Title
PROFILES OF SUPERMENISCUS ELECTROLYTE FILMS ON PARTIALLY SUBMERGED GAS ELECTRODES

Permalink
https://escholarship.org/uc/item/11d4b6pt

Author
Turney, John H.

Publication Date
1971-08-01
PROFILES OF SUPERMENISCUS ELECTROLYTE FILMS
ON PARTIALLY SUBMERGED GAS ELECTRODES

John H. Turney
(M.S. Thesis)

August 1971

AEC Contract No. W-7405-eng-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Contents

ABSTRACT ........................................................................... v
I. INTRODUCTION .............................................................. 1

II. THEORY
   A. Optical Interference in Thin Films ................................. 5
       1. Sign Convention ...................................................... 6
       2. Reflection Coefficients .......................................... 9
   B. Optimum Angle of Incidence ..................................... 22
       1. Double Beam Model ............................................... 24
       2. Multiple Beam Model .............................................. 26
   C. Colorimetry of Interference Colors .........................
       1. Elements of Colorimetry ........................................ 28
       2. Derivation of Color Charts .................................... 30

III. EXPERIMENTAL .......................................................... 37
   A. Optical
       1. Optical Bench ...................................................... 38
       2. Alignment ............................................................ 43
       3. Spectrophotometer ............................................... 44
   B. Chemical
       1. Cell ................................................................. 49
       2. Liquid System ...................................................... 49
       3. Gas System ......................................................... 54
       4. Electrodes ........................................................... 54
       5. Preparation of Surfaces and Solution ..................... 59
IV. ANALYSIS OF DATA
   A. Visual ................................................................. 67
   B. Spectrophotometer .................................................. 67
V. RESULTS ................................................................. 69
   A. Optimum Angle of Incidence ...................................... 69
   B. Color Charts ....................................................... 75
   C. Film Profiles ...................................................... 77

APPENDIXES
   I. FORTRAN IV COMPUTER PROGRAM MINIM .......................... 83
   II. FORTRAN IV COMPUTER PROGRAM CHROM .......................... 97
   III. FORTRAN IV COMPUTER PROGRAM MBINF ........................ 108

REFERENCES ............................................................... 122
Profiles of Supermeniscus Electrolyte Films On Partially Submerged Gas Electrodes *

John E. Turney

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California
Berkeley, California

ABSTRACT

The use of white light optical interference for the quantitative
determination of the local thickness of thin transparent films on metal
surfaces has been investigated. Two methods have been used: spectral
analysis and visual interpretation of interference colors. A ratio-
recording double beam spectrophotometer has been built for measuring the
spectral attenuation of reflected polarized light due to thin film inter-
ference. With a knowledge of the optical constants of film and substrate
material, comparison with computations yields a local film thickness.
Because the conventional series of interference color are not valid for
metal-supported films, the principles of tristimulus colorimetry have
been employed for the prediction of generalized interference color series,
valid for multiple beam interference with any phase change and a wide
range of amplitude changes due to reflection. Thus, quantitative film
thickness data can be derived from the visual or photographic observation
of interference colors. An optimum angle of incidence, which depends on
the optical properties of film and substrate, has been computed to maxi-
mize the visibility of thin film interference phenomena. Application of
these techniques has been demonstrated with aqueous KOH films on platinum
and stainless steel surfaces.

* M.S. thesis, research conducted under the direction of R. H. Muller.
I. INTRODUCTION

The spreading of thin liquid films on solid surfaces has been known for many years. Early observed films include those of hydrocarbons (1) and liquid helium (2). In 1961 Will postulated the existence of thin films of electrolyte above the intrinsic meniscus on partially submerged platinum-hydrogen electrodes (3). The presence of these films was proposed to explain current-voltage-height relations that he obtained experimentally. Will found that a partially submerged hydrogen-platinum electrode may supply up to 36 times the current of the same electrode totally submerged. Bennion (4) calculated and measured the current distribution on partially submerged silver and nickel electrodes. He found current densities up to 2000 times higher on the film covered surface than on the surface 2 mm below the liquid level. These high current densities were in the region of the top of the meniscus and decreased, due to ohmic resistance of the electrolyte, with height.

Thin liquid films are important and have been studied in several areas. In lubrication, the spreading of oils into inaccessible areas is important to the operation of penetrating oils. The spreading of oil is also of concern to makers of such instruments as watches and meters. In these applications oil should not spread away from the bearings (1).

Thin films are also of importance in porous gas evolution electrodes (5). A thin liquid film surrounds a gas bubble in a capillary allowing currents to flow around the bubble. With current flowing around the bubbles, interior areas of the electrode become useful.
Several mechanisms for the stabilization of these films have been proposed. Lightfoot and Ludviksson (6) have suggested that these films are dynamic in nature with the outer portion of the film rising due to surface tension gradients. These gradients could either be caused by concentration gradients due to reaction or caused by temperature gradients. A dynamic film with a surface tension gradient was also suggested by Chizmadzhev and Markin (7). They suggested that the surface tension gradient was caused by evaporation of the solvent when no current flows. Bikerman (8) has suggested that these films are held in place by surface roughness. Deryagain (9) has reported that the properties of water in thin films and capillaries is much different than in the bulk form.

The variation of film thickness with various parameters has also been investigated. These include variation of concentration, polarization and linear current density. The thickness of electrolyte films seems to vary with concentration in KOH. Electrical measurements by Belokopytov et al. (10) indicate that a thickness maximum occurs at a concentration of 5N. The effect of polarization is not so clear. Burshtein, et al. (11) found that for KOH and H₂SO₄ solutions, the films were thinnest with no polarization. The thickness increased with cathodic and anodic polarization, with the latter having the greater effect. Shepelin (12) was able to grow films on a dry surface if the reaction occurring at the electrode concentrated the electrolyte near the electrode i.e. H₂ oxidation in H₂SO₄ solution, or O₂ reduction in KOH solution. If the reaction was reversed, so that the electrolyte was diluted, no film would form. Muller (13) found that, in KOH, as the linear current
density (current per meniscus length) was increased cathodically, the film thickened and then broke into droplets.

The electrolyte films have generally been formed experimentally by pulling the electrode out of the solution and allowing the film to drain until it reached a stable profile. Two exceptions have been observed. Shepelin (12) has observed the creep of electrolyte up an electrode face as mentioned in the previous paragraph. He has also observed that with dilute (0.1 N) KOH solutions a film will form with no polarization on a dry surface. No film would form under the same conditions with a concentrated (5N) KOH solution. Muller (13) has observed a film of 3.4N KOH climb up an extremely thin film of distilled water previously covering the surface. The films of Shepelin did not reach as high as those of other workers who allowed the film to drain from a previously submerged electrode. Shepelin's films reached a height on the order of 0.5-1 cm. The major reason that films are formed by draining appears to be that it is difficult to clean the electrodes sufficiently and keep them clean while they are dry.

In order to quantitatively study these liquid films it is necessary to know their thickness profiles. There are several methods available which could be used. These include mechanical, electrical and optical methods. The first method disturbs the film to a large degree. The second method requires a knowledge of the local conductance of the solution, which is a strong function of concentration. The third, optical methods, includes light interference. This method disturbs the film little, is accurate, and has been used by most of the workers in this field. However, there are uncertainties in the interpretation of results.
which have been overlooked. These are: the uncertainty in interference order, the phase change at the metal-liquid surface, and the effect of multiple reflections on the interference colors. Wavy film profiles have been reported by Chesnokov and Chismadjev (14). These may have been the result of these uncertainties. The purpose of this work is to clarify these uncertainties.
II. THEORY

A. Optical Interference in Thin Films

Several methods can be considered for determining the thickness of transparent liquid films in the range of 0.1-1.5 microns. These may be divided into mechanical, electrical and optical techniques. Methods belonging to the last group offer the advantage of minimal disturbance to the film. In particular, light interference combines high resolution with the capability to simultaneously observe extended areas of film.

Optical interference in a transparent thin film not only depends on the thickness of the film but also on its refractive index, which is determined by chemical composition. For most aqueous solutions, the refractive index is a weak function of concentration; an approximate knowledge of composition is therefore sufficient for satisfactory thickness determinations of such liquid films. For instance, a change in concentration from 3N to 7N KOH causes an error in thickness of less than 2%.

Optical interference in a liquid film on a metal substrate is due to the interaction of light waves reflected from the air-liquid and liquid-metal interfaces. If monochromatic light is incident on the film, the interference results in intensity variations in the reflected light. These intensity variations are a function of the film thickness and repeat themselves with each increment of one wavelength optical path difference up to differences of tens of wavelengths or more (depending on the coherence of the light source). Each variation is identical with the previous ones. If white light is incident on the film, the interference similarly produces intensity variations, the period of which depends upon the
wavelength, which result in variations of color as a function of film thickness. These colors are non-repetitive for films up to a few wavelengths optical thickness but disappear for films thicker than about 2.5μ. The use of monochromatic light is therefore best for the study of thick films and thickness variations without regard to absolute value, while white light is preferable for thin films of interest in this work.

1. **Sign Convention**

The literature on optical reflection is confused by a great variety of conventions. Although the choice of any arbitrary set of conventions does not affect the end results, the consistent application of the same conventions throughout all derivations and the interpretation of results is crucial.

Figure 1 defines the directions of the positive electric field vector components (E) normal (s) and parallel (p) to the plane of incidence. With this coordinate system, the Fresnel reflection coefficients \( r_s \) and \( r_p \) for reflection from the interface of two dielectric media take the form given in Eqs. (1) and (2),

\[
\begin{align*}
    r_s &= \frac{E''}{E'} = -\frac{\sin(\phi - \phi')}{\sin(\phi + \phi')} \quad (1) \\
    r_p &= \frac{E''}{E'} = -\frac{\tan(\phi - \phi')}{\tan(\phi + \phi')} \quad (2)
\end{align*}
\]

where \( E \) and \( E'' \) are the electric field amplitudes of incident and reflected waves, respectively. \( \phi \) and \( \phi' \) are the angles of incidence and refraction, respectively, as defined in Fig. 2.
Fig. 1. Direction of positive electric field vectors for:

(a) s-polarization

(b) p-polarization
Fig. 2. Angle of incidence, $\phi$, refraction, $\phi'$, and reflection, $\phi''$. $\phi$ and $\phi'$ are related by Snell's Law:

$$n_1 \sin \phi' = n_0 \sin \phi$$

also,

$$\phi = \phi''$$
A plot of Eqs. (1) and (2) as a function of the angle of incidence \( \phi \) is shown in Fig. 3a.

The magnitude, \( r \), and phase, \( \delta \) of a complex number, \( r \), may be represented as:

\[
\mathbf{r} = r e^{i\delta} = (r \cos \delta) + i(r \sin \delta)
\]

The negative reflection coefficient in Fig. 3a represents a phase change of \( 180^\circ \) (since \( e^{i\pi} = -1 \)). Figure 3b shows the reflection coefficients with the absolute magnitude and phase separated. The latter representation will be used in this treatment: Reflection and transmission coefficients for amplitude and intensity will always be positive numbers. Phase changes will be given by \( \delta_n \), where the subscript \( n \) indicates the polarization or the interface of reflection. There is no phase change upon transmission through a dielectric interface. \( \delta \) without subscript designates a phase change due to the optical path in a film.

2. Reflection coefficients

For pure s and p polarization the reflection (amplitude) coefficients for a unit incident ray are ( ):

\[
r_s = \left| \frac{-\sin(\phi - \phi')}{\sin(\phi + \phi')} \right| = \left| \frac{n_o \cos \phi - n_1 \cos \phi'}{n_o \cos \phi + n_1 \cos \phi'} \right|
\]

\[
r_p = \left| \frac{\tan(\phi - \phi')}{\tan(\phi + \phi')} \right| = \left| \frac{n_o \cos \phi' - n_1 \cos \phi}{n_1 \cos \phi + n_o \cos \phi'} \right|
\]

where \( n_o \) is the index of refraction of the medium from which the ray is incident and \( n_1 \) is the index of refraction of the medium which the ray is incident upon.
Fig. 3. Alternate representations of the Fresnel reflection coefficient for reflection from a dielectric interface \( (n_1 > n_0) \).

(a) Phase change expressed as negative sign.

(b) Phase and amplitude (argument and modulus) of complex reflection coefficient separated.
The angle of incidence where $\phi + \phi' = \pi/2$ and $r_p = 0$ is known as Brewster's angle.

For dielectric reflection from a medium of higher refractive index than the incident medium (external) $\delta_s$ and $\delta_p$ are equal to $\pi$ below Brewster's angle. Above Brewster's angle, $\delta_p$ becomes 0. For reflection from a medium of lower refractive index than the incident medium (internal), $\delta_s$ and $\delta_p$ are equal to 0 below Brewster's angle. Above Brewster's angle $\delta_p$ becomes $\pi$. This results from the interchange of $\phi$ and $\phi'$ and $n_0$ and $n_1$.

The transmission (amplitude) coefficients for a unit incident ray are (15):

\[ t_s = \frac{2n_0 \cos \phi}{n_0 \cos \phi + n_1 \cos \phi'} \]  
\[ t_p = \frac{2n_0 \cos \phi}{n_1 \cos \phi + n_0 \cos \phi'} \]

For the case of reflection from an absorbing medium (e.g., metal) the index of refraction is a complex number. The complex index of refraction, $n_c$, can be written in the form:

\[ n_c = n(1+ik) \]

where $k$ is called the absorption coefficient. The values of $n$ and $k$ are available from the literature or by ellipsometric measurement of the surface.

The reflection coefficients for an absorbing medium in contact with a dielectric were derived by Mowat and Muller (16). These can be written as:
\[
\begin{align*}
\frac{E''}{E_s} &= \sqrt{\frac{A^2 + B^2 - 2A \cos \phi + \cos^2 \phi}{A^2 + B^2 + 2A \cos \phi + \cos^2 \phi}} \\
\frac{E''}{E_p} &= rs \sqrt{\frac{A^2 + B^2 - 2A \sin \phi \tan \phi + \sin^2 \phi \tan^2 \phi}{A^2 + B^2 + 2A \sin \phi \tan \phi + \sin^2 \phi \tan^2 \phi}}
\end{align*}
\] (9)

(10)

where \( E_s \) and \( E_p \) are defined in Fig. 1, and

\[
A^2 = \frac{1}{2} \left\{ + \sqrt{[N^2(1-K^2) - \sin^2 \phi]^2 + 4N^4K^2 + N^2(1-K^2) - \sin^2 \phi} \right\} \\
B^2 = \frac{1}{2} \left\{ + \sqrt{[N^2(1-K^2) - \sin^2 \phi]^2 + 4N^4K^2 - N^2(1-K^2) + \sin^2 \phi} \right\}
\] (11)

(12)

A and B are the positive square roots of \( A^2 \) and \( B^2 \). \( N \) is the real part of the complex index of refraction divided by the refractive index of the contacting dielectric medium.

\[
\delta_s = \tan^{-1} \left[ -\frac{2B \cos \phi}{A^2 + B^2 - \cos^2 \phi} \right] 
\] (13)

(14)

where \( 0 \leq \delta_s \leq \pi \).

\[
\Delta = \tan^{-1} \left[ -\frac{2B \sin \phi \tan \phi}{A^2 + B^2 - \sin^2 \phi \tan^2 \phi} \right] 
\]

and

\[
\delta_p = \Delta + \delta_s
\] (15)

where

\(-\pi \leq \Delta \leq 0\)
3. Thin Film Interference

In the following sections, the equations are valid for either polarization. The subscripts s and p will be omitted. The subscript 1 refers to reflection from the liquid-metal interface. The subscript 2 refers to internal reflection from the gas-liquid interface or transmission from the liquid to the gas. The subscript 3 refers to external reflection from or transmission through the gas-liquid interface with the beam incident from the gas (see Fig. 4).

a. Double beam model

Double beam interference results from the interaction of only two rays of light. It is realized in several interferometers (e.g., Michelson, Mach-Zehnder, Rayleigh) and in the polarizing microscope. Furthermore, it is of interest here as an approximation to thin film interference for film surfaces of low reflectivity. Because of its simplicity, it is useful as an aid to the understanding of the more correct multiple beam approach.

For the case of double beam interference, the intensity of the light reflected from a surface covered with a film of thickness d and index of refraction n (see Fig. 5) is the sum of rays a and b. The rays are added as amplitudes, considering the relative phase of the waves.

Using the notation of Section I-1, the complex amplitude of ray a in Fig. 5 is (assuming an incident ray of unit amplitude and phase zero):

\[ U_a = r_3 e^{i\delta_3} \]  

(16)
Fig. 4. Identification of reflection and transmission coefficients, with associated phase changes due to reflection from different interfaces.
Fig. 5. Double beam model of thin film interference.
The amplitude of ray b is:

\[ U_b = t_2^* t_3 r_1 e^{i(\theta + \delta_1)} \]  

(17)

\( \delta \) is the phase change of ray b relative to ray a in Fig. 5 due to b's passage through the film. The optical path difference, \( \Delta S \), due to the presence of the film is (13):

\[ \Delta S = 2nd \cos \phi' \]  

(18)

The corresponding phase change is:

\[ \delta = \frac{2\pi \Delta S}{\lambda} = \frac{4\pi nd \cos \phi'}{\lambda} \]  

(19)

where \( \lambda \) is the wavelength of the light. The resultant amplitude for a unit incident ray, due to the superposition of a and b, is:

\[ U = U_a + U_b = r_2^* e^{i\delta} + t_2^* t_3 r_1 e^{i(\theta + \delta_1)} \]  

(20)

The intensity is derived by multiplying by the complex conjugate, \( U^* \):

\[ I = (U)(U^*) = r_2^2 + (t_2^* t_3 r_1)^2 + 2t_2 t_3 r_1 r_2 \cos(\delta - \delta_1) \cos(\theta + \delta_1) \]  

(21)

It can be seen that the intensity varies as the cosine of the film thickness (see Fig. 6). The spacing of the maxima and minima is proportional to wavelength. The variation of intensity with wavelength, at constant film thickness, is proportional to the cosine of the inverse of the wavelength. This variation causes a film viewed in white light to be colored. As seen in Fig. 7, as the optical path difference increases, more maxima and minima fall in the visible region. This allows the spectra of different interference orders to be distinguished.
Fig. 6. Double beam interference. Variation of resultant intensity with optical path difference, $\Delta S$, between the two beams for two different wavelengths.
Fig. 7. Double beam interference. Variation of resultant intensity with wavelength for three optical path differences between the beams. (Refractive index independent of wavelength).
b. **Multiple beam model**

Multiple beam interference is a more exact model for thin film interference than double beam interference when multiples of the optical path difference are possible. Multiple beam interference results from the addition of rays which have been internally reflected from the air-liquid interface to the rays in the double beam case. See Fig. 8.

The derivation of the multiple beam intensity is similar to that of the double beam case. The amplitudes of the reflected rays are (17):

\[ U_a = r_3 e^{i\delta_3} \]  
\[ U_b = t_3 r_1 t_2 e^{i(\delta_1 + \delta_3)} \]  
\[ U_c = t_3 r_1 r_2 t_2 e^{i(\delta_1 + \delta_3 + \delta_2)} \]  
\[ U_d = t_3 r_1 r_2 r_2 t_2 e^{i(\delta_1 + 2(\delta_2 + \delta_3))} \]

In each additional reflected ray, the power of \( r_1 r_2 \) is increased by one. The amplitudes of multiple reflection \((c,d,\ldots)\) become progressively smaller by this amount. For low reflectivity surfaces (e.g. air-glass, air-liquid) the high order terms become insignificant compared to the first two terms, and double beam interference can be used as a good approximation. If either or both surfaces are highly reflective, with \( r_2, r_3 \) or \( r_1 \) close to one (e.g. metals, dielectrics at high angles of incidence), the multiple reflections are important.

The sum of the rays \( a, b, c, d, \ldots \) is an infinite series:

\[ U = r_3 e^{i\delta_3} + t_3 t_1 r_1 e^{i(\delta_1 + \delta_3)} \left[ 1 + r_1 r_2 e^{i(\delta_1 + \delta_3)} + \frac{2i(\delta_1 + \delta_3)}{1 + r_1 r_2} + \ldots \right] \]
Fig. 8. Multiple beam model of thin film interference.
Fig. 9. Multiple beam interference. Variation of resultant intensity with optical path difference, $\Delta S$, between successive reflections for three different amplitude reflection coefficients. The wavelength is 580 nm. Total phase change upon reflection, Eq. 46, is zero.
of the general form:

$$A e^{i\alpha} (1 + B e^{i\beta} + B^2 e^{2i\beta} + \ldots) = \frac{A e^{i\alpha}}{1-B e^{i\beta}}$$  \hspace{1cm} (24)

so that:

$$U = r_3 e^{i\beta} + \frac{t_2 t_3 r_1 e^{i(\delta_1 + \delta_2)}}{1-r_1 r_2 e^{i(\delta_1 + \delta_2)}}$$  \hspace{1cm} (25)

To derive the intensity, the amplitude must be multiplied by its complex conjugate $U^*$. This is most easily done by multiplying the numerator and denominator of the second term by the complex conjugate of the denominator and the resulting expression by the whole complex conjugate (17):

$$I = (U)(U^*) = r_3^2 + \frac{(t_2 t_3 r_1)^2 + 2t_2 t_3 r_1 r_3 \cos(\delta_1 - \delta_2) - 2t_2 t_3 r_1^2 r_2 r_3 \cos(\delta_2 + \delta_3)}{1 + (r_1 r_2)^2 - 2r_1 r_2 \cos(\delta_1 + \delta_2)}$$  \hspace{1cm} (26)

Here the dependence on the thickness and wavelength is more complicated. However, the location of the maxima and minima are the same as for the double beam case (18). Curves of intensity as a function of the phase difference, $(\delta_1 - \delta_2)$, are given in Fig. 9 for different reflectivities. Curves of intensity as a function of wavelength are given in Fig. 10.

**B. Optimum Angle of Incidence**

When the amplitude of the light reflected from the two interfaces is different the intensity minimum cannot go to zero. The contrast of the fringes is consequently reduced, making observation difficult. With a given film on a given substrate, the only method of substantially changing the relative reflectivity of the two interfaces is to vary the
Fig. 10. Multiple beam interference. Variation of resultant intensity with wavelength for three different amplitude reflection coefficients. Optical path difference 1.0 micron. Total phase change upon reflection, Eq. 46, is zero.
angle of incidence (see Eqs. 1-12). For a highly reflective liquid-metal interface, and a faintly reflective gas-liquid interface, increasing the angle of incidence from the normal increases the reflectivity of the gas-liquid interface and decreases the transmission coefficient as given by Fresnel's equations. At some angle between zero, where the liquid-metal surface is the more reflective, and grazing incidence, where the gas-liquid surface is totally reflective and not transmitting, an optimum angle can be found where the greatest contrast between interference maxima and minima occurs.

The Michelson fringe visibility, $V$, is (19):

$$V = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$$

(27)

At the optimum angle $V = 1$. This condition is equivalent to finding the angle where the minimum intensity is zero.

1. Double Beam Model

For the double beam model the intensity is given by Eq. 21

$$I = r_3^2 + (t_2 t_3 r_1)^2 + 2 t_2 t_3 r_1 r_3 \cos(\delta + \delta_1 - \delta_3)$$

(21)

Because the third term of Eq. 21 is the only possible negative term, and since all $r$'s and $t$'s are positive, a minimum will occur when:

$$\cos(\delta + \delta_1 - \delta_3) = -1$$

(28)

For polarization normal to the plane of incidence where $\delta_3 = \pi$, the conditions for a minimum intensity are:

$$\delta + \delta_1 = 0, 2\pi, 4\pi, \cdots$$

(29)
The minimum will be zero if:

\[ r_3^2 + (t_2 t_3 r_1)^2 - 2 t_2 t_3 r_1 r_3 = 0 \]  \hspace{1cm} (30)

or, taking the square root

\[ r_3 - t_2 t_3 r_1 = 0 \]  \hspace{1cm} (31)

For polarization parallel to the plane of incidence above Brewster's angle

\[ \delta_3 = 0 \]

The conditions for a minimum are:

\[ \delta + \delta_1 = \pi, 3\pi, 5\pi, \ldots \]  \hspace{1cm} (32)

The minimum will again be zero if:

\[ r_3 - t_2 t_3 r_1 = 0 \]  \hspace{1cm} (33)

for p polarization below Brewster's angle

\[ \delta_3 = \pi \]

The minimum condition is:

\[ \cos(\delta + \delta_1 - \delta_3) = -1 \]  \hspace{1cm} (34)

Thus,

\[ \delta + \delta_1 = 0, 2\pi, 4\pi, \ldots \]  \hspace{1cm} (35)

The minimum will be zero if

\[ r_3 - t_2 t_3 r_1 = 0 \]  \hspace{1cm} (36)

Thus, below Brewster's angle the phase change \((\delta + \delta_1)\) is the same for both polarizations. Above Brewster's angle the phase changes are
separated by $\pi$. This separation is the same as the separation of the maximum and minimum for either polarization. Above Brewster's angle the interference fringes for the two polarizations will be complimentary. For most metal-liquid combinations, the optimum angle will be above Brewster's angle for both polarizations. Since the minimum conditions are different above Brewster's angle, mixing of the two polarizations will reduce the contrast of the fringes. Thus, the polarizations should be separated for the best observation.

2. Multiple Beam Model

For the multiple beam model, since the maxima and minima occur at the same film thickness and wavelength as the double beam case (19), and since $\delta_2 = \delta_3 + \pi$, and $\delta_3$ is 0 or $\pi$, the minimum intensity can be derived from Eq. 26

$$I = r_3^2 + \frac{(t_2 t_3 r_1)^2 + 2 t_2 t_3 r_1 r_3 \cos(\delta_3 - \delta_1) - 2 t_2 t_3 r_1^2 r_3 \cos(\delta_2 + \delta_3)}{1 + (r_1 r_2)^2 - 2 r_1 r_2 \cos(\delta + \delta_2)}$$

The minimum intensity is

$$I_{\text{min}} = r_3^2 + \frac{(t_2 t_3 r_1)^2 - 2 t_2 t_3 r_1 r_3 + 2 t_2 t_3 r_1^2 r_3}{1 + (r_1 r_2)^2 - 2 r_1 r_2}$$

The intensity maximum, $I_{\text{max}}$, has an associated phase change due to film thickness, $\delta_{\text{max}}$, such that

$$\delta_{\text{max}} = \delta_{\text{min}} \pm \pi$$

where $\delta_{\text{min}}$ is the film thickness associated with $I_{\text{min}}$. Also,

$$(\delta_{\text{max}} + \delta_1) = (\delta_{\text{min}} + \delta_1) \pm \pi$$

so that

$$I_{\text{max}} = r_3^2 + \frac{(t_2 t_3 r_1)^2 + 2 t_2 t_3 r_1 r_3 + 2 t_2 t_3 r_1^2 r_3}{1 + (r_1 r_2)^2 + 2 r_1 r_2}$$

* Except for differences in $\delta_1$ between the two polarizations.
Eq. 37 is more complicated than the double beam equation and cannot be solved without trial and error (and a computer - see Appendix I).

A simpler expression can be obtained by using the amplitude expression Eq. 25.

\[ U = r_3 e^{i\delta_3} + \frac{t_2 t_3 r_1 e^{i(\delta+\delta_1)}}{1-r_1 r_2 e^{i(\delta+\delta_1+\delta_2)}} \]  

(25)

A zero minimum occurs when

\[ \pm U = r_3 - \frac{t_2 t_3 r_1}{1-r_1 r_2} = 0 \]  

(41)*

or

\[ \frac{r_3}{t_2 t_3 r_1} = +1 \]  

(42)

for low reflection coefficients, \( r_1 \) and \( r_2 \), then

\[ 1 - r_1 r_2 \approx 1 \]

and Eq. 41 becomes equivalent to Eqs. 31, 33 and 36 and the conditions for a zero minimum are the same as for the double beam case. A FORTRAN IV computer program was written using Eqs. 27, 37, 40 and 42 to find the optimum angles for any metal-solution combination for which the refractive indices are known. It is outlined in Appendix I.

---

* The \( +U \) is for \( p \) polarization above Brewster's angle. The \( -U \) is for either \( s \) or \( p \) polarization below Brewster's angle.
C. Colorimetry of Interference Colors

1. Elements of Colorimetry

According to the tristimulus theory the sensation of most colors can be reproduced using three primary or tristimulus colors. For additive color mixing these are usually red, green and blue. In 1931, the Commission Internationale de l'Eclairage (C.I.E.) adopted a system with three primaries. Unlike earlier primaries, these are always positive. With the earlier primaries, a portion of the spectrum in the blue-green region could not be reproduced without adding red to the unknown sample, essentially creating a negative red. With the C.I.E. primaries, any color can be given in quantitative terms.

The three tristimulus primaries are known as primary X, primary Y, and primary Z. The amounts of these in light of a single wavelength, \( \lambda_1 \), are \( x(\lambda_1) \), \( y(\lambda_1) \), \( z(\lambda_1) \), respectively. The functions \( x, y, z \) are tabulated for \( 380 \leq \lambda \leq 780 \) nm (see Fig. 11). The amount of the primaries in any light with spectral intensity distribution \( I(\lambda) \) is:

\[
X = \int_{380}^{780} I(\lambda)x(\lambda)d\lambda \quad \quad (43a)
\]

\[
Y = \int_{380}^{780} I(\lambda)y(\lambda)d\lambda \quad \quad (43b)
\]

\[
Z = \int_{380}^{780} I(\lambda)z(\lambda)d\lambda \quad \quad (43c)
\]

The value of \( Y \) was chosen to give a measure of the intensity of the light.
Fig. 11. Relative intensity of C.I.E. primaries $\bar{x}, \bar{y}, \bar{z}$ in spectral colors.
The value of $I(\lambda)$ is a combination of three factors: (1) The emissivity $P(\lambda)$ of the light source, (2) the history of the light after leaving the source (e.g., passing through filters, reflection from colored surfaces, interference), and (3) the response of the receptor. No correction is required when the eye is used as the receptor. The tristimulus values for the light can be normalized to specify the color without regard to intensity:

$$x = \frac{X}{X + Y + Z} \quad (44a)$$

$$y = \frac{Y}{X + Y + Z} \quad (44b)$$

$$z = \frac{Z}{X + Y + Z} \quad (44c)$$

These values are the chromaticity values. $x$ and $y$ are plotted on the horseshoe-shaped C.I.E. chromaticity diagram (see Fig. 12). $Y$ may be plotted on the third dimension.

2. Derivation of Color Charts

To find the color of a thin film in white light, the spectral distribution, $I(d, \lambda)$, is calculated for the multiple beam case using Eq. 26:

$$I(d, \lambda) = r_3^2 + \left(\frac{t_2t_3r_1^2 + 2t_2t_3r_1r_3 \cos(\delta_1 - \delta_3) - 2t_2t_3r_1^2r_2r_3 \cos(\delta_2 + \delta_3)}{1 + (r_1r_2)^2 - 2r_1r_2 \cos(\delta_1 + \delta_2)}\right)$$

The resulting intensity distribution is independent of the light source and receptor used for viewing the film. The distribution $I(d, \lambda)$ must then be multiplied by the emissivity $P(\lambda)$ of the source and the response of the receptor. Since, in this work, these were a tungsten lamp and the
Fig. 12. C.I.E. chromaticity diagram showing variation of hue (color) and variation of purity (saturation of color).
eye, respectively, $I(d, \lambda)$ was multiplied by the emissivity, $P_A(\lambda)$ of the standard tungsten source, C.I.E. source A. Values of $P_A(\lambda)$, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ were obtained from Wright (20). Values of $X$, $Y$, $Z$ may then be obtained from Eq. 43 a,b,c. The chromaticity values, $x$, $y$, $z$ are obtained using Eq. 44 a,b,c. By following this procedure, the numerical values of the thin film color can be obtained.

To translate these numbers into a color name, a color diagram, such as given by Kelly, is used (21). This diagram breaks the C.I.E. chromaticity diagram, Fig. 12, into areas which were given common color names. The diagram given by Kelly, however, is for the C.I.E. standard source C. This source is much more blue than tungsten light. For use with this work, and most work using white light, it was necessary to make a new diagram using tungsten light as the source.

The new diagram retained two elements of Kelly's diagram: the color names, and the intersection of the dividing lines between the colors with the outside of the diagram. New dividing lines were drawn from the points on the edge of the diagram to the new white point. These lines were straight, following the example of Bouma and others (22) in drawing straight lines of dominant wavelength. The white area was chosen to be 10 times the minimum color resolution of an observer as given by W. D. Wright (23). The resulting diagram is given in Figure 13.

By making calculations of the color of thin films in thickness increments of 100Å from 0 to 15,000 Å (1.5μ) and phase changes from 0 to 360° in 10° increments a generalized color chart was made. This plot of total phase change, $\delta_{tot}$ against optical path difference, $\Delta S$, with color as a parameter, allows one to determine the thickness of a
Fig. 13. Definition of color names employed in the colorimetric analysis of interference colors on the chromaticity diagram for tungsten white light.
tapered film by observing the colors in white light. (Fig. 14)

Three sets of calculations were made with the aid of a FORTRAN IV program CHROM (see Appendix II). The three sets were for low, medium and high reflectivity. The three solid substrates used were: a dielectric with index of refraction $n=2.25$, platinum, and silver. In all cases the liquid had an index of refraction of 1.50. The angle of incidence used was the optimum for each of the liquid-solid combinations as determined by the program MINIM. As the results are in terms of the optical path difference, any index of refraction and angle of incidence may be used by employing the relation:

$$d = \frac{\Delta S}{2n \cos \phi}$$  \hspace{1cm} (45)

which results from Eq. 18. The resulting charts are given in Fig. 14a, b. The resultant of the phase changes at the gas-liquid and liquid-solid interface is:

$$\delta_{\text{tot}} = \delta_3 - \delta_1$$  \hspace{1cm} (46)

This is the total phase change due to reflection.
Fig. 14 (a). Multiple beam interference. Generalized color chart for amplitude reflection coefficients of both interfaces: 0.20. (Typical of dielectric film on dielectric substrate and an approximation to double beam interference.) Color names as defined in Fig. 13, described by initials, in addition: Bl = black.
Fig. 14 (b). Multiple beam interference. Generalized color chart for amplitude reflection coefficients of both interfaces: 0.60. (Typical of dielectric film on platinum or stainless substrate). Color names as in Fig. 14(a).
III. EXPERIMENTAL

In order to compare the film thickness as measured with the spectrophotometer with that determined by observation of colors, liquid films were formed on flat, polished metal surfaces. In addition, measurements were made to test the theoretical determination of the optimum angle of incidence. Some earlier work was reproduced to check the thickness measurements, considering the effects of phase change upon reflection from the metal and multiple reflections.

The film profiles were measured using white, polarized light interference. The light reflected from the film was analyzed in two separate ways: (1) the color was recorded photographically, and the thickness estimated from the colors and color transitions, and (2) the spectral distribution measured at discrete points with a spectrophotometer. The photographic method was used originally by Muller (13).

White light was chosen for two reasons: (1) more data points are available than with monochromatic light, and (2) different interference orders can be distinguished since the colors are non-repetitive. More data points are available because in one interference order monochromatic light varies from dark to light to dark, while white light passes through two to five colors, depending on the interference order. For visual observation of a tapered film, one can make a measurement at the center of each color and each color transition, giving up to eight points per order. For monochromatic light, however, thickness can only be determined at the maxima and minima, giving two points per order.

For a film of uniform thickness, monochromatic light generally yields an area of constant intensity. White light
yields maxima and minima at specific wavelengths which depend on the film thickness. Because of non-linearity of the spectrophotometer response, and a tendency for the calibration to wander, monochromatic intensity measurements at a fixed wavelength were inaccurate. However, maxima and minima, with respect to wavelength, were easily and accurately located. Therefore, the technique of measuring the wavelength of maxima and minima was used.

Two beams were used, polarized parallel and normal to the plane of incidence (see Fig. 2). Polarized light was used to create well defined phase change conditions, since above Brewster's angle $\delta_s$ and $\delta_p$ are different. This difference in phase results in complimentary colors for the two polarizations at a given film thickness. By separating the two polarizations, better fringe contrast resulted.

A. Optical

1. Optical Bench

Figure 15 is a schematic diagram of the optical benches. Four images were recorded simultaneously on each frame of film in the camera: two images of the surface, a clock and potentiometer, and a thermometer. Figure 16 shows two typical views through the camera.

The light sources were two microscope lamps focused on ground glass screens. The bulbs were operated at 18 watts each. Between the screens and the lamps were neutral density step wedges. These were used to adjust the intensity of the sources relative to each other and to the intensity of the clock-potentiometer image for proper exposure in the photographs. A pair of irises were placed in front of the screens to define approximate point sources and to also provide a continuously variable intensity
Fig. 15. Schematic diagram of optical bench.
Fig. 15. Schematic diagram of optical bench.

(1) Microscope lamps
(2) Neutral density step wedges
(3) Source iris with diffusing screen
(4) First surface mirrors
(5) Collimating lenses
(6) Polarizing filter s-polarization
(7) Polarizing filter p-polarization
(8) Sample surface
(9) Field lens
(10) Stereo mirror system
(11) Camera objective
(12) Camera diaphragm
(13) Film plane
(14) Focusing lenses for clock and potentiometer
(15) Clock and potentiometer
Fig. 16. Two typical views through the camera for two angles of incidence: upper-75°. Film is 7N KOH on a platinum electrode, sodium light.
adjustment. A pair of collimating lenses was used to provide a collimated beam to reflect from the film surface. The two beams were polarized, using polaroid filters, normal and parallel to the plane of incidence, which was horizontal in this case.

The collimating optical bench was mounted on a table which could pivot about a common axis with the surface. Thus, the angle of incidence could be varied to obtain the optimum angle of incidence.

To refocus the collimated light reflected from the film surface, a field lens was placed near the cell. This lens focused the light to the diaphragm of the camera objective and allowed all the reflected light to be received at the camera.

Because the two beams diverged from each other after leaving the surface, a stereo mirror system was placed ahead of the camera. These mirrors were adjusted so that the two beams converged and crossed at the point where the source irises were in focus. This is the point where the diameter of the beams is smallest. To prevent vignetting of the interference pattern, the diaphragm of the camera objective should be placed at this point. Some vignetting might still occur at small lens openings but these were outside the proper exposure range.

The camera used was a Bolex H-16 16 mm reflex movie camera. This was used with a Vario-Switar 18-86 mm zoom objective. The camera and objective were mounted separately so that the camera could be removed to align the objective. The objective was held on two mounts, with one positioned below the diaphragm, so that the lens could be rotated without changing the position of the diaphragm.

The camera was set to take only one frame at a time. The shutter
release was an electric motor with a crank and connecting rod to the camera. A gentle release was necessary to prevent vibration from blurring the photos. The shutter release was actuated by a timer which turned the source lights and lights for the clock-potentiometer and thermometer on about two seconds before the exposure. Between exposures the lights were off to prevent absorption heating of the film. The room lights were off all the time to prevent reflections from the lenses, windows and mirrors. The photographs were taken on Ektachrome type EF color film balanced for 3200°K tungsten light.

To record the time of the exposure and the potential of the metal surface relative to a reference electrode, a clock and potentiometer were placed on another optical bench. A system of mirrors and lenses brought the image of the clock and potentiometer in focus next to the image of the metal surface. The potentiometer was a Heath pH recording electrometer, Model EUW-301. A pointer was attached to the pen carriage to make its position visible in the photographs.

2. Alignment

To minimize distortion of the images of the electrodes, the field lens should be placed as close to the cell as the rotation of the cell and stand will allow.

To prevent vignetting, the real image of each of the source irises must be centered at the plane of the diaphragm of the camera objective. With the camera and objective out of the way, the stereo mirror system was adjusted until the images of the irises converged about a foot behind the mirror assembly. This was best done with a screen at this point. Care was taken that no part of the beam was cut off by the
mirror edges. The images of the irises were centered over the optical bench. In order to have the images of the electrode coincide with the light reflected from them, it was necessary to make sure the electrode surface was vertical.

The camera objective with the camera attached was brought behind the mirror assembly, placing the diaphragm of the objective in line with the image of the irises vertically and laterally and approximately in place axially. The focus and focal length of the objective was then adjusted so that the image of the electrode was in focus and filled the frame. The camera was then removed and replaced with a photometric microscope (Gamma Scientific Model 700-10) which was mounted horizontally. The microscope was focused on the diaphragm of the objective. The camera objective and microscope were then moved together until the images of the source irises could be seen centered in the diaphragm. The axial position was adjusted by simultaneously bringing in focus the source irises and the objective diaphragm. The camera was then placed back behind the objective. The camera and objective were then pivoted around the mount located below the diaphragm to adjust the images of the potentiometer, electrode, and thermometer relative to the frame.

3. Spectrophotometer

Figure 17 is a diagram of the spectrophotometer. It was assembled using a pair of Gamma Scientific Photometers. A fiber optics probe was placed in the incident beam where they overlap. While making measurements the unused source was switched off. The probe was necessarily at

* A model 700 was originally purchased. When the second unit was purchased, the similar model was the model 2020. The characteristics of the two units are essentially the same.
Fig. 17. Schematic of ratio recording spectrophotometer.
Fig. 17. Schematic of ratio recording spectrophotometer.

(1) Thin film covered surface
(2) Reference fiber optic probe
(3) Reflected beam fiber optic probe
(4) Matched, synchronous motor-driven monochromators
(5) Matched photomultiplier tubes
(6) Photomultiplier electronics
(7) Unity gain amplifier
(8) Ratio recorder (see Fig. 18)
the edge of the beam to prevent the casting of a shadow on the surface. The probe in the reflected beam was mounted on a rack and pinion mount to move the probe vertically. A variable resistor, which moved with the pinion, allowed the position to be read on a recorder. It was placed in the center of the beam horizontally. The acceptance diameter of the probes was 1/8 inch. With an angle of incidence, \( \phi \), of 75° an ellipse about 1/8 inch high and 3/8 inch wide on the film surface was sampled. The fiber optic probes (Gamma Scientific Model 700-3C), which were of equal five foot length to even out any transmission losses, were connected to a matched pair of Bausch and Lomb monochromators (catalog number 33-86-02). The monochromators were geared together with a synchronous motor to give a uniform, reproducible sweep of wavelength. The input slit width was 0.75 mm. The exit slit width was 1.34 mm. This resulted in a bandwidth of 4 nm. A sweep of the usable range, 700 to 450 nm, took about 3 min. The usable range was limited on the blue end by the output of source, and on the red end by the response of the photomultiplier tubes, which were attached to the monochromators. To extend the red end a matched pair of Hamamatsu R136 extended range tubes were used. These were connected to the photometers, the output of which were connected to a modified Heath servorecorder, model EAW-20. This recorder was modified for ratio measurements by placing one of the inputs across the slide wire. Figure 18 is the modified circuit diagram. It was necessary to place a unity gain amplifier at this input to match the high output impedance of the photometer to the lower input impedance of the slide wire. By moving the recorder chart at a fixed rate, the wavelength scan was translated into time on the chart. An example
Fig. 18. Modifications of potentiometric recorder circuit for ratio recording.
output of the spectrophotometer is given in Fig. 19.

B. Chemical

1. Cell

The cell used for holding the metal surface was made by Muller. Since the metal surface was to be an electrode involved in an electrochemical reaction, provision was made for electrical contact to the metal, a counter electrode, and a capillary to a reference electrode. Figures 20a and b are views of the cell. To prevent attack and contamination of the solutions, the body of the cell was made totally of polypropylene. To minimize contamination of the solution around the metal surface by reaction products from the counter electrode, the counter electrode was made of nickel and placed in a separate chamber. Although glass windows were attacked by the potassium hydroxide solutions, no chemically more resistant material had sufficient optical properties. A weir separated them from the solution contacting the electrode. The same weir set the liquid level on the electrode. All the fittings attached to the cell were of Teflon. Initially, rubber gaskets were used to seal the windows to the cell. However, these could not be completely cleaned and also began to disintegrate. Because of this, these were replaced with Teflon gaskets. These were not entirely leak free, and required tightening to about twice the force as the rubber gaskets, 40 in.-lb. on the cell nuts, but leakage was minimal if the dried solids were kept washed off the outside.

2. Liquid System

The cell was drained for an experiment by a tube with a valve leaving the cell from the front, outside the weir. This fixed the
Fig. 19. Example of spectrophotometer output s-polarized light reflected from a 0.82 micron thick film of 7.0 N KOH on a platinum surface.
Fig. 20(a). Side sectional view of experimental cell.
Fig. 20(a). Side sectional view of experimental cell.

(1) Studs (6) for clamping windows to cell body
(2) Gas inlet
(3) Gas outlet
(4) Clamp and electrical contact
(5) Gas outlet for counter-electrode chamber
(6) Main chamber
(7) Glass capillary for reference electrode
(8) Optically polished experimental electrode
(9) Liquid drain
(10) Counter-electrode
(11) Counter-electrode chamber
(12) Liquid inlet
(14) Passage between chambers
(15) Weir to establish liquid level
Fig. 20(b). Top sectional view of experimental cell. Legend as in Fig. 20a, in addition:

(16) Frame to hold windows
(17) Plate glass windows
liquid level. The liquid was supplied from four 500 ml separatory funnels. These were connected in pairs, one pair for cleaning and one pair for the experimental solution. These were connected to the cell by polyethylene tubing, with Teflon diaphragm valves to control the electrolyte flow. Each gas outlet and vent was protected with a dust and carbon dioxide filter. Figure 21 is a flow diagram of the system.

3. Gas System

The system for supplying the gas to the cell included a washing bottle to saturate the gas so as not to dry the film. The gas, which was of tank purity was dried, had the dust removed, entered the wash bottle filled with the same solution as in the cell, had the flow rate measured with a rotameter and was delivered to the main chamber of the cell. The wash bottle could be bypassed to deliver dry gas to the cell, to evaporate the film, or the two streams could be mixed. Figure 22 shows this system.

4. Electrodes

The electrodes were 10.5 cm high and 4.0 cm wide. There were two electrodes used: a solid 316 stainless steel, and a platinum soldered to a stainless steel back. The face of these had been optically polished. The back and sides were coated with Scotchcast 8 epoxy. Electrical connection to the electrode was made with a stainless steel pin which also clamped the electrode in place. The counter electrode was a nickel screen. The reference electrode was connected to the cell by a glass capillary which came within one or two millimeters of the electrode below the liquid surface. For a potassium hydroxide electrolyte, the reference electrode was mercury-mercuric oxide (24).
Fig. 21. Liquid fill and drain system.
Fig. 21. Liquid fill and drain system.

(1) Dust filters
(2) 2 - 500 ml flasks containing cleaning solution
(3) 2 - 500 ml flasks containing experimental solution
(4) System flushing drain
(5) Experimental cell
(6) Drain vent
(7) Flexible connecting line
(8) Drain to start experiment
Fig. 22. Gas saturation system.
Fig. 22. Gas saturation system.

(1) Gas supply cylinder ($O_2$ or $N_2$)
(2) Drying tube
(3) Glass wool dust filter
(4) Dry gas flow rate rotameter
(5) Sparger with same solution as in experimental cell
(6) Glass wool mist filter
(7) Saturated gas flow rate rotameter
(8) Dust and $CO_2$ filters on outlet
(9) Experimental cell
(10) Flexible connecting line
5. Preparation of Surfaces and Solution

When the cell was disassembled the whole interior surface was cleaned with chromic acid and rinsed with distilled water to remove organic and inorganic contaminants. The electrodes were cleaned with nitric acid to remove oxidation. The stainless and nickel electrodes were especially subject to discoloration in potassium hydroxide electrolyte. A hot mixture of nitric and sulfuric acid removed this quickly with no harm to the polishing. Examination of the surface using the interference microscope confirmed this. Figures 23b and c are photographs taken before and after cleaning. The roughness of the electrodes checked regularly with the interference microscope. Figure 23 shows photos of the electrodes taken with the interference microscope.

After the cell was assembled, the cell was filled with electrolyte and hydrogen was evolved in large quantities to do the final cleaning. A current density of 35 ma/cm² was used, the limit of the power supply on hand. On the platinum electrode evolution of hydrogen and oxygen was alternated, always ending with evolution of hydrogen for about one-half hour. By draining the cell and observing the wetting of the film on the electrode it was possible to determine if the electrode was clean or if gas evolution would have to be repeated.

An experiment was begun by filling the cell with electrolyte and then draining it as fast as possible. Because of air in the valve, this usually took about 2 min. When the liquid level dropped to the top of the weir, the clock was started.

The potassium hydroxide solution was prepared from reagent grade pellets and distilled water. The solution was vacuum filtered. As
Fig. 23a. Interference micrograph of polished surface on 316 stainless electrode used in previous work (T1 light 535 nm).
Fig. 23b. Interference micrograph of 316 stainless electrode used in present work. Surface before acid cleaning.
Fig. 23c. Same surface as Fig. 23b after cleaning with hot concentrated $\text{H}_2\text{SO}_4 + \text{HNO}_3$. 
Fig. 23d. Interference micrograph of platinum surface (before use).
Fig. 23e. Interference micrograph of gold surface (not used in present work).
paper filters were attacked by the solution, fritted glass filters were used initially. After a large concentration of sodium silicate was discovered, Teflon and polypropylene filters were used (Greiner Scientific, Catalog Nos. 90116 and 90195-4). The finest filter had a porosity of 5μ. For experiments with a nitrogen atmosphere, the solution was then purged with nitrogen for two days. The concentration of KOH was then determined by titration with standard hydrochloric acid and phenolphthalein. The refractive index was taken with a Bausch and Lomb precision refractometer. Measurements were taken at several wavelengths throughout the spectrum. Table I gives refractive indices for solutions used.
Table I. Refractive index of KOH solutions.

<table>
<thead>
<tr>
<th>Concentration (Normal)</th>
<th>Temperature (°C)</th>
<th>Wavelength (Å)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.067</td>
<td>25</td>
<td>4360</td>
<td>1.36970</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5460</td>
<td>1.36329</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5892</td>
<td>1.36159</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6328</td>
<td>1.36118</td>
</tr>
<tr>
<td>1.012</td>
<td>25</td>
<td>5420</td>
<td>1.34461</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5892</td>
<td>1.34284</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6800</td>
<td>1.34038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7140</td>
<td>1.33944</td>
</tr>
<tr>
<td>0.985</td>
<td>23</td>
<td>4150</td>
<td>1.35167</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4470</td>
<td>1.34912</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5760</td>
<td>1.34304</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5892</td>
<td>1.34289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6800</td>
<td>1.34016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7140</td>
<td>1.33917</td>
</tr>
<tr>
<td>6.974</td>
<td>23</td>
<td>4150</td>
<td>1.40205</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4470</td>
<td>1.39891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5120</td>
<td>1.39434</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5892</td>
<td>1.39063</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6800</td>
<td>1.38775</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7140</td>
<td>1.38662</td>
</tr>
</tbody>
</table>
IV. ANALYSIS OF DATA

A. Visual

The thickness of the films was measured in two ways: (1) by visually observing the interference colors, (2) by measuring the spectral distribution of the reflected light.

The visual measurement was done by identifying the colors in the photographs. This was done using the results of the color scale in Figure 14. To use Figure 14, the phase change at the metal surface must be calculated using Eqs. 8, 9, and 10. The total phase change due only to reflections is

\[ \delta_{\text{tot}} = \delta_3 - \delta_1 \]  

(46)

This is the phase change used with Figure 14. A color series is taken from Figure 14 for each polarization for each metal electrode. The color series used for platinum is given in Fig. 24.

The interference order must be determined from the color sequence. Comparison of the two polarizations also served to also check the interference order.

B. Spectrophotometer

From the spectrophotometer chart the film thickness was determined using the maxima and minima. A FORTRAN IV computer program, MBINF, was used to find the thickness which corresponded to a maximum or minimum at any wavelength. This program gave a listing of wavelength with two lists of possible film thicknesses for which that wavelength would be a maximum or minimum. By taking the listings for each measured wavelength that was a maximum or minimum, the thickness that matched in all cases was the film thickness. Appendix III gives the program and an example solution for Fig. 19.
Fig. 24. Thin film interference color series for a platinum substrate.

(a) s-polarization, $\delta_{\text{tot}} = 338^\circ$

(b) p-polarization, $\delta_{\text{tot}} = 138^\circ$
V. RESULTS

Application of the techniques developed has been demonstrated briefly. Calculations were carried out leading to the generalized color charts, and data on the optimum angle of incidence for a dielectric film on different metal surfaces. Some attempt was made to use these results and check their validity experimentally. These can be divided into three areas: optimum angle of incidence, color series, and film profiles obtained using the color series and spectrophotometer.

A. Optimum Angle of Incidence

By using the computer program MINIM, the optimum angle of incidence for films on several metals was computed. Table II gives the results. These results were derived for the criteria of maximum Michelson fringe visibility, Eq. 27, or equivalently, zero intensity of the interference minimums.

To check these results, three methods were used: (1) calculation of the color series resulting from white light interference using a variation of the computer program CHROM; (2) visual observation of the colors while varying the angle of incidence; and (3) measurement of the fringe contrast in monochromatic (sodium) light.

The first method, using the program CHROM, consisted of calculating and plotting the chromaticity values \( x \) and \( y \) for angles of incidence in increments of 1°. The angle of incidence which gave the most saturated colors (i.e. those closest to the spectrum colors on the C.I.E. chromaticity diagram) was considered the optimum angle of incidence. The total phase change

\[ \delta_{\text{tot}} = \delta_3 - \delta_1 = 0 \]
Table II. Optimum angle of incidence for interference in a film of refractive index 1.50 on different metal substrates.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Optical Constants</th>
<th>Optimum Angle Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>κ</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.50</td>
<td>1.95</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>2.50</td>
<td>1.95</td>
</tr>
<tr>
<td>Platinum</td>
<td>2.63</td>
<td>1.35</td>
</tr>
<tr>
<td>Silver</td>
<td>0.18</td>
<td>20.6</td>
</tr>
</tbody>
</table>
was used. Chromaticity values were plotted for optical path differences up to 1.5 μ in increments of 0.1 μ using the Cal-Comp automatic plotting facility. These plots were similar to those in Figs. 25, 26 and 27.

Using the criterion of most saturated colors, agreement within 1° was obtained with the results of program MINIM using platinum as the substrate (amplitude reflection coefficient = 0.61).

When silver was used as the substrate, however, the colors were more saturated at angles less then the calculated optimum. This discrepancy has not been resolved. It appears that the discrepancy is caused by the sharp minima of intensity in the reflected spectrum (see Fig. 10, reflection coefficient = 0.98). The observed colors would be formed in this case by subtraction of the complimentary color from white. By subtracting a narrow band the reflected light is still almost white. By reducing the angle of incidence, the reflection coefficient is also reduced. It is possible that the reduced reflection coefficient causes the minimum to be broader, thereby subtracting more of the complimentary color. For the case of high reflectivity it may be necessary to develop a criterion other than maximum Michelson fringe visibility for use with white light. The best criterion would depend on the method of measurement, the maximum Michelson fringe visibility would be used with the spectrophotometer. The most saturated color would be best used with visual observation.

Observation of the optimum angle by visually observing the colors of films on stainless steel and platinum tended to confirm the calculations, although judging the optimum angle was difficult and inaccurate.

The measurement of the fringe contrast was done by photographing the
Fig. 25. Chromaticity of thin films as a function of optical path difference, $\Delta S$. Amplitude reflection coefficient of the two interfaces: 0.20, typical of dielectrics. (Film $n = 1.5$, substrate $n = 2.25$, $\delta_{tot} = 0$)
Fig. 26. Chromaticity of thin films as a function of optical path difference, $\Delta S$. Amplitude reflection coefficient of the two interfaces: 0.61, typical of most metals. ($\delta_{\text{tot}} = 0$)
Fig. 27. Chromaticity of thin films as a function of optical path difference, ΔS (in microns). Angle of incidence, φ=83°. Amplitude reflection coefficient of the two interfaces: 0.90, typical of silver. (δ = 0). For this high reflectivity the fringe shape and colors are very dependent on angle of incidence. At 89.3°, the calculated optimum angle based on fringe visibility = 1, the chromaticity values are bounded by the dotted rectangle.
the fringes in sodium light, and measuring the minimum and maximum net film density (the base film density was subtracted from each). The difference is the photographic contrast. For this, the Bolex 16mm camera and lens was replaced with a 35 mm Nikon camera with a 135 mm lens. The larger format reduced the effects of film grain. In addition, Kodak Panatomic-X film was used for its extremely fine grain and long characteristic curve. The density was measured using a microdensitometer which had a slit (sample) size of 0.1 mm by 20 microns. The difference between minimum and maximum net photographic density for different angles of incidence is given in Fig. 28. Not enough data was obtained by this method to reach any conclusions, but the results tend to agree with the calculations.

B. Color Charts

The color charts for a low and medium reflectivity substrate were given in Figs. 14 a and b. The low reflectivity surface had an amplitude reflection coefficient of 0.20. The medium reflectivity surface had an amplitude reflection coefficient of 0.61. A chart for high reflectivity, amplitude reflection coefficient = 0.90, was not made because the film color remained entirely within the white region of Fig. 13.

As a preliminary step to the color chart, the color must be located on the C.I.E. chromaticity diagram (Fig. 13) from the chromaticity values for each optical path difference. Plots of these values for amplitude reflection coefficients of 0.20, 0.61 and 0.90 are given in Figs. 25, 26, and 27. The reflection coefficients are typical of dielectrics, platinum or stainless steel, and silver, respectively. The white region in Fig. 27 is reduced to five times the minimum resolution from ten times the minimum
Fig. 28. Fringe contrast measured as difference in net optical density between interference minima and maxima on photographs of a tapered film of 7 N KOH on platinum for different angles of incidence. (a) s-polarization (wide image), (b) p-polarization (narrow image).
as in Figs. 13, 28 and 25. This was done because of the low saturation of the colors in Fig. 27. Kubota gives similar plots in his article (25). However, his plots are for double beam interference, and normal incidence. He also calculated his chromaticity values for standard illuminant C, typical of light from a northern sky. In both his work and this work the phase change due to reflection, $\delta_{\text{tot}}$, is equal to zero. He gives some plots for multiple reflections, for the same conditions as the double beam plots. A computation using program CHROM and light source C for the case of reflection coefficient equal to 0.20 agreed with Kubota's double beam case.

One should note the decreasing saturation of the interference colors with increasing reflectivity even at the optimum angle of incidence.

By knowing $\delta_1$ for the metal, the value of the total phase change

$$\delta_{\text{tot}} = \delta_3 - \delta_1 \quad (46)$$

can be calculated, and the chart can be used to determine film thickness from the color series. Typical values of $\delta_{\text{tot}}$ are given in Table III.

### C. Film Profiles

Several films were formed on electrodes and their thickness measured using both color photography and the spectrophotometer. Figure 29 shows the profile of a 1 normal KOH film on stainless steel. No electrochemical polarization was applied to the film. Figure 30 is a 3 normal KOH film on platinum. This figure shows the thinning as the film drained. At 22 hours the film is essentially stable. Figure 31 is the stable 3 normal film compared to a stable 7 normal KOH film. For the 7 normal film the results of the spectrophotometer and color photography are compared.
Table III. Phase changes $\delta_1$, $\delta_3$ and $\delta_{\text{tot}}$ for reflection from a dielectric film of refractive index $n_1=1.4$ on different metal substrates of optical constants listed in Table II.

<table>
<thead>
<tr>
<th>Angle of incidence (on film)</th>
<th>Polarization</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi = 45^\circ$</td>
<td>$\phi = 75^\circ$</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>$\delta_1$</td>
<td>$\delta_3$</td>
</tr>
<tr>
<td>Stainless, nickel</td>
<td>180 157.61 22.39</td>
<td>180 149.94 30.06</td>
</tr>
<tr>
<td>Platinum</td>
<td>180 154.48 25.52</td>
<td>180 145.83 34.17</td>
</tr>
<tr>
<td>Silver</td>
<td>180 144.53 35.47</td>
<td>180 132.07 47.93</td>
</tr>
</tbody>
</table>
Fig. 29. Steady state film profile 1.0 N KOH solution on 316 stainless steel saturated N₂ atmosphere.

- ♦ s-polarization
- ◇ p-polarization
Fig. 30. Draining of a 3.0 N KOH film on platinum, saturated 
N\textsubscript{2} atmosphere.

- O □ △ s-polarization
- • ■ ▲ p-polarization
Fig. 31. Steady state film profiles of 3.0 N and 7.0 N KOH films on platinum, saturated \( \text{H}_2 \) atmosphere.

- ♦ Visually determined thickness
- ◇ Thickness determined using spectrophotometer
Due to the larger number of maxima and minima the spectrophotometer is easier to use at film thicknesses greater than 0.5 microns, while color photography requires film thicknesses less than 0.8 microns to distinguish interference orders.

This work was done under the auspices of the U. S. Atomic Energy Commission.
VARIABLES

The following names are used in the program MINIM

<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN1, CN2</td>
<td>(c_{n1}, c_{n2})</td>
<td>Coefficients for a linear approximation of the real part of the index of the substrate.*</td>
</tr>
<tr>
<td>CK1, CK2</td>
<td>(c_{k1}, c_{k2})</td>
<td>Coefficients for a linear approximation of the absorption coefficient of the substrate.*</td>
</tr>
<tr>
<td>SCALE</td>
<td>-</td>
<td>Refractometer scale reading</td>
</tr>
<tr>
<td>RI, RIC</td>
<td>(n_1)</td>
<td>Index of refraction of the liquid film</td>
</tr>
<tr>
<td>TNA</td>
<td>(n)</td>
<td>Real part of the complex refractive index of the substrate</td>
</tr>
<tr>
<td>TKA, TK</td>
<td>(\kappa)</td>
<td>Absorption coefficient</td>
</tr>
</tbody>
</table>

* For the index of refraction of the substrate, written as in Eq. 8

\[
n_c = n(1+\kappa)
\]  

(8)

A linear approximation of \(n\) and \(\kappa\) with wavelength, \(\lambda\), was made such that:

\[
n = c_{n1} + c_{n2} (\lambda-3800 \text{ Å})
\]  

(A-1)

and

\[
\kappa = c_{k1} + c_{k2} (\lambda-3800 \text{ Å})
\]  

(A-2)

The values of \(c_{n1}, c_{n2}, c_{k1}\) and \(c_{k2}\) have been derived from Fig. 32 and are supplied as input parameters.
Fig. 32. Refractive index, $n$, and absorption coefficient, $\kappa$, for various metals used as substrates in this work (26).
<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN</td>
<td>n/n₁</td>
<td>Angle of incidence on film</td>
</tr>
<tr>
<td>PHID</td>
<td>φ(degrees)</td>
<td>Angle of incidence on film</td>
</tr>
<tr>
<td>PHI</td>
<td>φ(radians)</td>
<td>Angle of incidence on film</td>
</tr>
<tr>
<td>AMN</td>
<td>φᵣ_min</td>
<td>Minimum angle of incidence</td>
</tr>
<tr>
<td>AMX</td>
<td>φᵣ_max</td>
<td>Maximum angle of incidence</td>
</tr>
<tr>
<td>STEPS</td>
<td>Δφ</td>
<td>Increment of change of angle of incidence</td>
</tr>
<tr>
<td>PHIPR</td>
<td>φ'(radians)</td>
<td>Angle of refraction, angle of incidence on substrate</td>
</tr>
<tr>
<td>RL</td>
<td>r₃</td>
<td>Reflection coefficient from gas-liquid interface</td>
</tr>
<tr>
<td>RIL</td>
<td>r₂</td>
<td>Internal reflection coefficient from gas-liquid interface</td>
</tr>
<tr>
<td>R</td>
<td>r₁</td>
<td>Reflection coefficient from liquid-metal interface</td>
</tr>
<tr>
<td>TL</td>
<td>t₃</td>
<td>Transmission coefficient from gas to liquid</td>
</tr>
<tr>
<td>TIL</td>
<td>t₂</td>
<td>Transmission coefficient from liquid to gas</td>
</tr>
<tr>
<td>A,B</td>
<td>A,B</td>
<td>Intermediate variables</td>
</tr>
<tr>
<td>LAMBDA, WVLTH</td>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>MINT</td>
<td>I_min</td>
<td>Minimum intensity</td>
</tr>
<tr>
<td>MXINT</td>
<td>I_max</td>
<td>Maximum intensity</td>
</tr>
<tr>
<td>VISIB</td>
<td>V</td>
<td>Fringe visibility</td>
</tr>
<tr>
<td>RAT</td>
<td>r₃ ( t₂ t₃ r₁ / (1 - r₁ r₂) )</td>
<td>Ratio of amplitude of ray reflected from air-liquid interface to sum of all other reflected rays.</td>
</tr>
<tr>
<td>NAME</td>
<td>SYMBOL</td>
<td>DESCRIPTION</td>
</tr>
<tr>
<td>------------------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$R(1)/R(2-\text{INFIN})$</td>
<td></td>
<td>RAT</td>
</tr>
<tr>
<td>MINIMUM</td>
<td>$I_{\text{min}}$</td>
<td>EQ. 37</td>
</tr>
<tr>
<td>MAXIMUM</td>
<td>$I_{\text{max}}$</td>
<td>EQ. 40</td>
</tr>
<tr>
<td>MIN/MAX</td>
<td>$V$</td>
<td>EQ. 27</td>
</tr>
</tbody>
</table>
The input for program MINIM is on punched cards. All data is in a non-exponential form (e.g. 100, 0.0003, 100.7). Decimal points should be included in all numbers except $\lambda$ on cards 5 to 19. The cards used are:

<table>
<thead>
<tr>
<th>CARD</th>
<th>VARIABLE</th>
<th>UNITS</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Name of Substrate</td>
<td>Centered in Cols. 7-16</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$C_{n1}$</td>
<td>Dimensionless</td>
<td>Col. 11-20</td>
</tr>
<tr>
<td></td>
<td>$C_{n2}$</td>
<td>$1/\AA$</td>
<td>21-30</td>
</tr>
<tr>
<td></td>
<td>$C_{k1}$</td>
<td>Dimensionless</td>
<td>31-40</td>
</tr>
<tr>
<td></td>
<td>$C_{k2}$</td>
<td>$1/\AA$</td>
<td>41-50</td>
</tr>
<tr>
<td>3</td>
<td>$\phi_{\text{min}}$</td>
<td>Degrees</td>
<td>Col. 1-5</td>
</tr>
<tr>
<td></td>
<td>$\phi_{\text{max}}$</td>
<td>Degrees</td>
<td>6-10</td>
</tr>
<tr>
<td></td>
<td>$\Delta\phi$</td>
<td>Degrees</td>
<td>11-15</td>
</tr>
<tr>
<td>4</td>
<td>Concentration of electrolyte</td>
<td>Normal</td>
<td>Col. 11-20</td>
</tr>
<tr>
<td>5 to 19*</td>
<td>$\lambda$</td>
<td>$\AA$</td>
<td>Col. 1-4</td>
</tr>
<tr>
<td></td>
<td>$n_1$</td>
<td>Dimensionless</td>
<td>5-14</td>
</tr>
<tr>
<td></td>
<td>SCALE</td>
<td>Dimensionless</td>
<td>15-24</td>
</tr>
</tbody>
</table>

* From 1 to 14 of these cards may be used. If less than 14 are used, the last card must be blank.
The angles $\phi_{\text{min}}$ and $\phi_{\text{max}}$ are the minimum and maximum angles of incidence to be examined. $\Delta\phi$ is the size of the increments between calculations. $\Delta\phi$ must be equal to $0.01^\circ$, $0.1^\circ$, or an integral number of degrees. Also, the total number of increments

$$(\phi_{\text{max}} - \phi_{\text{min}}) \Delta\phi < 100$$

in addition

$$0^\circ < \phi_{\text{min}} < \phi_{\text{max}} < 90^\circ$$

$\lambda$ is the wavelength at which the refractive index of the liquid, $n_1$, is known. SCALE is the refractometer scale reading, from which the program will calculate the refractive index. The values of SCALE were obtained from a Bausch and Lomb precision refractometer, with prism series 749. Another prism would require that the prism constants, PC, in the function REFRXC be calculated for the new prism.

A listing of the program and a sample output follow. The two functions RIC and REFRXC from Program MBINF (Appendix III) should be added at the end of Program MINIM.
PROGRAM MINIM (INPUT, OUTPUT, TAPE 98, PLOT, TAPE 99= PLOT)

THIS PROGRAM CALCULATES THE MINIMUM INTENSITY FOR THE MULTIPLE BEAM CASE AT VARIOUS ANGLES OF INCIDENCE AT AN INTERMEDIATE WAVELENGTH (589 NM) FOR FINDING THE OPTIMUM ANGLE OF INCIDENCE.

REAL PHI(2), PHI2(2), PHIPI(2), TNA(100), TKA(100), RSO(100,2),
X R100,2, DEL(100,2), RL(2), RIL(2), RSQIL(2), TL(2), TIL(2),
X MINT(100,2), PHCGD(100,2), RSOL(2), PHCGM(100,2), DELD(2),
X LAMDA, RAT(100,2), MXINT(100,2), VISIB(100,2)

DIMENSION LAM(9)
DIMENSION WAVLTH(50), RI(50,1), W(50), RESID(50,1), S(1), AI(20,8),
X BI(20,8), TAVLTH(52), TRI(52),
X SCALE(50)
COMMON /CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
COMMON/RICOM/ BI, NO

500 FORMAT (1h1)
1 FORMAT (6X, A10)
2 FORMAT (1F5.2)
3 FORMAT (10X, 4F10.7)
4 FORMAT (10X, 4F10.6)
8 FORMAT (5X*ANGLE*12X*MINIMUM*17X*MAXIMUM*15X*VISIBILITY*11
X X*X*R(1)/R(2-INFINI*)6//10X*4.9X*5X*11X*X*P*2X1//1)
9 FORMAT (10X*MINIMUM INTENSITIES OF A **F6.4, **NORML FLM ON A
X+A10 **ELECTRODE, REFRACTIVE INDEX (D) IS **F6.4, **/
11 FORMAT(5X, F5.1, 8F12.5//)
18 FORMAT (F4.0, 2F10.5)

INPUT PARAMETERS ARE---(1) THE METAL SUBSTRATE, (2) FOUR COEFFICIENTS FOR A LINEAR APPROXIMATION OF THE COMPLEX INDEX OF REFRACTION OF THE METAL SUBSTRATE, (3) THE CONCENTRATION OF THE FILM, (4) THE REFRACTIVE INDEX OR REFRACTOMETER SCALE READING AT UP TO 14 WAVELENGTHS.

READ 1, TITLE
READ 3, CN1, CN2, CK1, CK2
READ 2, AMN, AMX, STEPS
READ 4, CONC
DO 401 N=1,14
READ 18, WAVLTH(N), RI(N), SCALE(N)
IF (WAVLTH(N)=EQ.0000) GO TO 402

401 CONTINUE
402 M=1=1
N=6
DO 403 M=1,N,1
IF (RI(N)=EQ.0.0) RI(N)=REFRXC(SCALE(N), WAVLTH(N))
W(N)=1.0

403 CONTINUE
IF (M.LT.2) GO TO 406
DO 404 I=1,M
WAVLTH(I)=WAVLTH(I)/4000

404 CONTINUE
CALL LSOPOL (WAVLTH, RI, W, RESID, MI, S, 1, AI, BI, NO)
DO 405 I=1, MI
WAVLTH(I)=WAVLTH(I)*4000

405 CONTINUE
XMIN=3000
XMAX=8000
YMIN=1.3
YMAX=1.4
CALL CCGRID (5,10,6,6,6,10,10)
CALL CCPLT (TVLTH, RI, MI, 6, 6, 4, 10, 6, 1)
TVLTH(1)=3000
DO 30 J=1,51
TRI=RI(TVLTH)
TVLTH(J+1)=TVLTH(J)+100
30 CONTINUE
CALL CCPLT (TVLTH, TRI, 50, 4, 6, 4, 10, 6, 1)
CALL CCEND
GO TO 407
406 RI(1)= RI(1)
RI(2)=0.
RI(3)=0.
RI(4)=0.
RI(5)=0.
RI(6)=0.
407 CONTINUE
PRINT 500
RID=RI(5892)
PRINT 9, CONC, TITLE, RID
PRINT 8
IF (STEPS.EQ.0.01) GO TO 201
IF (STEPS.EQ.0.1) GO TO 202
NSTEP=STEPS
FACT=1.0
MNA=AMN
MXA=AMX
GO TO 203
201 MNA=100.*AMN
MXA=100.*AMX
NSTEP=1
FACT=STEPS
GO TO 203
202 MNA=10.*AMN
MXA=10.*AMX
NSTEP=1
FACT=STEPS
203 CONTINUE
MNAI=MNA+1
MXAI=MXA+1
DO 213 J=MNAI, MXAI, NSTEP
LAMBDA=5892.
PHID(1)=(J-1)*FACT
PHID(2)=(J-1)*FACT
TNA(J)=CN1+CN2*(LAMBDA-3800)
TKA(J)=CK1+CK2*(LAMBDA-3800)
DO 10 I=1,2
PHI(I)=0.0174533*PHID(I)
PHIPRI(I)=ASIN(C1/RI(LAMBDA))*SIN(PHI(I))
10 CONTINUE
PI=3.14159

C SUBSECTION DLIR (DIELECTRIC LIQUID REFLECTION AND TRANSMISSION)
C FRESNEL-S EQUATIONS AND MULLER-S SIGN CONVENTION ARE USED
C AT ZERO ANGLE OF INCIDENCE THE POSITIVE P-POLARIZATION VECTORS C0-
C INCIDE.
C
C TEMP1=COS(PHI(1))
TEMP3 = RIC(LAMBDA) * COS(PHI(1))
RL(1) = (TEMP1 - TEMP3) / (TEMP1 + TEMP3)
RSOL(1) = (RL(1)) ** 2
RSOL(1) = RSOL(1)

TEMP2 = RIC(LAMBDA) * COS(PHI(2))
TEMP4 = COS(PHI(2))
TL(2) = (TEMP4 - TEMP2) / (TEMP4 + TEMP2)
RSOL(2) = (RL(2)) ** 2
RSOL(2) = RSOL(2)

TEMP1 = COS(PHI(1))
TEMP3 = RIC(LAMBDA) * COS(PHI(1))
TL(1) = 2 * TEMP1 / (TEMP1 + TEMP3)
TIL(1) = 2 * TEMP3 / (TEMP3 + TEMP1)

DO 153 M = 1, 2
IF (RL(M)) 150, 151, 152

150 DELD(M) = PI
RL(M) = -RL(M)
RIL(M) = RL(M)
GO TO 153

151 DELD(M) = 0.
RIL(M) = RL(M)
GO TO 153

152 DELD(M) = 0.
RIL(M) = RL(M)
153 CONTINUE

C SUBSECTION MER (METALLIC REFLECTION) M=1 IS S, M=2 IS P
C FROM A PROGRAM -MER- DEVELOPED BY MULLER AND USING HIS SIGN CON-
C VENTION.

TN = TNA(J) / RIC(LAMBDA)
TK = TKA(J)
DO 123 M = 1, 2
SX = SIN(PHIPR(M))
CX = COS(PHIPR(M))
TX = SX / CX

TEMP1 = (TN ** 2) * (1.0 - TK ** 2) - SX ** 2
TEMP2 = TEMP1 ** 2 + 4.0 * SQRT(TEMP1 * (TN ** 4) * (TK ** 2))
ASQ = 0.5 * SQRT(TEMP2)
IF (ASQ) 110, 112, 112

110 A = 0
GO TO 114

112 A = SORT(ASQ)

114 BSQ = 0.5 * SQRT(TEMP2 - TEMP1)
IF (BSQ) 116, 118, 118

116 B = 0
GO TO 120

118 B = SORT(BSQ)

120 IF (M.EQ.1) 121, 122

121 RSQ(J,1) = (ASQ + BSQ - 2.0 * A * CX * CX) / (ASQ + BSQ + 2.0 * A * CX * CX)
IF (RSQ(J,1)) 125, 124, 124

125 R(J,1) = 0
GO TO 126

124 R(J,1) = SORT(RSQ(J,1))
126 CONTINUE
GO TO 137
122 RSQ(J+2)=RSQ(J+1)*(ASQ+BSQ-2.0*A*X+TX*TX)/(ASQ+BSQ+2.0*A*X+TX*TX+X+X)
IF (RSQ(J+2)) 128,130,130
128 R(J+2)=0
GO TO 132
130 R(J+2)=SORT(RSQ(J+2))
132 CONTINUE
137 CONTINUE
123 CONTINUE

SUBSECTION MINIM

DO 250 M=1,2
TEMP2=TL(M)*TIL(M)
TEMP1= 2.*TEMP2*R(J,M)*RIL(M)
TEMP3=TEMP2*2*RSQ(J,M)+2.*TEMP2*RIL(M)*RIL(M)*RSQ(J,M)
TEMP4=1.+RSQ(J,M)*RIL(M)
TEMP5= 2.*R(J,M)*RIL(M)
MINT(J,M)=RSQ(M)+(TEMP3-TEMP1)/(TEMP4-TEMP5)
MXINT(J,M)=RSQ(M)+(TEMP3+TEMP1)/(TEMP4+TEMP5)
VISIB(J,M) = (MXINT(J,M)-MINT(J,M))/(MXINT(J,M)+MINT(J,M))
RAT(J,M)=RIL(M)/(TEMP2*R(J,M)/(1.-R(J,M)*RIL(M)))
250 CONTINUE
PRINT 11, PHID(1), MINT(J+1), MINT(J+2), MXINT(J+1), MXINT(J+2),
   VISIB(J+1), VISIB(J+2), RAT(J+1), RAT(J+2)
213 CONTINUE
STOP
END
APPENDIX I: FORTRAN IV COMPUTER PROGRAM MINIM

As shown in Sec. II-B, the optimum angle of incidence is that angle where the fringe visibility, \( V \), is equal to 1, or equivalently, the minimum intensity of a fringe, \( I_{\text{min}} \), is equal to 0. For the multiple beam model, the minimum intensity is given by Eq. 37

\[
I_{\text{min}} = r_3^2 + \frac{(t_2 t_3 r_1)^2 - 2t_2 t_3 r_1 r_3 + 2t_2 t_3 r_1^2 r_2 r_3}{1 + (r_1 r_2)^2 - 2r_1 r_2} \quad (37)
\]

Using Eq. 40 for the maximum intensity

\[
I_{\text{max}} = r_3^2 + \frac{(t_2 t_3 r_1)^2 + 2t_2 t_3 r_1 r_3 + 2t_2 t_3 r_1^2 r_2 r_3}{1 + (r_1 r_2)^2 + 2r_1 r_2} \quad (40)
\]

the fringe visibility is:

\[
V = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \quad (27)
\]

Program MINIM calculates these quantities for increments of angle of incidence. In addition, the quantity

\[
\frac{r_3}{t_2 t_3 r_1} = \text{reflection from air-liquid surface} \quad \frac{1 - r_1 r_2}{t_2 t_3 r_1} = \text{remainder of reflections} \quad (42)
\]

is calculated. This quantity is useful for interpolating to find the optimum angle of incidence precisely. The dependence of Eqs. 37, 40, 27, and 42 on the angle of incidence arises from the dependence of the reflection and transmission coefficients on the angle of incidence. The equation for these coefficients are given in Sec. II-A-2.

Since the indices of refraction of the liquid and substrate vary
with wavelength, it must be expected that the optimum angle of incidence also varies with wavelength. For observations in white light, only one angle of incidence can be used. As a compromise, the calculations were done for an intermediate wavelength (Sodium, $\lambda = 589.2$ nm).
<table>
<thead>
<tr>
<th>ANGLE</th>
<th>MINIMUM P</th>
<th>MAXIMUM P</th>
<th>MIN/MAX S</th>
<th>P(1) / B(2 - (1/FIN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.34825</td>
<td>1.40777</td>
<td>1.7214</td>
<td>-6.30900</td>
</tr>
<tr>
<td>4.0</td>
<td>1.36011</td>
<td>1.40332</td>
<td>1.60394</td>
<td>-1.19544</td>
</tr>
<tr>
<td>4.0</td>
<td>1.35756</td>
<td>1.47760</td>
<td>1.72110</td>
<td>-9.34695</td>
</tr>
<tr>
<td>4.0</td>
<td>1.34449</td>
<td>1.47061</td>
<td>1.72566</td>
<td>-11.34527</td>
</tr>
<tr>
<td>4.0</td>
<td>1.35199</td>
<td>1.45333</td>
<td>1.73714</td>
<td>-11.02367</td>
</tr>
<tr>
<td>4.0</td>
<td>1.34884</td>
<td>1.45574</td>
<td>1.73592</td>
<td>-10.47137</td>
</tr>
<tr>
<td>4.0</td>
<td>1.34041</td>
<td>1.44784</td>
<td>1.78064</td>
<td>-1.05820</td>
</tr>
<tr>
<td>4.0</td>
<td>1.34370</td>
<td>1.43061</td>
<td>1.74551</td>
<td>-1.03943</td>
</tr>
<tr>
<td>4.0</td>
<td>1.32747</td>
<td>1.43103</td>
<td>1.75075</td>
<td>-1.02493</td>
</tr>
<tr>
<td>4.0</td>
<td>1.33311</td>
<td>1.42205</td>
<td>1.75602</td>
<td>-1.02586</td>
</tr>
<tr>
<td>4.0</td>
<td>1.32840</td>
<td>1.41275</td>
<td>1.76119</td>
<td>-1.02776</td>
</tr>
<tr>
<td>4.0</td>
<td>1.33350</td>
<td>1.40362</td>
<td>1.76646</td>
<td>-1.02921</td>
</tr>
<tr>
<td>4.0</td>
<td>1.31800</td>
<td>1.39267</td>
<td>1.77243</td>
<td>-1.03243</td>
</tr>
<tr>
<td>4.0</td>
<td>1.31206</td>
<td>1.38227</td>
<td>1.77410</td>
<td>-1.03704</td>
</tr>
<tr>
<td>4.0</td>
<td>1.30564</td>
<td>1.37120</td>
<td>1.78632</td>
<td>-1.04070</td>
</tr>
<tr>
<td>4.0</td>
<td>1.29876</td>
<td>1.35966</td>
<td>1.78972</td>
<td>-1.04407</td>
</tr>
<tr>
<td>4.0</td>
<td>1.29133</td>
<td>1.34757</td>
<td>1.79468</td>
<td>-1.04745</td>
</tr>
<tr>
<td>4.0</td>
<td>1.29333</td>
<td>1.33630</td>
<td>1.80234</td>
<td>-1.05073</td>
</tr>
<tr>
<td>4.0</td>
<td>1.27474</td>
<td>1.32178</td>
<td>1.82749</td>
<td>-1.05407</td>
</tr>
<tr>
<td>4.0</td>
<td>1.26551</td>
<td>1.31062</td>
<td>1.84464</td>
<td>-1.05740</td>
</tr>
<tr>
<td>4.0</td>
<td>1.25640</td>
<td>1.29366</td>
<td>1.86064</td>
<td>-1.06070</td>
</tr>
<tr>
<td>4.0</td>
<td>1.24697</td>
<td>1.27661</td>
<td>1.87654</td>
<td>-1.06400</td>
</tr>
<tr>
<td>4.0</td>
<td>1.23358</td>
<td>1.26293</td>
<td>1.89347</td>
<td>-1.06731</td>
</tr>
<tr>
<td>4.0</td>
<td>1.22411</td>
<td>1.24856</td>
<td>1.90994</td>
<td>-1.07061</td>
</tr>
<tr>
<td>4.0</td>
<td>1.20842</td>
<td>1.22950</td>
<td>1.92639</td>
<td>-1.07392</td>
</tr>
<tr>
<td>4.0</td>
<td>1.19454</td>
<td>1.21175</td>
<td>1.94316</td>
<td>-1.07725</td>
</tr>
</tbody>
</table>

XBL 715-913
<table>
<thead>
<tr>
<th>Angle</th>
<th>S0</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
<th>S8</th>
<th>S9</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.0</td>
<td>.19574</td>
<td>.19674</td>
<td>.19524</td>
<td>.19567</td>
<td>.19579</td>
<td>.19590</td>
<td>.19590</td>
<td>.19590</td>
<td>.19590</td>
<td>.19590</td>
</tr>
<tr>
<td>90.1</td>
<td>.20574</td>
<td>.20431</td>
<td>.20092</td>
<td>.20073</td>
<td>.20071</td>
<td>.20070</td>
<td>.20069</td>
<td>.20068</td>
<td>.20067</td>
<td>.20066</td>
</tr>
<tr>
<td>90.2</td>
<td>.21574</td>
<td>.21424</td>
<td>.21194</td>
<td>.21165</td>
<td>.21161</td>
<td>.21159</td>
<td>.21158</td>
<td>.21157</td>
<td>.21156</td>
<td>.21155</td>
</tr>
<tr>
<td>90.3</td>
<td>.22574</td>
<td>.22397</td>
<td>.22168</td>
<td>.22141</td>
<td>.22137</td>
<td>.22134</td>
<td>.22132</td>
<td>.22130</td>
<td>.22128</td>
<td>.22126</td>
</tr>
<tr>
<td>90.4</td>
<td>.23574</td>
<td>.23357</td>
<td>.23132</td>
<td>.23098</td>
<td>.23087</td>
<td>.23077</td>
<td>.23067</td>
<td>.23058</td>
<td>.23049</td>
<td>.23040</td>
</tr>
<tr>
<td>90.5</td>
<td>.24574</td>
<td>.24347</td>
<td>.24112</td>
<td>.24079</td>
<td>.24069</td>
<td>.24060</td>
<td>.24050</td>
<td>.24041</td>
<td>.24032</td>
<td>.24023</td>
</tr>
<tr>
<td>90.6</td>
<td>.25574</td>
<td>.25337</td>
<td>.25102</td>
<td>.25069</td>
<td>.25060</td>
<td>.25051</td>
<td>.25042</td>
<td>.25033</td>
<td>.25024</td>
<td>.25015</td>
</tr>
<tr>
<td>90.7</td>
<td>.26574</td>
<td>.26321</td>
<td>.26087</td>
<td>.26055</td>
<td>.26046</td>
<td>.26037</td>
<td>.26028</td>
<td>.26019</td>
<td>.26010</td>
<td>.25991</td>
</tr>
<tr>
<td>90.8</td>
<td>.27574</td>
<td>.27314</td>
<td>.27071</td>
<td>.27039</td>
<td>.27030</td>
<td>.27021</td>
<td>.27012</td>
<td>.27003</td>
<td>.26994</td>
<td>.26985</td>
</tr>
<tr>
<td>90.9</td>
<td>.28574</td>
<td>.28308</td>
<td>.28067</td>
<td>.28035</td>
<td>.28026</td>
<td>.28017</td>
<td>.28008</td>
<td>.27999</td>
<td>.27990</td>
<td>.27881</td>
</tr>
</tbody>
</table>

MINIMUM INTENSITIES OF A 1.6000 FRIABLE FILM ON A SILVER ELECTRODE. REFRACTIVE INDEX (0) IS 1.6000.
APPENDIX II: FORTRAN IV COMPUTER PROGRAM CHROM

In Section II-C, a method was outlined, by which the color of a thin film of known thickness and refractive index could be calculated. In summary, the intensity as a function of wavelength and film thickness is calculated using Eq. 26

\[
I(\lambda,d) = r_3^2 \frac{(t_2 t_3 t_1)^2 + 2t_2 t_3 r_1 r_3 \cos(\delta_1 - \delta_3) - 2t_2 t_3 r_2^2 r_3 \cos(\delta_2 + \delta_3)}{1 + (r_1 r_2)^2 - 2r_1 r_2 \cos(\delta_1 + \delta_2)}
\]

(26)

The tristimulus values are found using the results of Eq. 26; tabulated \(\bar{x}, \bar{y}, \bar{z}\) values; and Eqs. 43a, b, c:

\[
\begin{align*}
x &= \int_{380}^{780} I(\lambda)\bar{x}(\lambda) d\lambda \\
y &= \int_{380}^{780} I(\lambda)\bar{y}(\lambda) d\lambda \\
z &= \int_{380}^{780} I(\lambda)\bar{z}(\lambda) d\lambda
\end{align*}
\]

(43a, b, c)

The chromaticity values are found using Eq. 44a, b, c:

\[
\begin{align*}
x &= \frac{X}{X+Y+Z} \\
y &= \frac{Y}{X+Y+Z} \\
z &= \frac{Z}{X+Y+Z}
\end{align*}
\]

(44a, b, c)
This program calculates and prints values of the six functions (43) and (44) for use with Fig. 13 to obtain a color series for determining the film thickness from visual observation. The index of refraction of the substrate and the reflection coefficients of the film-substrate interface are those for $\lambda = 589.2$ nm.
VARIABLES

The following names were used in the program CHROM:

<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN1, CN2</td>
<td>$C_{n1}, C_{n2}$</td>
<td>Coefficients for a linear approximation of the real part of the index of refraction of the substrate.*</td>
</tr>
<tr>
<td>CK1, CK2</td>
<td>$C_{\kappa 1}, C_{\kappa 2}$</td>
<td>Coefficients for a linear approximation of the absorption index of the substrate.*</td>
</tr>
<tr>
<td>SCALE</td>
<td>-</td>
<td>Refractometer Scale Reading</td>
</tr>
<tr>
<td>RI, RIC</td>
<td>$n_1$</td>
<td>Index of refraction of the film</td>
</tr>
<tr>
<td>TNA</td>
<td>$n$</td>
<td>Real part of the complex refractive index of the substrate</td>
</tr>
<tr>
<td>TKA, TK</td>
<td>$\kappa$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>TN</td>
<td>$n/n_1$</td>
<td></td>
</tr>
<tr>
<td>PHID, PHIN</td>
<td>$\phi$ (degrees)</td>
<td>Angle of incidence on film</td>
</tr>
</tbody>
</table>

* For the index of refraction of the substrate, written as in Eq. 8.

\[ n_c = n(1+\kappa) \]  \hspace{1cm} (8)

A linear approximation of $n$ and $\kappa$ with wavelength, $\lambda$, was made such that:

\[ n = C_{n1} + C_{n2}(\lambda-3800 \text{ Å}) \]  \hspace{1cm} (A-1)

and

\[ \kappa = C_{\kappa 1} + C_{\kappa 2}(\lambda-3800 \text{ Å}) \]  \hspace{1cm} (A-2)

The values of $C_{n1}$, $C_{n2}$, $C_{\kappa 1}$, $C_{\kappa 2}$ are supplied as input parameters.
<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHI</td>
<td>$\phi$ (radians)</td>
<td>Angle of incidence on film</td>
</tr>
<tr>
<td>PHIPR</td>
<td>$\phi'$(radians)</td>
<td>Angle of refraction, angle of incidence on substrate</td>
</tr>
<tr>
<td>DEL</td>
<td>$\delta_1$(radians)</td>
<td>Phase change upon reflection from solid surface</td>
</tr>
<tr>
<td>PHCGM</td>
<td>$\delta_1$(degrees)</td>
<td>Phase change upon reflection from solid surface</td>
</tr>
<tr>
<td>DELS</td>
<td>$\delta_1,s$(degrees)</td>
<td>Phase change upon reflection from solid surface for s-polarized light</td>
</tr>
<tr>
<td>DELP</td>
<td>$\delta_1,p$(degrees)</td>
<td>Phase change upon reflection from solid surface for p-polarized light</td>
</tr>
<tr>
<td>DELD</td>
<td>$\delta_3$(radians)</td>
<td>Phase change upon reflection from gas-liquid interface</td>
</tr>
<tr>
<td>PHCGD</td>
<td>$\delta_{tot}$(degrees)</td>
<td>Total phase change, Eq. 46</td>
</tr>
<tr>
<td>RL</td>
<td>$r_3$</td>
<td>Reflection coefficient from gas-liquid interface</td>
</tr>
<tr>
<td>RLS</td>
<td>$r_{3,s}$</td>
<td>Reflection coefficient from gas-liquid interface for s-polarization</td>
</tr>
<tr>
<td>RLP</td>
<td>$r_{3,p}$</td>
<td>Reflection coefficient from gas-liquid interface for p-polarization</td>
</tr>
<tr>
<td>RIL</td>
<td>$r_2$</td>
<td>Internal reflection coefficient from gas-liquid interface</td>
</tr>
<tr>
<td>R</td>
<td>$r_1$</td>
<td>Reflection coefficient from liquid-solid interface</td>
</tr>
<tr>
<td>NAME</td>
<td>SYMBOL</td>
<td>DESCRIPTION</td>
</tr>
<tr>
<td>-------------</td>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>RS</td>
<td>$r_{1,s}$</td>
<td>Reflection coefficient from liquid-solid interface for $s$-polarization</td>
</tr>
<tr>
<td>RP</td>
<td>$r_{1,p}$</td>
<td>Reflection coefficient from liquid-solid interface for $p$-polarization</td>
</tr>
<tr>
<td>TL</td>
<td>$t_3$</td>
<td>Transmission coefficient from gas to liquid</td>
</tr>
<tr>
<td>TIL</td>
<td>$t_2$</td>
<td>Transmission coefficient from liquid to gas</td>
</tr>
<tr>
<td>A,B</td>
<td>$A,B$</td>
<td>Intermediate variables</td>
</tr>
<tr>
<td>LAMBDA,WVLTH</td>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>INT(J,L,M)</td>
<td>$I$</td>
<td>Multiple beam intensity for a film thickness $100(L-1)$, wavelength $[380+5(J-1)]nm$, and polarization $M$, where $M=1$ is $s$ and $M=2$ is $p$</td>
</tr>
<tr>
<td>XBAR</td>
<td>$P_X$</td>
<td>Weighting function</td>
</tr>
<tr>
<td>YBAR</td>
<td>$P_Y$</td>
<td>Weighting function</td>
</tr>
<tr>
<td>ZBAR</td>
<td>$P_Z$</td>
<td>Weighting function</td>
</tr>
<tr>
<td>CAPX</td>
<td>$X$</td>
<td>Tristimulus value, Eq. 43a</td>
</tr>
<tr>
<td>CAPY</td>
<td>$Y$</td>
<td>Tristimulus value, Eq. 43b</td>
</tr>
<tr>
<td>CAPZ</td>
<td>$Z$</td>
<td>Tristimulus value, Eq. 43c</td>
</tr>
<tr>
<td>LOWX</td>
<td>$x$</td>
<td>Chromaticity value, Eq. 44a</td>
</tr>
<tr>
<td>LOWY</td>
<td>$y$</td>
<td>Chromaticity value, Eq. 44b</td>
</tr>
<tr>
<td>LOWZ</td>
<td>$z$</td>
<td>Chromaticity value, Eq. 44c</td>
</tr>
<tr>
<td>OPTIC PATH DIFF</td>
<td>$\Delta S$</td>
<td>Optical Path Difference, Eq. 18</td>
</tr>
</tbody>
</table>
The input for program CHROM is on punched cards. All data is in a non-exponential form (e.g. 100, 0.0003, 100.7). Decimal points should be included in all numbers except $\lambda$ on cards 5-19. The cards used are:

<table>
<thead>
<tr>
<th>CARD</th>
<th>VARIABLE</th>
<th>UNITS</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Name of Substrate</td>
<td>-</td>
<td>Centered in Cols. 7-16</td>
</tr>
<tr>
<td>2</td>
<td>$C_{n1}$</td>
<td>Dimensionless</td>
<td>Cols. 11-20</td>
</tr>
<tr>
<td></td>
<td>$C_{n2}$</td>
<td>$1/\AA$</td>
<td>21-30</td>
</tr>
<tr>
<td></td>
<td>$C_{k1}$</td>
<td>Dimensionless</td>
<td>31-40</td>
</tr>
<tr>
<td></td>
<td>$C_{k2}$</td>
<td>$1/\AA$</td>
<td>41-50</td>
</tr>
<tr>
<td>3</td>
<td>$\phi$</td>
<td>Degrees</td>
<td>Col. 11-20</td>
</tr>
<tr>
<td>4</td>
<td>Concentration of Electrolyte</td>
<td>Normal</td>
<td>Col. 11-20</td>
</tr>
<tr>
<td>5</td>
<td>Name of light source</td>
<td>-</td>
<td>Col. 21-40</td>
</tr>
<tr>
<td>6 to 87</td>
<td>$P(\lambda)\vec{x}(\lambda)$</td>
<td>Dimensionless</td>
<td>Col. 8-17</td>
</tr>
<tr>
<td></td>
<td>$P(\lambda)\vec{y}(\lambda)$</td>
<td>Dimensionless</td>
<td>18-27</td>
</tr>
<tr>
<td></td>
<td>$P(\lambda)\vec{z}(\lambda)$</td>
<td>Dimensionless</td>
<td>28-37</td>
</tr>
</tbody>
</table>

$\phi$ is the angle of incidence. For the color charts, Fig. 14a,b, this was the optimum angle of incidence, computed by Program MINIM. $P(\lambda)$ is the spectral emmissivity of the light source (380-780 nm, in 5 nm increments). $\vec{x}(\lambda)$, $\vec{y}(\lambda)$, $\vec{z}(\lambda)$ are the amounts of the C.I.E. primaries X, Y, Z in light of wavelength $\lambda$. The index of refraction of the film was set at 1.5 by setting BI(1) = 1.500 and BI(2-6) = 0.0.

A listing of the program and a sample output follow. The second listing under DELS and DELP is $\delta_{\text{tot}}$, Eq. 46, for s and p polarization, respectively.
PROGRAM CHROM (INPUT, OUTPUT, TAPE 98, PLOT, TAPE 99=PLOT)

THIS PROGRAM CALCULATES THE INTENSITY OF REFLECTED LIGHT FROM A
DIELECTRIC FILM COVERED METAL SURFACE OF KNOWN OPTICAL PARAMETERS
AS A FUNCTION OF WAVELENGTH AND FILM THICKNESS

REAL PHID(2), PHII(2), PHIPR(2), TNA(85), TKA(85), RSQ(85,2),
X R(85,2), DEL(2,85), RL(2), RIL(2), RSQIL(2), TL(2), TIL(2),
X INT(85,160,2), PHCGD(85,2), RSQ(2), PHCGM(85,2), DELD(2),
X LAMBDA
DIMENSION LAMBDA(9)
DIMENSION WAVLTH(50), RI(50,1), W(50), RESID(50,1), S(1), AI(20,8),
X BI(20,8), TWVLTH(52), TRII(52),
X SCALE(50)
REAL LOWX, LOWY, LOWZ, XBAR(81), YBAR(81), ZBAR(81), X, Y, Z
DIMENSION LOWX(160), LOWY(160), LOWZ(160)
COMMON/RICOM/ BI, NO

500 FORMAT (1HI)
1 FORMAT (6X, A10)
3 FORMAT (10X, 4F10.7)
4 FORMAT (10X, F10.6)
8 FORMAT (10X, *S POLARIZATION, /**)
9 FORMAT (10X, *P POLARIZATION, /**)
12 FORMAT (10X, *CONCENTRATION OF ELECTROLYTE IS *, F6.4, *, NORMAL. RE
XFRACTIVE INDEX (D) IS *, F6.4, *, ANGLE OF INCIDENCE IS *, F5.4, //
X/**)
15 FORMAT ( *OPTICAL PARAMETERS OF *, A10, * - LIQUID SURFACE *, //)
X *RLP*, //)
17 FORMAT (10X, F4.0, 11F10.4)
18 FORMAT (F4.0, 2F10.5)

INPUT PARAMETERS ARE---(1) THE METAL SUBSTRATE, (2) FOUR COEFFI-
CIENTS FOR A LINEAR APPROXIMATION OF THE COMPLEX INDEX OF REFRACT-
ION OF THE METAL SUBSTRATE, (3) THE ANGLE OF INCIDENCE ON THE LI-
QUID FILM, (4) THE CONCENTRATION OF THE FILM, (5) THE REFRACTIVE
INDEX OR REFRACTOMETER SCALE READING AT UP TO 14 WAVELENGTHS.

READ 1, TITLE
READ 3, CN1, CN2, CK1, CK2
READ 4, PHIN
READ 4, CONC
READ 5
DO 310 I=1,81
READ 6, XBAR(I), YBAR(I), ZBAR(I)
310 CONTINUE
NO=6
BI(1)=1.500
BI(2)=0.
BI(3)=0.
BI(4)=0.
BI(5)=0.
BI(6)=0.
PRINT 500
PRINT 15, TITLE
RID=RICM(589.2)
PRINT 12, CONC, RID, PHIN
PHIN(1)=PHIN
CHANGE IN OPTICAL CONSTANTS WITH WAVELENGTH

TNA(J)=CN1+CN2*(LAMBDA-3800)
TKA(J)=CK1+CK2*(LAMBDA-3800)
DO 10 I=1,2
PHI(I)=0.0174533*PHIDCII
PHIPR(I)=ASIN(1/RIC(LAMBDA))*SIN(PHI(I))
10 CONTINUE

SUBSECTION DLIR (DIELECTRIC LIQUID REFLECTION AND TRANSMISSION)
FRESNEL'S EQUATIONS AND MULLER'S SIGN CONVENTION ARE USED (AT
ZERO ANGLE OF INCIDENCE THE POSITIVE P-POLARIZATION VECTORS CO-
INCIDE).

TEMP1=COS(PHI(I))
TEMP3=RIC(LAMBDA)*COS(PHIPR(I))
RL(I)=(TEMP1-TEMP3)/(TEMP1+TEMP3)
RSQ(I)=(RL(I))*2
RSQ1(I)=RSQ(1)
TEMP2=RIC(LAMBDA)*COS(PHI(2))
TEMP4=COS(PHIPR(2))
RL(2)=(TEMP4-TEMP2)/(TEMP4+TEMP2)
RSQ(2)=(RL(2))*2
RSQL(2)=RSQ(2)
TEMP1=COS(PHI(I))
TEMP3=RIC(LAMBDA)*COS(PHIPR(1))
TL(I)=2*TEMP1/(TEMP1+TEMP3)
TIL(1)=2*TEMP3/(TEMP3+TEMP1)
TEMP2=COS(PHI(2))
TEMP4=RIC(LAMBDA)*COS(PHI(2))+COS(PHIPR(2))
TEMP6=RIC(LAMBDA)*COS(PHIPR(2))
TL(2)=2*TEMP2/TEMP4
TIL(2)=2*TEMP6/TEMP4
DO 153 M=1,2
IF (RL(M)) 150, 151, 152
150 DEL(M) = PI
RL(M)=-RL(M)
RIL(M)=RL(M)
GO TO 153
151 DELN(M)=0.
RIL(M)=RL(M)
GO TO 153
152 DELN(M)=0.
RIL(M)=RL(M)
153 CONTINUE

SUBSECTION MER (METALLIC REFLECTION) M=1 IS S*, M=2 IS P
FROM A PROGRAM -MER- DEVELOPED BY MULLER AND USING HIS SIGN CON-
VENTION.

TN=TNA(J)/RIC(LAMBDA)
TK=TKA(J)
DO 123 M=1,2
SX=SIN(PHIPR(M))
CX=COS(PHIPR(M))
TX=SX/CX
TEMP1=(TN**2)*(1.0-TK**2)-SX**2
TEMP2=TEMP1**2+4.0*(TN**4)*(TK**2)
ASQ=0.5*(SORT(TEMP2)+TEMP1)
IF (ASQ) 110, 112, 112
110 A=0
GO TO 114
112 A=SORT(ASQ)
114 BSQ=0.5*(SORT(TEMP2)-TEMP1)
IF (BSQ) 116, 118, 118
116 A=0
GO TO 120
118 R=SORT(BSQ)
120 IF (M.EQ.1) 120, 122
121 RSQ(J,1)=(ASQ+BSQ-2.0*A*CX+CX*CX)/(ASQ+BSQ+2.0*A*CX+CX*CX)
IF (RSQ(J,1)) 125, 124, 124
125 R(J,1)=0
GO TO 126
124 R(J,1)=SORT(RSQ(J,1))
126 CONTINUE
122 RSQ(J,2)=RSQ(J,1)*(ASQ+BSQ-2.0*A*SX+TX+SXSX*TX)/(ASQ+BSQ+2.0*
XA*SX+TX+SXSX*TX)
IF (RSQ(J,2)) 128, 130, 130
128 R(J,2)=0
GO TO 132
130 R(J,2)=SORT(RSQ(J,2))
132 CONTINUE
123 CONTINUE
DO 401 MI=1,37
LAMBDA=5892.*
DEL(1,MI)=10.*CMI-0.0174533
PRINT 16
DO 403 M=1,2
PHCGM(J,M)=RDICLAMBDAM)/0.0174533
PHCGM(J,M)=DEL(J,MI)/0.0174533
403 CONTINUE
RIS=RICLAMBDAM)
PRINT 17, LAMBDA, A, B, R(J,1), R(J,2), PHCGM(J,1), PHCGM(J,2),
X TN, TK, R(J,1), RL(1), RL(2)
PRINT 17, LAMBDA, A, B, R(J,1), R(J,2), PHCGD(J,1), PHCGD(J,2),
X TN, TK, R(J,1), RL(1), RL(2)
C SUBSECTION MBINT (MULTIPLE BEAM INTENSITY)
C USING AN EQUATION GIVEN BY FRANCON
DO 213 J=1,83
LAMBDA=3800.+50.*J-1)
DO 212 M=1,2
TEMP2=TL(M)*TIL(M)
DO 211 L=1,151
THK=100.*L-1)
TEMP1=4.0*PI*RICLAMBDAM)*THK*COS(PHIH(M))/LAMBDA+DEL(1,MI)
TEMP3=2.0*R(1,M)*RIL(M)*COS(TEMP1+DEL(M)+PI)
TEMP4=2.0*R(1,M)*RIL(M)*COS(TEMP1-DEL(M))
TEMP6=1.0+RSQ(1,M)+RSQIL(M)-TEMP3
TEMP7=(TEMP2**2)*RSQ(1,M)+TEMP4+2.0*TEMP2*RL(M)*RIL(M)*RSQ(1,M)
INT(J,L,M)=RSQ(L,M)+TEMP7/TEMP6
211 CONTINUE
212 CONTINUE
213 CONTINUE
C
C TRISTIMULUS AND CHROMATICITY VALUES
C PRINT 2* TITLE
C PRINT 5
C PRINT 4* DEL(1*M)
C DO 316 L=1*2
C IF (L.EQ.1) 311,312
C 311 PRINT 8
C GO TO 913
C 312 PRINT 500
C PRINT 2* TITLE
C PRINT 5
C PRINT 9
C 313 PRINT 11
C DO 314 M=1*151
C CAPX=0
C CAPY=0
C CAPZ=0
C DO 315 J=1*81
C X=INT(J*M*L)*XBAR(J)
C Y=INT(J*M*L)*YBAR(J)
C Z=INT(J*M*L)*ZBAR(J)
C CAPX=CAPX+X
C CAPY=CAPY+Y
C CAPZ=CAPZ+Z
C 315 CONTINUE
C ZUM=CAPX+CAPY+CAPZ
C LOWX(M)=CAPX/ZUM
C LOWY(M)=CAPY/ZUM
C LOWZ(M)=CAPZ/ZUM
C OP=2.*RIC(5892.)*100.*(M-1)*COS(PHIPR)
C PRINT 7*OP, CAPX, CAPY, CAPZ, LOWX(M), LOWY(M), LOWZ(M)
C 314 CONTINUE
C 402 CONTINUE
C 316 CONTINUE
C 401 CONTINUE
C 2 FORMAT (22X, * TRISTIMULUS AND CHROMATICITY VALUES OF AN ELECTROLY
C XTE FILM ON A *, A10*, * ELECTRODE*,//)
C 5 FORMAT (10X, 20H
C 6 FORMAT (7X, 3F10.4)
C 7 FORMAT (6X,F7.0, 7F17.4)
C X*LOWX*,
C X13X*LOWY*, 13X*LOWZ*,//)
C STOP
C END
C
C FUNCTION RIC(WAVLTH)
C THIS FUNCTION GIVES REFRACTIVE INDEX OF THE SOLUTION AT A SPECIFIED
C WAVELENGTH USING A POLYNOMIAL OF 6 TERMS.
C
C COMMON /RICOm/ B*NO
C DIMENSION B(2*8)
C REAL A
C A=WAVLTH
C C=0.0
C A=A/4000
C DO 601 K=1*NO
C C=C+(B(K)*(A**(K-1)))

601 CONTINUE
C RIC=C
C RETURN
C END
<table>
<thead>
<tr>
<th>ORIF</th>
<th>PATH DIFF</th>
<th>CAPE</th>
<th>CAPY</th>
<th>GAPZ</th>
<th>LONX</th>
<th>LORY</th>
<th>LORZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>45.3595</td>
<td>45.3595</td>
<td>25.3595</td>
<td>15.3595</td>
<td>20.3595</td>
<td>25.3595</td>
<td>15.3595</td>
</tr>
<tr>
<td>450</td>
<td>88.8385</td>
<td>88.8385</td>
<td>58.8385</td>
<td>38.8385</td>
<td>43.8385</td>
<td>58.8385</td>
<td>38.8385</td>
</tr>
<tr>
<td>1350</td>
<td>93.3017</td>
<td>93.3017</td>
<td>63.3017</td>
<td>33.3017</td>
<td>38.3017</td>
<td>63.3017</td>
<td>33.3017</td>
</tr>
<tr>
<td>1794</td>
<td>161.9556</td>
<td>161.9556</td>
<td>121.9556</td>
<td>81.9556</td>
<td>96.9556</td>
<td>121.9556</td>
<td>81.9556</td>
</tr>
<tr>
<td>2204</td>
<td>62.3427</td>
<td>62.3427</td>
<td>32.3427</td>
<td>22.3427</td>
<td>27.3427</td>
<td>32.3427</td>
<td>22.3427</td>
</tr>
<tr>
<td>2447</td>
<td>103.1873</td>
<td>103.1873</td>
<td>73.1873</td>
<td>43.1873</td>
<td>58.1873</td>
<td>73.1873</td>
<td>43.1873</td>
</tr>
</tbody>
</table>

**SOURCE**: 176533

**POLARIZATION**: 5

**LAMADA A**

| 5802 | 1.6537 | 2.4442 | 7.6222 | 6.6149 | 10.0000 | 10.0000 | 1.6498 | 1.4153 | 1.5000 | 1.8045 | 0.6080 |
| 5802 | 1.6537 | 2.4442 | 7.6222 | 6.6149 | 16.6998 | 10.0000 | 1.6498 | 1.4153 | 1.5000 | 1.8045 | 0.6080 |

**TRASTIVIAIUS AND CHROMATICITY VALUES OF AN ELECTROLYTE FILM ON A PLATINUM ELECTRODE**

**XBL 715-914**
This program calculates a table of the possible film thicknesses, for 5 nm increments of wavelength, which produce a maximum or minimum of intensity at that wavelength. For comparison with the observed maxima and minima, the range of wavelengths was 380 to 780 nm. The resulting table was used to determine film thickness from the spectrophotometer traces. To determine the film thickness it is necessary to know the optical constants of the substrate, n and \(\kappa\), the index of refraction of the liquid film, \(n_1\), and the angle of incidence, \(\phi\).

The program calculates the intensity at a particular wavelength in thickness increments of 10 nm (0.01 \(\mu\)). The first minimum of intensity is found by comparison with the intensity at the previous thickness. The spacing between minima or maxima is such that, from Eq. 19

\[
\frac{4\pi n (\Delta d) \cos \phi'}{\lambda} = 2\pi
\]

(A-3)

or

\[
\Delta d = \frac{\lambda}{2n \cos \phi'}
\]

(A-4)

The table is then filled out using this relationship.

To illustrate the use of the program, Fig. 19 is a sample spectrophotometer trace. Minima occur at 458 and 645 nm. A maximum occurs at 530 nm. Table A-I lists the film thicknesses for which maxima and minima occur at these wavelengths. The thickness which corresponds in all cases is (averaged): 0.82 \(\mu\).
### VARIABLES

The following names are used in the program MBINF.

<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM₁, CN₂</td>
<td>Cᵣ, Cᵣ₂</td>
<td>Coefficients for a linear approximation of the real part of the index of refraction of the substrate.*</td>
</tr>
<tr>
<td>CK₁, CK₂</td>
<td>C₉, C₉₂</td>
<td>Coefficients for a linear approximation of the absorption index of the substrate.*</td>
</tr>
<tr>
<td>SCALE</td>
<td>-</td>
<td>Refractometer scale reading</td>
</tr>
<tr>
<td>RI, RIC</td>
<td>n₁</td>
<td>Index of refraction of the film</td>
</tr>
<tr>
<td>TNA</td>
<td>n</td>
<td>Real part of complex refractive index of substrate</td>
</tr>
<tr>
<td>TKA, TK</td>
<td>κ</td>
<td>Absorption index</td>
</tr>
<tr>
<td>TN</td>
<td>n/n₁</td>
<td></td>
</tr>
<tr>
<td>PHID, PHIN</td>
<td>φ(degrees)</td>
<td>Angle of incidence on film</td>
</tr>
<tr>
<td>PHI</td>
<td>φ(radians)</td>
<td>Angle of incidence on film</td>
</tr>
</tbody>
</table>

* For the index of refraction of the substrate, written as in Eq. 8

\[
n_c = n(1+\kappa) \tag{8}
\]

A linear approximation of \( n \) and \( \kappa \) with wavelength, \( \lambda \), was made such that:

\[
n = C_{n1} + C_{n2} (\lambda-3800 \text{ Å}) \tag{A-1}
\]

and

\[
\kappa = C_{\kappa1} + C_{\kappa2} (\lambda-3800 \text{ Å}) \tag{A-2}
\]

The values of CM₁, CN₂, CK₁ and CK₂ are supplied as input parameters.
<table>
<thead>
<tr>
<th>NAME</th>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEL</td>
<td>$\delta_1$ (radians)</td>
<td>Phase change upon reflection from solid surface</td>
</tr>
<tr>
<td>PHCGM</td>
<td>$\delta_1$ (degrees)</td>
<td>Phase change upon reflection from solid surface</td>
</tr>
<tr>
<td>DELD</td>
<td>$\delta_3$ (radians)</td>
<td>Phase change upon reflection from gas-liquid interface.</td>
</tr>
<tr>
<td>PHCGD</td>
<td>$\delta_{\text{tot}}$ (degrees)</td>
<td>Total phase change</td>
</tr>
<tr>
<td>PHIPR</td>
<td>$\phi'$ (radians)</td>
<td>Angle of refraction, angle of incidence on substrate</td>
</tr>
<tr>
<td>RL</td>
<td>$r_3$</td>
<td>Reflection coefficient from gas-liquid interface</td>
</tr>
<tr>
<td>RIL</td>
<td>$r_2$</td>
<td>Internal reflection from gas-liquid interface</td>
</tr>
<tr>
<td>R</td>
<td>$r_1$</td>
<td>Reflection coefficient from liquid-metal interface</td>
</tr>
<tr>
<td>TL</td>
<td>$t_3$</td>
<td>Transmission coefficient from gas to liquid</td>
</tr>
<tr>
<td>TIL</td>
<td>$t_2$</td>
<td>Transmission coefficient from liquid to gas</td>
</tr>
<tr>
<td>A,B</td>
<td>A,B</td>
<td>Intermediate variables</td>
</tr>
<tr>
<td>LAMBDA, WYLTH</td>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>INT$(J,L,M)$</td>
<td>I</td>
<td>Multiple beam intensity for a film thickness $100(L-1)$, wavelength $[380+5(J-1)]$ nm, and polarization $M$, where $M=1$ is s and $M=2$ is p.</td>
</tr>
<tr>
<td>NAME</td>
<td>SYMBOL</td>
<td>DESCRIPTION</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>-------------------</td>
</tr>
<tr>
<td>THK</td>
<td>d</td>
<td>Film Thickness</td>
</tr>
</tbody>
</table>
The input for program CHROM is on punched cards. All data are in a non-expodential form (e.g. 100, 0.003, 100.7). Decimal points should be included in all numbers except $\lambda$ on cards 5-19. The cards used are:

<table>
<thead>
<tr>
<th>CARD</th>
<th>VARIABLE</th>
<th>UNITS</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Name of substrate</td>
<td></td>
<td>Centered in Cols. 7-16</td>
</tr>
<tr>
<td>2</td>
<td>$C_{n1}$</td>
<td>Dimensionless</td>
<td>Col 11-20</td>
</tr>
<tr>
<td></td>
<td>$C_{n2}$</td>
<td>$1/A$</td>
<td>21-30</td>
</tr>
<tr>
<td></td>
<td>$C_{k1}$</td>
<td>Dimensionless</td>
<td>31-40</td>
</tr>
<tr>
<td></td>
<td>$C_{k2}$</td>
<td>$1/A$</td>
<td>41-50</td>
</tr>
<tr>
<td>3</td>
<td>$\phi$</td>
<td>Degrees</td>
<td>Col 11-20</td>
</tr>
<tr>
<td>4</td>
<td>Separation</td>
<td>Degrees</td>
<td>Col 11-20</td>
</tr>
<tr>
<td>5</td>
<td>Concentration of electrolyte</td>
<td>Normal</td>
<td>Col 11-20</td>
</tr>
<tr>
<td>6 to</td>
<td>$\lambda$</td>
<td>$\AA$</td>
<td>Col 1-4</td>
</tr>
<tr>
<td>20 *</td>
<td>$n_1$</td>
<td>Dimensionless</td>
<td>5-14</td>
</tr>
<tr>
<td></td>
<td>Scale</td>
<td>Dimensionless</td>
<td>15-24</td>
</tr>
</tbody>
</table>

*From 1 to 14 of these cards may be used. If less than 14 are used, the last card must be blank.

$\phi$ is the nominal angle of incidence. It is one-half the reading on the track on which the movable optical bench rides. The separation between the S and P polarizations was 6°. The actual angles of incidence were $\phi + 3^\circ$, and $\phi - 3^\circ$.

$\lambda$ is the wavelength at which the refractive index of the liquid, $n_1$, is known. SCALE is the refractometer scale reading, from which the program will calculate the refractive index. The values of SCALE were
obtained from a Bausch and Lomb precision refractometer, with prism series 749. Another prism would require that the prism constants, PC, in the function REFRXC be calculated for the new prism. In contrast to the previous programs, this program calculates the amplitude reflection coefficients and phase changes upon reflection at each wavelength.
TABLE A-I

Example use of program MBINF with Fig. 18, WAVELENGTH

<table>
<thead>
<tr>
<th>Type of Extreme</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>458 nm</td>
<td>140 nm</td>
<td>30 nm</td>
<td>190 nm</td>
</tr>
<tr>
<td>530 nm</td>
<td>367</td>
<td>291</td>
<td>508</td>
</tr>
<tr>
<td>645 nm</td>
<td>593</td>
<td>552</td>
<td>826</td>
</tr>
<tr>
<td>Possible</td>
<td>820</td>
<td>814</td>
<td>1144</td>
</tr>
<tr>
<td>Film Thicknesses</td>
<td>1047</td>
<td>1075</td>
<td>1461</td>
</tr>
<tr>
<td></td>
<td>1273</td>
<td>1336</td>
<td>1779</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>1597</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1727</td>
<td>1858</td>
<td></td>
</tr>
</tbody>
</table>

The numbers that most closely correspond in the three cases are circled.

The average film thickness is then 0.82µ.
PROGRAM MBINF (INPUT,OUTPUT,TAPE 98, PLOT, TAPE 99=PLOT)

THIS PROGRAM CALCULATES THE INTENSITY OF REFLECTED LIGHT FROM A DIELECTRIC FILM COVERED METAL SURFACE OF KNOWN OPTICAL PARAMETERS AS A FUNCTION OF WAVELENGTH AND FILM THICKNESS.

REAL PHID(2), PHINE(2), PHIPR(2), TNA(85), TKA(85), RSQ(85,2), X R(85,2), DEL(85,2), RL(2), RIL(2), RSQIL(2), TL(2), TIL(2), X INT(85,16J,2), PHCGD(85,2), RSQI(2), PHCGM(85,2), DELD(2), X LAMBD

DIMENSION LAM(9),

DIMENSION WAVALT(50), RLI(50,1), W(50), RESID(50,1), S(1), AI(20,8), X BI(20,8), TWVLTH(52), TRI(52), X SCALE(50),

COMMON /CCPOOL/XMIN, XMAX, YMIN, YMAX, CCXMIN, CCXMAX, CCYMIN, CCYMAX

COMMON/RICOM/ BI, NO

500 FORMAT (1HI)

1 FORMAT (6X, A10)

3 FORMAT (10X, F10.7)

4 FORMAT (10X, F10.6)

8 FORMAT (10X, *S POLARIZATION* ///)

9 FORMAT (10X, *P POLARIZATION* ///)

12 FORMAT (10X, *CONCENTRATION OF ELECTROLYTE IS *, F6.4, * NORMAL, REFRACTIVE INDEX (D) IS *, F6.4, *, ANGLE OF INCIDENCE IS *, F5.2, */ X/)

15 FORMAT ( *OPTICAL PARAMETERS OF *, A10, * LIQUID SURFACE*, ///)


17 FORMAT (10X, F4.0, 11F10.4)

18 FORMAT (F4.0, 2F10.5)

INPUT PARAMETERS ARE---(1) THE METAL SUBSTRATE, (2) FOUR COEFFICIENTS FOR A LINEAR APPROXIMATION OF THE COMPLEX INDEX OF REFRACTION OF THE METAL SUBSTRATE, (3) THE ANGLE OF INCIDENCE ON THE LIQUID FILM, (4) THE CONCENTRATION OF THE FILM, (5) THE REFRACTIVE INDEX OR REFRACTOMETER SCALE READING AT UP TO 14 WAVELENGTHS.

READ 1, TITLE
READ 3, CN1, CN2, CK1, CK2
READ 4, PHIN
READ 4, SEP
READ 4, CONC
DO 401 N=1,14
READ 18, WAVALT(1), RI(1), SCALE(N)
IF (WAVALT(N).EQ.0000) GO TO 402
401 CONTINUE
402 M=I-1
NO=6
DO 403 N=1,MI
IF (RI(N).EQ.0) RI(N)=REFRxc(SCALE(N), WAVALT(N))
WIN(N)=1.0
403 CONTINUE
IF (MI.LT.2) GO TO 406
DO 404 I=1,MI
WAVALT(I)=WAVALT(I)/4000
404 CONTINUE
CALL LSOPOL (WAVALT, RI, W, RESID, MI, 5, 1, AI, BI, NO)
DO 405 I=1, MI
WAVALT(I)=WAVALT(I)*4000

-115-
405 CONTINUE
XMIN=3000
XMAX=8000
YMIN=1.3
YMAX=1.4
CALL CCGRID (5,10,6,10,10)
CALL CCPLLOT (WAVLTH, RI, MI, 6, 1)
TWVLTH(1)=3000
DO 30 J=1,51
TRI(J)=RIC(TWVLTH(J))
TWVLTH(J+1)=TWVLTH(J)+100
30 CONTINUE
CALL CCPLLOT (TWVLTH, TRI, 50, 4, 0, 1)
CALL CCEND
GO TO 407
406 RI(1)= RI(1)
BI(2)=0.
BI(3)=0.
BI(4)=0.
BI(5)=0.
BI(6)=0.
407 CONTINUE
PRINT 500
PRINT 15, TITLE
RID=RIC(5892)
PRINT 12, CONC, RID, PHIN
PRINT 16
PHID(1)=PHIN-0.5*SFP
PHID(2)=PHIN+0.5*SEP
DO 213 J=1,83
LAMBDA=3800.+50.*J
CALL CCGRID (LAMBDA)
CALL CCPLLOT (WAVLTH, RI, MI, 6, 1)
CALL CCEND
GO TO 407

CHANGE IN OPTICAL CONSTANTS WITH WAVELENGTH

TNA(J)=CN1+CN2*(LAMBDA-3800)
TKA(J)=CK1+CK2*(LAMBDA-3800)
DO 10 I=1,2
PHI(1)=0.0174533*PHID(I)
PHIPR(I)=ASIN((1/RIC(LAMBDA))*SIN(PHI(I)))
10 CONTINUE
PI=3.14159

SUBSECTION DLIR (DIELECTRIC LIQUID REFLECTION AND TRANSMISSION)
FRESNEL'S EQUATIONS AND MULLER'S SIGN CONVENTION ARE USED (AT
ZERO ANGLE OF INCIDENCE THE POSITIVE P-POLARIZATION VECTORS CO-
INCIDE).*

TEMP1=COS(PHI(1))
TEMP3=RIC(LAMBDA)*COS(PHIPR(1))
RL(1)=(TEMP1-TEMP3)/(TEMP1+TEMP3)
RSQLI(1)=(RL(1))**2
RSQLI(1)=RSQLI(1)
TEMP2=RIC(LAMBDA)*COS(PHI(2))
TEMP4=COS(PHIPR(2))
RL(2)=(TEMP4-TEMP2)/(TEMP4+TEMP2)
RSQLI(2)=(RL(2))**2
RSQLI(2)=RSQLI(2)
TEMP1=COS(PHI(1))
TEMP3=RIC(LAMBDA)*COS(PHIPR(1))
\[ TL(1) = 2 \cdot \text{TEMP1}/(\text{TEMP1+TEMP3}) \]
\[ TIL(1) = 2 \cdot \text{TEMP3}/(\text{TEMP3+TEMP1}) \]
\[ \text{TEMP2} = \cos(\phi(2)) \]
\[ \text{TEMP4} = \text{RIC} (\text{LAMBDA}) \cdot \cos(\phi(2)) + \cos(\phi(2)) \]
\[ \text{TEMP6} = \text{RIC} (\text{LAMBDA}) \cdot \cos(\phi(2)) \]
\[ TL(2) = 2 \cdot \text{TEMP2}/\text{TEMP4} \]
\[ TIL(2) = 2 \cdot \text{TEMP6}/\text{TEMP4} \]
\[ \text{DO 153 M}=1,2 \]
\[ \text{IF (RL(M)) } 150, 151, 152 \]
\[ 150 \text{ DELN(M) = PI} \]
\[ \text{RL(M)} = -\text{RL(M)} \]
\[ \text{RIL (M)} = \text{RL(M)} \]
\[ \text{GO TO 153} \]
\[ 151 \text{ DELN(M) = 0} \]
\[ \text{RIL (M)} = \text{RL(M)} \]
\[ \text{GO TO 153} \]
\[ 152 \text{ DELN(M) = 0} \]
\[ \text{RIL (M)} = \text{RL(M)} \]
\[ \text{153 CONTINUE} \]

**C SUBSECTION MER (METALLIC REFLECTION) M=1 IS S, M=2 IS P**

**C FROM A PROGRAM -MER- DEVELOPED BY MULLER AND USING HIS SIGN CON-**

**C VENTION.**

\[ \text{TN} = \text{TNACJ}/\text{RIC(LAMBDA)} \]
\[ \text{TK} = \text{TKA(J)} \]
\[ \text{DO 123 M}=1,2 \]
\[ \text{SX} = \sin(\phi(2)(M)) \]
\[ \text{CX} = \cos(\phi(2)(M)) \]
\[ \text{TX} = \text{SX}/\text{CX} \]
\[ \text{TEMP1} = (\text{TN}^{*}2) \cdot (1.0-\text{TK}^{*}2)-\text{SX}^{*}2 \]
\[ \text{TEMP2} = \text{TEMP1}^{*}2+4.0 \cdot ((\text{TN}^{*}4) \cdot (\text{TK}^{*}2)) \]
\[ \text{ASQ} = 0.5 \cdot (\text{SORT(TEMP2)}+\text{TEMP1}) \]
\[ \text{IF (ASQ)} 110, 112, 112 \]
\[ 110 \text{ A}=0 \]
\[ \text{GO TO 114} \]
\[ 112 \text{ A}=\text{SORT(ASQ)} \]
\[ 114 \text{ BSQ}=0.5 \cdot (\text{SORT(TEMP2)}-\text{TEMP1}) \]
\[ \text{IF (ASQ)} 116, 118, 118 \]
\[ 116 \text{ B}=0 \]
\[ \text{GO TO 120} \]
\[ 118 \text{ B}=\text{SORT(BSQ)} \]
\[ 120 \text{ IF (M, EQ, 1)} 121, 122 \]
\[ 121 \text{ RSQ(J+1)} = (\text{ASQ}+\text{BSQ}-2.0*A*CX+CX*CX)/(\text{ASQ}+\text{BSQ}+2.0*\text{A}*\text{CX}+\text{CX}^{*}\text{CX}) \]
\[ \text{IF (RSQ(J+1))} 125, 124, 124 \]
\[ 125 \text{ R(J+1)} = 0 \]
\[ \text{GO TO 126} \]
\[ 124 \text{ R(J+1)} = \text{SORT(RSQ(J+1))} \]
\[ 126 \text{ CONTINUE} \]
\[ \text{TEMP1}=2.0*\text{B}^{*}\text{CX} \]
\[ \text{TEMP2}=\text{ASQ}+\text{BSQ}-\text{CX}^{*}\text{CX} \]
\[ \text{DEL}(J+1)=\text{ATAN}(-\text{TEMP1}/\text{TEMP2}) \]
\[ \text{IF (DEL}(J+1)) 127, 123, 123 \]
\[ 127 \text{ DEL}(J+1)=\text{DEL}(J+1)+\text{PI} \]
\[ \text{GO TO 137} \]
\[ 122 \text{ RSQ(J+2)} = \text{RSQ}(J, 1) \cdot (\text{ASQ}+\text{BSQ}-2.0*A*\text{SX}+\text{TX}^{*}\text{SX}^{*}\text{TX}^{*}\text{TX}) /(\text{ASQ}+\text{BSQ}+2.0*\text{A}^{*}\text{SX}^{*}\text{TX}^{*}\text{SX}^{*}\text{TX}^{*}\text{TX}) \]
\[ \text{IF (RSQ}(J+2)) 128, 130, 130 \]
\[ 128 \text{ R(J+2)} = 0 \]
\[ \text{GO TO 132} \]
C

130 R(J+2)=SORT(RSQ(J+2))
132 CONTINUE
   TEMP5=2.0*R*SX*TX
   TEMP6=ASQ+RSQ-SX*SX*TX*TX
   DDEL=ATAN(-TEMP5/TEMP6)
   IF (DDEL) 136,136,135
135 DDEL=DDEL-PI
136 CONTINUE
   DEL(J+2)=DEL(J+1)+DDEL
137 CONTINUE
   PHCGD(J*M)=(DEL(J*M)-DELD(M))/0.0174533
   PHCGM(J*M)=DEL(J*M)/0.0174533
123 CONTINUE
   RID=RIC(LAMBDA)
   PRINT 17, LAMBDA, A, B, R(J+1), R(J+2), PHCGM(J+1), PHCGM(J+2),
   X TN, TK, RID, RL(1), RL(2)

C

SUBSECTION MBINT (MULTIPLE BEAM INTENSITY)

C USING AN EQUATION GIVEN BY FRANCON

C

DO 212 M=1,2
   TEMP2=TL(M)*TIL(M)
DO 211 L=1,151
   THK=100.0*L/(L-1)
   TEMP1=4.0*PI*RIC(LAMBDA)*THK*COS(PHIPRIM(I))/LAMBDA+DEL(J*M)
   TEMP3=2.0*R(1*M)*RIL(M)*COS(TEMP1+DELD(M)+PI)
   TEMP4=2.0*R(J*M)*RIL(M)*COS(TEMP1-DELD(M))*TEMP2
   TEMP6=1.0+RSQ(1*M)*RSQIL(M)-TEMP3
   TEMP7=(TEMP2**2)*RSQIL(M)+TEMP4+2.0*TEMP2*RIL(M)*RIL(M)*RSQ(1*M)
   INTCJLMI=RSQLCMI+TEMP7/TEMP6
211 CONTINUE
212 CONTINUE
213 CONTINUE

C

INTENSITY AS A FUNCTION OF FILM THICKNESS AND WAVELENGTH

C

PRINT 500
PRINT 2, TITLE
DO 310 I=1,9
   LAMCII=380+50*(I-1)
310 CONTINUE
PRINT 8
PRINT 5, (LAM(K),K=1,9)
PRINT 6, (PHCGM(J+1),J=1,81,10)
PRINT 13, (PHCGD(J+1),J=1,81,10)
PRINT 7
DO 311 M=1,151
   N=(M-1)*10
   PRINT 11, N, (INTCJ(J+1), J=1,81,10)
311 CONTINUE
PRINT 500
PRINT 9
PRINT 5, (LAM(K),K=1,9)
PRINT 6, (PHCGM(J+2),J=1,81,10)
PRINT 13, (PHCGD(J+2),J=1,81,10)
PRINT 7
DO 312 M=1,151
   N=(M-1)*10
   PRINT 11, N, (INTCJ(J+2), J=1,81,10)
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.