_R)_{\pm}=(B\pm C)^2$ in Eq. (1) is small. For curve (α), $BC=0.011$; for curve (β), $BC=-0.024$.

Cases of a different sort in which both B and C have values about 0.4 to 0.6 have been considered in previous papers.[6,8] They occur in practice when films of barium stearate are built on a polished chromium surface and are viewed at angles of incidence in the range 68° to 84°. Under these conditions the number of multiple reflections is sufficient to have a large effect on the variation of intensity with thickness. The intensity curve departs markedly from the type of cosine curve shown in Fig. 1(b), the curve assuming sharp minima and flat maxima.

In the curves of Fig. 1(a) and (b) the reflection I_g from a single surface of clean glass is $I_g=0.0426$, the intensity of the incident light being unity. This value was obtained from $I_g=(B_g)^2$ where B_g is the value of B from Eq. (3) when $n_1=n_g$.

In the case of film-coated glass, substituting the values of B and C from Eq. (3) and Eq. (4) in Eq. (5), we have the result

$$I_+=[(n_0-n_g)/(n_0+n_g)]^2. \qquad (8)$$

Therefore, *for the case of perpendicular light* I_+ is independent of n_1, and the value of I_+ is identical with the value of B_g^2. That is, when $n_1t=0.5a\lambda$ the intensity of light reflected by a film of any transparent substance is the same as the intensity I_g reflected by clean glass. In order to diminish the reflected intensity below this value the surface film must have a refractive index which is less than that of the glass. The minimum intensity is obtained when

$$n_1t=0.25\lambda(2a+1).$$

In interference phenomena the optical thickness n_1t is more useful as a unit of measurement than the actual thickness t. If a film is built in a series of steps which have increasing values of t and the same value of n_1, and the film is illuminated by monochromatic light of wavelength λ, the intensity minimum is seen at the step which has the thickness $t=0.25\lambda(2a+1)/n_1$. If the refractive index of the entire series is changed to n_2, the minimum is then seen at a different step of thickness $t_2=n_1t/n_2$. In other words, the minimum is seen to shift to thicker steps as the refractive index is lowered.

[8] K. B. Blodgett, J. Phys. Chem. **41**, 975 (1937).

Effect of angle of incidence

When glass covered with a film is illuminated by light at different angles of incidence i, the reflected light is affected in two ways (a) and (b) by the angle.

(a) *Effective thickness.*—The path difference D which appears in Eq. (1) may be called the "effective thickness" of the film. Eq. (2) shows that D is proportional to $\cos r_1$. Therefore a film of given thickness t has its greatest *effective* thickness when it reflects perpendicular light.

(b) *Reflection at B and C boundaries.*—The amplitudes of the reflected rays B and C can be calculated as a function of i, n_1, and plane of polarization by means of the following Fresnel formulae:

$$R_s=-\sin(i-r)/\sin(i+r), \qquad (9)$$

$$R_p=-\tan(i-r)/\tan(i+r). \qquad (10)$$

Here i and r are the angles of incidence and reflection at a given boundary, and R_s and R_p are the amplitudes of the reflected rays having the plane of polarization perpendicular and parallel, respectively, to the incident plane.

The dashed lines in Fig. 1(c) give the calculated values for the intensities $(I_g)_s$ and $(I_g)_p=(R_g)_p^2$, where R_g is the value of R for glass ($n_g=1.52$). The intensity $(I_g)_p$ falls to zero at Brewster's angle which is $\tan^{-1}1.52=56°\ 40'$.

The solid line in Fig. 1(c) was calculated for the case of glass coated with a film of an isotropic substance. The value of n_1 for the film was $n_1=1.233$ from Eq. (7), and D had the constant value $D=\lambda(2a+1)/2$. Therefore this curve does not represent the case of a single film reflecting light at a series of angles, but instead it represents a series of films having thicknesses which satisfy Eq. (2) for a constant value of D. The required thickness t increases with increasing values of i.

When glass is coated with a film there are two rays B_s and B_p reflected at the B boundary, and two rays C_s and C_p reflected at the C boundary. In the case of the data of Fig. 1(c) the values of B_s, B_p, C_s and C_p were calculated by substituting in Eqs. (9) and (10) the values of the angles of incidence and refraction at the B and C boundaries. These were obtained from the equations $n_1/n_0 = \sin i/\sin r_1$, and $n_g/n_1 = \sin r_1/\sin r_g$, where r_g is the angle of refraction in the glass.

A film for which $D = \lambda(2a+1)/2$ reflects light with an intensity I_- given by Eq. (6). Values of $(I_-)_s$ and $(I_-)_p$ can be calculated by means of Eq. (6) for different values of i by substituting in this equation the values of B and C derived from Eq. (9) and Eq. (10). In the particular case illustrated in Fig. 1(c) the relationship $n_1^2 = n_0 n_g$ results in the following simplification

$$\left(\frac{B-C}{1-BC}\right)_s = -\left(\frac{B-C}{1-BC}\right)_p = \frac{\cos(i-r_g)-1}{\cos(i+r_g)+1}. \quad (11)$$

The solid line of Fig. 1(c) gives the values of

$$(I_-)_s = (I_-)_p = [(\cos(i-r_g)-1)/(\cos(i+r_g)+1)]^2. \quad (12)$$

For the case where D is constant and has the value $D = a\lambda$, and $n_1^2 = n_0 n_g$, the equations for the amplitude $(B+C)/(1+BC)$ of the reflected light can be reduced to the form

$$[(B+C)/(1+BC)]_s = -\sin(i-r_g)/\sin(i+r_g), \quad (13)$$

$$[(B+C)/(1+BC)]_p = -\tan(i-r_g)/\tan(i+r_g). \quad (14)$$

Equations (13) and (14) are the Fresnel equations for the amplitudes $(R_g)_s$ and $(R_g)_p$ reflected by clean glass. We therefore have the result that at any angle i the maximum light reflected by a film having a refractive index given by $n_1^2 = n_0 n_g$ is equal to the light reflected by clean glass. In the case of perpendicular light the intensities were found to be equal for any value of n_1 (from Eq. (8)).

The formulae of Eqs. (1) to (14) are valid only for the case of a ray which obeys the ordinary laws of reflection and refraction. The equations for B and C for the case of the extraordinary ray of a uniaxial crystal have been given in a previous paper.[6]

Skeleton Films of Cadmium Arachidate

The technique of building films by depositing successive monolayers of barium stearate has been previously described.[5, 6] It was found in the early work that the refractive index of a film which had been built in this way could be greatly decreased by soaking the film in benzene. Before the film was soaked it consisted of a mixture of barium stearate and stearic acid. The benzene dissolved the stearic acid, and left the barium stearate as a skeleton with air filling the spaces previously occupied by stearic acid.

A large percentage of fatty acid can be removed from a film without causing the film to shrink in thickness. In an experiment described in an earlier paper the removal of 36.3 percent of the substance of the film was accomplished with a shrinkage of only 0.8 percent in thickness.

If a film has initially a refractive index $n_1 = 1.50$, and if 50 percent of the material is removed without causing the film to shrink in thickness, the refractive index of the skeleton is 1.232. This value was calculated by means of the law of Clausius and Mosotti:

$$(n^2-1)/(n^2+2) = kd, \quad (15)$$

where d is the optical density of the film and k is a constant. The value $n_1 = 1.232$ is equal to the value given by Eq. (7) which is needed to extinguish perpendicular light reflected by ordinary soda-lime glass ($n = 1.52$). Skeleton films of this type can be easily built.

Mr. S. Bernstein has measured the spacing of the layers of a skeleton film of lead arachidate by the methods of x-ray diffraction. A skeletonized film and an unskeletonized film were built by the writer, each having 300 layers. A test film taken from the same bath lost 43 percent of its material by being skeletonized in benzene and shrank one or two percent in its optically measured thickness. Mr. Bernstein found that the skeletonized film and the unskeletonized film gave the same x-ray grating space to within 0.1 percent. The photographic plate taken with the skeletonized film as the diffracting crystal was indistinguishable, on inspection, from the plate taken with the unskeletonized film with regard to relative intensities of the various orders and the sharpness of the x-ray lines.

In general practice the percentage of material removed from a film by the action of a solvent is approximately determined by the amount of fatty acid which is present in the monolayers of which the film is built. When a fatty acid spreads in a monolayer on water containing a dissolved metallic salt, the fraction θ of the acid which is converted to soap is determined by the salt concentration in the water, the nature of the dissolved salt, and the hydrogen ion concentration as measured by pH.[9] If the bath contains barium chloride in a concentration $10^{-4}M$, θ is 0.5 for barium stearate when the pH of the bath is 7.0. In the case of cadmium chloride in a concentration $10^{-4}M$, $\theta=1$ at pH 7.0, and in order to have $\theta=0.5$ the bath must be made slightly acid, the pH being lowered to 5.7.

Recent experiments have demonstrated that built-up films of cadmium arachidate (Cd-Ar), made by spreading arachidic acid on a bath containing cadmium chloride, form skeleton films which have several advantages over the skeleton films made from barium stearate (Ba-St). In the case of Ba-St it is difficult to establish a constant value for $(1-\theta)$, the fraction of stearic acid in the film. This difficulty arises from the fact that if minute traces of foreign salts, such as the salts of copper, aluminum or lead, are present in a barium bath at pH 7.0, the surface film tends to combine selectively with these salts.[10] This results in lowering the value of $(1-\theta)$ far below the value which the film has on a barium bath when these salts are absent. The effect is so marked that the value of $(1-\theta)$ for a film of Ba-St is often used as a test for the presence of traces of impurities in the barium bath. When a bath is used containing a cadmium salt at pH 5.7, the foreign substances have little tendency to combine selectively with the surface film. This is due to the decrease in pH, since the fraction θ of soap formed by a given concentration of a given substance tends to decrease with decreasing pH.

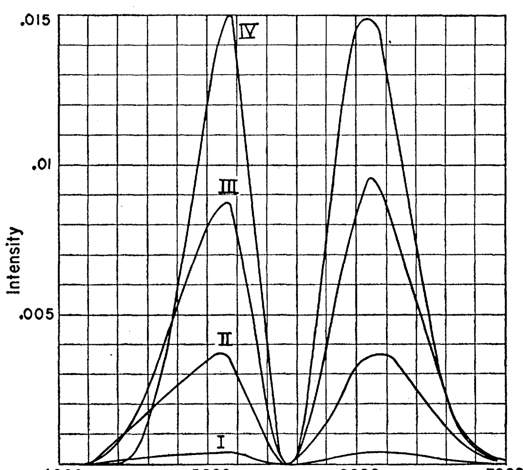

FIG. 2. Intensity of reflected light as a function of wavelength when film is illuminated by white light. Plotted for first four orders of interference minima. Curves calculated for the case of films having optical thicknesses 0.25 λ $(2a+1)$, where λ is 5550A and $a=0,1,2,3$.

Skeleton films of Cd-Ar have the further advantage that the optical quality of the films is exceptionally good. The optical quality depends on the size of the air spaces. In a perfect skeleton film these spaces are of molecular size and therefore scatter no light. If partial collapse occurs, crevices of larger size are formed which scatter more or less light and cause the film to have a fogged appearance.

The bath which is commonly used to build films of Cd-Ar is $10^{-4}M$ cadmium chloride, $10^{-3}M$ sodium acetate, $3\times10^{-5}M$ potassium cyanide, $1.2\times10^{-4}M$ hydrochloric acid. Distilled water is used which has a specific resistance 0.7 to 1.0×10^{6} ohm·cm. The sodium acetate is used as a buffer, and the potassium cyanide to remove traces of copper ions which are sometimes present in the distilled water. Oleic acid is used as piston oil. The films are built by the ordinary method. It has been found very desirable to apply the piston oil pressure immediately after the last drop of the spreading benzene solution of arachidic acid has vanished. If several seconds are allowed to elapse before the pressure is applied, the films built from the bath commonly have one or more bad streaks which are caused by imperfections in the monolayer on the water surface.

Skeleton films of Cd-Ar are made by soaking built-up films of Cd-Ar in ethyl alcohol or in acetone. One of the interesting features of skeleton films is the effect which different solvents have on films made of different substances. The most satisfactory solvent in the case of Ba-St is a mixture of 1 percent of 95 percent ethyl alcohol in benzene. This solvent acts many times more rapidly than pure benzene.

[9] I. Langmuir and V. J. Schaefer, J. Am. Chem. Soc. **58**, 284 (1936).
[10] I. Langmuir and V. J. Schaefer, J. Am. Chem. Soc. **59** 2400 (1937).

In fact, benzene is so slow in accomplishing the complete removal of stearic acid from Ba-St that the films which were supposed in the early work[6] to be completely skeletonized were found later to contain some stearic acid. In the case of calcium stearate pure benzene is as rapid as the alcohol-benzene mixture. Copper stearate forms wretched skeletons, the film collapsing to a large extent in the solvent. Lead arachidate is skeletonized very rapidly in pure benzene, to form skeletons of excellent quality. On the contrary, if Cd-Ar is soaked in benzene, carbon tetrachloride or carbon disulphide, it is nearly always cracked into a myriad of fine cracks which scatter a great deal of light. Cd-Ar films soaked in alcohol or acetone are perfectly clear.

A study of the optical properties of skeleton films can be made very simply by building a step-series of Cd-Ar monolayers on a glass slide. The layers are deposited on *both* sides of the glass. Ordinary microscope slides ($n_g=1.51$ to 1.52) are suitable for this purpose. The slides should be prepared by rubbing them with molten ferric stearate while the glass is hot (about 110°C) until every visible trace of the stearate has disappeared. Commercial lead stearate gives almost as good results. Cd-Ar monolayers attach themselves readily to a slide prepared in this way, the first layer being deposited as the slide is lowered into the water (*A* layer).

The step-series is built in about eight two-layer or four-layer steps with thicknesses ranging on either side of the thickness corresponding to $n_1t=0.25\lambda$ for visible light (Fig. 1(b)). For sodium light this thickness is built by 44 to 46 layers of skeletonized Cd-Ar when $\theta=0.5$. Before the series is skeletonized it is barely visible on a microscope slide, since the refractive index of the film ($n_1=1.54$ for Cd-Ar) is close to that of the glass. After it has been soaked in alcohol for ten sec. to two min. the steps appear as brightly colored bands. When the slide is first immersed in the alcohol the initial removal of stearic acid and corresponding lowering of n_1 is quite rapid, and with further time it proceeds more slowly. The slide should be raised fairly slowly from the alcohol to allow time for the surface to shed the alcohol which it does sometimes rapidly and at other times reluctantly. A hand windlass, of the type employed for building films, is convenient for this purpose.

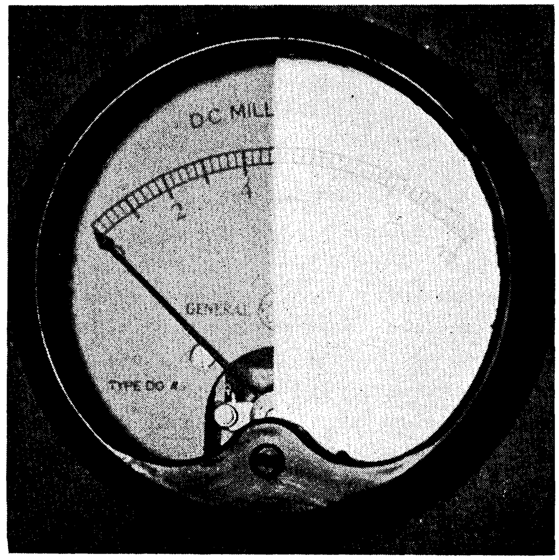

FIG. 3. Glass instrument cover illuminated by a flood light. The left side, in the photograph, was coated with a nonreflecting film.

When a slide, coated with a film, is removed from the solvent after a few seconds, the refractive index of the film in air is usually 1.35 to 1.30. At $n_1=1.35$ the steps seen by perpendicular white light form a series of colors which range continuously from yellow brown, to deep blue, to pale blue, as the steps increase in thickness. As n_1 is decreased toward the extinction value $n_1=n_g^{\frac{1}{2}}$, which is accomplished by soaking the slide for a longer time, the colors all become more vivid and the series changes to red brown, purple, deep blue and pale blue. That is, a red hue becomes very noticeable which was lacking at the higher refractive index. The progressive change as n_1 is decreased may be aptly described by saying that the colors show far more "fire." No step reflects a clear red when the thicknesses are in the range of the first minimum, but when $n_1=n_g^{\frac{1}{2}}$ the step having a thickness which extinguishes green light reflects a vivid magenta color.

The increase in the red hue serves as a very useful indicator of the approach of the refractive index to the extinction value. Dr. Langmuir has pointed out that the reason that the eye does not notice a red color in the reflected light until n_1 approaches $n_g^{\frac{1}{2}}$ is because the red color is due to the extinction of green from white light, and the wave-length corresponding to green lies at the maximum of the visibility curve for the eye.

At the first minimum the colors pass from brown to blue within a range of thickness which is quite narrow. When films are built with optical thicknesses $n_1t=0.75\lambda$, which correspond to the 2nd order of interference, the minima for the different wave-lengths extend over a range of thickness which is three times as great as for the first minimum. Consequently there is no film-thickness which reduces the reflection of white light to a value nearly so low as in the case of the first minimum. At the minima of the 3rd order and of higher orders the reflection of white light becomes increasingly greater, and approaches the value $I_g=I_B+I_C$, where I_B and I_C are the intensities of white light reflected at boundaries B and C, calculated by ordinary methods.

The reflection at the successive minima, *as seen by the eye*, can be calculated by multiplying the intensity given by Fig. 1(b) by the visibility corresponding to the different wave-lengths, as given by a visibility curve. Fig. 2 shows the result of these calculations for the minima of the first, second, third and fourth orders. The data were calculated for the case of skeleton films ($n_1=1.233$) having optical thicknesses $n_1t=5550(2a+1)/4$ A where $a=0, 1, 2$. The curves show that the first minimum is by far the most effective for diminishing reflection when white light is used. Also the first minimum is the only one for which the transmitted light appears colorless to the eye. The light transmitted by films corresponding to other minima is tinged by the color which is complementary to the color of the reflected light.

TABLE I. *Thickness and optical density of two types of film having refractive indices n_a and n_b. These are calculated for the case $n_a=1.50$. Thicknesses t_a and t_b refer to films which reflect minimum intensity of sodium light. Optical densities d_a and d_b are calculated by means of Eq. (15).*

(1)	(2)	(3)	(4)	(5)
γ	n_b	t_a/t_b ($i=0°$)	t_a/t_b ($i=80°$)	d_b/d_a
1.0	1.50	1.0	1.0	1.0000
0.9	1.45	0.9667	0.9404	0.9136
0.8	1.40	0.9333	0.8793	0.8242
0.7	1.35	0.9000	0.8159	0.7317
0.6	1.30	0.8667	0.7500	0.6358
0.5	1.25	0.8333	0.6804	0.5369
0.4	1.20	0.8000	0.6058	0.4349

The photograph in Fig. 3 shows the result of eliminating reflection from a glass instrument cover. One-half of the cover of a milliammeter was coated with a Cd-Ar skeleton film and the other half was left as clean glass. The coated half appears on the left in Fig. 3, the film being on the back and on the front of the glass. Mr. J. T. M. Malpica illuminated the instrument with a bright light in such a way that a strong glare was reflected by the clean glass, and photographed the meter in this position. The photograph shows that whereas the scale of the instrument was barely visible through the clean glass, the scale at the left was seen as plainly as though the glass were not there. People who have seen this instrument for the first time have been deceived by the illusion that there was no glass over the left side. The glass on the left actually reflected a deep purple color, but the intensity of the reflected light was so low that the color was not noticed when the attention of the observer was caught by the instrument-scale behind the glass.

The sharp boundary line between the coated and the uncoated glass, seen in the photograph, is a useful feature of films built from monolayers. This boundary is made by the line of intersection of the glass with the water surface when the film is dipped repeatedly to the same depth in the bath. A stripe can be built in the same way by dipping the glass between two fixed limits. In this case the end of the glass below the stripe receives one layer when the glass first enters the water and one layer when it leaves it, but a thickness of two layers on glass cannot be discerned by the eye.

The glass of which the instrument cover was made had a refractive index about 1.52. The procedure which was found most satisfactory in building skeleton films having $n_1=(1.52)^{\frac{1}{2}}$ was carried out in the following way. A film having 44 or 46 monolayers of Cd-Ar was built from the bath which has been described. This film was soaked for 2 min. in ethyl alcohol at room temperature, which reduced n_1 to a value which was usually less than 1.30. It was then soaked in acetone at 35°C to 40°C for 1-min. or 2-min. intervals of time, and after each interval the glass was withdrawn and the intensity with which it reflected sodium light was observed. As n_1 gradually approached the extinction value the film became nearly black when seen by sodium light, and at the extinction value it was completely black and reflected no image of the sodium lamp. When the process was carried out in this way the alcohol removed the greater part of the arachidic acid, and then the warm acetone continued the skeletonization by attacking the soap itself. The rate at which acetone dissolved Cd-Ar was found to increase rapidly with temperature and at 45°C to 50°C it dissolved the soap so rapidly that the film lost a thickness of several layers in about 5 min. and was completely dissolved after a longer period of time. At temperatures below 40°C, however, the rate at which acetone dissolved Cd-Ar throughout the body of a partially skeletonized film, i.e., the rate at which it continued to skeletonize the film, was sufficiently rapid compared with the rate at which it dissolved the surface so that the desired degree of skeletonization was accomplished before the film had lost a thickness of more than about 2 to 4 layers.

The method described in the preceding paragraph has usually given films of better quality than where fatty acid alone was dissolved. The method employed films which were built of monolayers for which the soap-fraction θ was a little greater than 0.5, rather than monolayers for which θ was 0.5 or less. From previous experience with films of other substances it seems probable that the films built with the higher value of θ had greater mechanical strength with which to withstand the strains of the processes of skeletonization. The value of θ can be varied over any desired range by adjusting the *p*H of the bath by means of HCl or NaOH.

In order to determine the correct number of monolayers for a light-extinguishing film of uniform thickness when the film is built from a given bath, it is usually desirable to test the films coming from the bath by building and skeletonizing a step-series. Films built by the processes described in the preceding paragraphs commonly suffer a loss of thickness of two to four layers, and after this number has been determined by a test run other films can be built so as to have exactly the correct thickness when skeletonized. The test is accomplished most conveniently by determining from a skeletonized two-layer step-series the number of layers having the desired thickness.

It has been shown that the thickness which a film must have in order to extinguish monochromatic light increases with increasing angles of incidence. When a film is to be built which will diminish the light as much as possible over a range of angles i_1 to i_2 this thickness can also be determined from a step-series. The film will have an effective thickness D which is greater than $0.25\lambda(2a+1)$ at $i=i_1$ and less than this value at $i=i_2$, where $i_1<i_2$.

The refractive index of a film can be measured by several methods, which will be described.

(a) When the film is a built-up film, so that a step-series can be duplicated on several different samples of glass, the most satisfactory method of measuring n_1 is to determine the glass for which the minimum of the step-series reduces the light to zero intensity. The refractive index of the film is then given by Eq. (7). The writer has used for this purpose a series of glasses ranging from lead glass, $n_1=1.7854$, to silica glass, $n_1=1.459$, which covers a range for the film from $n_1=1.336$ to $n_1=1.208$. When the refractive index of the step-series is given by $n_1^2>n_g$, the intensity of the minimum of the series increases as i is increased from $i=0$, and therefore the contrast shown by successive steps is diminished. On the contrary, in the case where $n_1^2<n_g$ the contrast increases and passes through a maximum as the angle increases.

(b) If one wishes to measure a series of values of n_1 on the same plate of glass, this may be done by measuring the intensity of the light reflected by the film. Measurements of this type have been made by Mr. Malpica, using a Hewlett cell as the light-sensitive element. The values of n_1 can then be determined by means of calculations of the type illustrated in Fig. 1(a). In many cases it is nearly as satisfactory to measure the transmission of light by the glass, and this measurement can be accomplished with a simpler optical set-up than the measurement of reflection. In the case of transmitted light due allowance must be made for the absorption of light by the glass. When the glass is a microscope slide the absorption can be measured by stacking together a pile of similar slides with a very thin layer of transparent oil between them, and measuring the

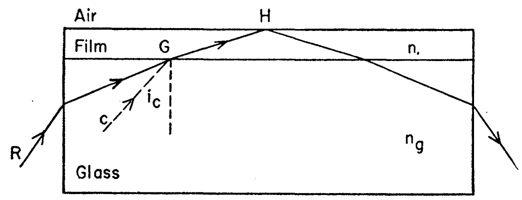

FIG. 4. Method of demonstrating the total reflection of light from the air-film boundary of a film built on glass.

decrease in transmission as the number of slides is increased. The oil should have a refractive index close to that of the glass. The effect of small differences of refractive index is small, however, for if $n_g=1.52$ for the glass and $n_1=1.49$ for the oil, the intensity reflected by a layer of oil between two glass plates is only $2(0.03/3.01)^2=2\times10^{-4}$. A batch of microscope slides, measured in this way, were found to have an absorption 0.007 per slide.

(c) A more sensitive method of measuring progressive changes of n_1 is carried out by building a step-series on a polished chromium plated slide. When films having a thickness corresponding to the first minimum for the R_s ray are built on chromium and are seen at angles of incidence 75° to 80°, a difference in thickness corresponding to 1 Cd-Ar layer (27A) is very plainly visible. If sodium light is used to illuminate a two-layer step-series on chromium, the step corresponding to the intensity minimum is seen as a black band which contrasts sharply with the brighter intensities reflected by the neighboring steps on either side.

It was shown in the section which dealt with the significance of the term "optical thickness" that as the refractive index decreases, the minimum for a given wave-length shifts to steps of higher thickness. At angles $i=75°$ to 80° the shift is nearly twice as great as for perpendicular light. This is shown by the data in columns 3 and 4, Table I.

Table I gives the values of t_a/t_b calculated for an "ideal" skeleton. An "ideal" skeleton is one which has the same thickness as the solid film from which it was made. The values were calculated by means of the equation $n_a t_a \cos r_a = n_b t_b \cos r_b$ which results from Eq. (2). Here r_a and r_b are the angles of refraction in the film corresponding to n_a and n_b. The calculations were made for the case $n_a=1.50$. The values in column 3 were calculated for $i=0°$ and in column 4 for $i=80°$. Column 1 gives values of γ where $\gamma=(n_b-1)/(n_a-1)$. Column 5 gives values of the relative density d_b/d_a calculated by means of Eq. (15). These values show that d_b/d_a is approximately equal to γ.

In order to determine the refractive index of a skeleton the value of t_a (in terms of Cd-Ar monolayers) is measured at $i=80°$ before the film is soaked. The values of n_b for the skeleton can then be determined from measurements of t_b at $i=80°$, and from the data for t_a/t_b in column 3.

The process can be carried out in another way when the skeleton is not built in a step-series. In this case the color of the skeleton film, can be matched to the color of a step-series of solid film built on a different slide. We then have $n_a \cos r_a/n_b \cos r_b = t_a'/t_b'$ where t_a' and t_b' refer to the solid film and are the thicknesses of the steps a and b of the solid film which match the skeleton before and after the latter is skeletonized. It is seen that $t_a/t_b=t_b'/t_a'$.

(d) A method for measuring n_1 has been previously described[6] which was carried out by making optical measurements of a series of eight steps having 119, 129, –189 layers of skeletonized Ba-St. This method depended for its validity on the condition that n_1 should be the same for all the steps in the series. If the steps should have a continuous variation of n_1 with thickness, this variation would result in a considerable error in the values of n_1 obtained by this method.

It has been found[8] that there are certain types of film for which the value of θ is not uniform over the area of the film, but increases continuously from one end of the slide to the other. This is due to the fact that the value of θ for each monolayer deposited as the slide descends into the water (A-layer) increases with the length of time which the slide spends under water before the next ascending layer (B-layer) is deposited. Therefore θ has a greater value at the lower end of the slide than at the upper end. In the case of a step-series built in the usual way with the thinner steps at the top of the slide and the thicker steps at the bottom, the variation in n_1 is accompanied by the variation in thickness.

The phenomenon of the increase of θ with time under water has been found to be especially characteristic of films of lead stearate, and to occur to a less marked degree with lead arachidate. In the case of lead stearate, films built from a bath which was $10^{-4}M$ $PbCl_2$, $pH=5.0$, consisted of Y layers at the top of the slide and X layers at the bottom. The results of skeletonization in benzene showed that θ was 0.75 at the top of the slide and 1.0 at the bottom. In the case of films of other substances which were built in Y layers the following method was used for testing this phenomenon. The test films were built on a chromium-plated slide with a thickness of about 40 layers over the entire dipping area. On each ascending trip, as a B layer was deposited, the slide was raised in about 1 sec. until one-half of the dipping area was out of water. It was held stationary in this position for 15 to 30 sec. and was then raised rapidly the remaining distance. The A layers were deposited in the usual manner by lowering the slide rapidly to the full depth of the dipping area. The film was skeletonized, and if θ for the A layers had increased during a time 15 to 30 sec. under water, the result was seen as a line of contrast between the colors reflected by the upper and lower halves. Tests were made with lead arachidate using the bath described above. They showed differences of refractive index amounting to two to five percent between the values of n_1 for the two halves.

(e) The method of measuring n_1 by means of Brewster's angle i_B has also been previously described.[6] This is a very useful method in the case of isotropic substances. Built-up films of the soaps of fatty acids are uniaxial crystals and retain their property of birefringence after being skeletonized. In the case of a birefringent substance the value of i_B is a function of the two refractive indices n_1 and n_3 of the ordinary and extraordinary rays. Therefore a measurement of i_B does not lead to a determination of the value of either n_1 or n_3 unless further data are available, such as the data giving the birefringence (n_3-n_1) of the substance. However, measurements of i_B have frequently proved useful in the present experiments as a rough indication of the progressive decrease of n_1 where a film is soaked for successive intervals of time. Since the film remains birefringent, i_B decreases with n_1.

Skeleton films absorb oil very readily. Oil fills the pores of the skeleton, and if the refractive index of the oil is the same as that of Cd-Ar the oil restores the refractive index of the film to the value which the film had before it was skeletonized. Oil is used to determine whether a skeleton is an ideal skeleton or has a partially collapsed structure. A drop of mineral oil is allowed to flow across the film. The oil does not wet the surface of the film permanently but withdraws from the path which it has traveled, leaving the pores of the film over which it has traveled filled with oil. If the skeleton has the thickness t of the solid film from which it was made, the oil restores the color exactly to the color of the original film; if the skeleton has shrunk in thickness the color is different.

Total Reflection

The phenomena of interference, as exhibited by thin films, have no effect whatever on the phenomena of total reflection which occur when light is reflected from a surface at angles greater than the critical angle. It follows from Eqs. (5) and (6) that if either B or C is unity, $I_+=I_-=1$. Lord Rayleigh[11] pointed out this interesting fact in the following way. "When a thin transparent film is backed by a perfect reflector, no colours should be visible, all the light being ultimately reflected whatever the wave-length may be. The experiment may be tried with a thin layer of gelatin on a polished silver plate."

[11] "Wave Theory of Light." Published in *Scientific Papers*, Lord Rayleigh (Cambridge University Press, 1902), Vol. III, p. 67.

TABLE II. *Spacings of laminae. The optical thicknesses are given in column 4 and column 5. The amplitudes B, C_1 and C_2 of the rays reflected at the air-P, PQ and Q-glass boundaries, respectively, were calculated by means of Eqs. (3) and (4). Column 9 gives the expression for the resultant of the three rays (neglecting the effect of multiple reflections).*

(1)	(2) n_P	(3) n_Q	(4) $(n_1t/\lambda)_P$	(5) $(n_1t/\lambda)_Q$	(6) B	(7) C_1	(8) C_2	(9) Resultant Amplitude
(a)	1.52	1.236	0.25	0.5	−0.206	0.103	−0.103	$B+C_1-C_2$
(b)	1.52	1.87	0.25	0.25	−0.206	−0.103	0.103	$B-C_1+C_2$

The experiment may be done very convincingly by building a film n_1 on a block of glass n_g and illuminating the film by means of light R traveling in the direction shown in Fig. 4. It is found that the glass then reflects light as though the film were not there whether n_1 is greater or less than n_g. Let i_C be the critical angle for glass at a glass-air boundary. It follows from the laws of reflection and refraction that a ray C which is incident on the film at an angle i_C at the glass-film boundary is refracted in the film and arrives at the film-air boundary at an angle which is the critical angle for that boundary. Therefore all rays, such as R, which arrive at G at an angle greater than i_C are totally reflected at H. A film illuminated in this way can be said to be "backed" by a perfect reflector for every wave-length, the air serving as the "backing" material. Fig. 4 illustrates the case for glass $n_g=1.50$, $n_1=1.45$.

It should be mentioned in this connection that since built-up films of Ba-St and Cd-Ar are uniaxial crystals, the birefringence can be studied in an interesting way by the method of illumination illustrated in Fig. 4. If the films are built in a series of about 8 steps having 40, 80, . . . 320 layers on glass $n_g=1.52$, and the glass is held between parallel or crossed Polaroid screens, the colors which are seen due to birefringence are very striking. Quantitative measurements of the path difference between the R_s and the R_p rays can be made as a function of film thickness, angle, and n_g. An interesting demonstration of the range of phase changes which occur at total reflection can be made by "backing" one-half of the film with a strip of paper wet with water while the remainder is backed by air. The series of colors of the steps seen between Polaroid screens is shifted, the steps backed by water having colors which correspond to a smaller phase difference between the two rays than the steps backed by air.

Laminated Films

Several types of crystals occur in nature which are composed of alternating laminae of substances of different refractive index, the laminae having spacings which are comparable with a quarter-wave-length of light. These crystals have interesting optical properties which have been studied by Lord Rayleigh, R. W. Wood,[12] and others. In the present experiments laminated films were built with combinations of skeleton and solid films, and with evaporated films of zinc sulphide and built-up Ba-St films.

Table II illustrates the spacings which laminae of two different substances of refractive index n_P and n_Q must have in order that a film composed of one lamina of each substance shall extinguish the light reflected from glass ($n_g=1.52$). The data were calculated for the case where one lamina of Q was built on the glass, and one lamina of P on top of Q.

Laminated films built in this way have total optical thicknesses greater than 0.25λ. Therefore when they are used with white light they reflect more light than a film which corresponds to curve I, Fig. 2.

Etching of Glass by Chemical Treatment

Various types of lead glass and barium glass having refractive indices 1.61 to 1.72 have been etched with nitric acid to produce films which showed interference colors. The films that were formed by the etching process were found to have a refractive index approximately 1.46. This is the refractive index of fused quartz. The film is hard and can be rubbed vigorously with a cloth or with a mild abrasive such as Shamva without being scratched or showing a decrease of thickness. It is completely dissolved by boiling NaOH. The porosity of the film is very slight. When oil is placed on part of the film and is then rubbed off with a towel, no visible trace is left of the effect of the oil on the film. This shows that the film takes up no oil, or takes up so small an amount that the refractive index is not altered by an amount which causes the interference colors seen with white light to be visibly changed.

Mr. Malpica has made the following measurements of the reflection of light by two samples of glass, No. 1 and No. 2, which were etched so as to have films of optical thickness 0.25λ:

	No. 1 $n_g=1.72$	No. 2 $n_g=1.61$
Etched glass	2.4 percent	2.83 percent
Unetched glass	11.2 percent	9.66 percent

[12] R. W. Wood, *Physical Optics* (Macmillan Co., 1914), second edition, p. 161.

It was usually found necessary to prepare a glass surface for the etching treatment by polishing the glass with a fine grade of polishing rouge or by immersing it in boiling N/5 NaOH. This preparation accelerated the rate at which the glass was etched when it was put into acid. One sample of lead glass which had not received this preliminary treatment was not visibly attacked by nitric acid after many hours in the acid, but after being boiled in NaOH to remove the surface skin it was etched quite rapidly.

Measurements were made of the rate at which glasses No. 1 and No. 2 were etched in 1 percent nitric acid. Glass No. 1 was a sample of lead glass, of the type used to make x-ray screens. Dr. L. Navias measured the refractive index of this glass and found $n_g=1.695$ which corresponds to 60 percent PbO_2. This sample was etched in 1 percent HNO_3 at 100°C. Four pieces of the glass were boiled in NaOH until all stains had been removed, and were then plunged immediately into the boiling acid. The pieces were withdrawn one at a time, after measured intervals of time, and plunged into hot distilled water to rinse off the acid. After being removed from the water they were rubbed with molten paraffin to prepare the surface to receive built-up layers of Ba-St. The thickness of the film which resulted from the etching was measured in terms of layers of Ba-St by counting the number of layers which were needed to bring the film to the thickness corresponding to the first minimum for perpendicular sodium light, $N_I=40$, or to the second minimum, $N_{II}=122$. The data in Table III were obtained in two series of measurements, A and B. The same glass was used for both series, the silica film which produced the colors being completely removed by boiling NaOH after each series of measurements. The thicknesses in the table are given in terms of number of Ba-St layers ($n_1t=36$A per layer). When the data in Table III are plotted on double-log paper they lie quite closely on a straight line. The slope of the line shows that the thickness increases with the 0.37 power of the time.

TABLE III. *Thickness of film produced on lead glass, $n_g=1.72$, by etching in boiling* HNO_3 *for lengths of time t. Thickness is given in terms of number N of layers of* Ba-St. *($n_1t=36A$ per layer).*

t	Thickness N_A	Thickness N_B
15 sec.	30	32
1 min.	47	51
3 "	70	72
8 "	109	
9 "		113

Glass No. 2 was received from Dr. C. E. K. Mees. It was a sample of glass obtained from Bausch and Lomb Optical Company, of a type described in their most recent catalog as "DBC-3", $n_D=1.61088$. This sample was etched far more readily by 1 percent HNO_3 than sample No. 1. Therefore the etching was carried out in acid at 40°C since the rate of etching decreased rapidly with decreasing temperature. The rate was found to be linear with time, the thickness increasing at a rate equal to 26 Ba-St layers per min. in the acid.

A step-gauge was made by etching this glass in steps. The glass was polished with rouge and was then held in a vertical position and lowered to successive depths of 0.5 cm, 1.0 cm, etc., for one minute at each depth. The result was a step-series showing bright colors which were matched by the colors of a Ba-St series having 20, 46, 72, 98, 124 layers.

The step-gauge made with etched glass is well suited to measurements made with the gauge under water, such as are made in studying adsorption of substances from solution. The colors are more vivid when seen under water than when seen in air, since n_1 for the film has more nearly the value given by Eq. (7) when $n_0=1.33$ for water than when $n_0=1.0$ for air. On the contrary the colors of the usual type of step-gauge, which is made of Ba-St steps built on polished chromium, are so faint under water as to be almost invisible when seen by perpendicular light.

Films of Evaporated Substances

Dr. C. W. Hewlett has reported the following experimental results:

"Thin films were made by evaporating in vacuum various substances such as calcium fluoride, sodium fluoride, and lithium fluoride. The films were evaporated on glass microscope slides. After the glass was cleaned by the ordinary processes, and heated in a blue Bunsen flame, it was subjected to a glow discharge for a few minutes before evaporation began.

"The material to be evaporated was melted down to a clear bead on a platinum or tungsten filament, and a small amount was allowed to evaporate before the glass plate was moved into position to receive the deposit. Special magnetic rotating devices were provided for moving the plate, and also for rotating it during the evaporation so as to deposit a film on each side of the plate. The thickness of the evaporated film was controlled by observing the reflected image of the filament in the surface of the deposit, and discontinuing the evaporation when the correct color was reached.

"Films of calcium fluoride, CaF_2, were found to have the lowest refractive index of the films which were made in this way. When the CaF_2 was evaporated in vacuum the refractive index of the film was 1.22. The refractive index was determined from a measurement of Brewster's angle for the film. Glass of refractive index 1.52 transmitted 92 percent of white light when the glass was not coated, and 99 percent when both surfaces were coated with CaF_2. These films had very poor mechanical properties, being easily scratched by light pressure from a handkerchief. Various heat and chemical treatments were ineffectual in hardening them. The films were not removed by being immersed in hot water.

"Sodium fluoride films were harder, but were not quite so good optically, and were soluble in water. The refractive index of the NaF films was 1.29, and glass coated on both sides with films having an optical thickness of a quarter-wave-length transmitted 98 percent of white light. It required considerable pressure and rubbing with a soft cloth to scratch them. A mixture of four parts CaF_2 and one part NaF, by molecular weight, produced a film of intermediate hardness, refractive index 1.27, and transmission 98.5 percent.

"Lithium fluoride produced films which were quite satisfactory mechanically, they would stand vigorous rubbing with a soft cloth without being scratched. Glass covered on both sides with quarter-wave-length films transmitted 98 percent. Unfortunately these films were readily soluble in cold water.

"The refractive index of each of these three substances could be controlled within certain limits by adjustment of the gas pressure during evaporation, the greater the pressure the lower the refractive index. However, if the pressure was as high as 5μ there resulted a perceptible decrease in the hardness of the film, and if the pressure was as high as 10μ there was non-uniformity in the thickness of the evaporated layer, owing apparently to the presence of convection currents."

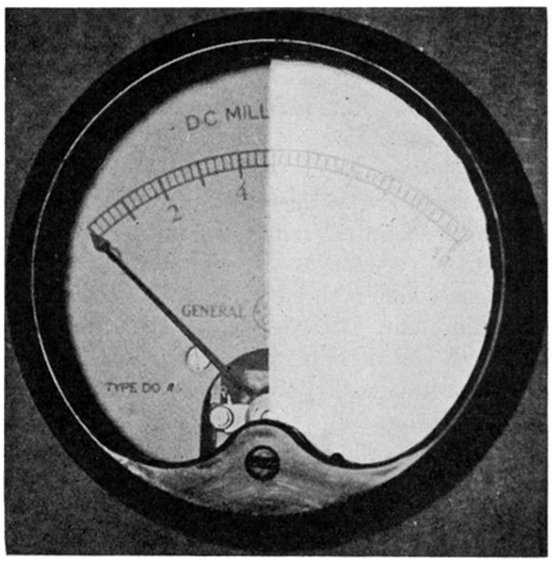

FIG. 3. Glass instrument cover illuminated by a flood light. The left side, in the photograph, was coated with a nonreflecting film.