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Report 1134

PREPARATION OF HARD OXIDE FILMS
ON EVAPORATED ALUMINUM SURFACES AND
APPLICATIONS OF SUCH FILMS

Project 8-23-02-002

28 July 1949

Submitted to

THE CHIEF OF ENGINEERS, U..S. Army

by

The Commanding Officer
Engineer Research and Development Laboratories

Prepared by

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FOREWORD

The material here presented is the result of work carried on by
Dr. Georg Hass of the Radiation Branch, Engineer Research and
Development Laboratories, Fort Belvoir, Virginia, from July 1948 to
February 1949. A resume of this report was presented at the meeting
of the Optical Society of America, on 11 March 1949, at New York City,
New York.

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ABSTRACT

By increasing the thickness of the natural oxide film on evaporated aluminum mirrors, a much better surface protection can be achieved. Heat treatment in air is not a practical method for producing protective coatings on aluminum because a temperature of more than 400 C is required, and oxide films formed at this temperature are rough. Oxide films of precisely controlled thicknesses can be produced on evaporated aluminum mirrors by anodic oxidation in electrolytes such as ammonium tartrate. The thickness of the oxide layer formed in a given length of time increases linearly with the applied voltage and is 13.0 Angstrom units (A) per volt for 2 minutes' anodizing time. The current efficiency of the anodic process in ammonium tartrate is approximately 80 percent. The oxide coatings are 1.38 times thicker than the aluminum layers replaced. The anodic oxide films formed in ammonium tartrate are amorphous and free of pores. They exhibit no noticeable absorption of ultraviolet, visible, or infrared light. Their refractive index between $\lambda = 3000$ A and $\lambda = 6000$ A varies from 1.67 to 1.62. Anodized aluminum mirrors show excellent abrasion resistance. To obtain the highest reflectivity in the visible light region, the anodic oxidation must be performed with 120 volts for 2 minutes. The precisely controlled uniform anodic coatings on opaque aluminum mirrors are suitable for the preparation and investigation of reflection-type interference filters. The thickness of a pure aluminum film can be determined by the voltage required for complete oxidation. The anodic coatings are suitable as temperature resistant films for electron diffraction and electron microscope investigations.

PREPARATION OF HARD OXIDE FILMS ON EVAPORATED ALUMINUM

SURFACES AND APPLICATIONS OF SUCH FILMS

I. INTRODUCTION

The fact that evaporated aluminum mirrors do not tarnish in normal atmosphere is a result of the protective qualities of their natural oxide films. For many mirror applications, however, the natural oxide films are too thin to furnish sufficient mechanical and chemical protection. Therefore, various methods have been developed to coat the aluminum mirror surface with a hard and adherent dielectric layer. Since the extremely thin natural oxide film has a relatively good protective effect, a satisfactory protection of an evaporated aluminum mirror can be expected after the thickness of its oxide coating has been increased. Electrolytically brightened massive aluminum reflectors show good scratch and corrosion resistance because of their hard anodically produced surface layers of aluminum oxide.[1]

The thickness of the oxide film on aluminum can be increased by chemical methods such as heat treatment in air or by anodic oxidation. The present paper presents data on the formation and properties of oxide films produced on evaporated aluminum mirrors at various temperatures in air and by anodic oxidation in ammonium tartrate. The applications of anodically produced films, the thicknesses of which can be precisely controlled, are discussed herein.

The study was conducted under authority contained in a letter from the Chief of Engineers to the Engineer Research and Development Laboratories, dated 14 October 1946, file ENGNC (14 Oct 46), subject: Infrared Optical Materials, Approval of Military Characteristics, and Authorization of Development Project XR 750. A copy of the project card (RDB Form 1A) is included in the appendix to this report.

II. ON THE OXIDATION OF EVAPORATED ALUMINUM MIRRORS IN AIR AT VARIOUS TEMPERATURES

By Drude's optical polarization method, a study was made of the thicknesses of oxide layers formed in air on evaporated aluminum films. The special vacuum apparatus in which the films can be evaporated and examined before and after initial exposure to air has been described in a previous paper.[2] The oxide film formed on aluminum

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1. J. D. Edwards, Trans. Ill. Eng. Soc., 29,351 (1934); and N. D. Pullen, J. Inst. Met. (London), 59:151 (1936).
2. G. Hass, Zeits. f. anorg. Chemie, 254,96 (1947).

when exposed to air at normal temperature for 2 hours is about 10 A thick. It continues to grow very slowly for about one month, reaching a thickness of about 45 A and then stops almost completely. The same thickness for the oxide film formed on evaporated aluminum was calculated from the increase of the electrical resistance caused by oxidation in air. The fact that the oxide film on aluminum reaches this limiting thickness is in good agreement with Mott's[3] theory of the formation of oxide films on metals.

Fig. 1 shows the thicknesses of oxide films formed on aluminum at different temperatures after 2 hours' exposure to air. The rate of oxidation of a fresh aluminum surface changes very little below 300 C. Above 300 C, it increases slowly and above 450 C, very rapidly. An increase of humidity in the air increases the rate of oxidation and shifts the beginning of more rapid oxidation to lower temperatures. By introducing steam into the oxidation furnace a rapid oxidation could be detected at 350 C. The oxidation of aluminum in oxygen at various temperatures and pressures has been studied by Gulbransen and Wysong[4]. They, too, found a rapid increase of oxidation rates at high temperatures beginning at about 475 C. The fact that high humidity increases the rate of oxidation of aluminum slightly at low and strongly at higher temperatures has been reported previously.[5]

The electron diffraction investigations on aluminum oxide films showed the following results. The oxide films formed on poly-crystalline aluminum in a temperature region where the oxidation rate is low are amorphous. Those formed at higher temperatures are crystalline, consisting of γ-Al_2O_3 with a = 7.90 A. At low humidity the formation of crystalline γ-Al_2O_3 begins at approximately 450 to 500 C, while in the presence of steam γ-Al_2O_3 and rapid oxidation can be found at 350 C. The change in structure of the aluminum oxide film seems to be responsible for the rapid change in oxidation rates with increasing temperature. Furthermore, the electron diffraction investigations showed that during the formation of crystalline γ-Al_2O_3 in air at higher temperatures the lattice constant of the underlying aluminum increased from 4.04 A to 4.10 ± 0.02 A. The increase of the lattice constant must be caused by the diffusion of oxygen into aluminum and may be considered as the first step in oxidation.

3. N. F. Mott, Trans. Faraday Soc., 36,472 (1940), and 43,429 (1947).
4. E. A. Gulbransen and W. S. Wysong, J. Physical and Colloid Chemistry, 51,1087 (1947).
5. N. Cabrera and J. Hamon, Comptes Rendus, 225,59 (1947); and H. Röhrig and L. Lux, Korrosion metallischer Werkstoffe, Band 3 Verlag S. Hirzel, Leipzig (1940).
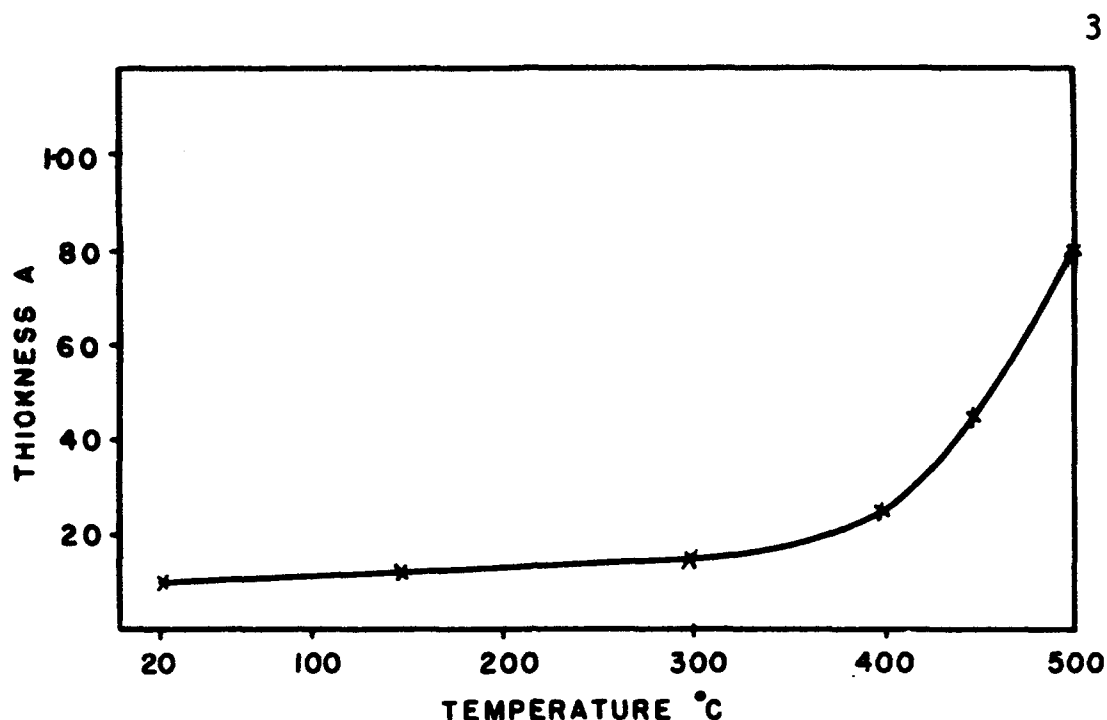
Fig. 1. Thicknesses of oxide films formed on aluminum at different temperatures after 2 hours' exposure to air.

Heat treatment in air is not a practical method for producing protective coatings on evaporated aluminum mirrors. The temperature required for producing the desired thickness of oxide is very high, and the films thus produced, being rough and nonuniform, result in diffused reflection.

III. ON THE ANODIC OXIDATION OF EVAPORATED ALUMINUM MIRRORS IN 3 PERCENT AMMONIUM TARTRATE

Unlike aluminum oxide films produced by oxidation at high temperatures, those formed anodically in a suitable bath are smooth and uniform and can be prepared in precisely controlled thicknesses. The method used to anodize evaporated aluminum mirrors and data on the properties of Al_2O_3 films thus formed, together with their applications, are given in the following subparagraphs.

a. **Method for Anodizing Evaporated Aluminum Films.** When aluminum is made the anode in an electrolyte containing oxygen-

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bearing anions, a coating consisting predominantly of aluminum oxide is formed on its surface as long as a current flows. The electrolytes used for the anodic oxidation must be divided into those, such as dilute sulfuric and oxalic acids, which have an appreciable solvent effect on the oxide films formed, and those, such as boric acid and solutions of acidified organic ammonium salts, which have no solvent action on aluminum oxide. The oxide films formed in electrolytes such as dilute sulfuric acid are characterized by substantial thickness and porous structure. Within quite a wide range, these oxide coatings continue to grow as long as potential is applied. Film thicknesses of more than 100 microns can be attained under suitable conditions. In electrolytes in which the aluminum oxide is insoluble, the dielectric coating forms rapidly and the high current which flows when contact is first made decreases to less than 1 ma/dm^2 in a few minutes, indicating that the growth of the coating has almost ceased. The thicknesses of the oxide films which are produced in a given time depend only on the applied anodizing voltages, and can therefore be controlled. This type of oxide film is nonporous and is called an anodic barrier-layer. It has been found to be especially suitable as a protective coating on thin evaporated aluminum mirrors.

The electrolyte used for producing anodic barrier-layers on evaporated aluminum is a solution of 3 percent tartaric acid with ammonium hydroxide added to make the pH about 5.5. It permits the formation of uniform films up to about 5000 A thick on evaporated aluminum mirrors of any size.

Fig. 2 is a sketch of the anodizing arrangement. The evaporated aluminum surface is made the anode in the electrolyte and a plate of aluminum is used as cathode. The strong initial current is limited to 2 amperes by a resistor. As the oxidation increases, the current decreases to a few ma/dm^2 in about one minute, after which continued application of the voltage produces little change in film thickness.

The glass form on which the aluminum film is evaporated must be extremely clean; otherwise, the aluminum film will loosen during the anodic oxidation process. Also, impurities will cause pin holes in the anodic treatment. Thus, the anodic oxidation provides an excellent means for checking the adherence and purity of evaporated aluminum mirrors.

b. _Thickness of the Anodic Coatings Produced in 3 percent Ammonium Tartrate_. The thickness of Al_2O_3 layers formed in 3 percent ammonium tartrate as a function of voltage and time as determined by means of multiple reflection fringes. Thi optical
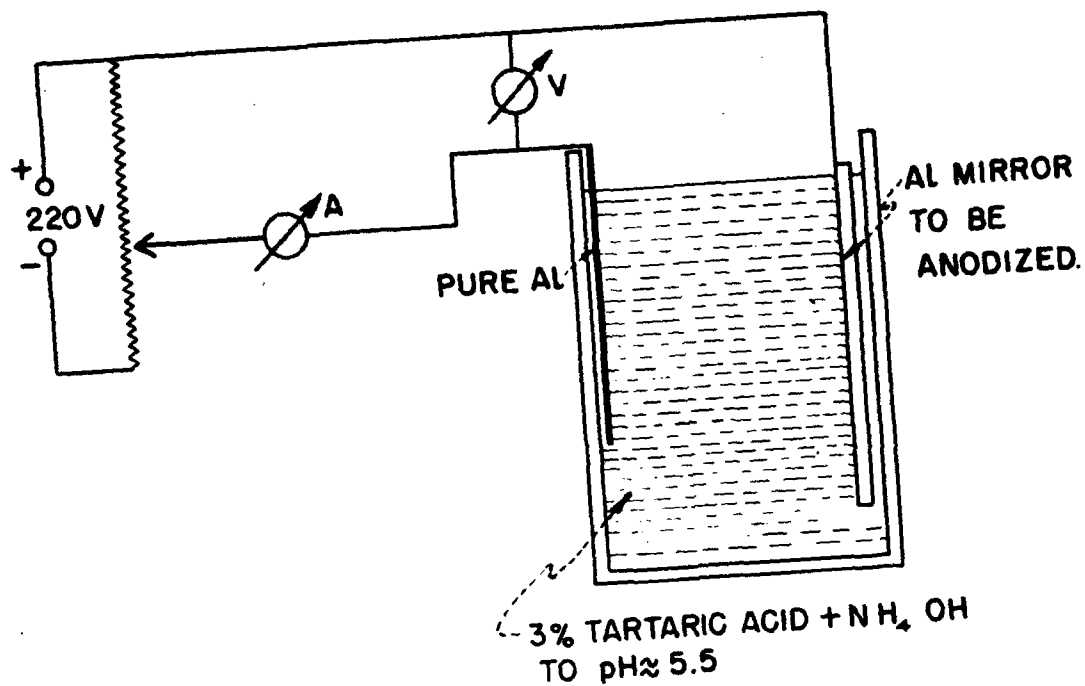
Fig. 2. Arrangement used to anodize evaporated aluminum mirrors.
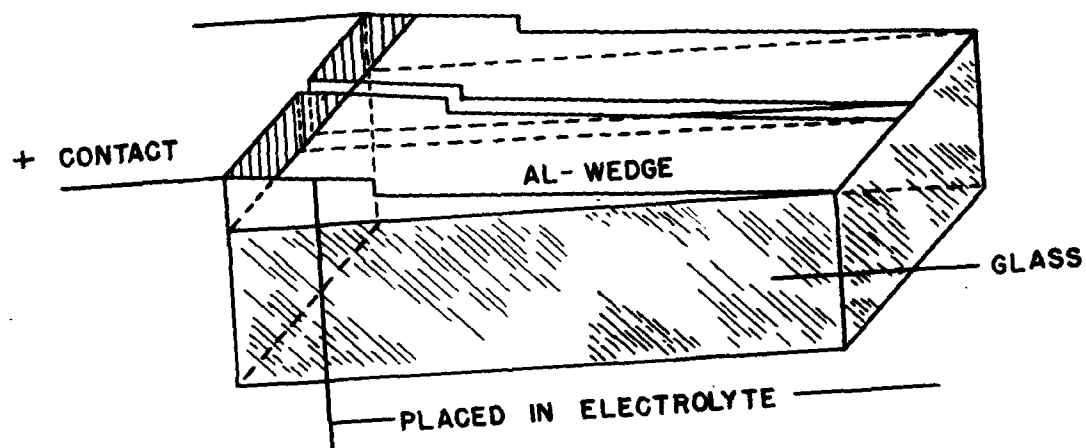
V

A

220V

PURE AL

AL MIRROR
TO BE
ANODIZED.

3% TARTARIC ACID + N H₄ OH
TO pH≈ 5.5

+ CONTACT

AL- WEDGE

GLASS

PLACED IN ELECTROLYTE

Fig. 3. Aluminum wedge to measure thickness of anodic coating as function of voltage and time.

method (Fig. 3) was developed by Tolansky[6] and is based on the consideration of these fringes as Newton's rings greatly sharpened through a multiple beam action between two highly reflecting surfaces placed close together. The extreme sharpness of these fringes permits a determination of Al_2O_3 film thicknesses accurate to about 10 A.

In this method, a wedge of aluminum is evaporated on a flat glass plate while a narrow central area of the glass is shielded. The top of the wedge is increased in thickness to furnish good contact for the anodizing process. The wedge coated glass is immersed in the ammonium tartrate bath and the aluminum is oxidized anodically with constant voltage. The thinner part of the aluminum wedge becomes transparent and completely oxidized in a few seconds. The boundary up to which the evaporated aluminum is completely changed to its oxide moves rapidly during the first 10 seconds and then more and more slowly up to the thicker part of the aluminum film. The thickness of the coating on glass at this boundary represents the thickness of the aluminum oxide film formed with the applied voltage and time. It was measured by the relative fringe displacement, which is observed at the boundary of the narrow uncoated central area after a flat glass plate is placed close to it. The interference fringes are very diffuse between low reflecting surfaces and are extremely sharp between high reflecting plates (Fig. 4). For accurate measurements of the fringe displacements, a high reflecting opaque aluminum film was evaporated over the whole aluminum oxide coated base plate and a silver film with 90 percent reflectivity and 7 percent transmission was condensed into the top plate. Thus, the thicknesses of the anodic coatings produced with various voltages in various times were determined (Fig. 5). The thickness of the oxide layer formed in a given time on aluminum in 3 percent ammonium tartrate increases linearly with the applied voltage. Layers produced in 2 minutes have a thickness of 13.0 A units per volt. The increase of thickness in the next 15 minutes is only 5 percent. After about 40 minutes the anodizing current reaches a very small constant value, resulting in a constant increase in thickness of only about 1 percent per hour. Walkenhorst[7] determined the thickness of anodic barrier-layers formed on aluminum in ammonium citrate to be 13.7 A per volt; and Taylor and Edwards[8] found for films produced in aqueous solution of boric acid a thickness of about 11.6 A per volt. The thicknesses of oxide coatings formed in different electrolytes in which aluminum oxide is insoluble seems to be in the same order of magnitude.

c. <u>Current Efficiency of the Anodic Process</u>. The amount, m, of Al_2O_3 formed on aluminum during the anodic oxidation should be, according

6. S. Tolansky, J. Sci. Instr., 22,161 (1945).
7. W. Walkenhorst, Naturwiss., 34,373 (1947).
8. C. S. Taylor and J. D. Edwards, Heating, Piping, and Air Conditioning, 11,59 (1939).

Fig. 4. Interference fringes. Top: between low reflecting surfaces (glass and aluminum oxide). Bottom: between high reflecting surfaces (opaque aluminum and transparent silver with reflectivity = 90 percent and transmission = 7 percent.

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to Faraday's law, proportional to the quantity of electricity (It) passing through the electrolyte: $m = $ Ite. The electrochemical equivalent e for Al_2O_3 is 17.6 x 10^{-5} g per amp-sec.

This means that the thickness of the oxide coating (t Al_2O_3) increases with the amount of electricity according to the following relationship:

$$t_{Al_2O_3} \text{ (in A units)} = \frac{17.6 \text{ It}}{\rho Al_2O_3 \text{ F}}$$

where   It   = the amount of electricity in ma. sec

ρAl_2O_3 = density of Al_2O_3 in g/cm^3 and

F   = area of the aluminum surface to be anodized in cm^2.

The density of γ-Al_2O_3 calculated from x-ray data[9] is 3.62 g/cm^3. The values measured for anodic coatings are smaller, about 3.0 g/cm^3 for the porous type of films[10] and between 3.1 and 3.3 g/cm^3 for nonporous anodic barrier-layers.[11] Assuming the density is 3.2 g/cm^3 for the films formed in 3 percent ammonium tartrate, their thicknesses may be calculated from:

$$t_{Al_2O_3} \text{ (in A units)} = \frac{5.50 \text{ It(ma-sec)}}{F \text{ (cm}^2)}$$

In electrolytes which have a solvent effect on Al_2O_3 the increase in thickness must be smaller, while in those in which the coating formed is insoluble, an agreement with the values calculated by Faraday's law may be expected. The amount of ampere second was measured with a recently described coulometer[12] and checked with a fast recording ammeter. Fig. 6 shows the measured and the theoretical thickness increase of Al_2O_3 films with 50 and 100 volts as a function of time. The apparent current efficiency is in the neighborhood of 80 percent only, although no solvent effect on Al_2O_3 by ammonium tartrate could be measured after 65 hours of exposure.

d.   Relationship between Thickness of Anodic Coating Formed and Thickness of Aluminum Layer Removed. If all of the aluminum reacting appears as oxide, the thickness ratio of the oxide film formed to the

9.   E. J. W. Verwey, Zeits. Kristallogr., 91,65 (1935).
10. J. D. Edwards, Proc. Am. Soc. for Testing Materials, 40,14 (1940).
11. W. G. Burgers, A. Claasen, and J. Zernike, Zeits. f. Phys., 74,593 (1932).
12. E. L. Abers and R. F. Newton, J. Physical and Colloid Chemistry, 52,955 (1948).
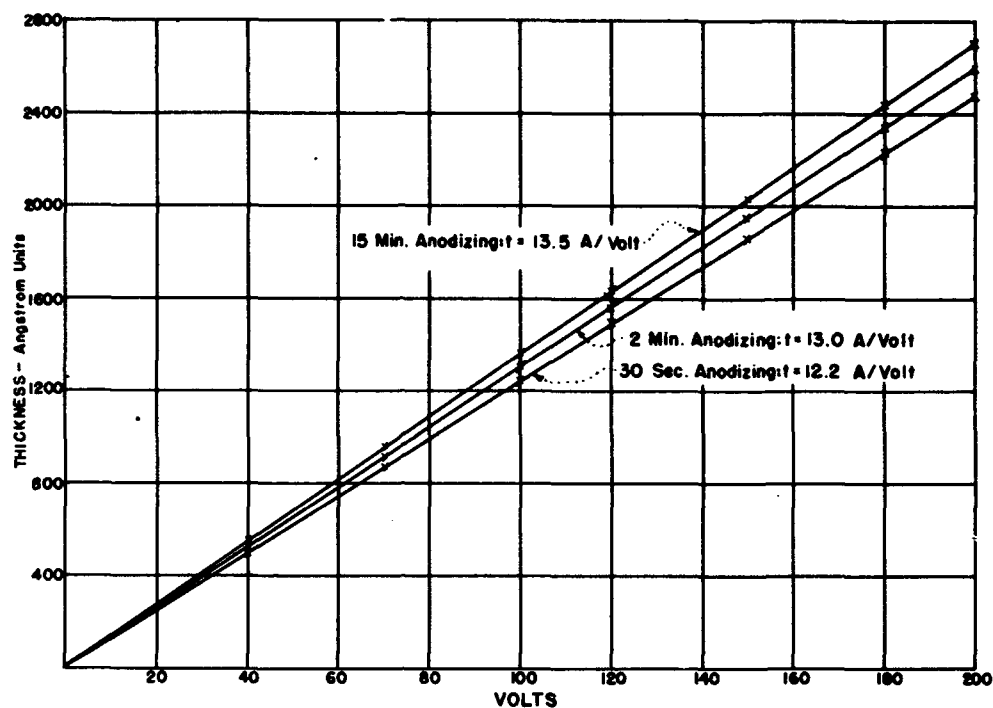
Fig. 5. Thickness of anodic coating formed in 3-percent ammonium tartrate as a function of voltage for 30 seconds', 2 minutes', and 15 minutes' anodizing time.
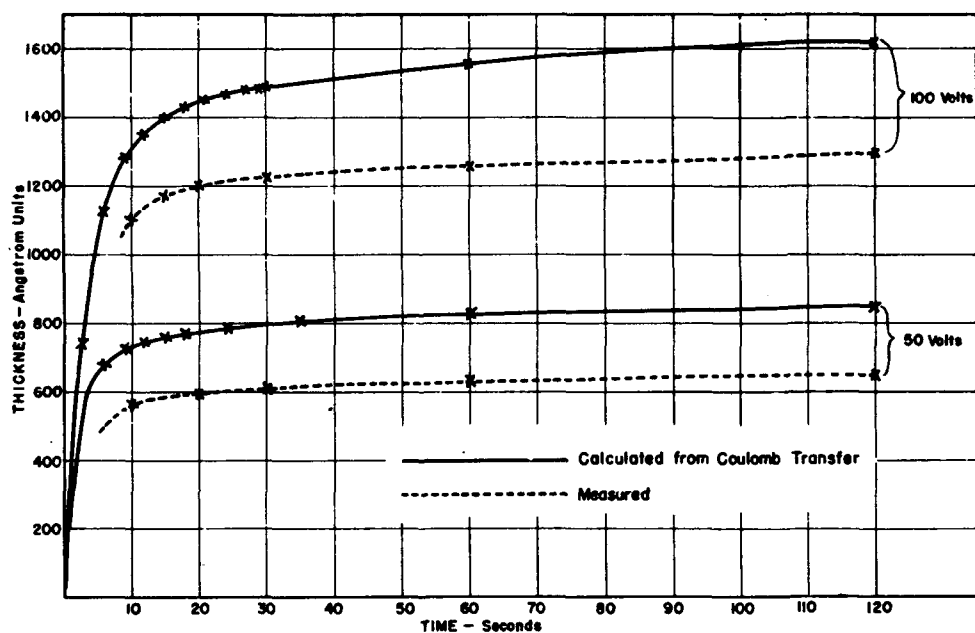

Fig. 6. Calculated and measured thickness of Al_2O_3 coating formed in 3-percent ammonium tartrate with 50 and 100 volts as a function of time.

aluminum layer replaced should be:

$$\frac{t_{Al_2O_3}}{t_{Al}} = \frac{M_{Al_2O_3}}{2M_{Al}} \cdot \frac{\rho\,Al}{\rho\,Al_2O_3} = 1.60$$

where $M_{Al_2O_3}$, the molecular weight of Al_2O_3 = 101.94

M_{Al}, the atomic weight of Al = 26.97

ρ_{Al}, the density of Al = 2.7 g/cm^3
(Aluminum films produced by fast evaporation under good
vacuum conditions have, according to Walkenhorst,[13]
normal density)

$\rho_{Al_2O_3}$, the density of Al_2O_3 = 3.2 g/cm^3

By measuring the thickness of ten different films before and after
complete oxidation in ammonium tartrate the thickness ratio was
determined as:

$$\frac{t_{Al_2O_3}}{t_{Al}} = 1.38 \pm 0.03$$

The measured value is considerably smaller than the theoretical one.
An agreement between the two values could be obtained by assuming a
density of 3.70 g/cm^3 for the anodic films. But this value is higher
than any known for anodic aluminum oxide films and, since the refrac-
tive index of these films is very low (subpar. f), this assumption is
not justified. The fact that the thickness of the oxide is only 1.38
instead of 1.60 times greater than that of the aluminum from which it
is formed may be explained by a theory recently developed by Anderson.[14]
According to this theory, one-third of the anodizing current is carried
through the anodical barrier-layer by aluminum-ions and the rest is
transported by oxygen ions, and only two out of every three aluminum
ions that leave the parent metal combine with oxygen ions to form Al_2O_3,
while one diffuses through the oxide film into the electrolyte, where
it may become lost for oxide formation. The loss of one out of three
aluminum ions during the oxide formation would lead to a thickness
ratio which agrees with the one measured here.

13. W. Walkenhorst, Zeits. techn. Phys., 22,14 (1941), and Diss.
    Hannover, 1940.
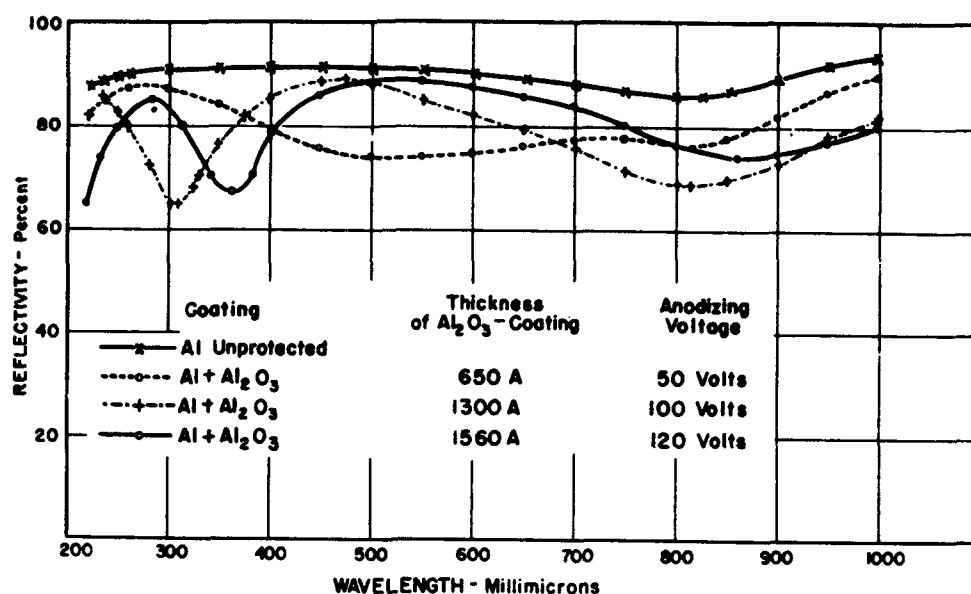14. Scott Anderson, J. App. Phys., 15,477 (1944).

Fig. 7. Reflectivity of evaporated aluminum mirrors coated with anodic Al_2O_3 films of different thicknesses as function of wavelength from 220 to 1000 mu.
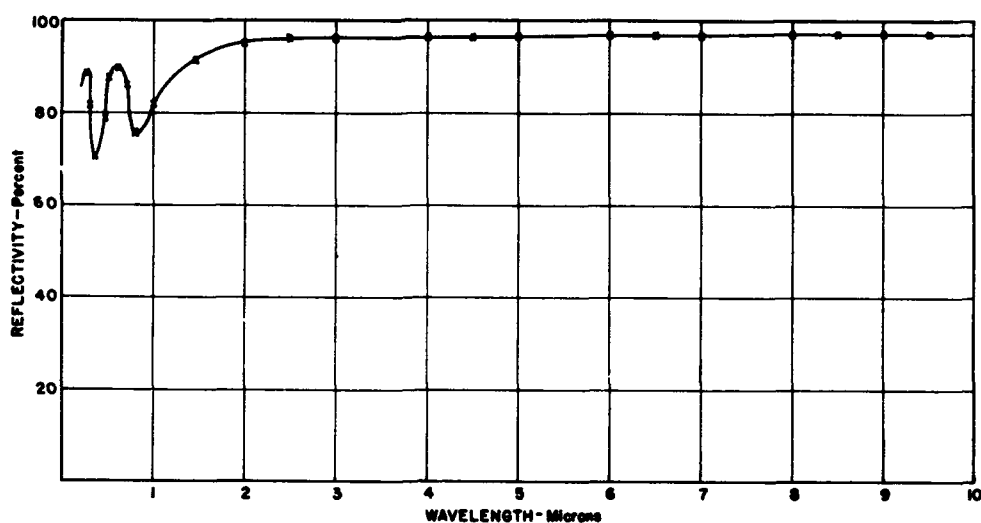

Fig. 8. Reflectivity of evaporated aluminum mirror coated with an anodic Al_2O_3 film 1560 A thick as function of wavelength from 0.2 to 10 u.

The thickness of an evaporated aluminum film t_{Al} can be readily determined from the voltage required for its complete oxidation in ammonium tartrate, since

$$t_{Al} = 0.725t_{Al_2O_3} \quad \text{and}$$

$$t_{Al_2O_3} \text{ (in A)} = 12.2 \text{ x volts for 30 seconds anodizing time}$$

Then t_{Al} (in A) $= 8.85$ x volts

For complete anodic oxidation of an aluminum film that is just opaque to a bright tungsten filament, a 30-second application of approximately 70 volts is required. Its thickness is therefore about 620 A.

e. **Properties of Aluminum Oxide Protected Aluminum Front-surface Mirrors.** Figs. 7 and 8 show the reflectivity in the wavelength region from 0.22 u to 10 u of evaporated aluminum mirrors protected by anodic films of various thicknesses. The interference maxima and minima which, with increasing thickness of the aluminum oxide coating, shift to longer wavelength, can be brought to a desired position by adjusting the applied anodizing voltage. To obtain highest reflectivity in the visible, the anodic oxidation must be performed with 120 volts (2 minutes). The oxide film formed with this voltage is 1560 A thick and yields a first order maximum at $\lambda = 550$ mu. Front-surface mirrors for use in the ultra-violet and infrared can be advantageously protected with an anodic coating, because the thin layer of aluminum oxide used for protection shows no appreciable absorption. The infrared reflectivity from 2 to 10 u (Fig. 8) is therefore practically the same as that of an unprotected aluminum mirror, since the Al_2O_3 coating is too thin to produce any interference minimum in this region.

The abrasion resistance of evaporated aluminum mirrors protected with aluminum oxide is good. They cannot be damaged by strong rubbing with rough linen and are extremely resistant to scratching with most metal points. They are, however, more sensitive to boiling water and salt spray than silicon monoxide protected aluminum mirrors.

f. **Refractive Index of the Anodically Produced Al_2O_3 Films.** The refractive index (n) of the anodic coatings was determined by dividing the difference in optical thickness, n $(t_2 - t_1)$, of two films produced with different voltages by their actual difference in thickness, $t_2 - t_1$. To eliminate from the calculations, the phase change on reflection the thicknesses of the oxide films were adjusted so that interference maxima or minima of different orders were produced at the same wavelength. Thus, the difference in optical thickness of two films can be calculated from:

$$n(t_2 - t_1) = \frac{\lambda}{4} (m_2 - m_1)$$

where $m_2 - m_1$ represents the difference in the interference order. The actual difference in thickness was determined by the difference in voltage used for the anodic oxidation. The refractive index, which was determined to be n = 1.62 for λ = 600 mu, increases uniformly with decreasing wavelength to n = 1.67 for λ = 300 mu. These values are smaller than those known for $\gamma - Al_2O_3$ (n = 1.73 for λ = 589 mu)[15] but are in agreement with the refractive indices for anodic coatings as determined by Edwards.[16]

g. **Absolute Phase Change of Light Waves at Boundary Al_2O_3 - Al**

and Its Effect on the Position of Reflection Minima and Maxima. If light is reflected at normal incidence from a metal surface covered with a thin dielectric film of the optical thickness $n_1 t$ the spectral position of reflection minima and maxima can be calculated by the following equation:

$$2n_1 t + \delta_1 - \delta_2 = m \frac{\lambda}{2}, \tag{1}$$

where m is the interference order, δ_1 the absolute phase change at the boundary air-dielectric film, and δ_2 the absolute phase change at the boundary dielectric film-metal surface. While δ_1 has a constant value of $\frac{\lambda}{2}$ or 180°, δ_2 depends upon the optical constants n and k of the metal and the refractive index n_1 of the dielectric and is defined by:

$$\tan \delta_2 = \frac{2n_1 k}{N_1^2 - N^2 - k^2} \tag{2}$$

δ_2 can be determined directly from equation (1) where it is the only unknown quantity and can be calculated from equation (2) using the optical constants of aluminum, which have been reported in a recent paper.[17]

Table I gives the optical constants of aluminum and the obsolute phase change on light reflected at the boundary dielectric-aluminum under normal incidence for various wavelengths and various refractive

15. E. Kordes, Zeits. Kristallogr., 91,193 (1935).
16. J. D. Edwards, Monthly Rev. Am. Electroplaters' Soc., 26,513 (1939).
17. G. Hass, Optik 1,2 (1946).

Table I. Optical Constants of Aluminum and Absolute
Phase Change on Light Waves Reflected under Normal
Incidence at the Boundary Dielectric-aluminum for
Various Refractive Indexes of the Dielectric Material

Wave-length mu	Optical Constants of Al		Phase Change in Degrees at Boundary Dielectric-aluminum					
	n	k	$n_{diel} = 1$	$n_{diel} = 1.40$	$n_{diel} = 1.50$	$n_{diel} = 1.60$	$n_{diel} = 1.65$	$n_{diel} = 1.80$
435	0.40	4.16	153.3	143.1	140.7	138.2	136.5	133.5
491	0.57	5.19	158.4	150.1	148.1	146.1	145.1	142.3
546	0.76	5.49	159.7	151.8	149.9	148.1	147.1	144.3
578	0.89	5.68	160.5	152.9	151.1	149.2	148.3	145.6
644	1.12	6.26	162.5	155.6	153.9	152.2	151.4	148.9

indexes of the dielectric material as calculated from equation (2).
Fig. 9 shows the δ-values in degrees and A units (units of the
wavelength) for the system Al + Al_2O_3 as function of wavelength
from 300 to 650 mu. There is a good agreement between the calcu-
lated and directly determined δ values. ($\delta air-Al_2O_3$ - δAl_2O_3 -Al)
in A units is almost constant throughout the wavelength region
studied and behaves like a fixed increase in optical thickness of
the Al_2O_3 film of 250 A. Therefore, equation (1) becomes simple
for this special case:

$$2(n_1 t + 250) = m \frac{\lambda}{2} \qquad \text{(t and λ in A units).}$$

The shift of the interference positions is directly proportional
to the increase in optical thickness of the aluminum oxide layer
(Fig. 10).

h. Reflection Type Interference Filters with Al_2O_3 As
Dielectric Layer. A reflection-type interference filter normally
consists of a highly reflecting opaque mirror coating on which is
first applied a thin layer of dielectric material and then a very
thin semi-transparent metal film.[18] Fig. 11 shows the arrangement
of the three layers in the reflection-type interference filter.
The spectral positions of minimum and maximum reflections and
the shape of the spectral reflectivity curve depend on the optical
thickness of the dielectric layer and the thickness of the semi-
transparent metal film. The anodizing process permits the pro-
duction of uniform Al_2O_3 layers of desired thickness on opaque

18. L. N. Hadley and D. M. Dennison, J. Opt. Soc. Am., 37,451
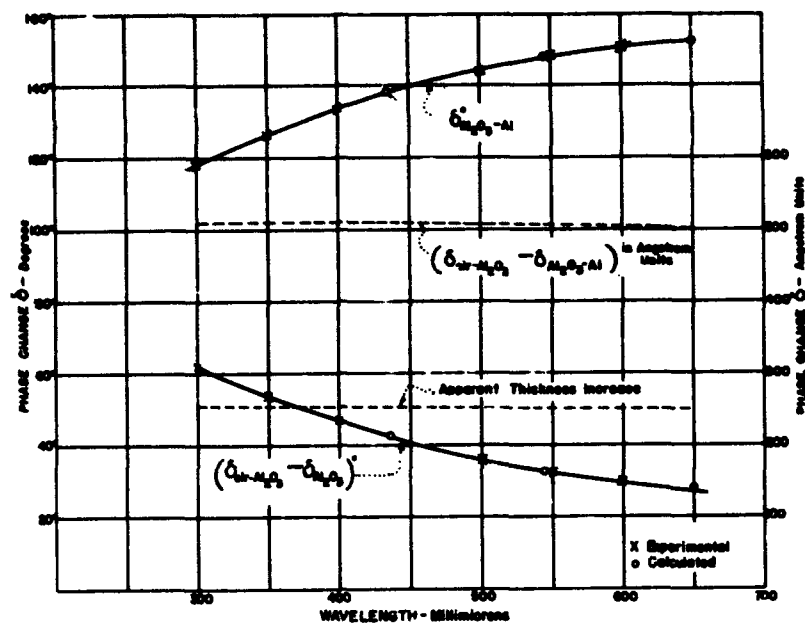(1947); and 38,483 (1948).

Fig. 9. Phase changes occurring on reflection at Al_2O_3-coated aluminum as function of wavelength from 300 to 650 mu.
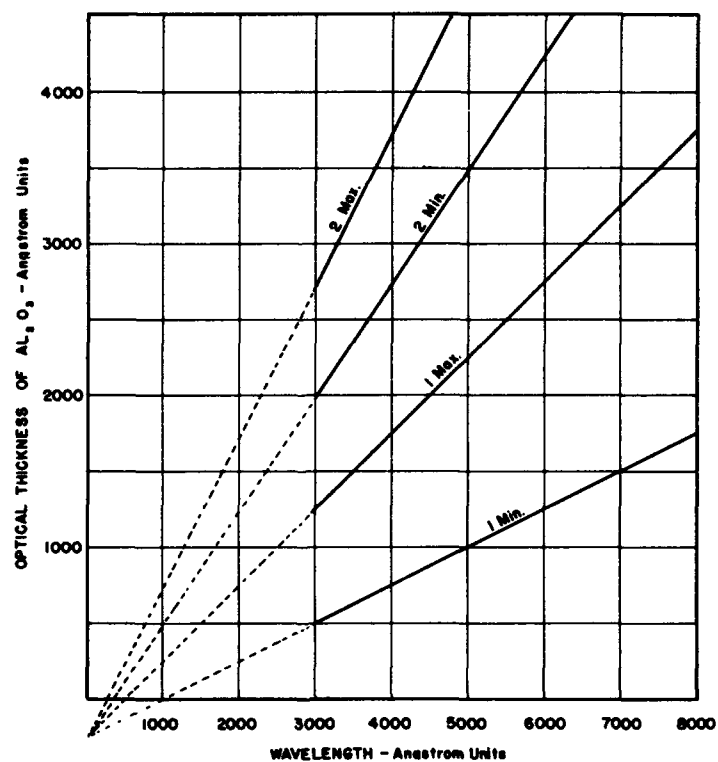

Fig. 10. Optical thickness of aluminum oxide film on aluminum as function of wavelength position of reflection minina and maxima.

aluminum mirrors, thus providing a simple method for shifting the spectral positions of maximum and minimum reflectivities to desired wavelengths and for studying the influence of the thickness of the transparent metal film on the reflection properties of reflection-type interference filters.

Fig. 12 shows the reflection properties of a simple reflection filter. It consists of an evaporated aluminum mirror which has been oxidized anodically with 45 volts (585 A Al_2O_3) and coated with aluminum about 50 A thick. This type of reflection filter reduces the visible reflectivity to less than 2 percent, but exhibits high reflectivity in the ultraviolet and infrared where it may have useful applications.

1. Solubility of Anodic Films in Dilute Solutions of Sulfuric Acid. As mentioned previously, very thick coatings of aluminum oxide can only be produced in electrolytes in which the oxide has an appreciable solubility, such as solutions of sulfuric acid. All commercial anodic protective coatings are made in these electrolytes and have thicknesses of from 2 to 20 u. An exact study of the solubility of aluminum oxide in sulfuric acid of varied concentration and temperature is therefore of technical interest. Aluminum mirrors, coated anodically in ammonium tartrate with oxide films 2000 to 4000 A thick, were exposed various times to sulfuric acid solutions of various concentrations and temperatures. The wavelength positions of reflection minima and maxima were determined before and after exposure and their shift was used to calculate the decrease in thickness caused by the sulfuric acid treatment. The decrease in thickness thus determined is accurate to ± 20 A. This corresponds to accuracy of a ± 6 x 10^{-7} g/cm^3 in weight decrease. The results of the measurements are represented in Fig. 13. The rate of dissolving increases slightly with the concentration but very rapidly with the temperature of the sulfuric acid solution. The aluminum oxide films decrease uniformly in thickness during their exposure to sulfuric acid.

j. Structure of Anodic Coatings Produced in Ammonium Tartrate and Their Use As Temperature Resistant Films for Electron Microscope and Electron Diffraction Investigations. Anodic coatings produced with various voltages (10 to 150 volts) were released from their substrate by dissolving the aluminum in a solution of mercuric chloride and were examined by the electron diffraction method and with electron microscope.

The electron diffraction patterns of all these anodic coatings consist only of diffuse rings indicating an amorphous, or glass-like structure. The films become crystalline when subjected to temperatures of 700 C or higher. Fig. 14 shows the electron diffraction pattern of an anodic film before and after one hour of heat treatment at 800 C. The electron diffraction patterns of films heat treated at
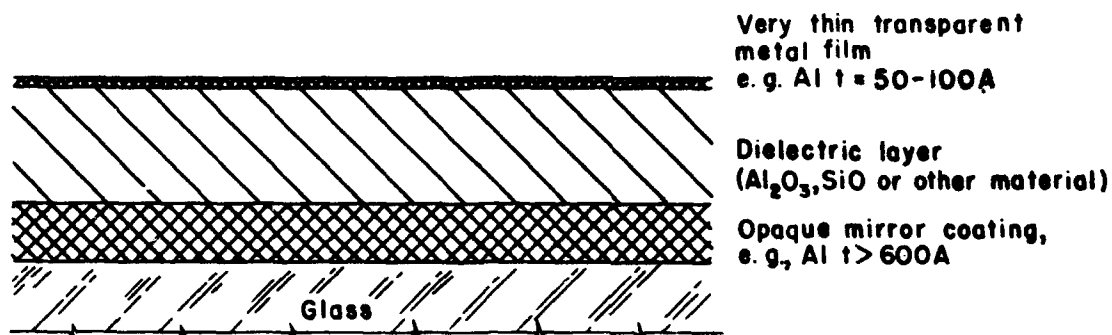
Very thin transparent
metal film
e. g. Al t = 50-100Å

Dielectric layer
(Al$_2$O$_3$,SiO or other material)

Opaque mirror coating,
e. g., Al t > 600Å

Glass

Fig. 11. Arrangement of three layers in reflection-type
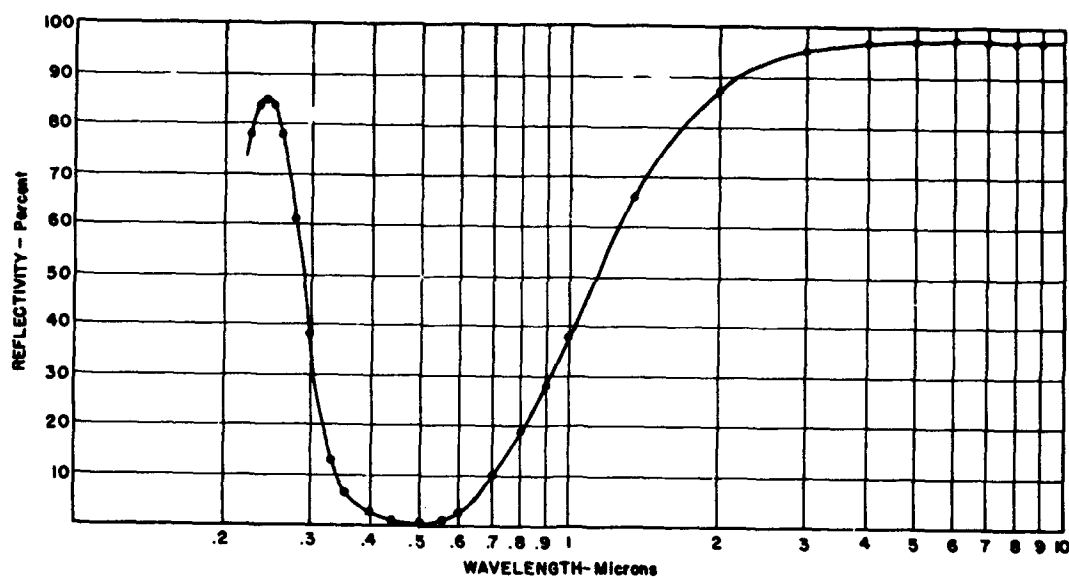interference filter.

Fig. 12. Reflectivity of reflection-type interference fil-
ter as function of wavelength from 0.2 to 10 u. Filter con-
sists of opaque aluminum + Al$_2$O$_3$ (580 A thick) + transparent
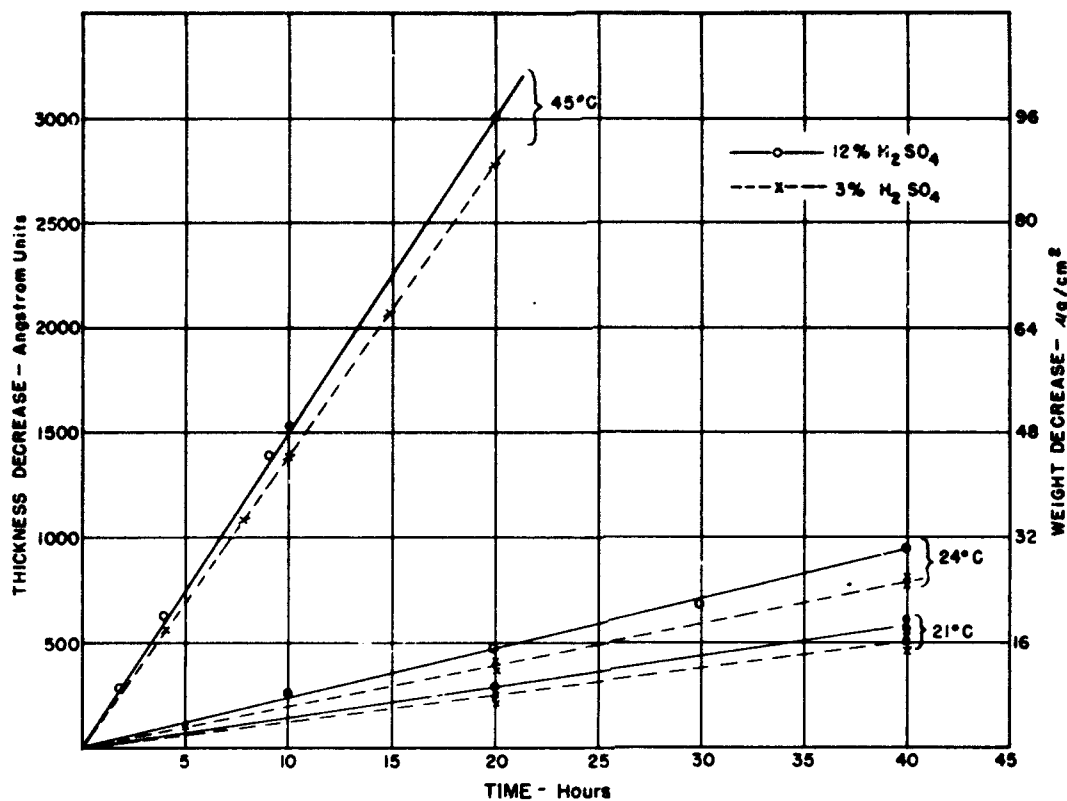aluminum (approx 50 A thick).

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Fig. 13. Dissolving rates of anodic Al_2O_3 films in H_2SO_4 solutions of various concentrations and temperatures.

temperatures between 700 and 950 C correspond with those for γ-Al_2O_3, while at higher temperatures α-Al_2O_3 is formed.

The electron micrographs show no evidence of pores or grain structure in the oxide layer even at magnifications of 50,000 diameters. A characteristic grain structure appears only when the films are heated to more than 700 C. They are, therefore, suitable as temperature resistant support films for electron diffraction and electron microscope investigations.[19] When used for this purpose the films are made 100 to 200 A thick. Fig. 15 shows the electron diffraction pattern of a 400 A thick aluminum coating evaporated on such an aluminum oxide support film at a temperature of 450 C. Only the sharp diffraction rings

19. G. Hass and H. Kehler, Kolloid Zeits. 95,26 (1941); and 97,27 (1941).
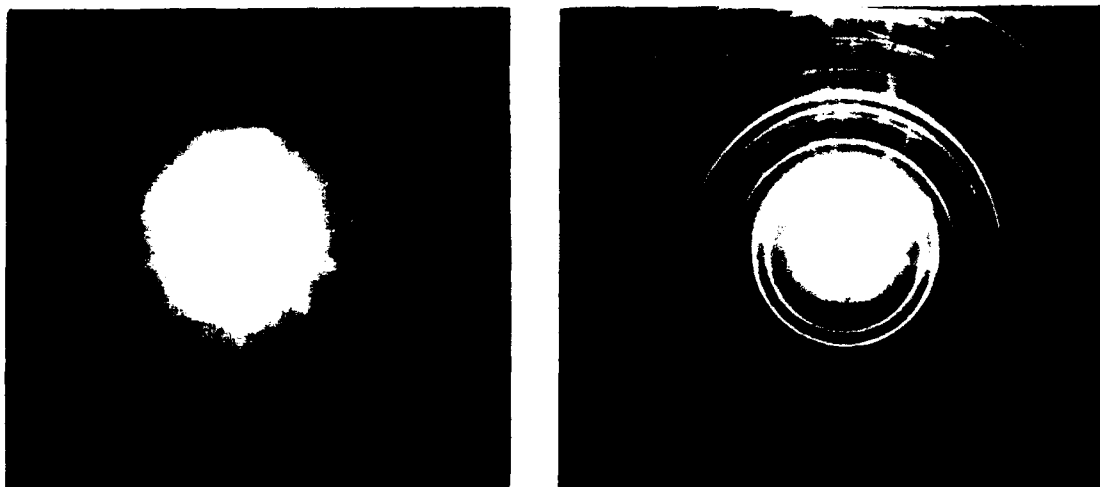
Fig. 14. Electron diffraction pattern of anodically produced aluminum oxide film. Left: before 1-hour's treatment at 800 C; and right: after 1-hour's treatment at 800 C.
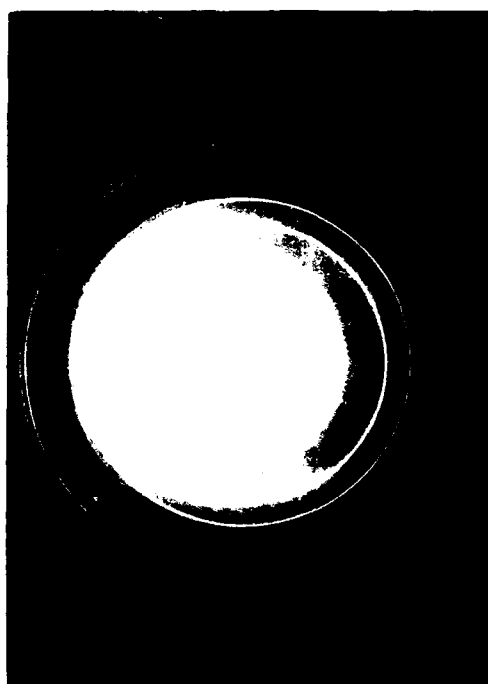

Fig. 1ȷ. Electron diffraction pattern of an aluminum film condensed 400 A thick on aluminum oxide at 4ȷ0 C.
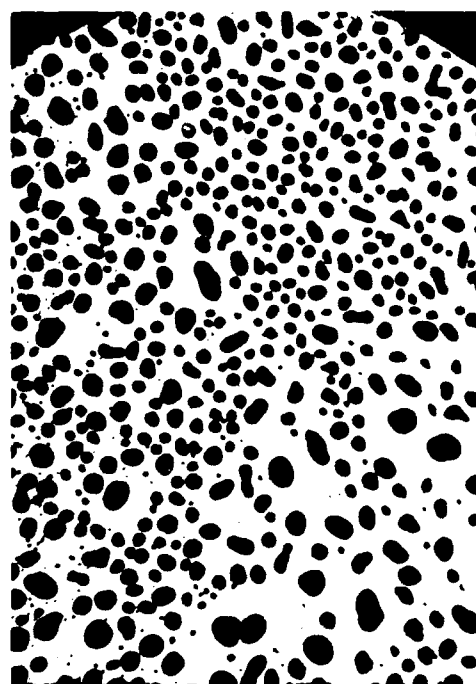

Fig. 16. Electron micrograph of silver condensed 150 A thick on aluminum oxide at 300 C. Magnification: 30,000.
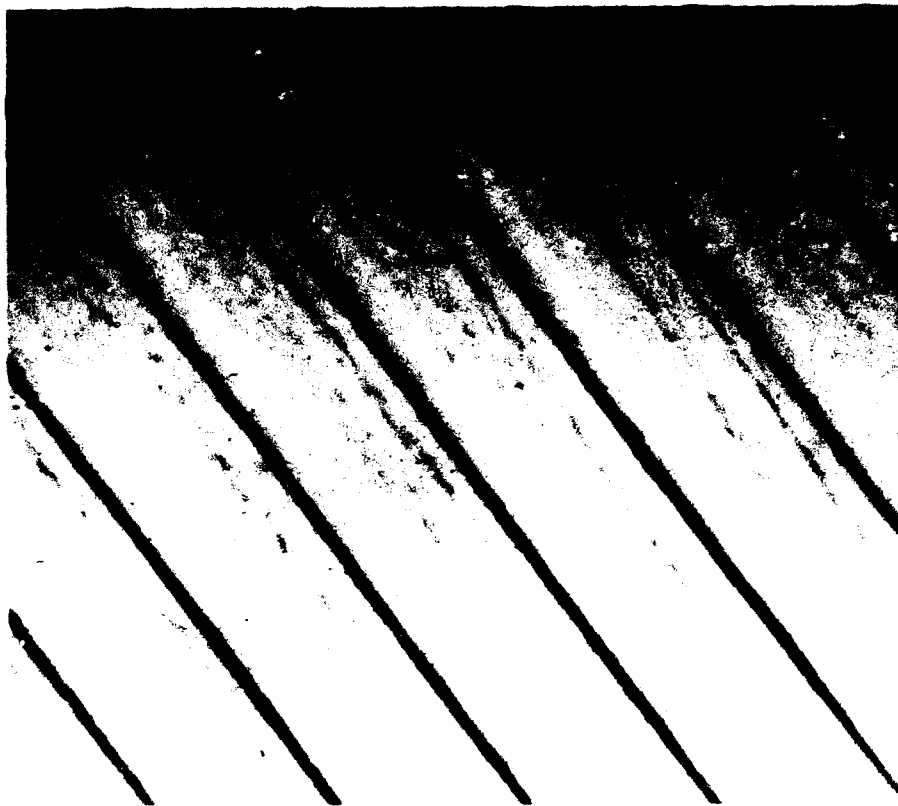
Fig. 17. Electron micrograph of a 30,000 lines per inch grating obtained by the aluminum-aluminum oxide method.

of the aluminum can be recognized while the diffused rings of aluminum oxide are practically invisible. Fig. 16 represents an electron micrograph of a silver film evaporated 150 A thick on an aluminum oxide support at 300 C. The film consists of insulated grains which can be seen clearly on the structureless aluminum oxide layer. Thus, the anodic films are very valuable for studying the structure of evaporated films which are condensed on a heated base.

To study the surface structure of materials with the electron microscope a thin replica film must be prepared on the specimen and released from it by a suitable method.[20] The anodic oxide coatings have proved particularly valuable as replica films. However, their application has been restricted to aluminum and aluminum alloys on which they can be produced directly.

20. H. Mahl, Metallwirtsch., 19,488 and 1082 (1940).

By using a double replica method similar to the silver-collodion method first suggested by Zworykin and Ramberg[21] a more general application of aluminum oxide as replica film can be obtained. The specimen to be investigated is placed in a vacuum chamber and a thick film of aluminum ($t > 2$ u) is evaporated onto its surface. The specimen is removed from the vacuum chamber and the aluminum film is pulled off the surface with Scotch tape. If the aluminum is sufficiently thick, the film can be readily removed from most specimens without damaging their surfaces. Aluminum oxide is now formed on the side of the aluminum film which was in contact with the specimen surface by anodizing in 3-percent ammonium tartrate with about 40 volts. The aluminum oxide film, which represents a positive replica of the specimen surface, is released from its substrate in mercuric chloride, washed with dilute hydrochloric acid and distilled water, and mounted on a support screen for the electron microscope investigation. Fig. 17 shows an electron micrograph of a 30,000 lines per inch grating obtained with the aluminum-aluminum oxide method and used to calibrate the magnification of the electron microscope.

21. V. K. Zworykin and E. G. Ramberg, J. App. Phys.,
    12,692 (1941).

22

Submitted by:

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Approved 28 July 1949 by

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OSCAR P. CLEAVER
Chief, Technical Department II

APPENDIX

AUTHORITY

RESEARCH AND DEVELOPMENT PROJECT CARD (NEW PROJECTS)	SEC. R	HDG. NO. 8-23-02-002

1. PROJECT TITLE
INFRARED OPTICAL MATERIALS

4. OLD PROJ.NO. XR750
5. REPORT DATE 30 Sept.47

6. BASIC FIELD OR SUBJECT
Infra-Red and Ultra-Violet

7. SUB FIELD OR SUBJECT SUB GROUP
Components and Accessories

8. COGNIZANT AGENCY
Office, Chief of Engineers

9. DIRECTING AGENCY
Engr. Res. & Dev. Div., MO, OCE

10. REQUESTING AGENCY
Office, Chief of Engineers

11. CONTRACTOR AND/OR LABORATORY
Engr. Res. & Dev. Laboratories
Ohio State University
Baird Associates

CONTRACT/W. O. NO.
W44-009ENG400
W44-009ENG473

12. RELATED PROJECTS

17. EST. COMPL. DATE
REQ. June 49
REV. Dec. 49
TEST
OR EVAL.

11. PARTICIPATION AND/OR COORDINATION
Signal Corps (C)
Ordnance (C)
Air Force (C)
Navy (C)

14. DATE APPROVED
27 September 1946 by WDGS

15. PRIORITY 1-B
16.

18. FISCAL EST. $.

FY	
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19.
Item No. 1039, CETC Meeting #160

20. REQUIREMENT AND/OR JUSTIFICATION There is a requirement for optical materials which have special properties for the transmission, refraction and reflection of infrared radiation for use as filters for infrared light sources and for protective coverings and optical elements of infrared equipment. This project will result in essential optical materials for night viewing devices sensitive to radiation from heat targets and useful in IR Guided Missiles, a new concept of warfare.

21. BRIEF OF PROJECT AND OBJECTIVE
a. REFERENCES:
  (1) Letter from Engineer Board to Chief of Engineers, file No. 400.1 (XR 750), subject: "Request for Project Infrared Optical Materials," dated 1 August 1946, with two inclosures thereto.
b. OBJECTIVE:
  (1) Development of optical materials which have special properties for the transmission, refraction, and reflection of infrared radiation for use as filters for infrared light sources and for protective coverings and optical elements of infrared equipment and to develop techniques for laboratory and production line testing of the optical and physical properties of such materials.
c. MILITARY CHARACTERISTICS:
  (1) Transmission of useful infrared radiation shall be the maximum obtainable.
  (2) Materials designed for use as filters shall have a minimum transmission of those wavelengths which are to be excluded.
  (3) The transmission properties and physical strength shall be unaffected by the temperatures resulting through use with associated equipment, in ambient temperatures from -70°F to 150°F, or by heat shocks from maximum equilibrium temperatures to 70°F.
  (4) Materials shall be moisture and fungus resistant, and shall be capable of withstanding normal field usage.
  (5) Materials shall have physical properties suitable for various treatments, as being blown, cast, machine ground or polished.
  (6) Materials shall be adaptable to manufacture in quantity production with close control of optical and physical properties.

22. JRDB SR. | **PC.** | **IC & P.** | **L.** | **I.** | **C.**

d. DISCUSSION:

(1) There are at present no entirely satisfactory infrared optical
materials, even though considerable research on this problem has
been conducted by the NDRC and other research agencies. The lack of
satisfactory materials, such as filters, protective windows,refractive &
reflective materials, and low reflectance coatings, has limited the
performance of present infrared equipment. It is believed that the
initiation of the subject project will result in more satisfactory
materials thereby resulting in better performance of the present and
future infrared equipment.

(2) The agencies interested in the subject project are Signal Corps,
Ordnance Department, Army Air Forces and the Navy Department.

e. PROJECT PLAN:

(1) The work under this project will be directed towards collection of
all pertinent information and development of new or improved infrared
optical materials to be considered as a stockpile from which may be
selected the best available components for incorporation in new or
modified items of infrared equipment as they are developed.

(2) All presently available materials will be studied, cataloged, and
samples will be obtained, through library research, contact with
manufacturers and other research agencies, and evaluation of
captured enemy equipment.

(3) Research will be conducted at the Engineer Board Laboratories on
important basic studies, of which the following list may be
considered typical:

    (a) Growth of sizable crystals of thallium halides and other snythetic
crystals, and study of methods of shaping, grinding, and polishing
of such crystals.

    (b) Application of low reflectance coatings to optical elements which
are designed for transmission of infrared radiation, and com-
parative tests to determine the most suitable methods of applying
these coatings.

    (c) Application of high reflectance materials, by evaporation, to
reflectors in order to provide surfaces of adequate hardness,
high reflectivity and selective reflectance to infrared radiation.

    (d) Application of protective coatings, by evaporation, to mirrors
and reflectors in order to provide more durable surfaces and to
prevent early tarnishing and surface deterioration.

    (e) Preparation of interference filters and filter mirrors for use in
the infrared region of the spectrum, and study of methods of
application.

    (f) Preparation of inorganic heat-resistant filters which will cut
off radiation to which caesium-silver-oxide is sensitive, and
transmit that to which lead sulfide is sensitive.

(4) Studies will be conducted to establish definite photometric stand-
ards for the comparison and evaluation of infrared optical materials.

APPROVAL OF

Report 1134

PREPARATION OF HARD OXIDE FILMS
ON EVAPORATED ALUMINUM SURFACES AND
APPLICATIONS OF SUCH FILMS

28 July 1949

AND

DISTRIBUTION

ADDRESS REPLY TO
COMMANDING OFFICER
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FORT BELVOIR, VA.

17 AUG 1949

IN REPLY
REFER TO:

TECRD I
400.1 (8-23-02-002)

SUBJECT: Transmittal of Report 1134, Preparation of Hard Oxide Films on
Evaporated Aluminum Surfaces and Applications of Such Films

THRU: Commanding General
The Engineer Center and Fort Belvoir
Fort Belvoir, Virginia

TO: Chief of Engineers
Department of the Army
ATTENTION: Chief, Engineer Research and Development Division

1. Transmitted herewith is Report 1134, "Preparation of Hard Oxide
Films on Evaporated Aluminum Surfaces and Applications of Such Films,"
dated 28 July 1949, which was prepared by the Technical Staff of the Engineer
Research and Development Laboratories and is submitted for technical informa-
tion only.

2. By increasing the thickness of the natural oxide film on evaporated
aluminum mirrors, a much better surface protection can be achieved. Heat
treatment in air is not a practical method for producing protective coatings
on aluminum because a temperature of more than 400 C is required, and oxide
films formed at this temperature are rough. Oxide films of precisely con-
trolled thicknesses can be produced on evaporated aluminum mirrors by
anodic oxidation in electrolytes such as ammonium tartrate. The thickness
of the oxide layer formed in a given length of time increases linearly with
the applied voltage and is 13.0 Angstrom units (A) per volt for 2 minutes'
anodizing time. The current efficiency of the anodic process in ammonium
tartrate is approximately 80 percent. The oxide coatings are 1.38 times
thicker than the aluminum layers replaced. The anodic oxide films formed
in ammonium tartrate are amorphous and free of pores. They exhibit no
noticeable absorption of ultraviolet, visible, or infrared light. Their
refractive index between $\lambda = 3000$ A and $\lambda = 6000$ A varies from 1.67 to
1.62. Anodized aluminum mirrors show excellent abrasion resistance. To

TECRD I
400.1 (8-23-02-002)
Subject: Transmittal of Report 1134, Preparation of Hard Oxide Films on
Evaporated Aluminum Surfaces and Applications of Such Films

obtain the highest reflectivity in the visible light region, the anodic
oxidation must be performed with 120 volts for 2 minutes. The precisely
controlled uniform anodic coatings on opaque aluminum mirrors are suitable
for the preparation and investigation of reflection-type interference
filters. The thickness of a pure aluminum film can be determined by the
voltage required for complete oxidation. The anodic coatings are suitable
as temperature resistant films for electron diffraction and electron micro-
scope investigations.

    3. The report and its contents are approved.

                                        O. B. BEASLEY
2 Incls   O. B. BEASLEY
  1. Proposed distr list   Colonel, CE
     (in trip)   Commanding
  2. Rpt 1134 (in dup)

TEC GD 400.1   1st Ind

Hq, The Engr Cen & Ft Belvoir, Ft Belvoir, Va. 18 AUG 1949

To: C of Engrs, DA, Washington 25, D. C.

SUBJECT: Transmittal of Report 1134, Preparation of Hard Oxide
Films on Evaporated Aluminum Surfaces and Applications
of Such Films.

ENGMA (17 Aug 49)   2nd Ind.

Office of the Chief of Engineers, Washington 25, D. C.   25 August 1949

TO: The Commanding General, The Engineer Center, Fort Belvoir, Va.

        The report including the proposed distribution list is approved.

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   1 and 2 w/d   Lt. Colonel, Corps of Engineers
   ADDED   Acting Chief, Engr. Res & Develop. Div.
   3. Cpy ltr to Dir.Log.   Military Operations
      GSUSA dtd 25 Aug 49.

TEC GD 400.1   3d _____ Ind

Hq, The Engr Cen & Ft Belvoir, Ft Belvoir, Va.   29 AUG 1949

To: CO, E.R.D.L., Ft Belvoir, Va.

1 Incl:
   n/c

                          FOREST PATRICK
                          1st Lt.   AGD
                          Asst Adjutant General

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Joint Communications Committee (4)

	ATI- 80 426

TITLE: Preparation of Hard Oxide Films on Evaporated Aluminum Surfaces and Applications of Such Films - and Appendix

REVISION
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July' 49	Unclass.	U.S.	English	30	table, diagrs, graphs	(Same)

ABSTRACT:

Data are presented on the formation and properties of oxide films produced on evaporated aluminum mirrors. These oxide films are produced at various temperatures in air, or by means of anodic oxidation in ammonium tartrate. Applications of anodically produced films are discussed with respect to reflection-type interference filters, and temperature-resistant films for electron diffraction and electron microscope investigations. The anodically produced films can be precisely controlled in thickness, and are 1.38 times thicker than the aluminum layers replaced. The current efficiency of the process is 80%, and the thickness of the oxide layer formed in a given length of time increases linearly with the applied voltage (13.0 A per v for 2 min anodizing time).

*Labs., Fort Belvoir, Va.

DISTRIBUTION: Copies of this report obtainable from CADO.

DIVISION: Sciences, General (38)
SECTION: Optics (3)

SUBJECT HEADINGS: Optical materials, Infrared Mirrors
Coatings, Protective

CADO

CAL INDEX