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Notes on Solution of Problems in Odd Job Vapor Coating

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Charts are presented for the solution of the problems pertaining to vapor coating in general. These charts are intended to be adequate to explain and describe the conditions necessary to produce high-quality metal coatings of given optical transmission and given electrical resistance as well as given thicknesses or given weight per unit area.

IF one wants ten thousand small pieces of glass coated with gold of, say, 50 percent light transmission or perhaps to have 50 ohms resistance across a square, it is not uneconomic to devise the setup by "cut and try." If, however, a vaporizer is used for odd jobs, no two successive jobs being much alike, it is important to eliminate the "cut and try" and "call one's shots" rather accurately. It is also important to avoid lengthy calculations for each job. Hence one needs to plan general procedure rather carefully to get flexibility and simplicity. This paper presents graphical aids for coating problems.

The simplest vapor coating "picture" we can get is of evaporation onto the walls of a hollow sphere from a small concentric sphere. If the small sphere is heated, atoms will fly off it in all directions at speeds of about two thousand feet per second and if in the space between the two spheres there are very few air molecules, the metal atoms will travel in straight lines and strike the outer sphere. We will assume that the atoms stick where they hit; exceptions will be considered later.

Since the volume of the metal is the same after transference as before, when the metal of the small sphere is completely transferred to the inner wall of the hollow sphere, the thickness of coating t is such that

$$v = 4\pi r^2 t, \quad (1)$$

where v is the volume of the small sphere and r is the radius of the spherical cavity: If the small sphere was made by melting a piece of wire of diameter d mils, length l centimeters, and if we replace t in centimeters by T° , the deposit thickness in angstroms, and express

r in centimeters, Eq. (1) may be written

$$T^\circ = \frac{40.3d^2 l}{r^2}. \quad (2)$$

This "picture" and Eq. (2) are very useful because the results are nearly the same for deposit from a short cylinder falling perpendicularly onto a small flat surface which is not too near. Before we consider this problem in detail we will dispose of the problem of interference by air molecules.

Air is 78 percent nitrogen, N_2 , and in collision studies air can be considered to be N_2 . At low pressures the molecules of N_2 are farther apart than at higher pressures and hence molecules can travel farther between collisions. This "mean free path" between collisions varies with pressure in the manner shown in Fig. 1. Since most metal atoms are of roughly the same size as the N_2 molecule, the mean free path of the metal atoms between collisions with gas molecules is about the same as that given in Fig. 1. At a pressure of 10^{-4} mm the mean free path is seen to be about 70 cm. Hence in traveling, say, 10 cms, few metal atoms are bounced out of their paths. Hence, the metal can throw sharp shadows. At atmospheric pressure an atom will make 100 000 collisions in traveling a cm. At the end of this, the atom will be but little nearer the surface it started for. Hence, the metal cannot give sharp shadows. If the atom can be oxidized, it has an excellent chance to do so as it meets so many oxygen atoms on its way. Hence we get dirty, nonadhering coats. Figure 2 shows the fraction of atoms that collide with gas molecules

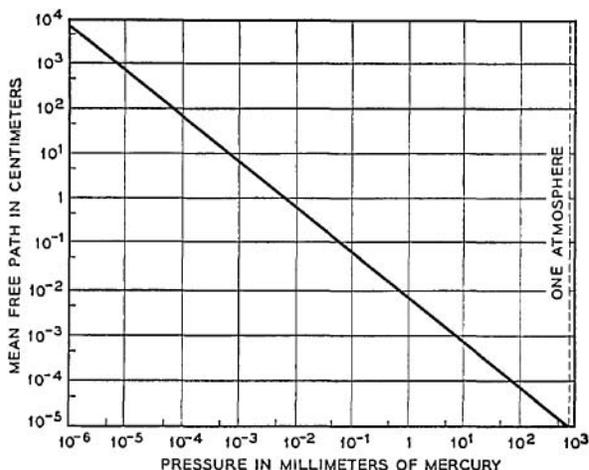


FIG. 1. Mean free path vs air pressure.

within the distance r for a mean free path L . It is seen that if the metal falls on a surface one mean-free-path distance away, 63 percent of the atoms have gas encounters enroute, but at a distance of one-tenth a mean free path only 9 percent have encounters. Hence the importance of evaporating at low pressures only. As an example, at 10^{-4} mm pressure the mean free path is 70 cm. If the path length is 7 cm and 9 percent of the metal atoms suffer encounters on the way, about $\frac{1}{5}$ or 1.8 percent of these encounters are with oxygen. Not all these metal atoms will oxidize, but if they did and the deposit were stacked in an orderly cubic arrangement, on the average the oxidized atoms would be spaced only 3.8 times as far apart as the unoxidized atoms would be $[3(100/1.8)^3=3.8]$. With a pressure of 2×10^{-5} mm, which is commonly used in evaporation work, this factor is 7.3 instead of 3.8.

Consider now a small sphere evaporating onto a plane surface which is at a distance r from the sphere center. At the foot of the perpendicular from the sphere center to the plane the deposit is of the same thickness as the deposit on the wall of the hollow sphere first considered. Hence, Eq. (2) applies at the foot of the perpendicular. At other points on the plane the deposit is thinner. At a distance x from the foot of the perpen-

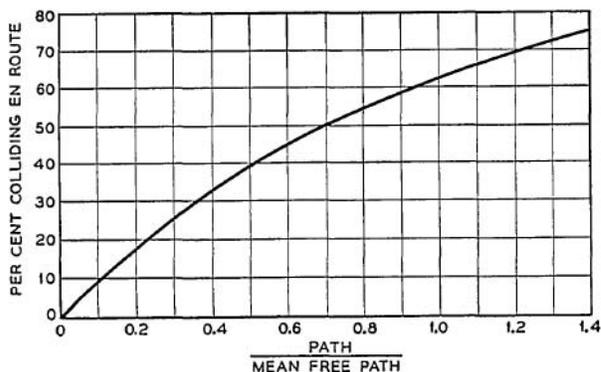


FIG. 2. Percent metal atoms colliding with air atoms enroute.

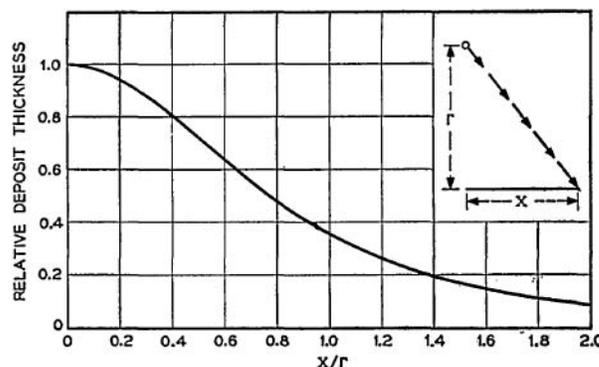


FIG. 3. Deposit thickness variation over an extended surface for evaporation from a point source.

dicular the distance to the sphere center, namely $(r^2+x^2)^{\frac{1}{2}}$, is greater than at the foot. Also the metal lands here obliquely, so that it must cover a greater area than it would at distance $(r^2+x^2)^{\frac{1}{2}}$ if it landed perpendicularly. Therefore, the deposit will be thinner in the ratio $\cos\theta$ to 1 where θ is the angle between the surface normal at x and the line joining x to the sphere center. Hence, at a point distant x from the foot of the perpendicular the deposit thickness is

$$T^\circ = \frac{40.3d^2l}{r^3} f, \tag{3}$$

where

$$f = \frac{r^2 \cos\theta}{r^2+x^2} = \left[1 + \frac{x^2}{r^2} \right]^{-\frac{3}{2}}. \tag{4}$$

In Fig. 3, we have plotted values of f against values of x/r . This curve tells us that for example a disk of diameter D will have a deposit 95 percent as thick at the edges as at the center if it is distant $2.7 D$ from the sphere center.

Another concept that one can use is the evaporation of an infinitely long cylinder onto the inner walls of a hollow concentrically placed cylinder. A cylinder d mils in diameter in a hollow cylinder of radius R cm gives, on evaporation, a coating of thickness

$$T^\circ = \frac{80.5d^2}{R^2} \text{ angstroms.} \tag{5}$$

If the wire length is not great as compared to r , this equation does not hold. It takes an infinite amount of material to make and load an infinitely long wire so we prefer spherical radiation as being less wasteful of material. Since the spherical equation, Eq. (2), is solved for nearly every job, we have prepared a nomograph, Fig. 4, to solve the equation. As an example of its use suppose we want a deposit 1000A thick and that we wish to have the receiving surface 10 cm from the source and to use 20-mil load wire. We draw a line from the point marked 1000 on the deposit thickness scale (top line) through the point 10 on the distance scale and

extend the line until it crosses the reference line. From this intersection we draw a new line that passes through the point marked 20 on the load wire diameter scale and extend this line until it crosses the load wire length scale. We observe that this intersection comes at a scale reading of 6.2 cm. Hence we use 6.2 cm of 20-mil wire.

Some materials, such as chromium, are not available as wire. Here we weigh a piece of about the right size and figure the distance necessary to get the proper thickness of coat. The weight of metal in milligrams is given by $M = 1.95\sigma r^2$, where σ is the coat weight in milligrams per square inch. For metal of density ρ gm/cm³: $\sigma = 6.45 \times 10^{-5} \rho T^{\circ}$. Figure 5 makes this computation for us. For example: 750A chromium being required, a convenient distance being about 10 cm, we draw a line through Cr on the material scale and 750 on the T° scale and observe that it cuts the reference of σ scale at 0.33. Hence 750A of chromium weighs 0.33 milligrams per square inch (msi). We now draw a line from this intersection through the point 10 on the r or distance scale and observe that it cuts the milligram scale at 68. Hence 68 milligrams of chromium would be required for a distance of 10 cm. We weigh a few pieces but find none that weigh 68 mg but do find one weighing, say, 55 mg. Drawing a line through 55 to the intersection on the reference scale, we observe that it cuts the r scale at 9.1 cm. This is the distance to use with the 55 mg lump.

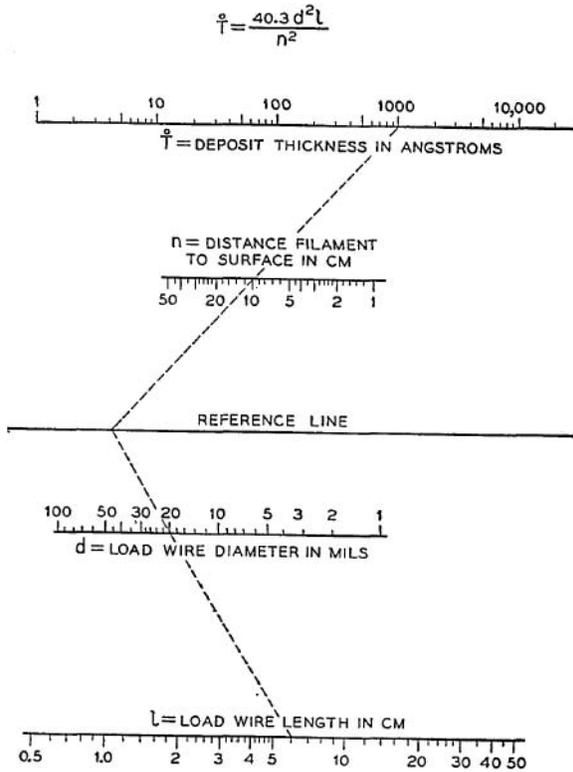


FIG. 4. Deposit thickness vs load wire size nomograph.

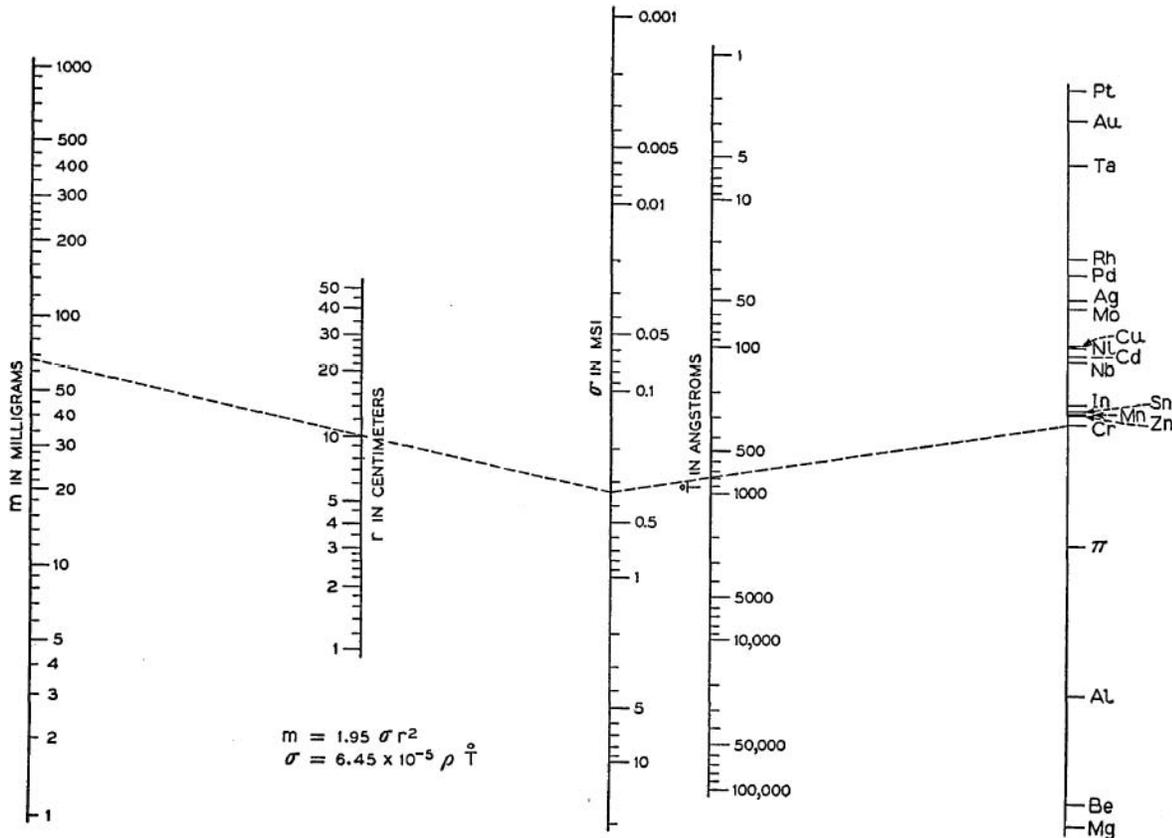


FIG. 5. Deposit thickness and weight per unit area vs load weight nomograph.

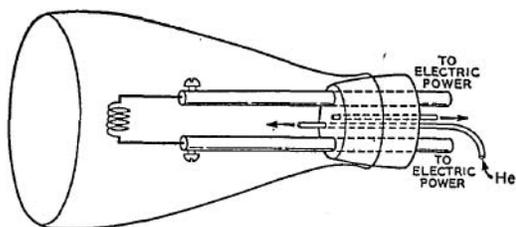


FIG. 6a. A helium bottle for melting sublimating materials such as chromium onto the filament.

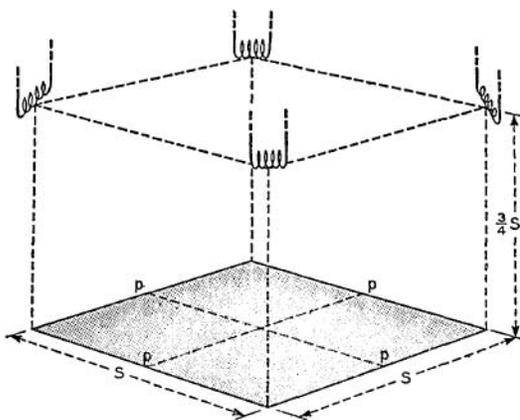


FIG. 6b. Arrangement for uniform coverage of an extended area.

Chromium does not melt at the low pressures we use. It will sublime so fast that it will disappear completely and never become liquid. As it sublimates it gives off gas all over the surface and hence jumps around in the filament coil like popcorn in a popper. It will not heat quickly unless it is firmly fastened to the hot wire. Since it will not melt onto the filament in a vacuum, we melt it onto the filament at room pressure in a helium bottle, Fig. 6(a). Also it is quite practical to electroplate the chromium onto the filament coil.

We now inquire as to the effect of departure from sphericity of the vaporizing surface. The important property of the sphere from our viewpoint is that from all points equidistant from its center is subtends the same solid angle. Let us consider a uniformly hot cylinder whose length is greater than its diameter. It is centered in a hollow sphere whose radius is great as compared to the cylinder length. At a point on the sphere in line with the cylinder axis the evaporating surface subtends the smallest solid angle and here the deposit will be thinnest. At a point on the sphere 90° from here (directly off the cylinder center) the solid angle subtended by the evaporating surface is greatest and the deposit is thickest. The deposit thickness at any point is directly proportional to the solid angle subtended by the source. This is perfectly general—

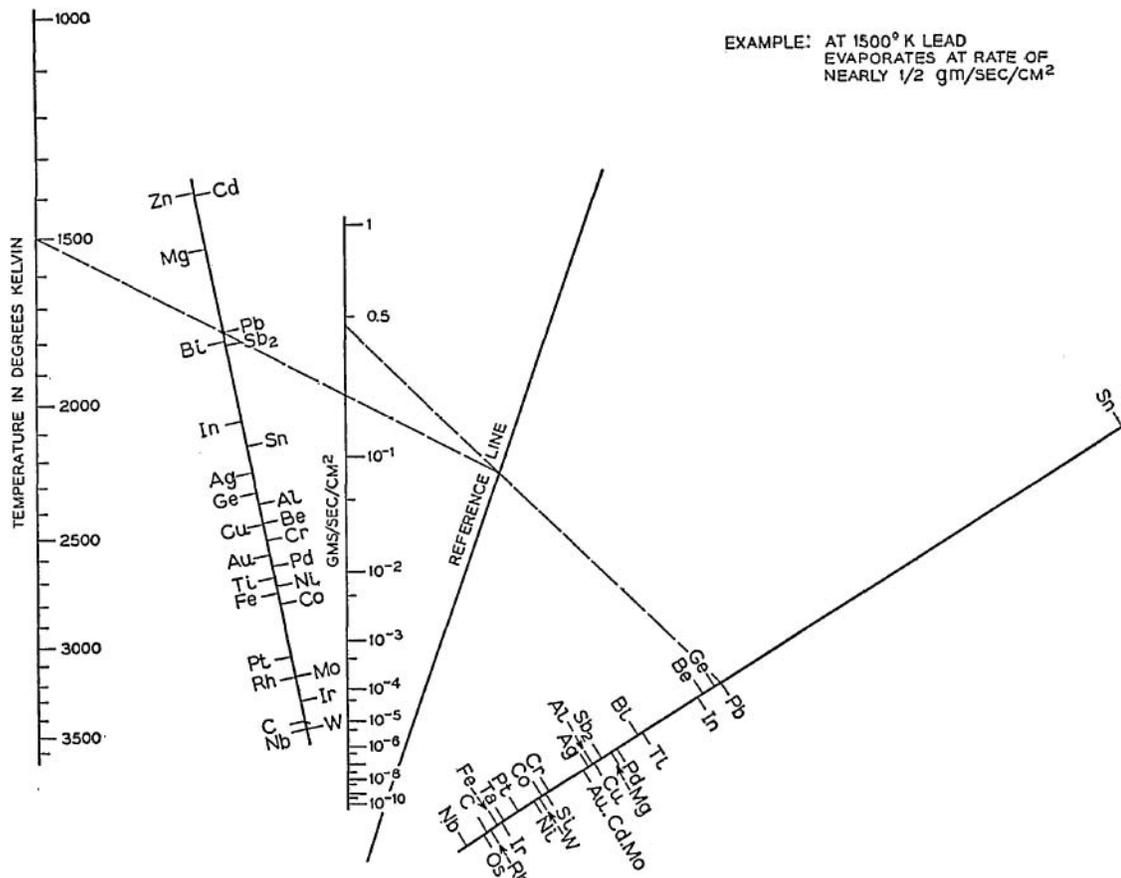


FIG. 7. Temp-rate of evaporation nomograph.

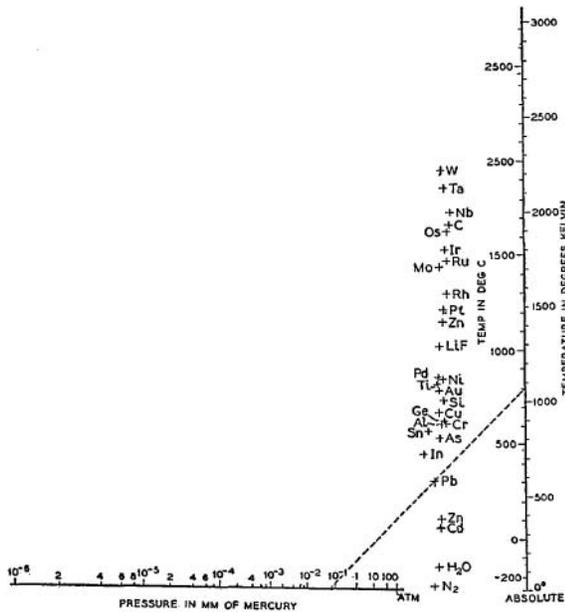


FIG. 8. Nomograph showing temperature vs vapor pressure for metals.

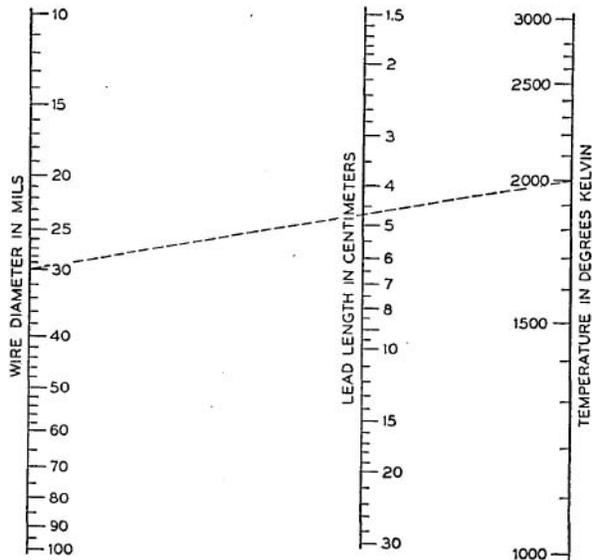


FIG. 9. Lead length allowance nomograph for tungsten.

the cylinder and spherical shell may be discarded and we may say that any uniformly heated surface will deposit its substance on a "cool surface" to an amount directly proportional to the solid angle subtended by the source at that point and proportional to the cosine of the angle the path of the metal atoms makes with the normal of the "cool surface." If the hot source subtends a large solid angle at points on the "cool surface," the incoming path is not defined. In this case we imagine breaking the hot surface up into small areas, figure the effect of each area at a given point, and add the effects. Examining in this way the "cylinder in a sphere" we find that the spherical Eq. (2) is correct in case we place the surface to be coated on the axis of a cylinder whose length is half its diameter, or else place the surface parallel to the length of a cylinder whose length is 1.83 times its diameter. Both these are useful since they can be approximated by placing the metal to be evaporated on a refractory metal wire filament wound into a spiral or helix of the proportions mentioned.

Tungsten is the most generally useful metal for this because of its high melting point. Since the metal to be evaporated should be spread out over the tungsten surface, a stranded wire is better than a solid wire as it acts like a wick. Hence we usually use helical coils of four strand tungsten wire. The metal to be evaporated should alloy slightly with tungsten so that it "wets" tungsten and hence does not fall off (or out) but spreads over the surface. If the alloy has too low a melting point, it may not be possible to get the metal to a temperature sufficiently high without melting the filament. Evaporation of platinum from tungsten is such a case. For example, if we want to deposit 500A of platinum from a filament with a square centimeter of evaporating sur-

face at a distance of 5 cm from the receiving surface the "loading by weight" chart tells us that we will need 33 milligrams of platinum on the filament. At a temperature of 3000°K this would be evaporated in less than a second. At 2500°K it will evaporate off in a little over a half minute while at 2000°K it will require about four hours. (This data comes from the evaporation rate nomograph, Fig. 7). Obviously, one must use high temperatures in evaporating platinum to avoid intolerably long evaporation time. One should employ a very heavy filament to keep the platinum-tungsten alloy very tungsten rich—and hence of high melting point. Otherwise, the filament will melt before a satisfactory temperature is reached. An increase in filament temperature increases the rate of metal dep-

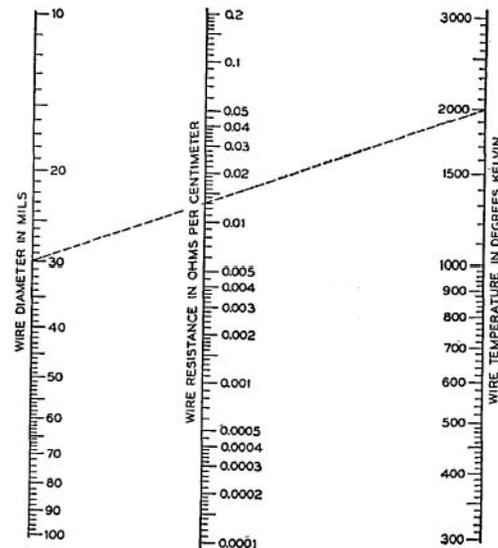


FIG. 10. Wire diameter-temperature-resistance nomograph for tungsten.

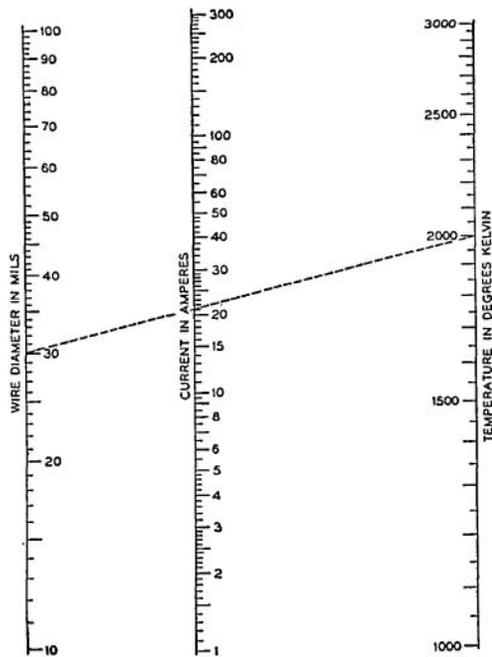


FIG. 11. Wire diameter-current-temperature nomograph for tungsten.

osition but also increases the rate of heating of the surface being coated. However, the deposition rate is increased more than the heating rate. Hence, bodies that will be damaged by temperature rise are most quickly coated by short flashes of the filament with cooling time between flashes rather than by using a continuous filament temperature low enough to avoid damage.

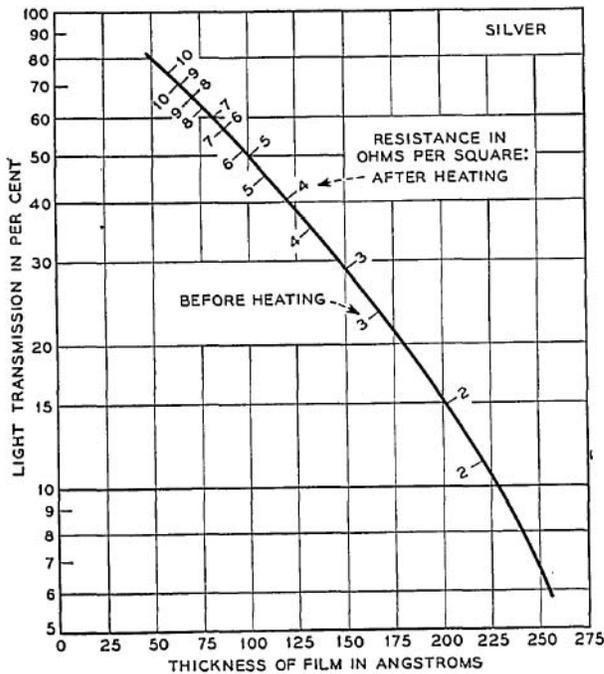


FIG. 12. Light transmission and resistance per square vs thickness of silver.

The temperature-vapor pressure nomograph, Fig. 8, gives the vapor pressures of a number of substances as a function of temperature. It will be noticed that zinc and cadmium have high vapor pressures at fairly low temperatures. At 300°C zinc has a vapor pressure of 2×10^{-3} mm. Brass clamps used to support the filament could easily get hotter than 300°C. Zinc would then distill out of the brass and raise the operating pressure. Zinc and cadmium are not good in high vacuum systems, especially if they get warm in use.

In spite of this reputation of zinc, it is interesting to note that at 27°C a zinc sphere one centimeter in diameter would lose weight by evaporation at the rate of a milligram in a million years. Also, it is useful to note that at 2000°K silver evaporates 200 000 times as fast as platinum, while platinum evaporates about a million times as fast as tungsten does. At 3000°K platinum evaporates 20 000 times as fast as tungsten.

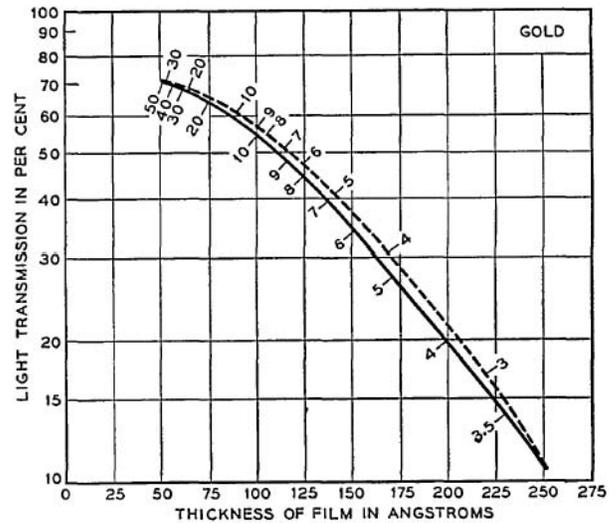


FIG. 13. Light transmission and resistance per square vs thickness of gold.

From this we see how small is the amount of tungsten that is deposited along with the other metal. If the tungsten has been heated in air and has a colored coat of tungsten oxide the case is different. Tungsten oxide has a higher vapor pressure than tungsten does. To avoid depositing this oxide on the surface along with the metal one is trying to deposit, one should heat the filament in vacuum or helium to clean it before using it. Also, one should not open the vacuum chamber until the filaments are cold. Experiments have shown that gold evaporated at 10^{-3} mm pressure contains 5 percent tungsten. This tungsten must have been first oxidized by the excess gas, then transported.

One can get an idea of the temperature of a filament by viewing simultaneously a distant long straight filament that seems to cut across the evaporation filament because the two filaments are in line with the eye. The current in the comparison filament is adjusted until

it seems to blend into the evaporation filament because their colors are the same. One may need dark glasses to make the observation, but since both filament colors are reduced in the same way, the glasses should not influence the result. Figure 9 gives the relation between comparison filament current and temperature for filaments of diameters between 10 mils and 100 mils, and Fig. 10 gives the resistance of such wires at temperature T° so that one may compute the voltage given the current and filament length. We have said that the comparison filament should be "long." If the filament is too short, the end supports cool the filament excessively. The cooled ends of the filament may be considered as leads to the hotter part. The allowance for leads is given in Fig. 11. A filament that is two lead lengths long will have its center within $\frac{1}{10}$ percent of true temperature. The wire size—current—temperature

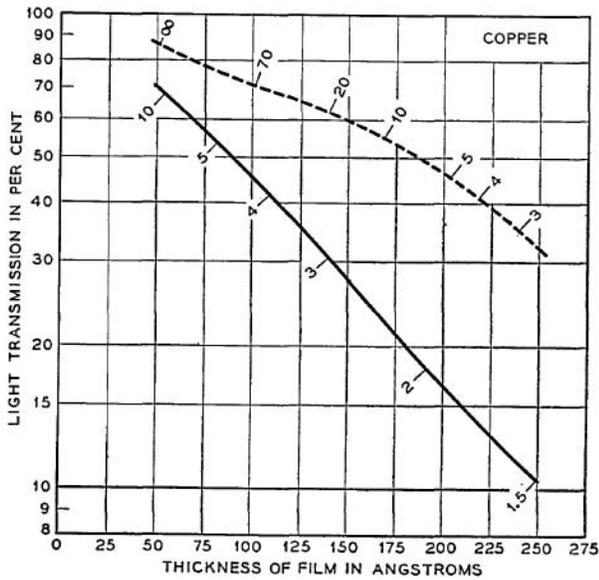


FIG. 14. Light transmission and resistance per square vs thickness of copper.

chart applies to round wire. The evaporation filament will make rather quick changes in temperature as the molten metal moves around shorting the filament in various ways. This is particularly true if the filament is heavily loaded. For a very lightly loaded filament the temperature will approach that of an empty filament. If the evaporation filament is a straight wire we can approximate its temperature by Fig. 9. If the evaporation filament is a helical coil, when empty it will be hotter than Fig. 8 indicates. Figure 8 assumes that the heat loss is all by radiation from the entire wire surface and that no radiation falls on the wire. In a coil, radiation from one turn falls on the other coil turns. Hence the coil gets hotter than a straight wire.

So far we have not met the problem of getting a uniform coat over a large area. If we use four identical filaments, one over each corner of a square of side s and

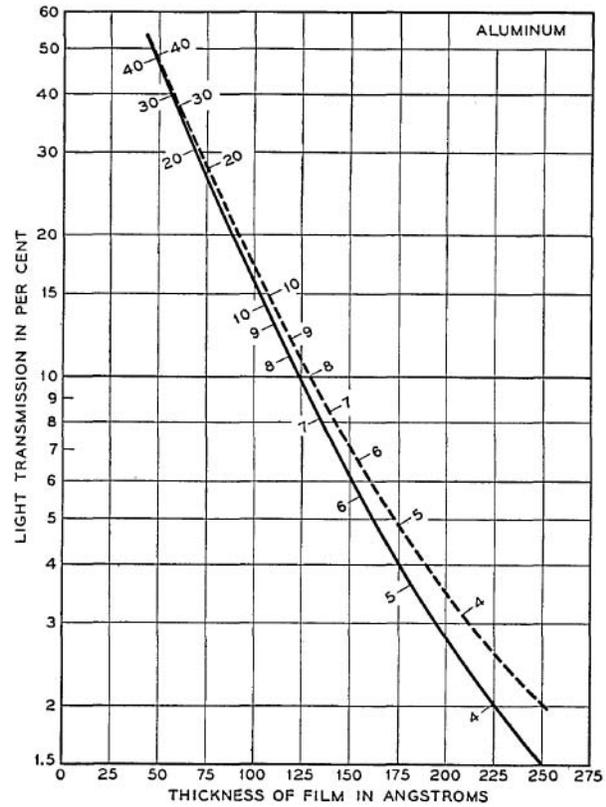


FIG. 15. Light transmission and resistance per square vs thickness of aluminum.

at a distance $\frac{3}{4}s$ from the surface, as in Fig. 6(b), we will get a coating uniform in thickness to about 3 percent. Furthermore, if we put in *each* filament $\frac{2}{3}$ of the amount called for in Fig. 4 or Fig. 5, the coating will have the thickness indicated in the charts. We have described

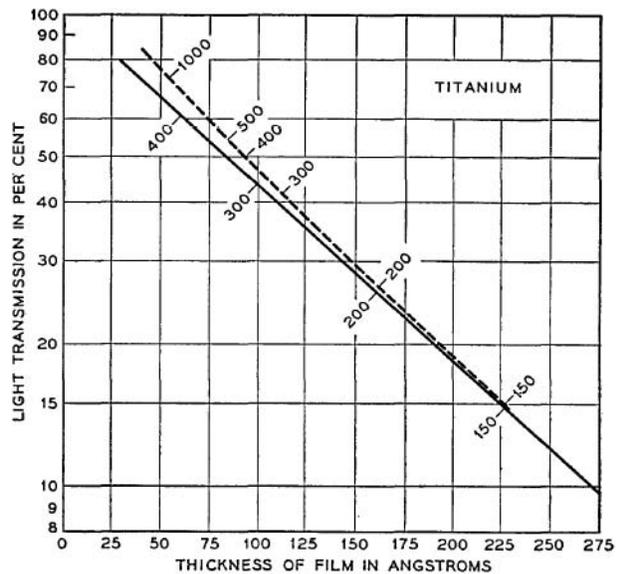


FIG. 16. Light transmission and resistance per square vs thickness of titanium.

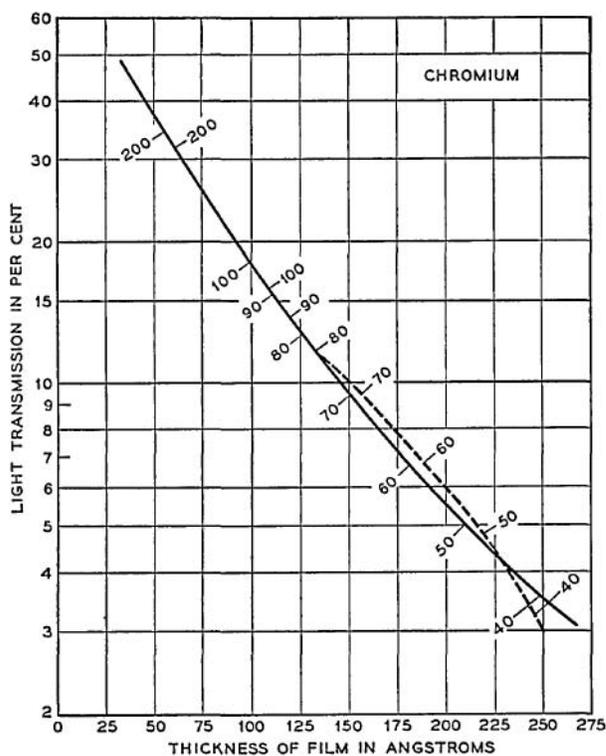


FIG. 17. Light transmission and resistance per square \propto thickness of chromium.

this as a deposit on the upper surface of a horizontal sheet because this is the easiest way to describe it. Actually this is the least desirable position because anything falling from the filament falls on the surface to be coated, "shading" the surface from the metal "rays." The result is "pin holes" in an otherwise continuous metal coating.

THE ELECTRICAL AND OPTICAL PROPERTIES OF THIN FILMS

As metal is deposited on a substrate such as glass it does not immediately form a continuous sheet. The first atoms to land skate around on the surface, some perhaps escape from the surface, some come to rest.

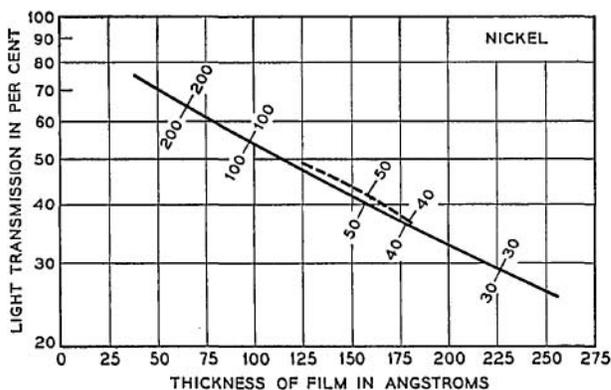


FIG. 18. Light transmission and resistance per square \propto thickness of nickel.

Those that come to rest serve as nuclei for newcomers. Those newcomers which strike such a nucleus come to rest enlarging the nucleus. This means that the surface layer must grow in patches which eventually coalesce as more material is added. This is called agglomeration. Since the patches increase in thickness as well as in area, one may have considerable material on the surface before electrical continuity is established.

Just how much material is on the surface when continuity starts depends on several things: the nature of the material being evaporated, the nature of substrate temperature of substrate, residual gas pressure, and speed of deposition. Metals with low boiling points such as cadmium and zinc are reluctant to stick to nonmetallic surfaces unless the surfaces are very cold. If, however, a fraction of a layer of silver is on the surface, zinc

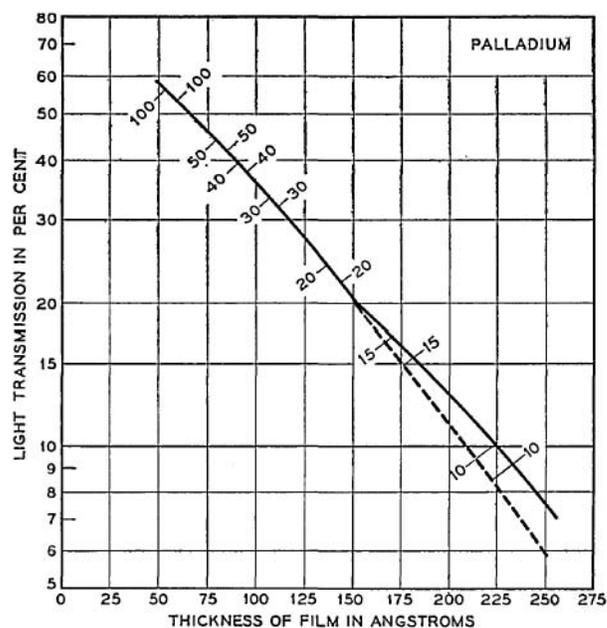


FIG. 19. Light transmission and resistance per square \propto thickness of palladium.

sticks well even at room temperature. Fast evaporation achieves electrical continuity with less metal than does slow evaporation. A thin conducting metal coat may become nonconducting, if warmed for a short time or if allowed to stand a long time. Because of agglomeration, aging may greatly alter the resistance of a thin film. From the foregoing we can see that the electrical resistance and optical transmission of thin films cannot be computed by equations that assume a continuous metal. Empirical data is necessary for the production of given resistances or optical transmissions. In Figs. 12 to 19 we give for silver, gold, copper, aluminum, titanium, chromium, nickel, and palladium the empirical relation between optical transmission and resistance across a square as a function of the nominal film thickness.

These films were deposited at 2×10^{-5} mm pressure

with the substrate at room temperature. The metals were melted on the filament, then flashed off as quickly as possible. They were aged by heating to 135°C for 15 minutes. The transmission measurements were made in a "Lumetron colorimeter" without a filter. Here the nominal film thickness means the thickness according to Eq. (2). The actual film thickness has been found on occasion to be double the nominal thickness and also on occasion to be little more than half. This is apparently due to gravity keeping more of the molten metal at the bottom of the horizontal axis coil than at the top. This means more metal is available for downwards evaporation than for upwards evaporation. It can also be caused by using a very small charge in a large filament coil. If the charge is insufficient to fill the interstices of the four strand wire, only the lower parts of the coils will be filled since the charge will normally be placed at the coil bottom. Ideally, the filament coil should be of such a size as to just soak up the charge. If the charge in such

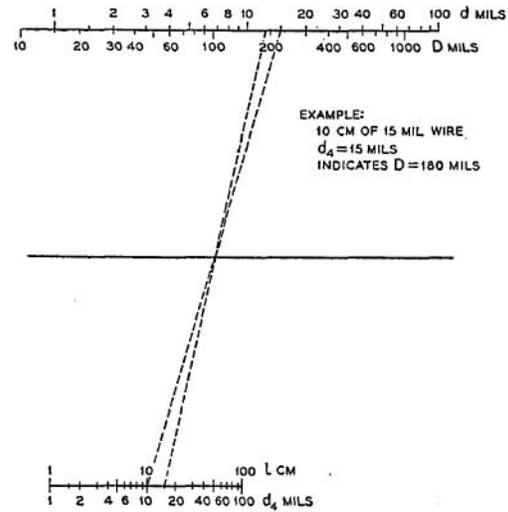


FIG. 20. Coil diameter for least directional evaporation.

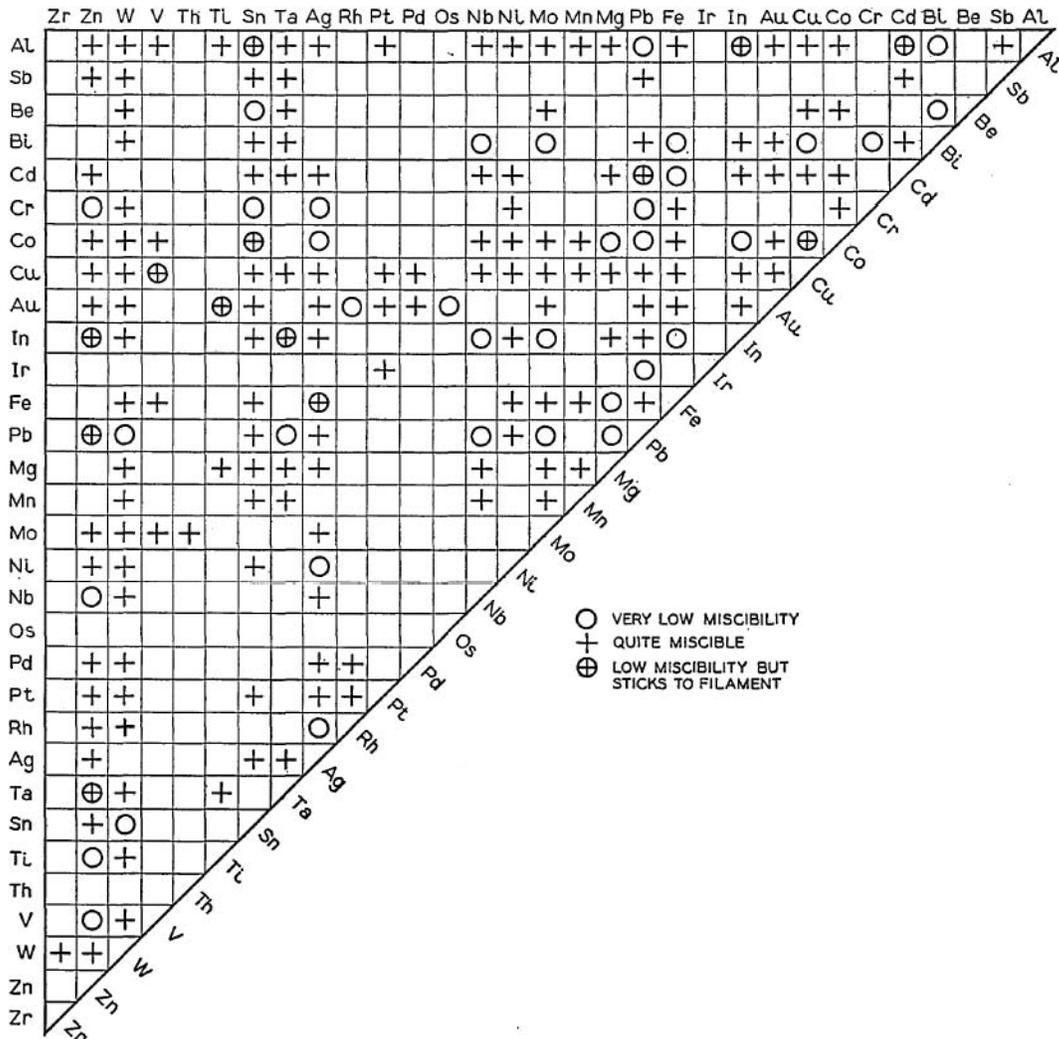


FIG. 21. The mutual solubility of metals.

a filament is carefully melted and allowed to distribute before being flashed off, the directionality is reduced as can be shown by evaporating onto the inner walls of a cylinder. Figure 20 is a nomograph that indicates the diameter of coil for d mil loading wire in the interstices of a cable composed of four strands of d_4 -mil tungsten wire, the coil length being 1.83 times its diameter. This should serve as a rough guide in making filament coils.

Alloys

Although distillation is a common method of separating mixtures of elements or compounds one can vapor

coat with alloys by fast evaporation. One's probability of success is greatest for those metals that have nearly the same evaporation rate. Another aspect of alloying is that mentioned before, the alloying of the load with the filament. A small mutual solubility is necessary if the load is to cling to the filament. A guide to the mutual solubilities of metals is given in Fig. 21. For example, Sn does not cling to tungsten enough to make it feasible to evaporate tin from an open coil of tungsten. The chart tells us, for example, that silver and chromium do not alloy. Hence, one coated over the other should not diffuse into it.

Reflection from a Mirror Surface with an Absorbent Coating*

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The problem of a plane-wave incident obliquely on a layer of absorbent (dissipative) material uniformly coated on a mirror (highly conducting) plane surface is considered. The results of extensive numerical calculations, carried out for a wide range of values of the parameters, are reported. Approximate formulas for the reflection coefficients to supplement these calculations are derived for the case when the "absorption" in the layer is small.

IT is well known in optics that the reflection coefficient for a highly conducting mirror surface is modified if a layer of absorbent material is coated on the surface. In fact, it can be demonstrated that the reflection coefficient vanishes if the optical constants, layer thickness, and the angle of incidence are suitably chosen.¹ It is the purpose of this paper to consider the problem further and to report the results of rather extensive calculations that were carried out at the computation center of the University of Toronto.²

The general problem to be investigated is described as follows. A plane wave, whose wavelength is λ , is incident with angle of incidence θ onto the plane surface of a homogeneous film of thickness h whose complex dielectric constant is $K(1-iq)$ relative to free space. That is, the real dielectric constant is K and the loss tangent is q . In the language of optics the refractive index of the film is n and the absorption coefficient is k so that³

$$n^2(1-ik)^2 = K(1-iq),$$

* Work carried out under Defense Research Board, Project No. D48-95-11-14.

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‡ Computation Centre, University of Toronto, Toronto, Canada.

¹ L. N. Ridenour, *Radar System Engineering* (McGraw-Hill Book Company, Inc., New York, 1947), Massachusetts Institute of Technology, Radiation Laboratory Series No. 1.

² K. F. Hill and W. A. Fraser, Problem No. 114, "Microwave Reflection Coefficients" Computation Centre, University of Toronto, (June 1953).

³ Max Born, *Optik* (Julius Springer, Berlin, 1933), p. 260.

or

$$n^2 = (1/2)[(K^2 + K^2q^2)^{1/2} + K] \quad (1)$$

and

$$n^2k^2 = (1/2)[(K^2 + K^2q^2)^{1/2} - K].$$

The lower medium has an absorption coefficient or loss tangent that is very large so it is equivalent to a perfect conductor.

There are two reflection coefficients to be considered which are designated by $R_{||}$ and R_{\perp} where the subscripts $||$ and \perp denote that the electric field of the incident wave is parallel to and perpendicular to, respectively, the plane of incidence. These reflection coefficients are equal to the complex ratio between the

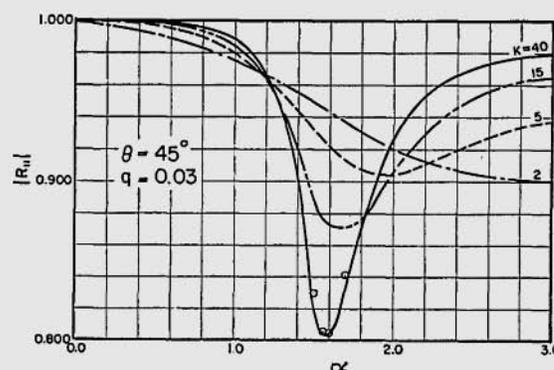


FIG. 1. The magnitude of the reflection coefficient of a coated conductor as a function of the optical thickness of the film in radians.