TI-2362

4101-F-15

ECHNICAL REPORT 52-36

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DEVELOPMENT OF TRANSPARENT MATERIALS WHICH REDUCE EFFECTS OF PRECIPITATION STATIC IN AIRCRAFT

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BALCO RESEARCH LABORATORIES

MARCH 1952

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WADC TECHNICAL REPORT 52-36

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Balco Research Laboratories

March 1952

Materials Laboratory
Contract No. 33(038)-12240
RDO No. 606-62

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

McGregor & Werner, Inc., Wakefield, Mass.
Oct. 17, 1952 200

FOREWORD

This report was prepared by the Balco Research Laboratories, Newark, New Jersey, under USAF Contract No. AF 33(038)-12240, "Development of Transparent Materials which Reduce Effects of Precipitation Static in Aircraft". This work was initiated under Research and Development Order No. 606-62, "Optical Coating for Aircraft Materials", and was administered by the Materials Laboratory, Research Division, Wright Air Development Center, with Mr. Jules I. Wittebort acting as Project Engineer.

The work was directed by Doctors M. U. Cohen and George A. Dalin and was carried out by Mr. S. Levinson and S. Temel. Messrs. A. Schneider and R. Hanson also participated.

Professor Chas. Overberger of the Polytechnic Institute of Brooklyn served as consultant on the work dealing with organic polyelectrolytes.

ABSTRACT

Methods of laying a transparent electrically conductive film on plastic airplane canopies are discussed. The purpose of such films is to conduct to the aircraft frame the static charges developed on the canopies by friction with air, dust, snow, etc., during flight. Unless these charges are properly dissipated, precipitation static results, producing serious interference with radio communication.

The types of film studied include metal oxides, metals, phosphors, polyelectrolytes, electrolytes dispersed in waxes, and electrolytes dispersed in non-polar polymers.

Special techniques employed in the research include film-forming by withdrawing slides from solution at a controlled rate, vacuum-evaporation of metals, metallic oxides and phosphors, a convenient method of measuring surface resistance, and the deposition from solution of adherent metal-oxide films on acrylic sheet.

Preliminary studies indicate that the mono-butyl ester of orthophosphoric acid in polymethyl methacrylate and analogous systems merit further detailed investigation.

PUBLICATION REVIEW

Manuscript Copy of this report has been reviewed and found satisfactory for publication.

FOR THE COMMANDING GENERAL:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Research Division

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INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

It has been observed that aircraft are subject to serious radio interference as a result of the accumulation of electric charge on plastic or otherwise insulated surfaces, when the rate of accumulation is greater than that at which the charge can be dissipated by normal surface leakage. As the charge accumulates, the electric potential rises until disruptive sparks or streamers occur across the insulating surfaces towards the adjacent air frame. The interference which ensues is known to have caused numerous operational failures of radio compass and low frequency communication receivers. The necessity for installing receiving antennas within the transparent plastic enclosures of high speed aircraft has intensified the problem.

Two methods of attack on the problem have been suggested. The first proposal is that a surface treatment be developed to reduce the charging rate, so that charges formed may be dissipated through the usual conductivity mechanisms which do not cause interference. The second proposal is that a surface treatment or plastic composite be developed which will provide a sufficiently high conductivity to allow the transfer of high charging currents (as high as 100 microamperes per square foot) from the transparent areas to the metal structure without the arcing and attendant ionization effects which disrupt radio reception.

In order that the coating may dissipate the charge referred to, it has been estimated that the surface resistance should be in the range of 3 megohms per square to 10 megohms per square. It is believed that a lower resistance would cause attenuation of radio frequency signals. It is also required that the dielectric loss factor of the coating and plastic sheet combination should preferably be below 0.01 at frequencies up to 150 megacycles. Moreover, the coating should be of a permanent or semi-permanent nature, resistant to erosion and to extremes of temperature, humidity and atmospheric pressure variations.

Also, the coating should not unduly affect the transparency of the plastic, and if applied prior to forming the plastic it should be sufficiently flexible and adherent to retain its desirable characteristics during and subsequent to the forming operations. If the coating is of semi-permanent nature, it should be possible to apply it in the field.

The origin of the charge and the mechanism by which the charge forms have been studied by R. H. George (58) and by I. Langmuir and H. E. Tanis (59). The various physical forms of water appear to be the worst offenders. This is to be expected since the dielectric constant of water is so high; electrons are easily removed from water by the methyl-methacrylate of the canopy surface and accumulate as negative charge.

1.2 METHODS OF ATTACK ON THE PROBLEM

1.2.1 Charge Dissipation by Conduction

Since corona discharge or arcing at the plastic surface cannot take place unless a high potential is reached at the surface of the plastic, removal of the charge by conduction as rapidly as it is formed should provide a solution to the precipitation-static problem. The achievement of surface conductivity is an objective which has received much study. A number of the methods which have been developed are manifestly inapplicable; for instance, methods depending on ionization of the air in the vicinity by high energy radiations would introduce serious hazards and operational difficulties.

Coatings which are both transparent and conductive have been developed for a number of applications, among which are conductive layers on glass and anti-static coatings on motion picture films. These examples illustrate the two principal methods of transferring electric charge, namely, by electron conduction and by ion conduction.

1.2.1.1 Electron Conduction and Semi-Conductivity

Lying between the familiar conductors, typified by the metals and graphite, and the familiar insulators such as glasses, rubber and plastics, is the group of materials known as semi-conductors, having resistivities ranging from 10^{-2} to 10^{7} ohm-cm. The semiconductors include distilled water and alcohols, metals such as silicon, germanium, and selenium, and a group of compounds including titania and tin oxide, which are of particular interest because of the fact that they can be deposited in the form of transparent films. Titania films have been studied in connection with reflection problems by this laboratory and by others (67). It has also been shown that titania can be made semi-conductive by effecting partial reduction (16,19). Coated glass is commercially available which has a surface conductivity high enough to permit the passage of relatively large currents. The coating consists of tin oxide and is completely transparent.

The mechanism by which semi-conductors function appears to be fairly well elucidated (6,30,31,32,33,42,43,47). It is believed that the phenomenon of semi-conduction can be explained on the following assumptions (44). Electrons, in metals such as silicon and germanium, when in their normal levels, are unavailable for conduction. In order for conduction to take place, electrons must be supplied to a band of levels of higher energy, termed the conductive band or zone. This can take place, as in selenium, by the absorption of a photon of light which imparts enough energy to lift an electron into the conduction band. A second possibility is by the introduction of an impurity into the crystal lattice, which impurity contains in its valence shell an electron in excess of the number needed for the formation of valence bonds (24,40). In the silicon lattice, for instance, each atom is joined to its neighbors by four bonds, each bond utilizing one of the four valence electrons in the outer shell of the silicon atom. If a phosphorus atom is introduced into the lattice, it will still have only four neighbors with which to form bonds; the fifth electron in its valence shell will therefore be unpaired.

The transfer of this electron to a neutral atom by the so-called tunnel effect requires little or no energy of activation, and the material can therefore conduct. This type of conduction is known as N-type or excess-type, and depends upon the fact that the impurity introduced has more electrons in its valence shell than are required by the lattice for bond formation. Stated more generally, the impurity lies to the right of the lattice metal in the periodic table.

Where the impurity lies to the left of the lattice metal in the periodic table, the foreign atom will lack one electron of the number required by the lattice structure. It will therefore tend to acquire an electron from another atom; the resulting electron deficiency can travel through the crystal in a manner exactly analagous to that expected from a positive electron. This type of conduction is known as P-type or deficiency-type and is referred to as 'positive hole' transfer.

It is worth noting that it is futile to attempt to increase conductivity by adding both N-type and P-type impurities since the effects counterbalance each other.

Materials which can readily undergo valence change by gain or loss of an electron can also give rise to conduction. The normal configuration of the cuprous ion is $(3d)^{10}$. A 'positive hole' is formed in the transition to $(3d)^9$ by loss of an electron The same is true for the reaction $Ni^{++} \longrightarrow Ni^{+++}$.

Although most of the experimental work done to date on semi-conductors has involved the use of metals, the metallic oxides are promising coatings for precipitation static removal since they can be rendered insoluble, and are transparent and hard. Information as to the mechanism of conduction in oxides is incomplete at the present time. It is likely, however, that it will be found to be similar to that in metallic semi-conductors. For this reason, the study of the effect of impurities in metallic oxide films, and in particular the effect of partial reduction of the oxides are of importance.

It should be noted that the reduction of a metal oxide can be regarded either as the introduction of an impurity or as causing an imperfection in the lattice. Thus, in the process of decreasing the valence of an individual metal atom, this atom accepts an electron which is then in an energy level from which it can easily be transferred to nearby metal atoms, thereby giving rise to conduction. From the other point of view, an oxygen atom has been removed, causing a lattice imperfection and giving rise to an unpaired electron. The lattice imperfection in this case is the site of a positive charge since the negative oxide ion is missing. Coupled with it is the unpaired electron forced on the metallic ion. Such singularities can be separated by thermal excitation, giving rise again to conduction.

As mentioned above, both titania and tin oxide have been investigated with respect to electrical conductivity. It has been found that the electrical resistance of titania can be sharply decreased by partial reduction (20). However, the transparency of the material is also affected. Thus, TiO_2 is water-white whereas $TiO_{1.97}$ is dark blue (18,23). Samples of plastic coated with titania have definite anti-static properties, as previously demonstrated by us to the Air Force Materials Laboratory. The film is completely transparent, but the conductivity is much lower than that of the product obtained by reduction. Tin oxide, on the other hand, is free of this disadvantage. It has been reported that adherent, transparent, conductive films of tin oxide on glass can be prepared from organo-tin solutions (66); we have verified this claim.

Verwey and his associates have studied a group of mixed oxides known as the spinels which have been found to be conductive (52). In his discussion of the spinel structure, Verwey restricted the domain to include only combinations of the oxide of a monovalent or a divalent metal with the oxide of a trivalent metal. In the examples which he gave, however, he included Zn_2TiO_4, in which compound the titanium is tetravalent. Dana (5) also lists the titanates as possessing the spinel structure, but points out that they do not occur naturally.

The titanates offer the best point of departure for this type of study for more than one reason. In the first place we are already skilled in the deposition of titania films; the preparation of a titanate spinel merely requires then, at least so far as the composition is concerned, the modification of the deposition solution. In the second place, as we are aware from our previous experience, some of the trivalent metal oxides are difficult to deposit from solution. This is particularly the case with aluminum.

Verwey pointed out that the conductivity of a spinel is a function of the amount by which the composition differs from the stoichiometric. In general, the conductivity rises as the difference increases. Compositions which bracket the spinels are therefore of more interest than the spinels themselves.

It is a distinguishing characteristic of semi-conductors that conductivity increases with rise in temperature. This is due to the fact that electrons can be lifted from the lower non-conducting band into the conducting band by thermal excitation.

The dependence of conductivity upon temperature has been found in many cases to follow the law:

$$s = Ae^{-E/2kT}$$

where

s = conductivity

A = 30 to 3000 mho/cm

E = the energy required for an electron transfer

k = the Boltzmann constant

and T = the absolute temperature in $^{\circ}K$

A negative temperature coefficient of resistivity has been found to be associated so consistently with semi-conductivity that it is used as a criterion of the presence or absence of the phenomenon. By this test it has been established that in sufficiently thin films, even highly conductive materials such as silver are semi-conductors. The list of semi-conductors is constantly being extended, and now includes not only the metalloids and oxides, but many of the compounds known as phosphors.

1.2.1.2 Ionic Conduction

The phenomenon of conduction by ions in solution has been well known and understood for many years. In order for conduction to take place in a liquid medium, the liquid must have a substantial dielectric constant, and a solute which can disassociate into charged atoms or groups must be present. The medium most commonly studied is water, which possesses a dielectric of 80, and the commonest solutes are salts.

Speaking more generally, the solute should be polar in nature. Since electrolytes of high molecular weight which are highly polar and yet insoluble are known, the possibility of conduction by means of ions in a solid medium therefore arises. Experimentally it has been found that the sulphonated divinylbenzene-styrene combinations are conductive provided that water is present. The water in this case is not evident as liquid, but is, rather, adsorbed within the polymer.

Commercial applications of this principle have already been made. Lauryl pyridinium chloride in an ethylene-vinyl acetate copolymer base (65) and potassium acetate with a wetting agent in starch (60) have been used as anti-static coatings on motion picture film.

In both of the above formulations an electrolyte has been added to a polymer in order to increase the conductivity. However, where the polymer is sufficiently polar to ionize, conduction can take place without added electrolyte, provided only that some water is present. Examples of such polymers are polyacrylic acid and the sodium salt of the copolymer of maleic anhydride and styrene.

Theoretically, solvents of high dielectric constant, other than water, could also be used, but very little work directed toward actual application has been done in this field. Water suffers from the disadvantage of high volatility, as a result of which it is easily lost from films; a dielectric of comparable efficacy and lower vapor pressure would be desirable.

1.2.2 Reduction of Charging Rate

It has been found that solid particles impinging against a surface at high velocity deposit charge upon the surface. This charge may be either negative or positive, depending upon the relative positions in the triboelectric series of the materials of which the particles and the surface are composed. This series was proposed originally by Faraday and is related to Coehn's rule which states that substances of high dielectric constant become positively charged when rubbed against materials of low dielectric constant. The triboelectric series is constructed according to the rule which states that of two materials which are rubbed against each other, the one which becomes positively charged is to be placed higher in the series than the other. The rule is somewhat imperfect in that inversions in the series occur.

The charging effects produced by the high velocity impingement of a variety of particles on a number of surfaces were studied; the results indicate that the charge accumulated by aircraft transparent surfaces is caused by the impingement of snow, ice, rain, dust, and by the friction of air flowing past the transparent surfaces.

The rate of charging is dependent on the velocity of the airstream carrying the particles, the angle of impingement and the exact nature of the particles. Different crystalline forms of ice, for instance, give different charging rates. The possibility of exploring this approach was discussed with the Project Engineer. It was then decided that the difficulties involved in making measurements which would reliably predict the variable effects of snow, ice, rain and dust were such as to make this approach less desirable than that by way of surface conduction.

We have, however, prepared 11" x 11" samples of titania- and silica-coated methyl-methacrylate sheet by techniques which will be described below. The samples are available to the Project Engineer for test in actual flight.

SECTION II

2.1 GENERAL CHEMISTRY OF COATING FROM SOLUTION

A standard method of obtaining metal oxides from solution is to start with the metal chloride and treat with water. The steps then are (for a tetravalent metal, M):

Hydrolysis - $MCl_4 + 4H_2O \longrightarrow M(OH)_4 + 4HCl$

Condensation - $M(OH)_4 + \text{heat} \longrightarrow MO_2 + 2H_2O$

The oxide, MO_2, is of high molecular weight and insoluble, and, therefore, potentially of use as a film composition. In some cases the dehydration reaction proceeds rapidly enough at room temperature so that no heat need be provided.

Where the above sequence fails to yield coherent films, an additional step may be introduced. The metal chloride is first reacted with an alcohol and then hydrolyzed and condensed. The first stage is then

$$MCl_4 + 4ROH \longrightarrow M(OR)_4 + 4HCl$$

where ROH may be any alcohol such as ethyl or isopropyl, but is usually low boiling. The advantage of using $M(OR)_4$ rather than MCl_4 lies principally in the fact that the rate of hydrolysis can thereby be controlled. In fact it is possible to let the hydrolysis proceed part way in solution rather than on the treated surface and then to store the solution until it is needed. The preparation of silica films by this technique has been studied intensively, and although these films are not conductive, the chemistry involved is instructive.

Using silicon tetrachloride, for example,

$$SiCl_4 + 4C_2H_5OH \longrightarrow Si(OC_2H_5)_4 + 4HCl$$

Then, $nSi(OC_2H_5)_4 + \text{insufficient water} \longrightarrow (\text{-SiO-})_n(OC_2H_5)_{2n+2} + 2nC_2H_5OH$

The polymeric ethyl silicate which consists of a mixture of polymers of various molecular weights is stable, and is marketed for a number of uses (56,57). Finally, the solution is applied by any of the standard methods and the hydrolysis is completed by means of atmospheric moisture. To increase the rate of hydrolysis a small quantity of concentrated hydrochloric acid may be added to the solution.

The reaction of a metal chloride with an alcohol is unquestionably more complex than the above description would indicate. Taking the reaction of titanium tetrachloride with ethyl alcohol as an example, the primary step is

$$TiCl_4 + C_2H_5OH \longrightarrow TiCl_3(OC_2H_5) + HCl$$

This process is repeated until the chlorine atoms are completely replaced, giving $Ti(OC_2H_5)_4$ as the end product. When water is added the ethylate groups are split off and the formation of $Ti(OH)_4$ can be postulated. Condensation then ensues to give two-dimensional chains of 'Titanium oxy-hydrate'. The chains finally cross-link to form a three-dimensional structure. It is believed that the condensation is never complete at moderate temperatures because of the loss of mobility which follows partial cross-linking and the consequent difficulty in orienting the hydroxyl groups so as to complete the elimination of water. Also, condensation must certainly start before the hydrolytic removal of the ethylate groups is complete; it is therefore probable that the pure $Ti(OH)_4$ stage is never reached.

There are yet more ramifications to this problem. In the first place the chloride split off from the titanium tetrachloride is adsorbed to a considerable extent by the polymeric titanium oxy-hydrate. Although this chloride, strictly speaking, is an impurity, it probably functions as a peptizing agent in stabilizing the colloidal titania (8).

Secondly, the film-forming capacity of the solution is unquestionably a function of the average molecular weight of the titania sol, as well as of the distribution of molecular weights. We have found that because of this fact the solution should be permitted to age or be otherwise treated for a specific length of time before using, in order that polymerization may take place.

Finally, titanium tetrachloride is an oxidizing agent, and the metal goes readily to the +3 valence state. In the process, alcohol is oxidized. This phenomenon is particularly important since as discussed above, conductivity is associated with the lower valence state.

The presence of foreign ions may be avoided completely by preparing the tetraalkoxytitanium compound from titanium tetrachloride and sodium alcoholate. The pure compound, theoretically, can be obtained by distillation, but undoubtedly some decomposition will take place during the operation.

Formally, the chemical behavior of tin tetrachloride in the sequence of operations through which oxide films are attained resembles that of titanium tetrachloride. Both metals are tetravalent in the highest oxidation state, are reducible, and yield oxide films which are conductive. Tin has the advantage in that its lower oxidation state is not associated with color.

2.2 METHODS OF COATING FROM SOLUTION

Films may be applied in a number of ways, some of which are sufficiently well-known so that little or no comment is necessary. When forming the film by spraying, brushing, or wiping, for example, the principal concern is to adjust the concentration, the viscosity, and evaporation rate so that a film of the desired thickness is deposited. It is, of course, possible, though somewhat less convenient, to lay down successive coats.

The solutions utilized must be formulated in accordance with the fact that the base on which the precipitation-static film is to be laid down is composed of plastic, and more specifically of acrylate. The formulation must therefore be free of components which attack acrylate or tend to craze it, and the method of application must not include steps such as heat treatment at high temperatures, which would decompose the plastic base.

The following sections describe the application of oxide coats by methods which meet these limitations.

2.2.1 Coating by Dipping

In order to prepare films of uniform thickness by dip coating, it is necessary to arrange to remove the specimen from the coating bath at a constant rate. This is due to the fact that the thickness is a function of the withdrawal rate. More rapid withdrawal gives a thicker film, and vice-versa. To effect constant withdrawal, a mechanical lifting device has been constructed which operates through a constant speed motor, reducing gears and a cable which passes over a windlass on a vertical frame down to the sample in the bath.

In previous work in this laboratory, it has been found advisable to provide some control of the drying rate. This can be effected by mounting strip or radiant heaters close to the surface of the sample as it is withdrawn from the bath. The electrical input to the heaters is adjusted so that the drying rate of the film is substantially the same as the withdrawal rate.

2.2.2 Coating by Doctor-Blade Casting

The doctor blade is essentially a rigid, carefully machined straight-edge with side panels so adjusted as to locate the straight edge at a pre-determined distance from the surface on which the side panels rest. To prepare a film, a portion of the solution, which should preferably be fairly viscous, is poured upon the surface. The doctor blade is placed on the surface and pulled across, sweeping before it that portion of the solution which cannot pass underneath the blade because the depth of the solution is too great. As the solvent evaporates, a film is left behind, the thickness of which is always less than that of the original wet film. The method in the form described is applicable only to flat surfaces, since the doctor blade is a straight edge. Airplane canopies are, in general, curved surfaces, however, so it is not anticipated that this method will be particularly useful in the current problem, except as a research tool.

2.2.3 Spin-Coating

Our preferred method for preliminary research is spin-coating. In this method, the sample to be coated is set into rotation at a pre-determined speed and the solution is pipetted onto the center of the surface of the rotating sample. As a result of centrifugal force, the liquid spreads uniformly over the whole surface to the edge of the sample, the excess liquid being automatically cast off. The film which remains on the surface is permitted to dry; if desired, additional coats may be formed. The coated sample is then removed from the chuck.

The rate of rotation during the coating operation is an important factor since the thickness of the film can be varied by altering the rate. It has therefore been found convenient to measure the speed of the rotation by means of a stroboscope. The stroboscope illumination also makes it possible to observe the spreading of the film and to observe when the film is touch dry. The air circulation produced by the rotation also increases the rate of drying.

The spin-coating unit which we have constructed consists of a 110 volt universal motor with a vertical shaft, a chuck mounted on the motor shaft which holds the specimen to be coated so that the surface is horizontal, and a variable transformer, which controls the speed of the motor by varying the applied voltage. The motor and the specimen chuck are located inside of an open box at such a level that the spinning surface is below the top of the box; the operator and the surroundings are thus protected from the liquids which are thrown off the spinning specimen.

For a particular spinner the rotational speed of the motor varies with voltage as shown in the following table:

A. C. Input (volts)	Speed of Spinner (RPM)
40	700
45	1050
50	1380
55	1680
60	1950
65	2250
70	2530
75	2820

The degree of control obtainable with spin-coating is not as great as with dip-coating. The latter is definitely the more suitable method where reproducible results are required.

The ambient humidity and temperature can readily be controlled by placing the entire unit, which is quite small, in a proper chamber, preferably made of glass or transparent plastic.

It is usually necessary to provide some form of after-treatment to render the film adherent and water resistant. This treatment may consist of the application of mild heat. An oxide film cannot be laid down directly as such since the oxides are high molecular weight compounds and therefore insoluble. It is necessary to lay the film down as a sol and subsequently to complete the removal of the solvent and the condensation of the hydroxyl groups, thus transforming the sol into the final stable oxide form. The "cure" or bake must be carried out at temperatures below approximately 100°C in order to avoid deforming the acrylic sheet.

2.2.4 Preparation for Coating

Methyl-methacrylate is not readily wet by water or water solutions. To prepare uniform films from water solution it is therefore necessary to clean the surface effectively before coating.

In selecting solvents for use on methyl-methacrylate, compounds which are either very low or very high in polarity are preferable. Thus, aliphatic hydrocarbons have little or no effect on acrylate; cyclic paraffins show some slight action, chlorinated hydrocarbons still more, and the aromatics are very active. The aliphatic alcohols are almost as satisfactory as the aliphatic hydrocarbons; of the common alcohols methyl alcohol is best.

We have used normal hexane followed by iso-propyl alcohol to clean methacrylate. This sequence gives a surface which in general is immaculate, but occasionally has a few isolated blemishes. These blemishes can be removed with wetting agents; XL-6 sold by the Alexander Distributing Corporation of Stanford, Connecticut, is particularly effective. The dilute wetting agent is rinsed off with tap water and then with distilled water. To obtain a surface free of 'water' spots, adhering droplets are removed with adsorbent tissue.

Wetting agent must also be incorporated in the coating solutions; these will be described in connection with the specific formulations.

2.3 SILICA AND TITANIA COATINGS

Coatings of silica and titania had previously been laid down, for the most part, on glass. It was therefore of interest to determine whether the same type of formulation and the same techniques would be applicable to the coating of acrylic.

Stock solutions were prepared which were then diluted for use. Typical formulations follow:

Stock Solution AS21

$TiCl_4$		10 ml
Isopropanol	(dist.)	80 ml
H_2O	(dist.)	20 ml

Stock Solution AS92

$SiCl_4$	10 ml
Isopropanol 99%	80 ml
H_2O (dist.)	20 ml

Stock Solution AS97

$Si(OC_2H_5)_4$	400 ml
H_2O (dist.)	65 ml
HNO_3(conc.)	4 drops

Stirred vigorously for 2 hours in ice bath

To prepare coating solutions, stock solutions were diluted as follows:

	Solution AS23
AS21	5 ml
Isopropanol 99%	5 ml
Tethyl Acetate	0.5 ml

	Solution AS40
AS21	5 ml
Isopropanol 99%	13 ml
Tergitol 08	2 drops

	Solution AS99
AS97	10 ml
Isopropanol 99%	20 ml

In general, it was found that wetting agent must be added to the formulation in order to produce uniform films. Carbide and Carbon Tergitol EH and Tergitol 08 proved effective.

A number of coatings, several of multiple thicknesses, were prepared by dip-coating and by spinning. The films were cured after each dip, by baking at 90°C. In all cases, the films were anti-static, as determined by rubbing with a rough cloth, but the conductivities were below the specified range.

A number of films were built up by multiple dips until interference colors became apparent, but the conductivities were still too low. In all cases, hard, adherent, completely transparent coatings were obtained.

2.4 TIN OXY-HYDRATE FILMS

Solutions of tin tetraisopropylate can be prepared by reacting tin tetrachloride with either excess alcohol, or with sodium alcoholate in excess alcohol. Both methods were used.

2.4.1 The Stannic Chloride-Isopropanol Reaction Product

The reaction of tin tetrachloride with isopropanol proceeds smoothly and vigorously with the evolution of heat. The principal product is tin tetraisopropylate, but it is known that side reactions involving reduction of the tin and oxidation of the alcohol also occur. Moreover, the hydrogen chloride formed is only partially removed by prolonged refluxing. Despite these disadvantages, the method is the simplest for preparing tin hydrous oxide coating solutions. Also, our previous experience in the preparation of the analogous silica and titania coating solutions has indicated that the method should be generally suitable.

One hundred ml of isopropanol were placed in a 250 ml flask under a reflux condenser. Ten ml of tin tetrachloride were added slowly through the condenser, which was then washed down with 90 ml of isopropanol. Finally, 10 ml of water were added. The solution was refluxed for two hours to ensure that the tin tetrachloride was completely reacted and to 'age' the tin hydrous oxide produced by hydrolysis of the tin alcoholate. The solution is ready for application as soon as it is cool.

In general, it is necessary to refrigerate alcohol solutions of metal hydrous oxide to defer gelation. However, the tin compositions do not gel in this manner.

Tin tetraisopropylate solutions have been prepared with added hydrochloric acid, after the technique found useful with ethyl silicate. No advantage in use was noted.

Tin hydrous oxide solutions can be applied by spinning, dipping, or by spraying, exactly as with the other film forming solutions described in earlier reports. The deposits are uniform, have appreciable thickness, and are gummy to the touch. The last property is characteristic of partially polymerized hydrous oxides. However, they fail to cure at 100°C which is the highest temperature to which polymeric methyl-methacrylate substrates can be exposed.

2.4.2 The Stannic Chloride-Sodium Isopropylate Reaction Product

It is well-known that tin hydrous oxide strongly adsorbs various ions from solution. In some cases the adsorption is so pronounced as to cause precipitation. This phenomenon is utilized in the analytical procedure for the determination of phosphoric acid. Tin foil added to nitric acid produces the beta-oxide which carries down the phosphoric acid. The term 'beta-oxide refers to the relatively high molecular weight hydrous oxide of the tin (8).

When the tin oxide sol is prepared by the hydrolysis of stannic chloride, hydrochloric acid is formed which acts as a peptizing agent. Although the sols are positively charged due to preferential adsorption of hydrogen ions (12), it is likely that some chloride ions are adsorbed also.

Qualitative tests have shown that despite prolonged boiling of the tin hydrous oxide solutions, the chloride ion cannot be eliminated. It is therefore to be expected that a portion of this electrolyte will remain in the films laid down from such a solution. The presence of this electrolyte gives rise to a number of problems. It can cause the cured film to be hygroscopic, it can give rise to a spurious conductivity dependent on adsorbed water, and it can effect the curing process itself. Since it was found that the films deposited from the stannic chloride-alcohol reaction product could not be cured within a temperature range suitable to the plastic base, we decided to investigate the behavior of tin oxide sols prepared so as to be as free of foreign ions as possible.

The procedure which was used was essentially that of Meerwein and Bersin (39). Eleven grams of sodium were added to 400 ml of anhydrous isopropanol. The mixture was warmed slightly to start the reaction and then cooled to moderate it. When the sodium was completely reacted, addition of 14 ml of $SnCl_4$ anh. in 56 ml of benzene was started. The solution was stirred constantly. The addition was completed in forty minutes, after which the mixture was refluxed for 1-1/2 hours.

The completion of the reaction was indicated by neutral reaction of a sample dissolved in water, using methyl orange as the indicator. The sodium chloride formed in the reaction was separated off by centrifuging and decantation.

Part of the resulting solution was placed in a flask fitted with a two-hole rubber stopper through which passed inlet and outlet tubes terminating above the surface of the solution. The solution was warmed gently, and dried air was passed through the flask until most of the solvent was removed. The remainder of the solvent was eliminated by heating in an oven at 100°C. Despite the moderate conditions used, the solid when finally obtained was brown, and analyzed higher in tin than was to be expected for tin tetraisopropylate. It is likely that some reduction of the tin or some thermal decomposition of the alcoholate to the oxide took place.

Although the system was anhydrous, it could be assumed that the solution would deposit a film which would hydrolyze and cross-link to form tin oxide. It was therefore pertinent to calculate the tin oxide content of the solution. The result was approximately 4%. Qualitative tests showed that the solution was relatively chloride-free.

Films were then laid down on acrylic by the methods described above. Coatings, made by dipping or by spinning, were uniform, and had the usual **slightly** gummy consistency characteristic of the other metal hydrous oxide films. When oven-cured at 100°C for as long as sixteen hours, the films failed to harden. To make certain that the atmosphere could supply enough **moisture** to hydrolyze off the isopropylate groups, containers of water were in some cases placed in the oven. It became evident that thermal treatment alone is insufficient for the cure of tin hydrous oxide films on plastic.

These results indicate that the failure of tin hydrous oxide deposits to harden cannot be related to the concentration of chloride ion.

2.4.3 The High Temperature Cure of Tin Oxy-Hydrate

As described above, we found that tin oxide films could not be cured at 100°C. In order to determine whether cure by thermal treatment alone is possible, glass slides were spin-coated and cured at progressively higher temperatures. The compositions used were prepared from stannic chloride by hydrolysis in alcohol.

We found that apparently hard coatings could be produced by curing at 350°C for two hours, but that the films were slightly water soluble. They could also be removed by vigorous rubbing with a cloth. Nevertheless the films were hard enough so that successive coats could be laid down.

After building up the thickness by means of multiple coating, films showing considerable conductivity were obtained. The resistances ranged as low as one megohm per square. However, when the resistances were measured in a dry chamber, the values rose slowly from one megohm per square to several hundred megohms per square. The resistivities became substantially constant in this region after the films were dried for several hours. It was evident that the fall in conductivity was due to the removal of adsorbed water.

The curing temperature was then raised by 50° steps to determine whether the film could be rendered non-hygroscopic. Curing at 400°C for sixteen hours was found to be ineffective. Curing for one hour at approximately 500°C, however, effected the desired result. The coatings produced were also much harder and were strongly adherent.

Films were built up by multiple coating which had resistances of 300 megohms per square. It is significant that the conductivity was not a linear function of the thickness, that is, thin films showed much higher resistances than only slightly thicker films. It is possible that this effect is due to 'island' structure of thin films. Successive coats would be expected to bridge the channels between the islands and cause a large increase in conductivity without a proportionate increase in thickness.

This phenomenon has been observed with evaporated metal coatings. It can also appear in reverse, as when a thin but conductive coating recrystallizes and forms fissures.

It is interesting and significant that films with the resistivities described should have been obtained as is evident from the following calculation.

Commercial films of tin oxide on glass are approximately one wave length or about 6000 angstroms thick; they have resistivities of the order of 200 ohms per square. Assuming that resistivity is inversely proportional to thickness, the thickness of the films we have prepared should then be

$$6000 \times \frac{200}{3 \times 10^{8}} = 4 \times 10^{-3} \text{ angstroms.}$$

This calculated value is much less than the thickness of a monomolecular layer. However, interference phenomena observed during the multiple-coating operations indicated that our films must be far heavier.

In view of the fact that the specific resistance of the films produced by our process is about 10^{6} times greater than that of the commercial films, it would seem that an inherent difference in composition or in structure exists.

2.5 IMPURE OXIDES

Interest in the subject of mixed oxides and defect structure in general was stimulated by a series of papers by Verwey and others (22,25,29,35,36,51) describing semi-conductive materials in these categories. Starting with Stock Solution AS21, consisting of

$TiCl_4$	10 ml
Isopropanol (dist.)	80 ml
H_2O (dist.)	20 ml
Tergitol 08	0.5 ml

we tested the following materials as addition agents for the purpose of preparing mixed oxide films: phosphorus trichloride, phosphorus pentachloride, hydrazine hydrochloride, yellow phosphorus (dissolved in benzene), titanium trichloride and arsenious oxide. These all are of valence other than four. The hydrazine hydrochloride would be expected to reduce some titanium to the titanous form. Films were cast, but in no case was any conductivity noted.

It seemed possible that curing in air might result in oxidation of the titanous ion. A small oven through which nitrogen or hydrogen could be circulated was constructed to test this possibility. In a series of tests, films of titanous chloride in isopropanol were deposited and cured. The results were uniformly negative.

Turning then more in the direction of Verwey's compositions, films of the following compositions were laid down:

Exp. #	Metal Oxides	Ratio of Metals in Gram Atoms
SL 10	TiO_2 - MgO	$Ti_1Mg_{0.1}$ $Ti_1Mg_{1.66}$
SL 14	Fe_2O_3- MgO	Fe_1Mg_1 $Fe_1Mg_{1.7}$ $Fe_1Mg_{3.3}$
SL 15	TiO_2 -Fe_2O_3	$Ti_1Fe_{0.03}$ $Ti_1Fe_{0.06}$ $Ti_1Fe_{0.5}$ $Ti_1Fe_{1.4}$ Ti_1Fe_5
SL 16	TiO_2 - Sb_2O_3	$Ti_1Sb_{0.015}$ $Ti_1Sb_{0.03}$
SL 18	Fe_2O_3- ZnO_2	$Fe_1Zn_{0.2}$ $Fe_1Zn_{0.4}$

The results were again negative.

Although mixed oxides in compositions approximating the spinels are known to be semi-conductors, at least when prepared at high temperature, we had found that such compositions, laid down from solution, showed no conductivity. In order to determine whether the mixed oxides when so prepared do in fact form spinels, we prepared films by our usual methods for examination by electron diffraction. A mixture of magnesium and iron oxides near the spinel ratio was spin-coated onto lucite[1] and cured as usual at 90°C. The resistivities were beyond the range of the meter. The samples were cut up into 1/8" square pieces and the films were floated off with ethyl bromide. The film segments were "fished" onto wire screens and examined under the electron microscope. The films were found to be continuous and appeared to be about 150 A thick. Very little crystal structure was apparent.

Examination of the films by electron diffraction disclosed only very weak and diffuse lines indicating that the crystal size was extremely small. The d spacings were 2.52 A, 1.49 A and 1.56 A; these spacings could not be definitely interpreted. The 2.52 A spacing was to be expected if our magnesium oxide-iron oxide samples were indeed spinels; however, no conclusion could be drawn. A spin-coated titania film was similarly investigated and found to consist of very small crystals. Again, no definite structure could be deduced. We are grateful to Dr. R. D. Heidenreich of the Bell Telephone Laboratories in Murray Hill, New Jersey, who examined the films and supplied the interpretation.

Synthetic spinels are usually formed at high temperatures (about 1200°C) where the rate of crystal growth is large compared to the extent of nucleation. It appears that films cured at our comparatively low temperatures show much greater nucleation so that the resultant crystal size is small. The question of crystal structure type then becomes irrelevant, since even if the mixed oxides films we prepared were in fact spinels, the characteristic electrical properties could not be expected in such minute crystals. This phase of the study was therefore terminated.

SECTION III

THE DEPOSITION OF FILMS BY VACUUM EVAPORATION

The limitations of the solution method with respect to the preparation of oxide films of certain metals, especially as mixtures, made it desirable that other methods of preparing films be investigated. A vacuum evaporation program was therefore initiated.

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[1] The term "lucite" in this report refers to the high molecular weight polymethyl-methacrylate sold by E. I. DuPont deNemours Co., Inc., under the designation Lucite HC-202.

The original intent was to use vacuum evaporation strictly as an exploratory technique; any coatings prepared by this method which were found to meet the requirements of the problem would then be deposited by methods more suitable to quantity production. The program, however, did not develop according to expectations, primarily because the optical transmission, electrical conductivity, and stability of the evaporated films were such as to merit more detailed investigation.

In the first experiments, the evaporation of metal oxides was attempted. However, as is well known, the metal oxides are much less volatile than the corresponding metals. Aluminum, for instance, boils at 1800°C; aluminum oxide must be heated to 2250°C. Titanium can be evaporated without much difficulty, but titanium oxide decomposes in the process. In general, our attempts to evaporate oxides resulted in films which were unmistakably metallic, at least in part.

This decomposition was not unexpected since all oxides have a dissociation pressure which is a function of temperature. Under the conditions of the evaporation, the oxygen produced can be removed by the pumps. The dissociation equilibrium, according to Le Chatelier's principle, is therefore displaced, and the oxygen content of the resultant film will be lower than that of the charge.

The evaporation of the oxides of titanium, iron, and aluminum, and particularly of tin oxide, resulted in the production of metallic, highly reflecting films. It is unlikely that the films were completely devoid of oxide, but any conduction by the oxide would certainly be masked by the presence of the metal.

The films thus prepared, even though metallic, were considered so interesting because of the relatively high ratio of transparency to resistivity that it was decided to interrupt the experimental work to investigate the literature on thin metallic films and also to prepare suitable specimen holders so that experimental conditions could be properly controlled.

3.1 METAL-FILM LITERATURE

Julius Neubauer in a German patent (68) described the coating of polymers, by cathode sputtering, with metallic films thick enough to carry current adequate for resistance heating. It seems most unlikely that films thick enough for this purpose could have the transparency claimed. No substantiating examples were given in the patent.

Considerable theoretical work has been done on the correlation of the nature of the metal comprising the film, with transparency and electrical resistivity. R. W. Weale, in two papers (53,54), discusses this problem. According to Weale, film performance may be predicted from theoretical considerations.

The results of experimental work on a variety of films have been presented in a number of papers, three of which are listed (15,37,48). The paper by Van Itterbeek and de Greve is particularly interesting because data are given to support the theory that thin metallic films are actually semi-conductors.

The oxidation of iron and other metallic films has been discussed in considerable detail by Gulbransen (21), and by Edwards (17).

This study indicated that it would be profitable to evaporate those metals which either do not oxidize, or which form protective oxide coatings.

3.2 SPECIMEN SUPPORTS AND AUXILIARY EQUIPMENT

The slide size, namely 2" x 2" x 1/8", used in the coating experiments was selected for the vacuum evaporation study as well, largely because of the convenience for storage.

The first jig consisted of a wire circle, 10" in diameter, across which were soldered parallel rods to hold the plates. The jig was supported 7" above the boat containing the evaporation charge. As was to be expected, the specimens directly over the boat were coated somewhat more densely than those at the edge of the jig. The difference in density was readily apparent on visual examination. A quantitative measure of the distribution was obtained by evaporating a sufficiently large charge of tin so that the increase in weight of the individual slides could be determined on an analytical balance.

The center slides were found to have accumulated more than twice as much tin as slides at the periphery.

In order to produce more uniform deposits, this jig was replaced by the design shown in Figure 1. Up to ten 2" x 2" samples can be coated simultaneously. In addition, a 6" x 6" piece can be laid across the top for coating; the size of the inner decagon is such that only the corners of the piece are shadowed.

In order to determine what portion of the vaporized charge is intercepted by each plate, a sample of tin weighing one gram was evaporated from a molybdenum boat onto weighed slides. The slides were reweighed and found to have gained from 0.011 to 0.016 grams. The average increase was 0.0143 ±0.0016 grams. This value is more useful when expressed percentage-wise, since in general, much smaller charges will be evaporated. It can be assumed that 1.43% of the charge evaporated from a boat falls upon each 2" x 2" plate.

During the course of the work, it was found advantageous to use the method of Sennett and Scott (46), in which a rectangular strip is tipped so as to receive a deposit of varying thickness. The rectangle was a 9" x 2" x 1/8" strip placed at an angle such that the end furthest from the boat received a much lighter deposit than the nearer end.

The difference is a function of the inverse square law and also of the angle between the line from a given point to the source and the normal from the source to the slide. It was also demonstrated that the nature of the deposit is independent of the angle of incidence at which the metal impinges upon the slide.

This information, combined with a technique of measuring resistance during the evaporation, yielded us a method of preparing a metal wedge with a resistance range bracketing a selected value. As a preliminary, we constructed a jig to hold six 9" x 2" slides and coated three such slides with a large weighed charge of tin. The slides were then cut up into 1" x 2" sections and weighed. After weighing, the metal films were stripped from the sections with hydrochloric acid, and the pieces were reweighed. From the weight differences, the fraction of the tin charge deposited on each section was found. Blanks showed that the treatment with hydrochloric acid had no effect on the plastic itself.

The curves of Figure 2 show the distributions found for the positions A, C and E of the jig. The curves B, D and F are interpolations. The small dip to the side of the maximum on some of the curves is probably due to shadowing by the support. At any rate, a thickness range of approximately 5 to 1 is obtainable in one evaporation. As will be apparent from the experimental results presented below, this range is ample for our requirements.

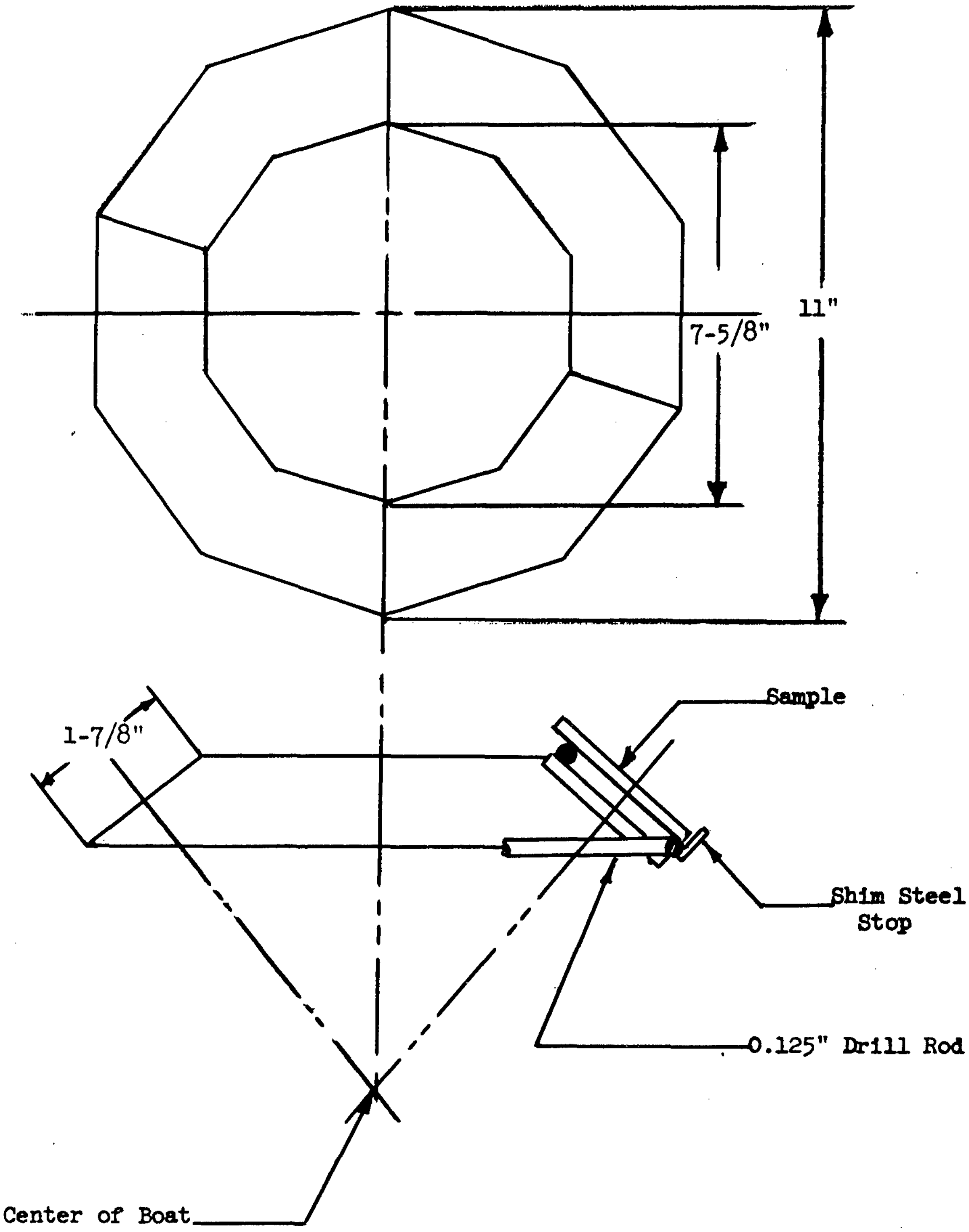


FIGURE 1
Sample Support Grid for Vacuum Evaporation

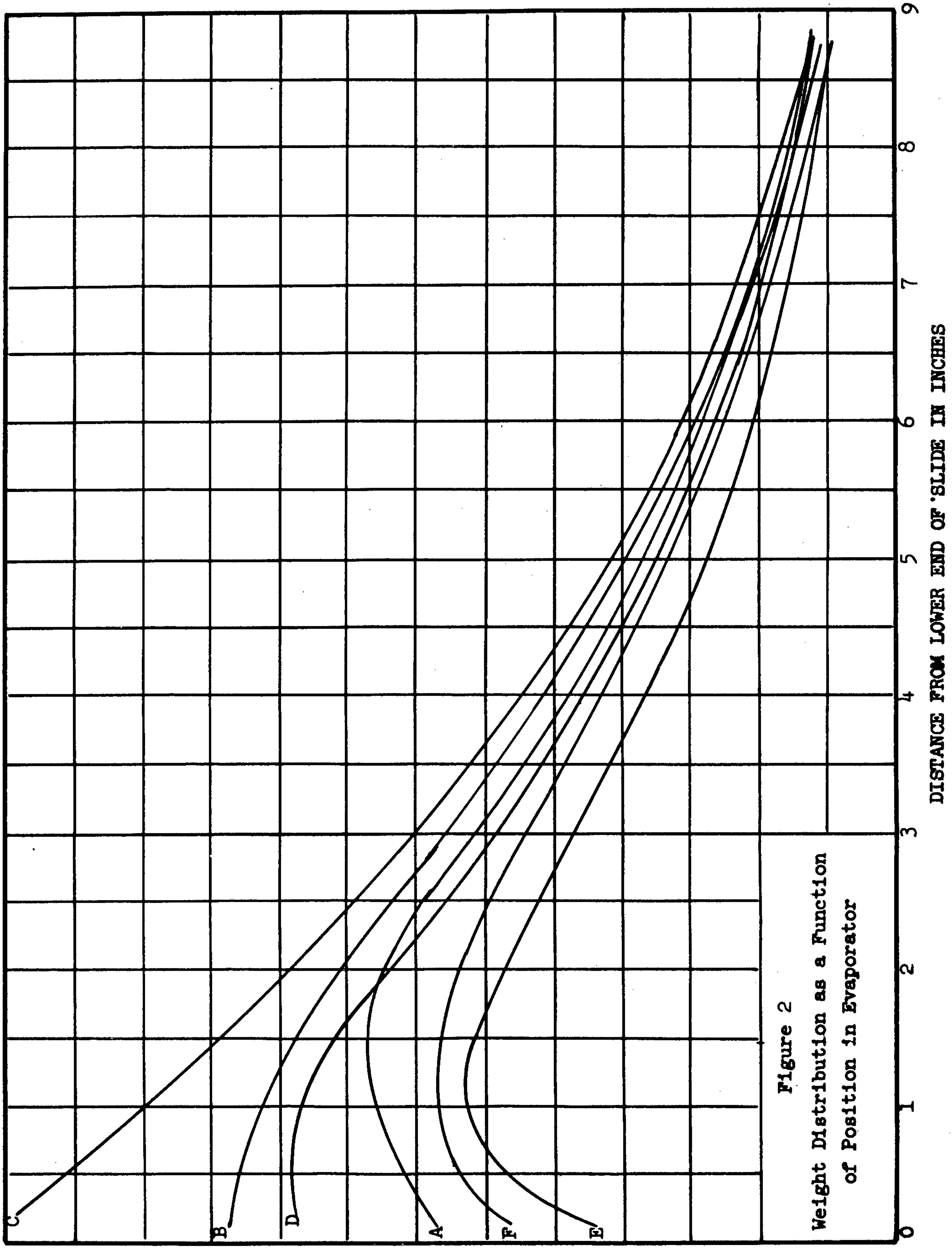


Figure 2
Weight Distribution as a Function
of Position in Evaporator

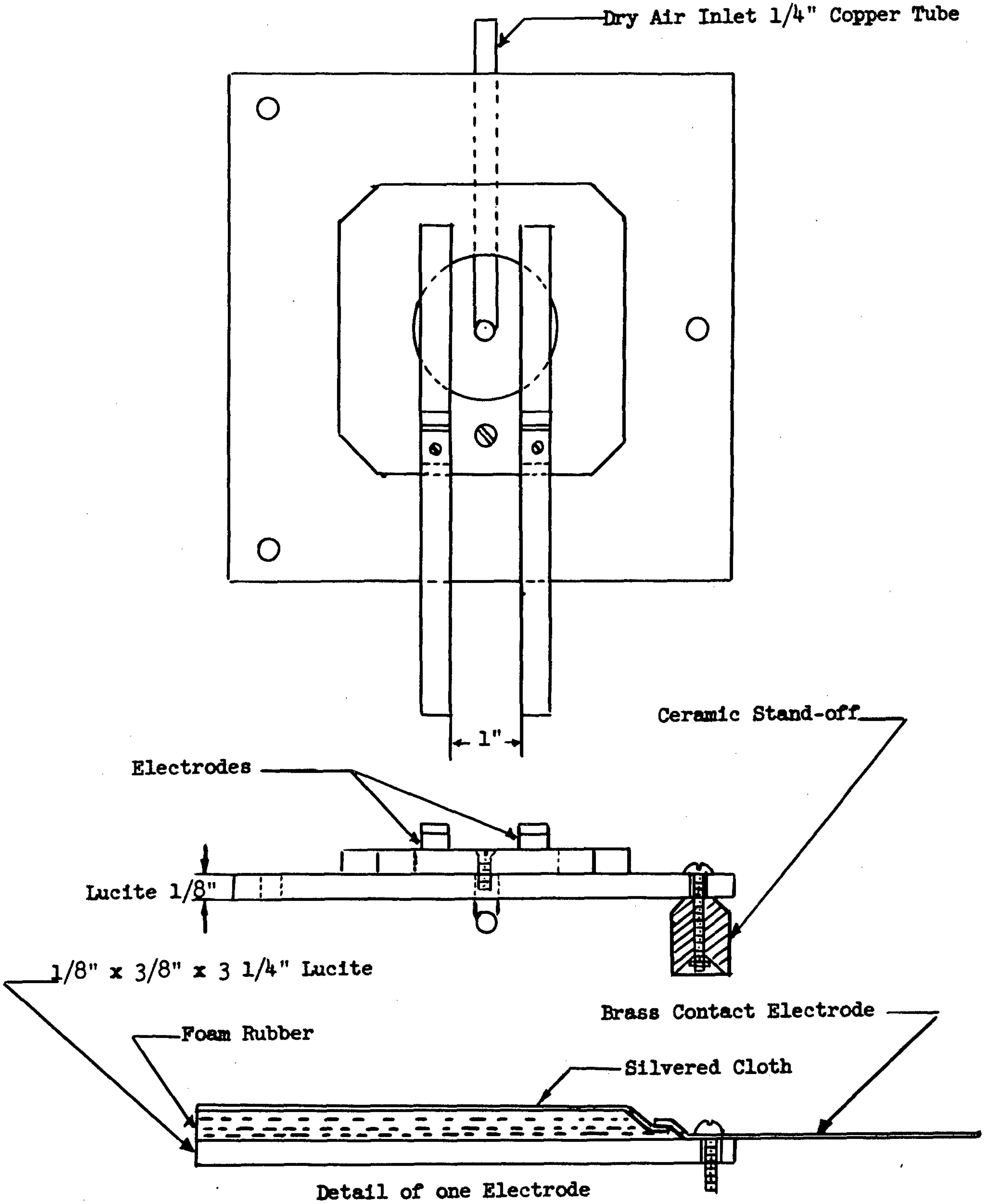
In order to simplify the process of measuring resistances, we modified the apparatus shown in Figure 22 to render unnecessary the use of painted-on electrodes. For these last, silver-painted tape on sponge rubber was substituted as shown in Figure 3. We have found that these contacts give very reproducible results and are soft enough so that they do not mar even non-adherent coatings. Also, they are flexible enough to conform to relatively irregular or moderately curved surfaces.

The modification proved to be especially advantageous in the examination of the wedges. Since the resistance of each film varies continuously over the length of the sample, it is necessary to be able to determine the resistance at several points along the 9" dimension of the piece. However, each resistivity determination actually yields an average of the point-to-point values across the section between the two strip-electrodes. Moreover, as will become evident, the variation in resistivity between two points an inch apart on the wedge is great. It is therefore desirable to diminish the range over which averaging takes place.

With this objective in view, the distance between the electrodes was decreased to one-half inch. Also, a ruled plastic strip was placed across the ends of the electrodes to serve as a gage against which the wedges could be positioned. Using this modified jig, the resistivity per square as a function of distance from one end of the wedge could be readily measured.

Our light transmission meter has similarly been modified with a slit so that the transmission of sections one-half inch long can be determined. This meter has also been fitted with a position gage.

With the establishment of the weight distribution curves it now is feasible to describe the properties of a metal film in terms of (1) resistance as a function of transmission, (2) resistance as a function of weight or thickness, (3) transmission as a function of weight or thickness. The first form shows with one evaporation whether a film of a specific metal can have an adequate transmission in the desired resistance range. The second form discloses the proper thickness to be laid down in making samples with a specific resistivity. The third form discloses whether there are any maxima in the transmission curve; this might occur as the result of interference phenomena at specific thicknesses. Strictly speaking, we have data only with reference to weight, since the thickness is also a function of the porosity or state of aggregation of the deposit. Nevertheless, for purposes of calculation and comparison, it may be assumed that thickness and weight are essentially equivalent.



Detail of one Electrode

FIGURE 3
JIG FOR MEASURING FILM RESISTANCE

3.3 EVAPORATION OF METAL OXIDES

Work on the deposition of silicon and titanium suboxides has shown that the degree of reduction during evaporation can be increased by including pure metal with the oxide in the charge. An additional variable can be introduced by using a foreign metal. Samples ST 9 and ST 13 exemplify this situation and are particularly interesting, as can be seen from Table III-1.

Since the conduction of oxides is attributable to lattice defects, the formation of a non-stoichiometric film is a desirable objective. This would more definitely be the case if the homogeneity of the film could be ascertained. Unfortunately, the metallic appearance of the deposit indicates that the product is a mixture rather than a non-stoichiometric compound, or true sub-oxide. This situation, potentially, can be remedied by proper after-treatment of the film. For this reason both chemical and thermal oxidation of these 'sub-oxide' films were included in the program.

Films ST 9 and ST 13 have a relatively high conductivity and are far from opaque. In order to determine the nature of the conductive process in these films, we evaporated charges with different amounts of the two components. In the series of experiments were included the vaporization of the pure metal and pure metal oxide. It was in this series that a blank was run, as a result of which we found that the molybdenum boat was evaporating along with the boat contents.

We have found that films deposited on lucite are from two to 200 times less conductive than films of the same composition and thickness on glass. Furthermore, the lucite-based films are at least as readily oxidized at room temperature. There is no apparent reason for the difference in conductivity; however, the difference may be a function of the surface roughness, or possibly of the presence of a relatively volatile fraction in the lucite. Again, the adhesion mechanism may be a factor, but this seems unlikely since the adhesion seems to be about equally good for the two substrates.

The stability of oxide films on glass and on lucite, as indicated by resistivity, is shown in Figure 4. As can be seen, the curves are somewhat irregular; except for sample ST 17D, no real trend seems to be evident.

The resistivity values given in the tables above were taken on a vacuum tube voltmeter using only one of the several resistance ranges. When the resistance of a sample was measured on two overlapping ranges, the resistance values obtained were found to differ by an amount definitely outside the limit of error of the meter.

TABLE III-1

PROPERTIES OF EVAPORATED METAL-OXIDE FILMS

Sample No.	Substrate	Resistivity in Megohms	Percent of Transmission	% Reflection (Both Surfaces)	Heated in Air		Resistivity in Megohms	Percent of Transmission
					°C	t (hrs)		
ST 17 80 TiO_2	glass	1.4	42	26.1	300	1/2	120	60
30 Fe_2O_3	glass	1.4	42	26.1	100	1/2	1.7	45
	lucite	425	40	24.7	---	---	-----	--
ST 18 43 Fe_2O_3	glass	0.133	46	25.4	300	1/2	335	61
	glass	0.133	45	25.4	100	1-1/2	0.750	49
	lucite	0.220	46	30.7	---	---	-----	--
ST 21 62 TiO_2	glass	1,340	11	----	400	1/2	4.6	58
38 Ti	glass	1,340	11	----	300	1/2	0.038	21
	lucite	12,000	16	----	---	---	-----	--
ST 22 12 Fe_2O_3	glass	14,500	--	----	Room	350	0.110	59
	lucite	90,000	--	----	---	---	1.5	66
ST 23 5 Ti	glass	6.75	66	20.2	300	1/2	Open	
12 TiO_2	glass	6.75	66	20.2	100	1/2	52	70.5
	lucite	13	66	20.3	Room	2 days	460	71
ST 9 80 TiO_2 10 Fe	glass	280	68	32	300	1/2	1,000	72
ST 13 60 TiO_2 20 Fe	glass	1300	32	19	300	1/2	24	65.6

Note: Data following sample number is weight of charge in milligrams.

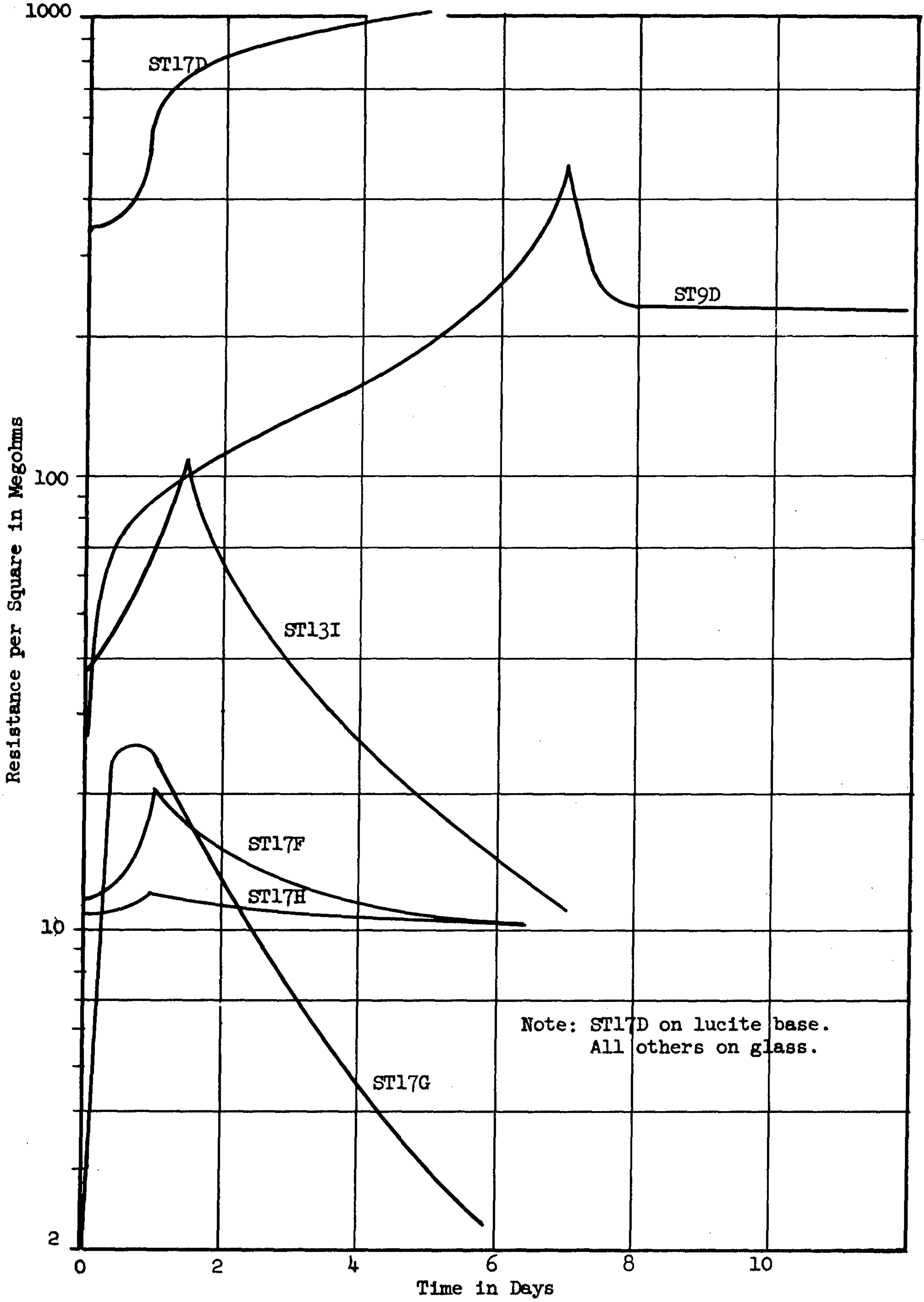


FIGURE 4

RESISTANCE OF EVAPORATED FILMS AS A FUNCTION OF TIME

The meter was then checked by testing a standard resistor element on the two ranges; the readings were found to be identical. Now the multiplicity of meter ranges is obtained by changing the voltage across the test specimen. The voltages on the high and low ranges designated H and L in Table III.3.1 are 30 and 3 respectively. It appears, therefore, that the resistance is a function of the applied voltage.

The manner in which the film resistivity varies is potentially of considerable interest. A low resistance is advantageous for the discharge of high voltage precipitation static. However, a low resistance film would impair the reception of the low voltage radio signals; for this voltage range, therefore, a high resistance film is desirable. The data of Table III.3.1 indicate that the direction of change of the film resistance with change in impressed voltage is exactly that desired. Naturally, it remains to be shown that this trend continues to the extremes of the range in question.

3.4 EVAPORATION OF METALS

In each experiment, ten 2" x 2" slides were coated; usually, two of these were plastic and the remainder glass. In order to keep tabulations within reasonable bounds, the values in each group have been averaged. The multiplicity of samples makes it feasible to carry out life tests and tests to destruction on samples of the same group.

Table III.4.1 shows the properties of a group of metal films. The first two column headings are self-explanatory except for one point: in experiments ST26 and ST27, the metal was evaporated from a notched strip rather than from a boat. It is evident that in the latter case no metal can be deposited below the plane defined by the rim of the boat, whereas a heated strip can 'radiate' in all directions. We shall, therefore, assume tentatively, when comparing films made by the two methods, that only half the metal evaporated from a strip is available for deposit. The column heading "Resistivity" gives the resistance per square. The next column gives the percentage of white light transmitted by the sample. The following column shows the fraction reflected. The reflectivity of glass, for reference, is approximately 8%.

Some of the samples were heated for a period as shown in the next column. The changes in properties, where measured, are also shown. Treatment with reagents, etc., is described in the footnote.

TABLE III.3.1

MEASURED RESISTIVITY AT TWO IMPRESSED VOLTAGES

Sample	Resistivity in Megohms	
	High	Low
ST 9D	160	220
ST 13I	4	11
ST 17G	1.2	1.8
ST 17H	84	100
ST 23H	560	800
ST 23A	84	100
ST 19A	48	52

NOTE: Column High, Impressed Voltage = 30
Column Low, Impressed Voltage = 3

TABLE III.4.1

PROPERTIES OF EVAPORATED METAL FILM

Sample No.	Substrate	Resistivity in Megohms	% Transmission	% Reflectivity (Both Surfaces)	Heated in Air °C	Heated in Air t (hrs)	Resistivity in Megohms after heating	% Transmission after heating
ST 19	glass	5.1	82	9.3	300	1/2	Open	83
	lucite	140	80	9.3	---	---	----	--
ST 25	glass	1380	39	23.4	300	1/2	2100	42
	glass	1380	39	23.4	100	1/2	1860	42
	lucite	5200	44	20.0	100	1/2	11,500	49
ST 26	glass	200	85		Room	1/3	Open	85
ST 27	glass	4200	48	23.3	---	---	----	--
	lucite	72,500	44	22.6	---	---	----	--
JB 8	glass	1.8	50	21.9	500	1/2	6.75	80

Note: Film ST 19 can be removed by washing with soap and water, or by dipping in dilute hydrochloric acid and rinsing. The reflectivity after treatment is not recorded because the changes were negligible.

	Charge	Support
ST 19		Mo Boat
ST 25	12 mg Ti	Mo Boat
ST 26	5.5 mg Ti	Ti Strip
ST 27	19.2 Ti	Ti Strip
JB 8	10 mg Fe	Mo Boat

The possibility of oxidizing metal films to the oxide was given some attention, because of the transparency and stability of oxides in general. Regardless of the oxidation method studied, two limitations must be kept in mind. The plastic substrate cannot be heated higher than 100°C, and no oxidizing agent may be used which will convert the metal to a soluble salt or otherwise render the film discontinuous. Although temperatures of 300°C and higher are useful for oxidizing tin films on glass, they cannot be employed in production where the substrate will be polymeric methylmethacrylate. Similarly, liquid oxidants such as peracetic acid, and ammonium persulfate are suspect because of the possibility that a soluble metal salt will be formed.

Thermal oxidation of the metal films has been studied at temperatures up to 400°C. Not all of the films are oxidized even at this elevated temperature. No changes are apparent as a result of oxidation at 100°C; however, treatment at 100°C may be useful as an accelerated test method for stability.

Hydrogen peroxide (100 vol.) and ammonium persulfate have been studied as possible oxidizing agents. These reagents have been tested only against chromium and tin. Chromium is oxidized by both, but the tin is attacked only by the persulfate. In all the tests, the oxidation process destroyed the film continuity and conductivity. This may indicate that oxidation does not take place by removing electrons from the metal atoms and adding oxygen ions, but rather by splitting metal atoms or ions from the lattice. If this is indeed the case, then oxidation by liquid oxidants cannot be expected to produce a continuous, conductive film.

Oxygen can be rendered more active through the medium of the high-voltage electric discharge. At normal pressures, ozone is formed. This compound is fairly stable and should be considerably more reactive than oxygen itself for the oxidation of our films. A simple ozonizer was constructed, the efflux of which was passed over a tin film. The results, however, were completely negative with respect to change of both transparency and conductivity.

At low pressures, that is from about three millimeters downward, the passage of an electric discharge through gaseous oxygen produces free atoms and ions of high reactivity. Tin placed in such a discharge seemed to be completely unaffected.

In view of the consistently negative results obtained, this section of the work was discontinued.

The results described thus far constitute an exploratory phase in the evaporation study. The main course of the development will be covered under the heading of the specific metals.

3.4.1 Iron

The preparation of iron films by vacuum-evaporation was considered worth-while for a number of reasons. Iron is known to evaporate readily, the metal is relatively transparent, its conductivity is fairly high and it can be rendered passive. This last property is important since the rapid and complete conversion of the iron to iron oxide would otherwise be a foregone conclusion.

For the charge we used fine iron wire of a diameter such that a piece 1/2 inch long weighed about 5 milligrams. We mention this point because of an effect which was noted. A piece of wire of about this length usually constituted the entire charge. The wire when placed in the boat lay along the main axis of the boat. When the heating current was turned on, the wire rose from the bottom and generally came to rest with one edge supported by the rim. As the boat temperature was increased, the wire finally returned to the boat, usually at some region other than the center, and fused and finally evaporated. This illustrates one reason why samples from the same batch varied with respect to the weight of deposit.

We pointed out above that plastic slides coated under identical conditions with glass slides showed far higher surface resistivities. The reason for the difference is not apparent but could be due to effects such as the relative magnitudes of cohesive and adhesive forces at the interfaces. Specifically, the ratio of cohesive to adhesive forces on the plastic surface might be large, as a result of which the deposit would tend to form aggregates rather than a continuous film.

Acting on this supposition, a number of plastic slides were prepared for evaporation coating with iron by first coating with metallic oxides. Both silica and titania were applied from solution by our usual methods.

During the evaporations the slides were held in the jig shown in Figure 1. In loading the jig, the substrates to be compared were interspersed so as to eliminate, in so far as possible, the effect of position. Thus, in experiment ST28, lucite slides were placed in positions A, D and G, and glass slides were placed at the remaining positions. The iron charge weighed five milligrams and was evaporated from a molybdenum boat. The results are shown in Table III.4.1.1.

It is immediately evident that the slides between the D and G positions are higher in resistance, but it is also quite evident that the lucite resistances are higher than the others. The last entry in the table shows the average ratio of the lucite resistances to those of the immediately neighboring glass slides. Although the ratios are irregular, they are definite larger than unity.

TABLE III.4.1.1

RESISTANCE OF IRON FILMS ON GLASS AND LUCITE

Experiment ST28

Sample No.	Material	Resistance in megohms/square
A	Lucite	12.4
B	Glass	1.7
C	Glass	2.4
D	Lucite	60
E	Glass	11.8
F	Glass	19.0
G	Lucite	300
H	Glass	5.0
I	Glass	2.0
J	Glass	1.2

Average resistance of films on glass = 4.7 ± 2.7

Average resistance of films on lucite = 124 ± 117

Average ratio of films on lucite resistance to neighboring films on glass resistances = 20.4 ± 14.4

Table III.4.1.2 shows the effect of the two types of undercoat. Again, 5 milligrams of iron were evaporated from a molybdenum boat, but in this experiment only undercoated lucite samples were treated.

Comparing the results given in the above tables it can be seen that

(1) the resistances of films on glass are generally much lower than the resistances of similar films on lucite.

(2) Coating lucite with metal oxide before evaporation-coating, renders the surface comparable with that of glass so far as the resistivity of superposed metal films is concerned.

(3) Silica and titania are essentially equally effective as undercoats.

We have stated these conclusions without reference to the specific metal comprising the top-coat, because the results are substantially the same for most of the metals we have studied thus far.

It is expected that oxide undercoats should influence the adhesion between the metal film and the lucite substrate. However, no effect has been observed with iron films deposited on these undercoats.

We have also tested evaporated magnesium fluoride as an undercoat. Although satisfactory in every other way, this material can be washed off the substrate very easily, which eliminated it from further consideration for this use.

Silicon monoxide undercoats have been recommended (64). Coatings were prepared, but were found to possess no advantage. Furthermore, the monoxide reduces the light transmission and is non-adherent.

Iron was selected for study because of the possibility that the film might become passive. In general, we confined our attention to the noble metals and to those metals which form transparent, protective oxides.

The resistivities of the iron films for a time seemed to be approaching stationary values. However, as the measurements continued, it became apparent that the resistivities were increasing. It seems likely that the increase will continue until the films are converted entirely to the oxide form.

TABLE III.4.1.2

EFFECT OF UNDERCOATING ON THE RESISTANCE OF IRON FILMS

Experiment SL22

Sample No.	Undercoating	Resistance in megohms/square
A	Titania	9
B	Silica	80
C	Titania	4.4
D	Silica	9.6
E	Titania	2.0
F	Silica	1.2
G	Titania	1.5
H	Silica	3.6
I	Titania	2.0
J	Silica	6.0

Average resistance of Titania undercoated films = 3.8 ± 2.3

Average resistance of Silica undercoated films = 5.1 ± 2.7

(Sample B excluded)

We have taken a number of representative samples from experiments SL22 and ST28 and plotted (Figure 5) the resistivities as a function of time on log-log scales. Since a zero value cannot be plotted in this way, we have arbitrarily taken the time of the first resistance measurement as one-tenth day, so that the initial resistance value could be included.

As can be seen from the curves, the rate at which the resistance increases does not seem to be approaching zero. In fact, it appears that the rate of increase is at least proportional to the resistance. Also, a few slides have been baked at 90°C to accelerate the aging process, but without any indication of a limiting value being approached. Considering these results, the iron films do not seem to merit further study.

It is significant that the transmissions of the films did not change appreciably while the resistivities were increasing so rapidly. This was also found to be the case with the other metal films (one exception will be discussed). Since the oxidation of metals should result in a large change in transparency, particularly for metals such as titanium which are relatively opaque, it therefore appears probable that conversion to an oxide film is not the primary cause of the change in resistivity.

It is possible that the change is due to a recrystallization which increases the extent of "aggregation", or island formation. Lennard-Jones (34) has given evidence to show that sections of the crystal can be "floated" apart by the incursion of gas molecules along faults in the crystal. The absorbed gas in the iron-air system would probably be oxygen, but it is not necessary to postulate actual oxidation in order to explain the resistivity rise. This theory thus accounts for an increase in resistivity without a concomitant change in transmission.

3.4.2 Titanium

Titanium films were first formed by evaporating the powder from molybdenum boats. However, the boat weights before and after evaporation showed that some molybdenum was also being vaporized. Subsequent evaporations were, therefore, made from notched titanium strip.

In order to simplify the process of laying down coatings with resistances in the desired range, we painted and baked a pair of silver electrodes on one slide in each batch and connected the electrodes to a vacuum-tube-volt-ohmmeter. This was done first in the titanium evaporations.

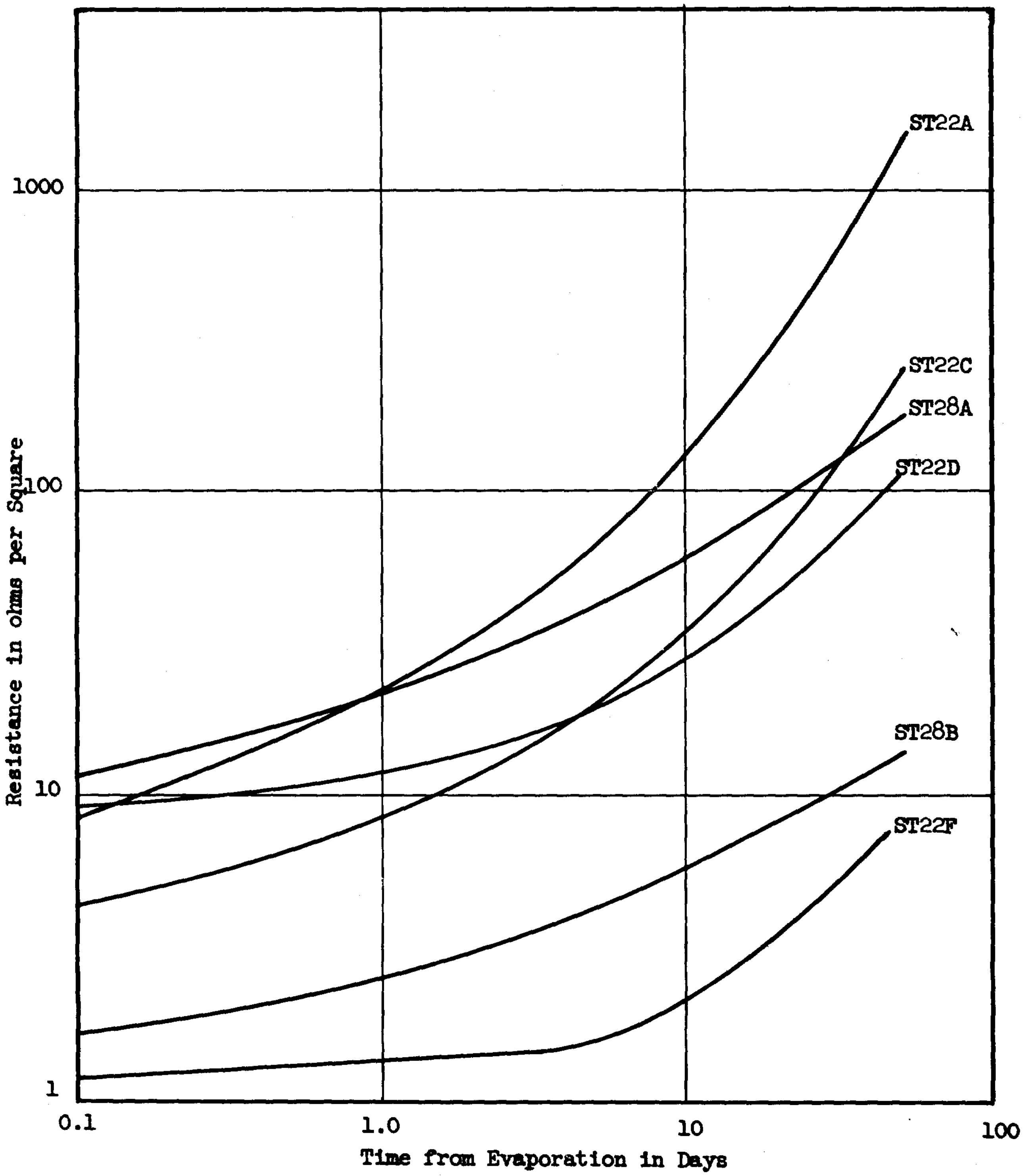


FIGURE 5
AGING CHARACTERISTICS OF EVAPORATED
IRON FILMS

We expected to prepare films of the proper resistance, that is, 3 to 10 megohms, and then to remove the coated slides for life testing. However, we noted that as soon as the evaporation was terminated, the resistance began to increase. The resistance went from 2 up to 12 megohms per square within nine minutes, even though the pressure was less than one micron. When the diffusion pump was cooled, and air was introduced into the inclosure, the resistance in one minute rose beyond the meter limit, which was 10,000 megohms. Similar phenomena have been noted elsewhere (49).

Since the transmission of the films was less than 80%, it appeared that titanium could not meet our objectives. However, we were interested in determining whether much thicker coatings would also show the same increase in resistance. Thirty milligrams of titanium were evaporated from a molybdenum boat onto a batch of slides. One coated slide had a resistance of 1400 ohms/square immediately after removal from the evaporator and a transmission of 8%. After 49 days the resistance rose to 4000 ohms/square and the transmission was unchanged. Evidently, the ratio of increase with these thicker films is much smaller than with the thin films.

Titanium, in bulk, is considered very resistant to oxidation. The lack of stability, again, cannot be due only to a crystallization or orientation effect, since the resistance rise is so much more rapid in the presence of air. The phenomenon, therefore, appears to fall within the domain covered by the Lennard-Jones theory.

3.4.3 Molybdenum

Molybdenum was evaporated, though with some difficulty. Undercoated films with a resistance of 2 megohms per square transmitted only 50% of the incident light. This was considered low. Since molybdenum washes off easily, the problem of improving the transmission did not warrant further study.

The fraction of molybdenum in the titanium films evaporated from molybdenum boats was found to be much higher than would be expected from vapor-pressure data (2). The discrepancy was probably due to the ratio of the relative areas from which the evaporation took place. At any rate, the presence of molybdenum did not improve the stability of titanium films.

3.4.4 Platinum

Platinum films were laid down on 2" x 2" slides by evaporating the metal from a heated tungsten spiral. Table III.4.4.1 lists the properties of the coated pieces. As the table shows, platinum films of the proper resistivity have relatively high transmissions. Also, undercoating the films reduces the resistance but simultaneously decreases the transmission. As will become evident from data on wedges, it is unlikely that the decrease in transmission caused by undercoating can be compensated for by decreasing the film thickness to bring the resistance up into the desired range.

Life test disclosed no change in any of the above properties. However, the adherence of platinum to all of the substrates in the table was poor. Films were baked at 90°C in the hope that some recrystallization or orientation which would improve the adherence might take place. The results were negative.

For no obvious reason, the results obtained with platinum were quite irregular. Samples ST 36J and H opened completely. Samples ST 36A and E from the same batch (see Figure 6) remained relatively constant. Figure 7 shows the data of samples ST 36F and G over a longer period.

3.4.5 Nickel

Silver electrodes were painted on at one end of a 9" x 2" lucite strip (no undercoat). The electrodes were one-half inch apart. The strip was placed with two undercoated and two uncoated strips in the evaporator. Five and one-half milligrams of nickel were evaporated. Figure 8 shows the resultant resistivity-transmission relationship for sample ST 64B, on uncoated strip, taken shortly after the evaporation. For the specific sample, the most important point is the transmission at the high end of the target resistance range. The value is 70% at 10 megohms per square.

For more general application the most significant characteristic of the curve is the change in resistivity with transmission. The resistivity increases fifteen thousand fold while the transmission increases from 68.5% to 78%. This is shown even more strikingly in Figure 9 which gives the resistance as a function of the weight of the deposit. It is very evident from the curve that the resistance of thin films is a completely different function from the resistance of the bulk material. The curve thus confirms

TABLE III.4.4.1

PLATINUM FILM PROPERTIES

Experiment ST36

Sample Number	Material	Resistance in megohms/square	Per cent Transmission	Per cent Reflectance (2 surfaces) Glass = 8%
A	Glass	4	77	9.65
B	Glass	14	78	9.33
C	Lucite	5	78	9.33
D	Lucite	5.8	78	8.33
E	Lucite + 1/2 AS168	1	74	14.0
F	Lucite + 1/2 AS168	0.6	72	14.7
H	Lucite + 1 AS168	0.56	68	18.5
I	Lucite + 1-1/2 AS168	1.4	73	14.0
J	Lucite + 1-1/2 AS168	4	73	12.4

Note: AS168 refers to undercoating of titania on lucite. The fraction refers to the thickness of the undercoat in terms of an arbitrary "normal" coat. These are 2" x 2" slides.

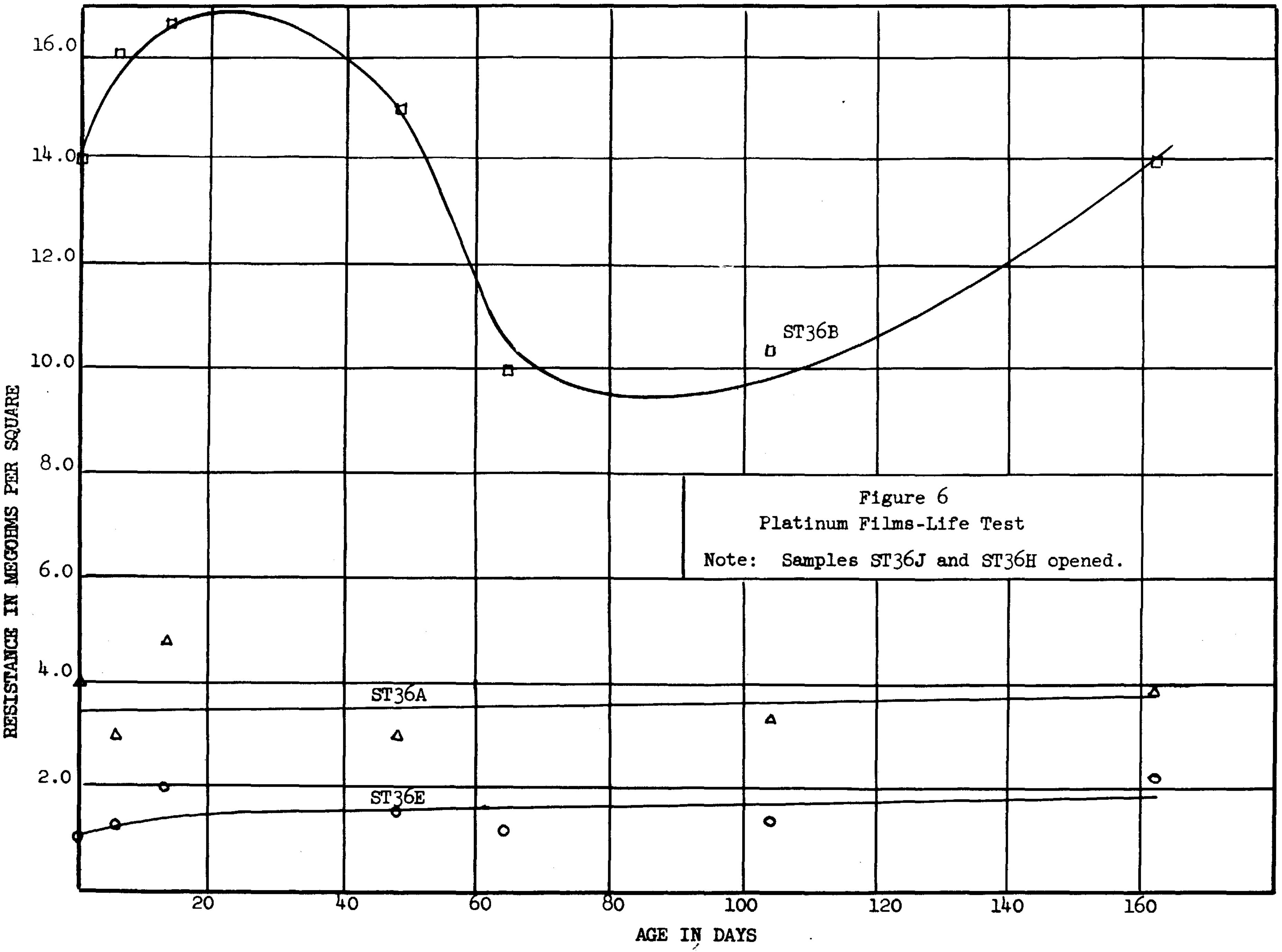
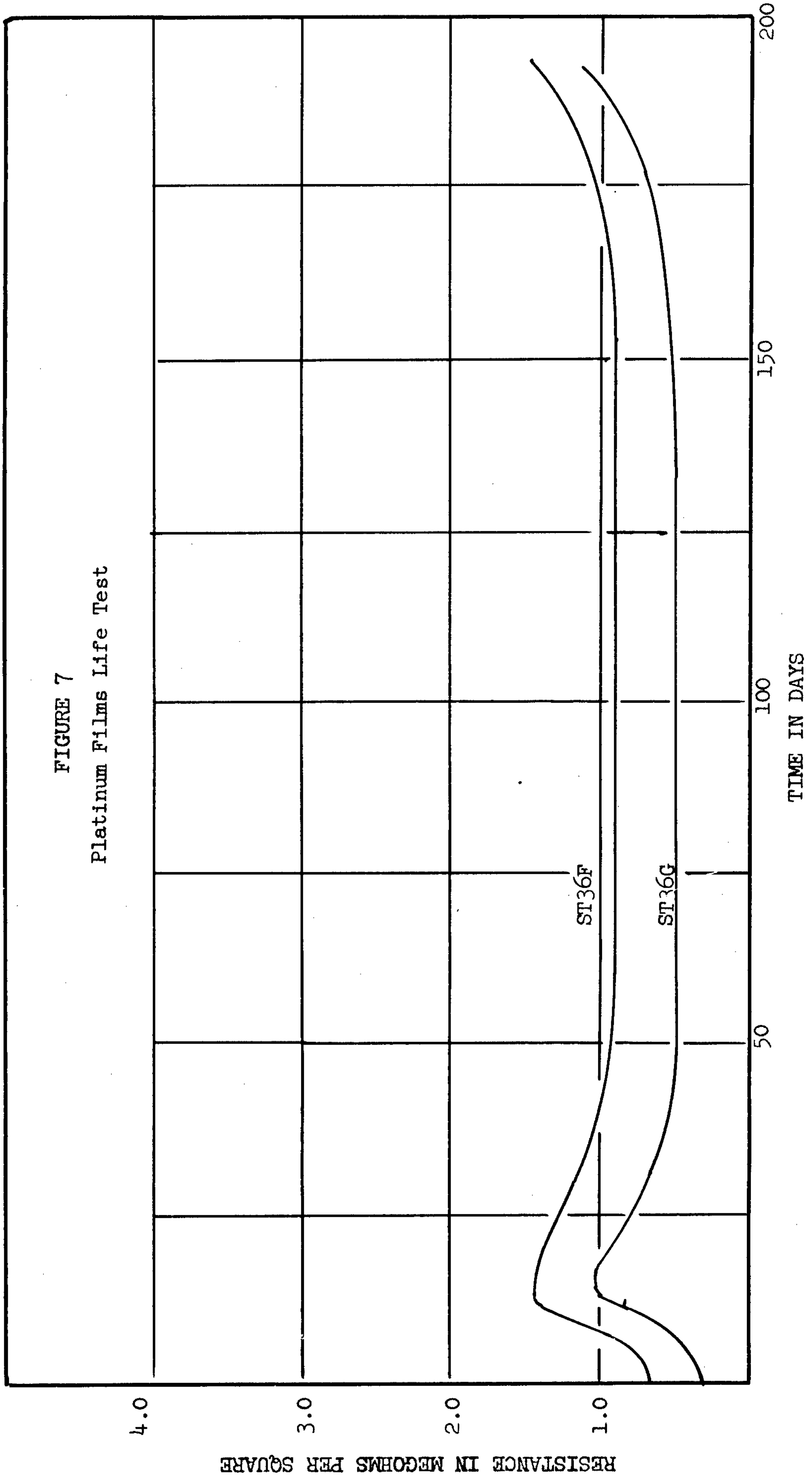


Figure 6
Platinum Films-Life Test

Note: Samples ST36J and ST36H opened.

FIGURE 7

Platinum Films Life Test



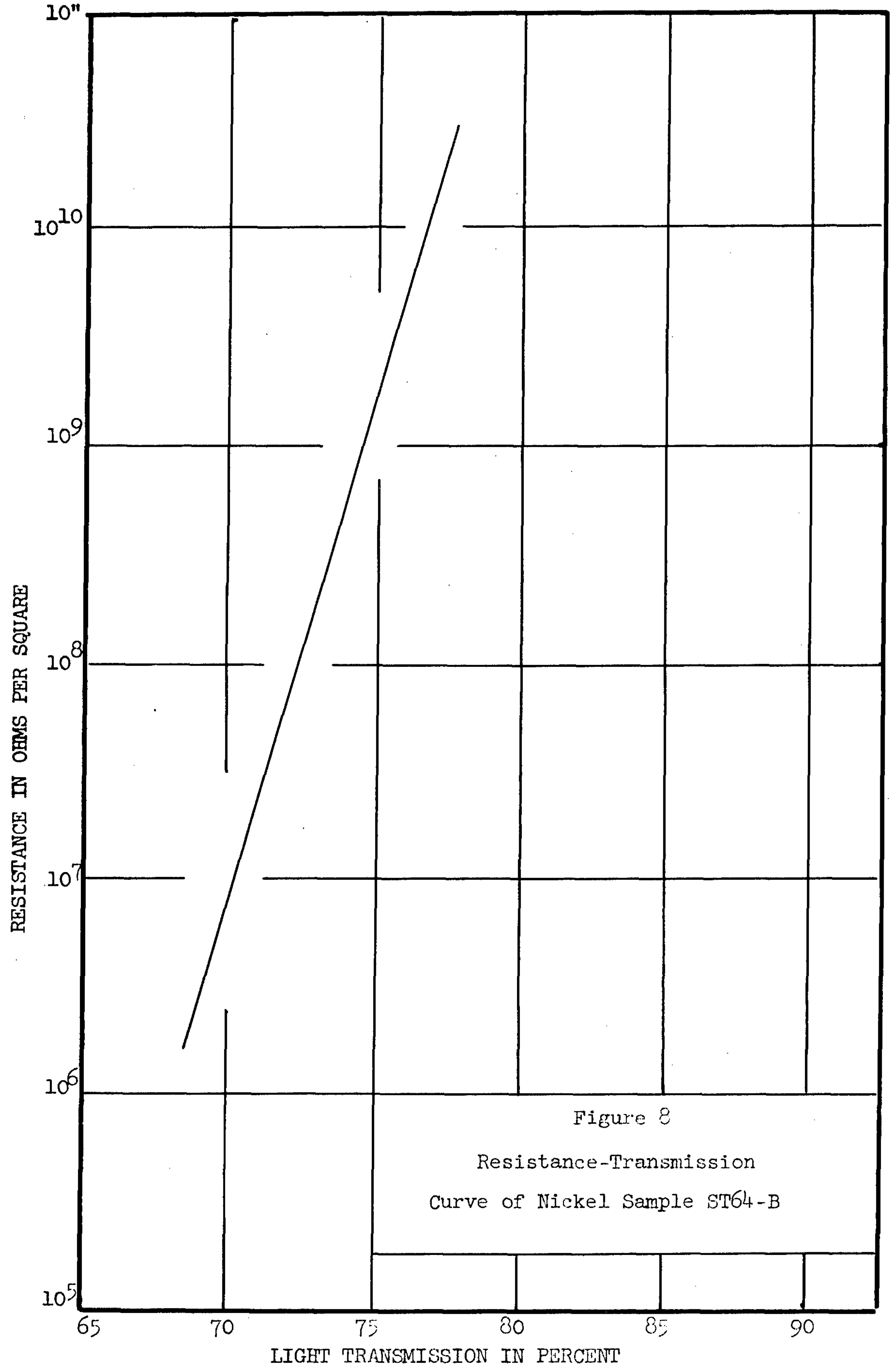


Figure 8

Resistance-Transmission Curve of Nickel Sample ST64-B

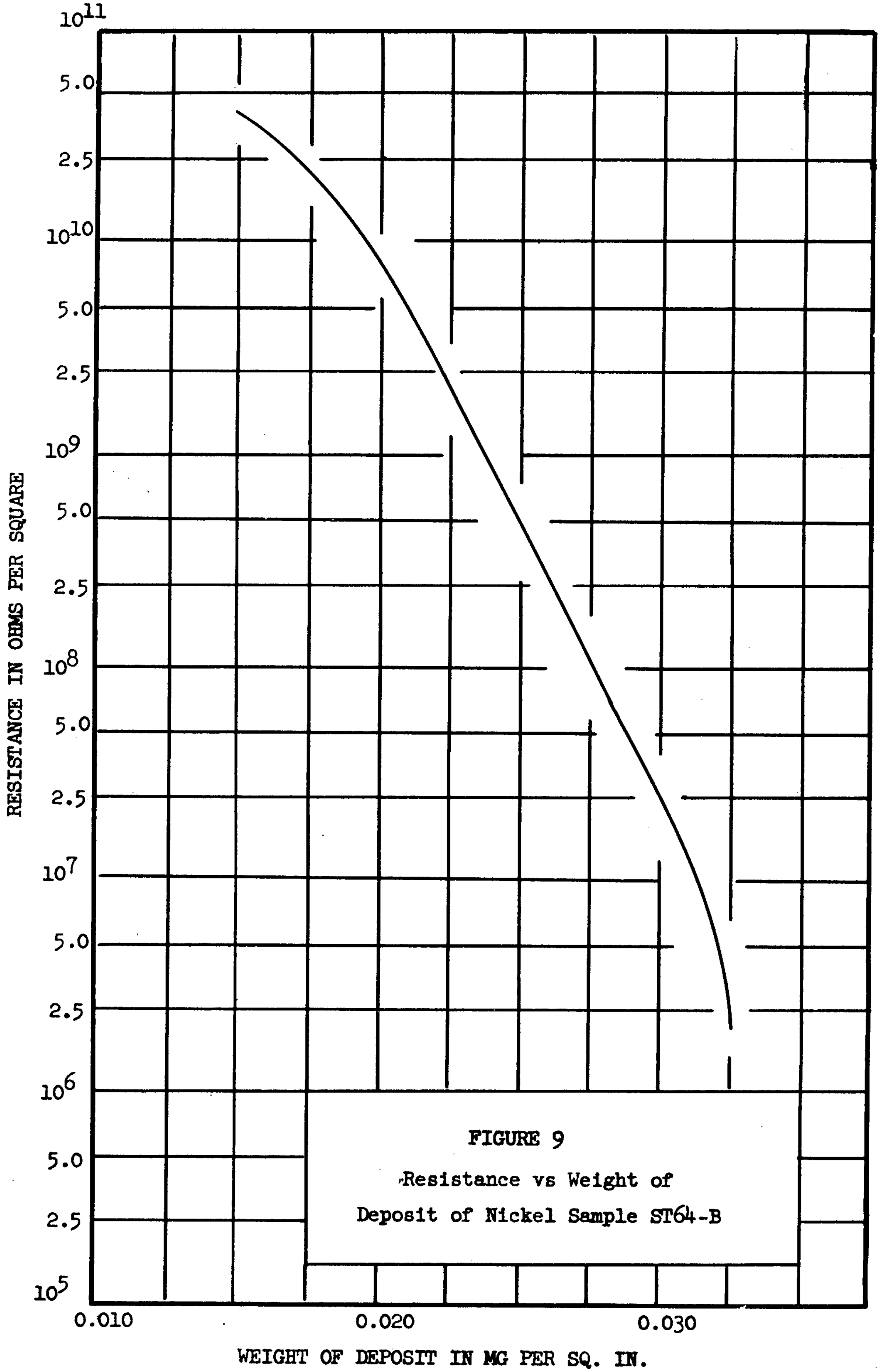


FIGURE 9

Resistance vs Weight of Deposit of Nickel Sample ST64-B the work of Aron (11), and others who stated that below a critical value, conductivity is an exponential, rather than a linear, function of the thickness.

The group of figures, describing the properties of sample ST64-B, is completed by Figure 10. Evidently, the transmission is not so sensitive to the weight of the deposit as is the resistance. As a consequence, the utility of undercoatings is markedly decreased. The undercoating increases the conductivity but also decreases the transmission. To compensate for the loss in transmission, the film thickness must be decreased. The increase in resistance which results more than offsets the initial decrease afforded by the undercoat.

Figure 11 gives the resistance-transmission curve (solid line) for a fresh nickel coat of somewhat greater density than the film of ST64-B. Three and seven-tenths milligrams of nickel were evaporated in preparing this film. Ideally, the curve of Figure 11 for sample ST65-B should form an extension of the ST64-B curve. Actually, the slopes are different, indicating the presence of another variable. This variable may be the rate of evaporation, or the condition of the surface.

The broken-line curve of Figure 11 shows the change in resistance after five days. As can be seen, the change is appreciable; the measurements were continued to determine whether a limiting value is reached. The transmission remained constant throughout. Figures 12 and 13 complete the group.

In another evaporation nickel films were deposited on 2" x 2" lucite slides. Electrodes, leading to an ohmmeter, were attached to one of the slides throughout the evaporation and the meter reading was used to determine the end point of the vaporization. It was noted that when air was admitted to the bell jar, the resistivity of the test piece increased rapidly from the initial value of one thousand megohms per square. The air was pumped out of the bell jar and additional nickel was evaporated to bring the resistance down to one hundred megohms. When air was re-admitted, the resistance rose somewhat more slowly. The procedure was repeated twice more, finally bringing the resistivity to one megohm per square. The samples were removed for testing by which time the resistivity had risen to 16 megohms per square.

It was noted that the adherence of these films appeared to be appreciably better than that of films deposited uninterruptedly and without interim exposure to air. The resistivities, however, continued to increase indicating that nickel films are unstable. Table III.4.5.1 shows the life charts for three of the samples. As can be seen, the resistivities show no tendency to stabilize. However, the transparency and the adhesion are relatively good.

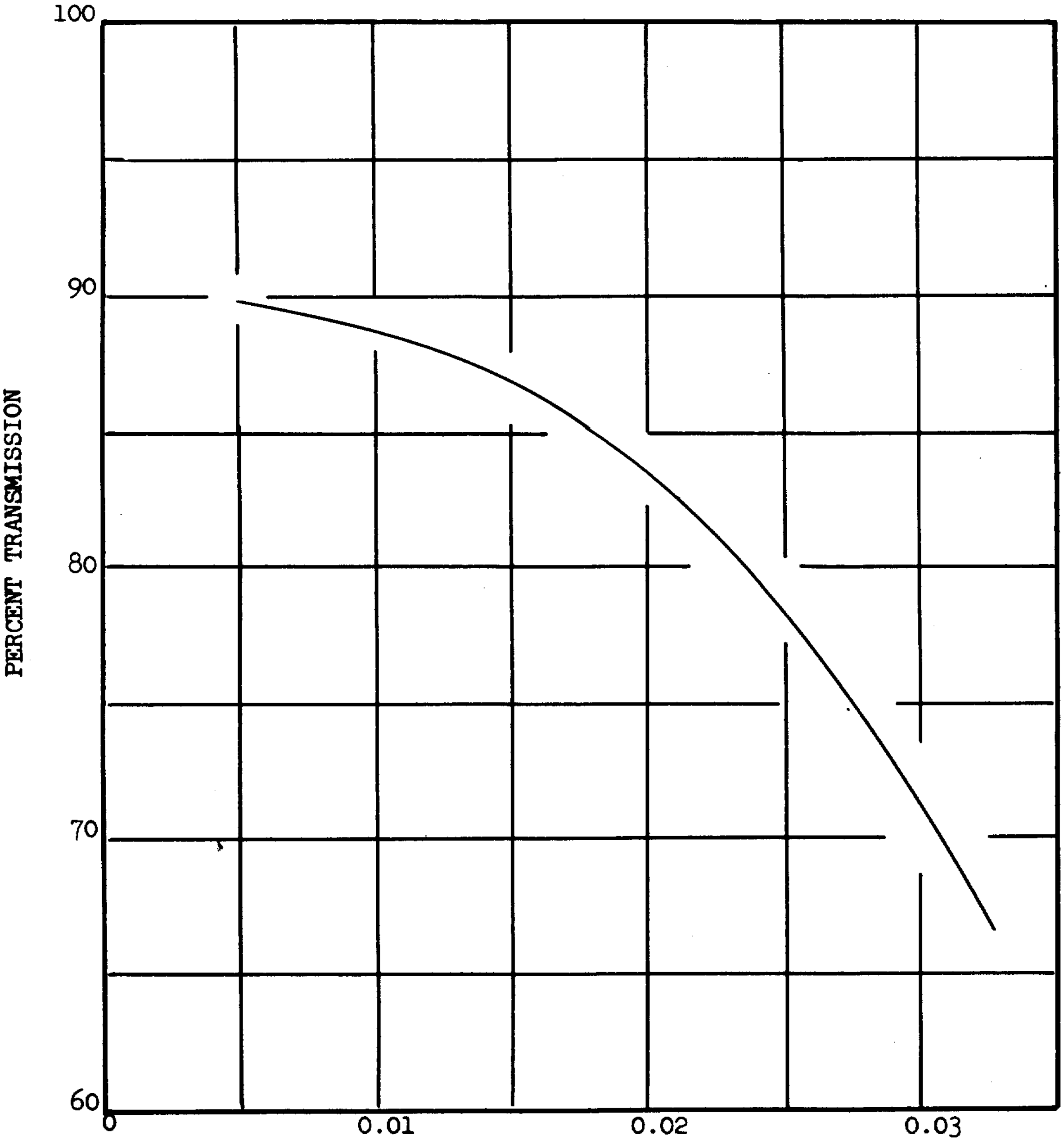


Figure 10 TRANSMISSION VS WEIGHT OF DEPOSIT OF SAMPLE ST64-B NICKEL

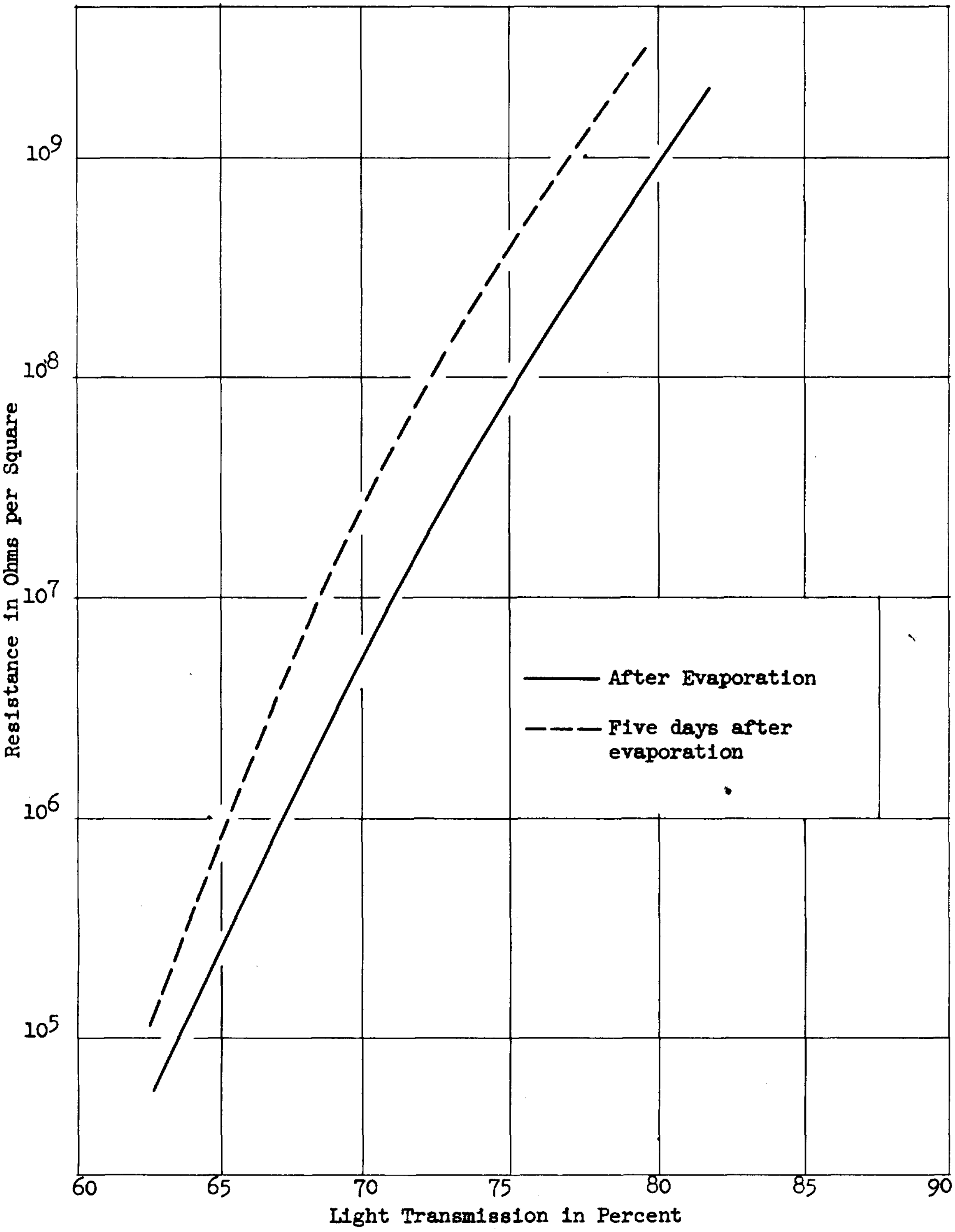


FIGURE 11
RESISTANCE-TRANSMISSION CURVE OF
NICKEL SAMPLE ST65-B

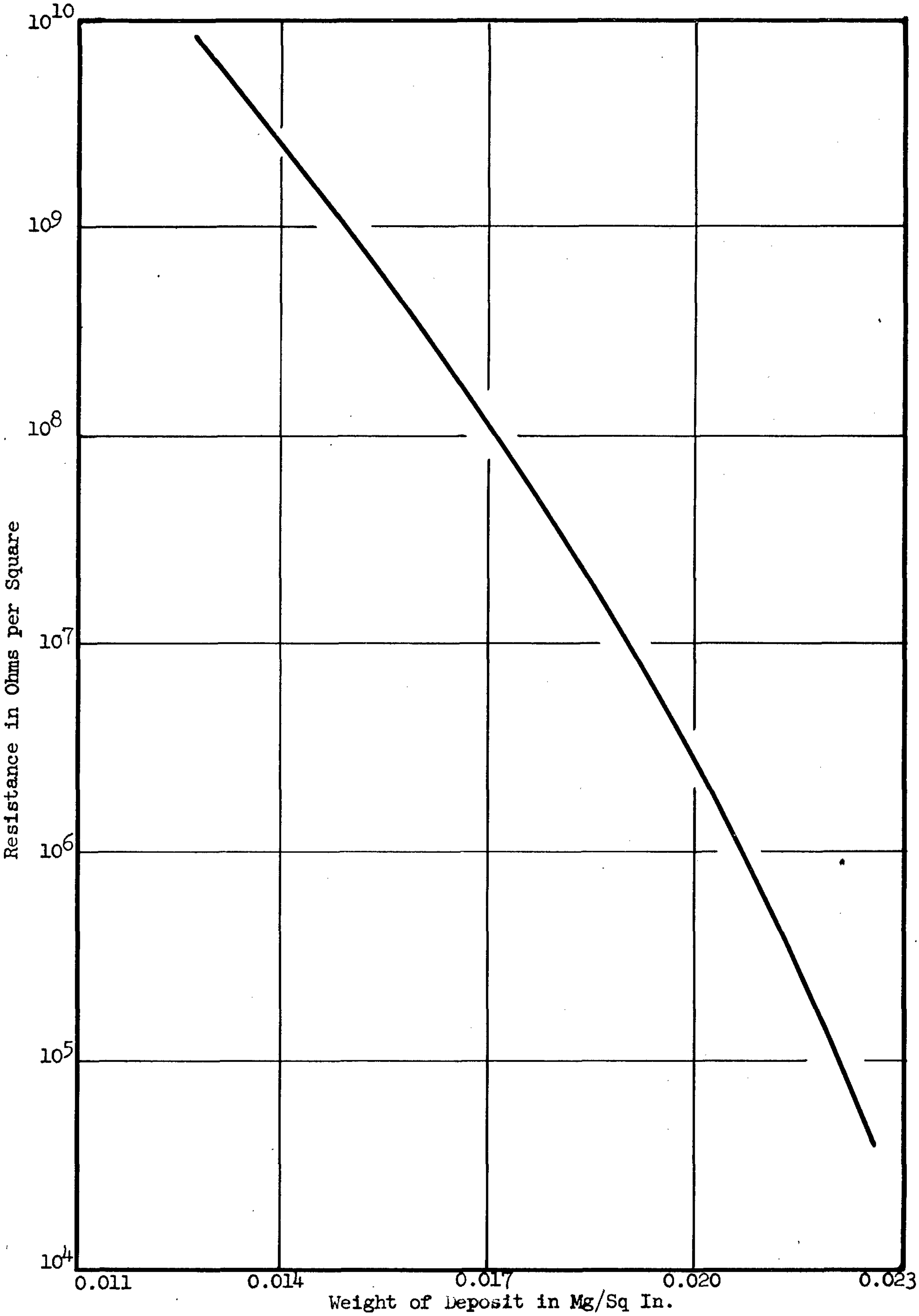


FIGURE 12

RESISTANCE VS WEIGHT OF DEPOSIT
OF NICKEL SAMPLE ST65-B

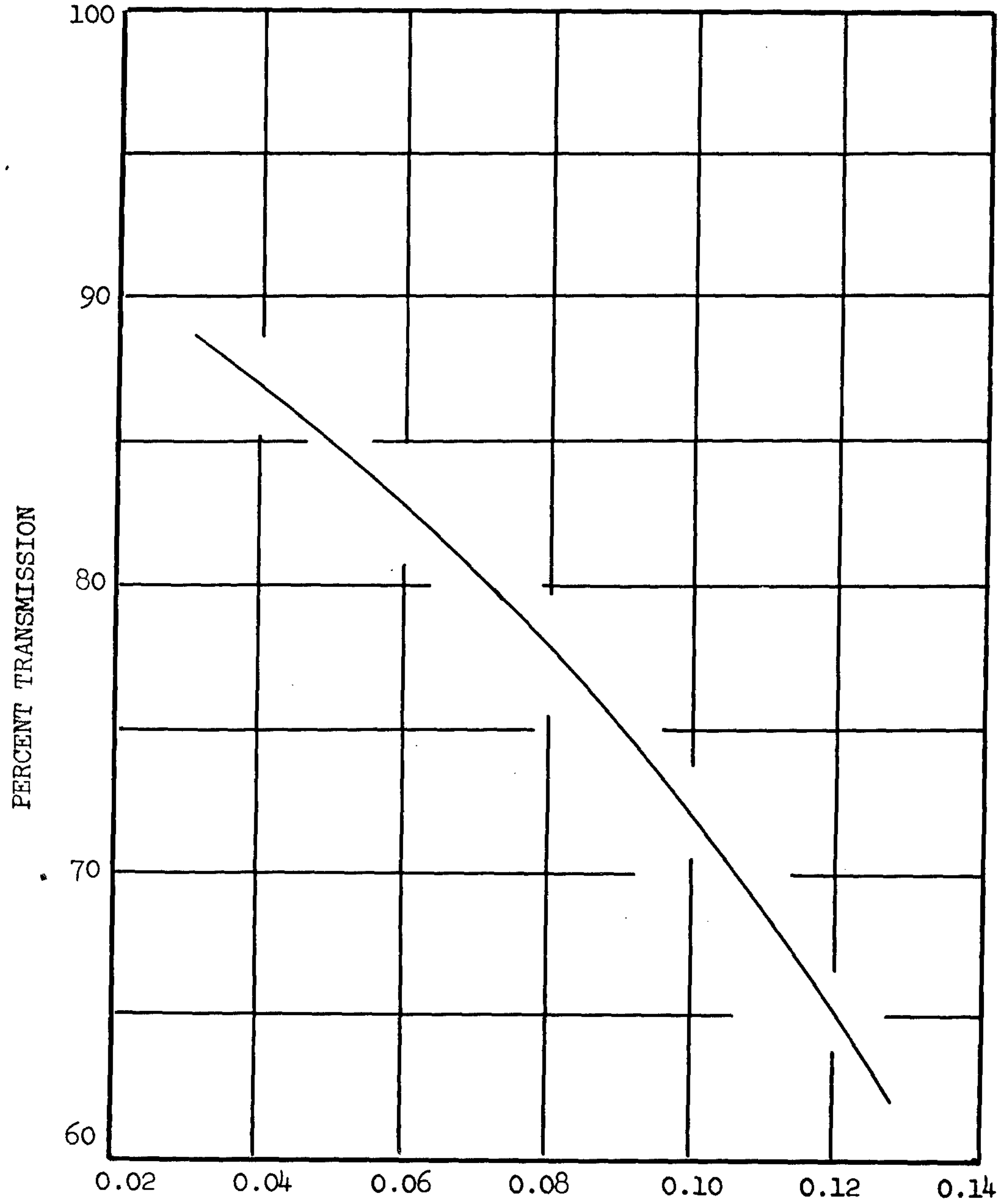


Figure 13 TRANSMISSION VS WEIGHT OF DEPOSIT OF NICKEL SAMPLE ST65-B

TABLE III.4.5.1

NICKEL FILM LIFE CHARTS

(Interrupted evaporation)

Age of Film in Days	Sample ST86A Res.	Trans.	Ref.	Sample ST86B Res.	Trans.	Ref.	Sample ST86C Res.	Trans.	Ref.
0.1	48 Meg	76%	15%	23 Meg	76%	15%	10.6 Meg	75%	16%
1	280			104			48		
2	1,000			300			120		
3	2,000			480			170		
4	3,000			600			190		
8	10,000			1,200			280		
10	open			2,000			400		
15	open			2,600			600		

Res. = Resistance

Trans. = Transmission

Ref. = Reflectance

The effect of the intermittent oxidation is similar to that described in three Libby-Owens-Ford patents (61,62,63).

3.4.6 Silver

Thin silver films on 2" x 2" slides were prepared and were found to be pink, non-conductive and non-adherent. After standing for thirty days, the color faded. Heavier silver films were rendered adherent by baking overnight at 90°C. The increase in adherence may be due to an orientation effect. This effect received considerable attention. Reference (45) is specific to the problem; for additional papers, refer to the extensive bibliography under (1).

It was at first thought that the pink color of the thin films might have been caused by carrying out the evaporation at too high a pressure. It was demonstrated by means of the wedge technique that the color is actually a function of film thickness, and not of the pressure.

The adherence of silver to lucite is known to be relatively poor. In an attempt to improve the adherence of the silver to the acrylic, the lucite strip was first undercoated with titania and then evaporation-coated in wedge form with 1.7 milligrams of chromium. Finally, silver was evaporated until the resistivity between the painted electrodes reached two megohms per square.

Examination of the wedges showed that they were conductive only at the heavy end. At this heavy end the resistivity was seven megohms per square and the transmission was 41.6%.

The wedges showed a strong color gradation from blue at the dense end through red to a light yellow at the thin end. Only the blue end was conductive. Evidently the film at the red section was too thin and was discontinuous, which explains the lack of conductivity mentioned above.

In the attempt to improve adhesion, a silver film was deposited by evaporation on lucite slides, each of which was coated over half its surface with Ciba's Araldite cold setting adhesive Type 102. This material adheres strongly to polymethylmethacrylate; it is an epoxy resin. Some improvement in the adhesion of the silver was noted. The comparison could readily be made, since treated and untreated portions of the surface were contiguous.

3.4.7 Chromium

Chromium films are of particular interest because they have been shown to be continuous at thicknesses as low as 20 Angstroms (46). The films were laid down in experiment ST66 by evaporating 10.8 milligrams onto lucite, undercoated with titania. The resistance-transmission curve is shown in Figure 14. The curve indicates that the highest transmission obtainable in the specified resistance range is 44%. This result is surprising, since from the above statement concerning continuity, the chromium film should be conductive at low densities and high transmissions.

Figures 15 and 16 complete the group.

3.4.8 Rhodium

Rhodium wedges were prepared by evaporation. Vaporization was continued until the electroded sample reached a resistivity of 0.5 megohms per square. The resistivity remained constant while the diffusion pump cooled, but rose to 12 megohms per square when exposed to the air. This sequence is of particular interest since the resistivity increase seems so definitely to be a consequence of contact with air, despite the fact that bulk rhodium at room temperature is inert to oxygen. Figure 17 gives the resistivity-transmission curve. The transparency is excellent in the target resistance range, but the adherence of the film is poor.

The resistance continued to rise over a period of several months, though not rapidly, as can be seen from Figure 18.

3.4.9 Ruthenium

Ruthenium samples were laid down as wedges. Transmission was high in the required conductance range, but the adhesion was poor. The adhesion improved perceptibly with aging.

Figure 19 shows the results of the life tests.

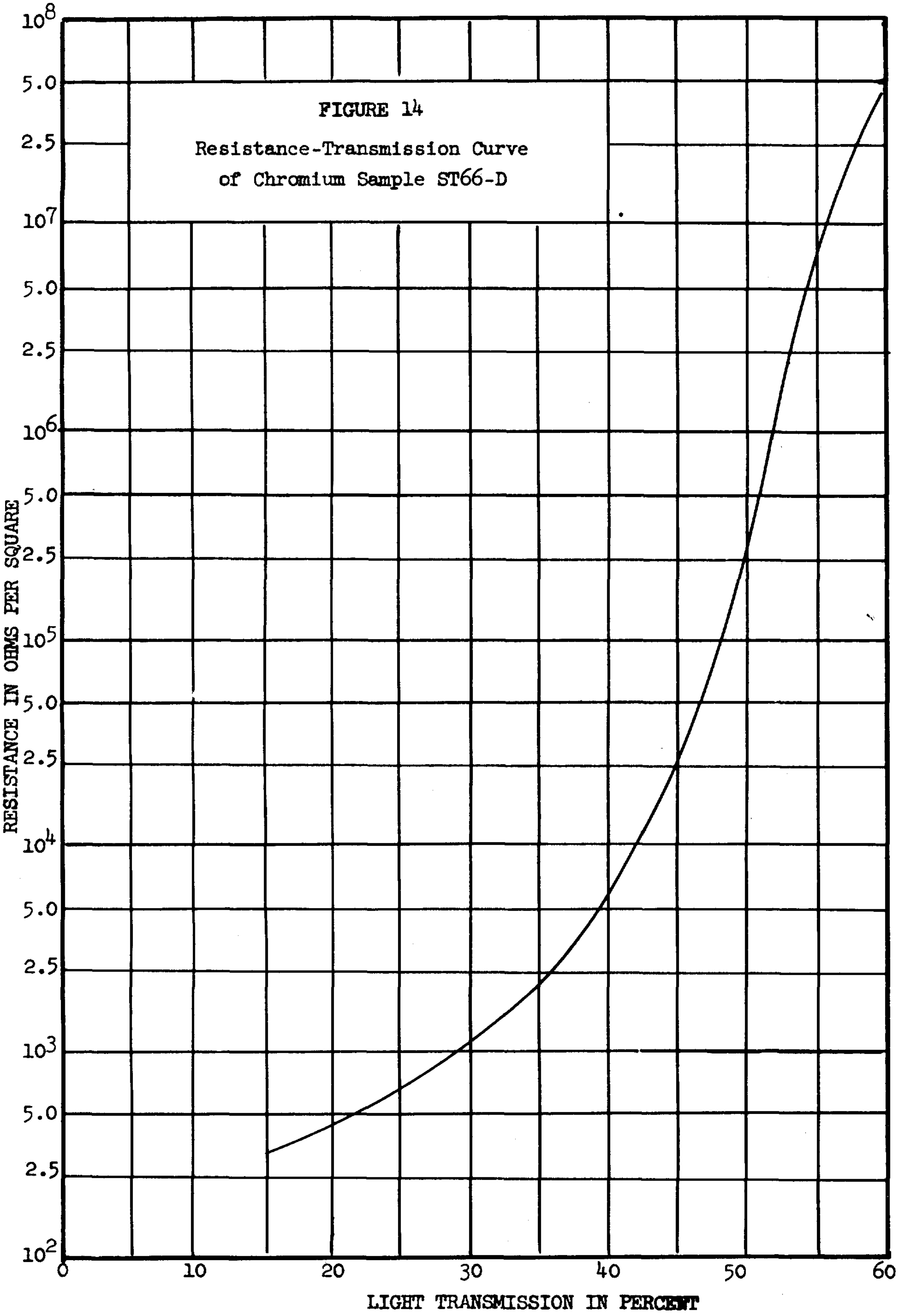


FIGURE 14

Resistance-Transmission Curve of Chromium Sample ST66-D

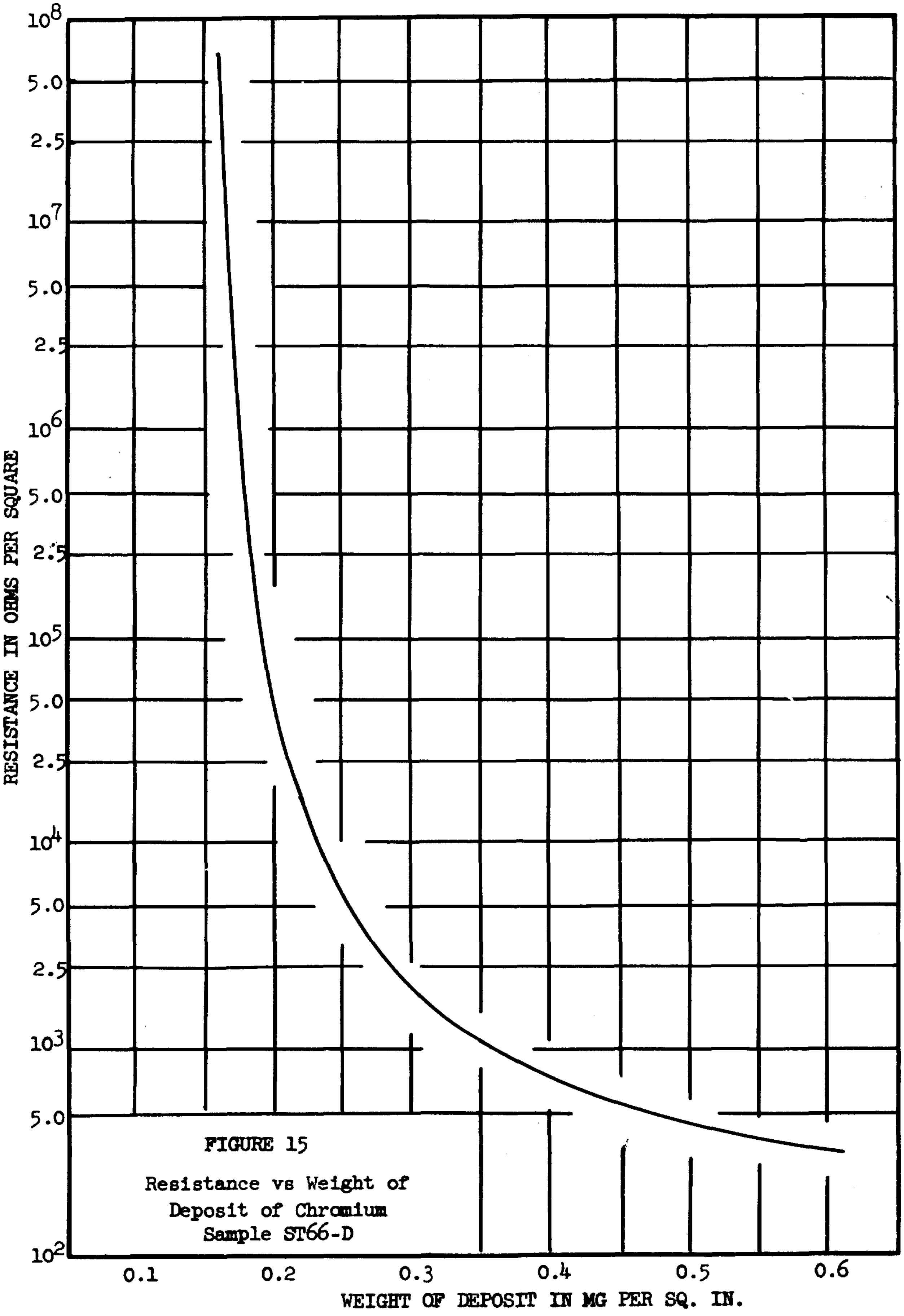


FIGURE 15

Resistance vs Weight of Deposit of Chromium Sample ST66-D

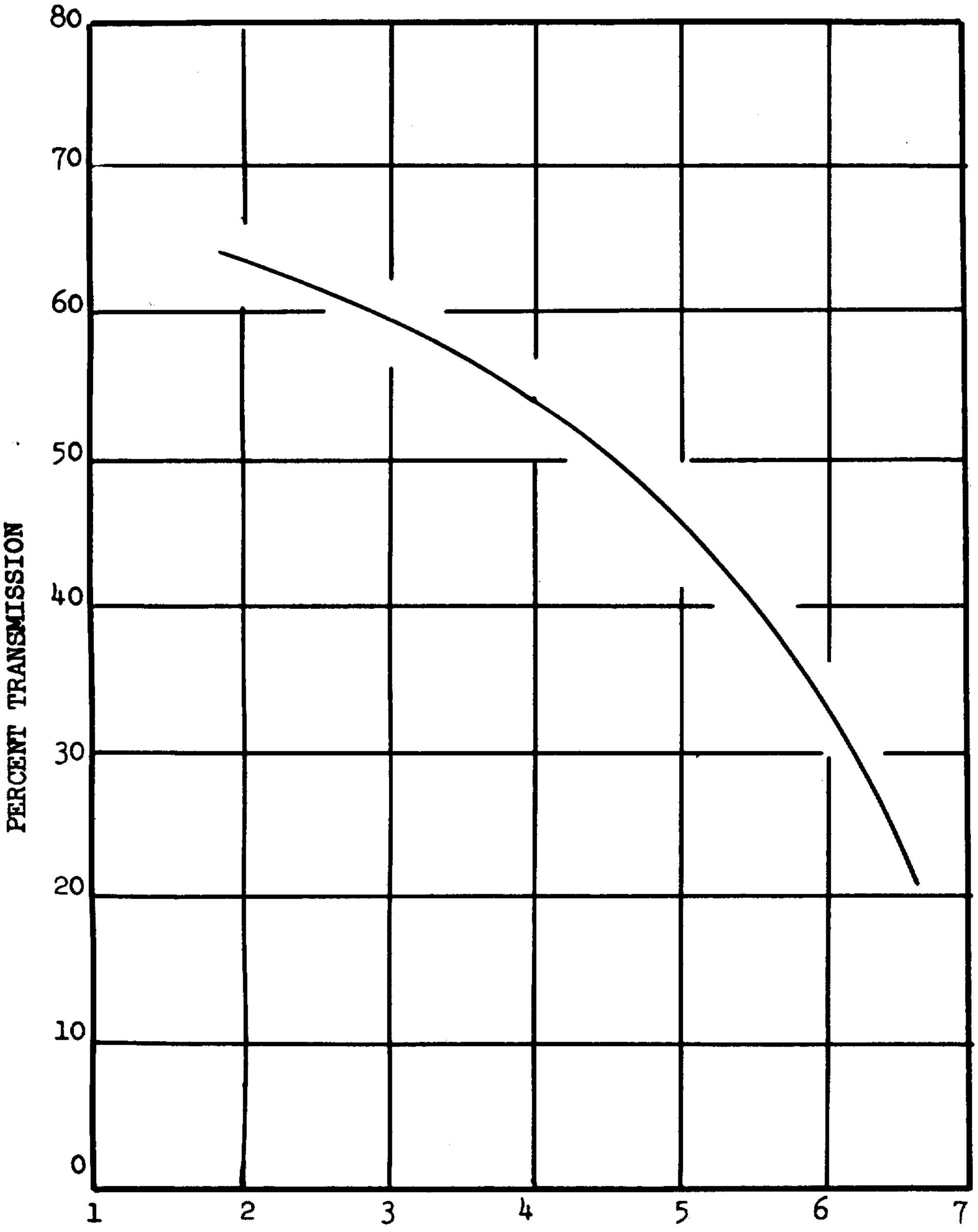


Figure 16 TRANSMISSION VS WEIGHT OF DEPOSIT CURVE OF CHROMIUM SAMPLE ST66-D

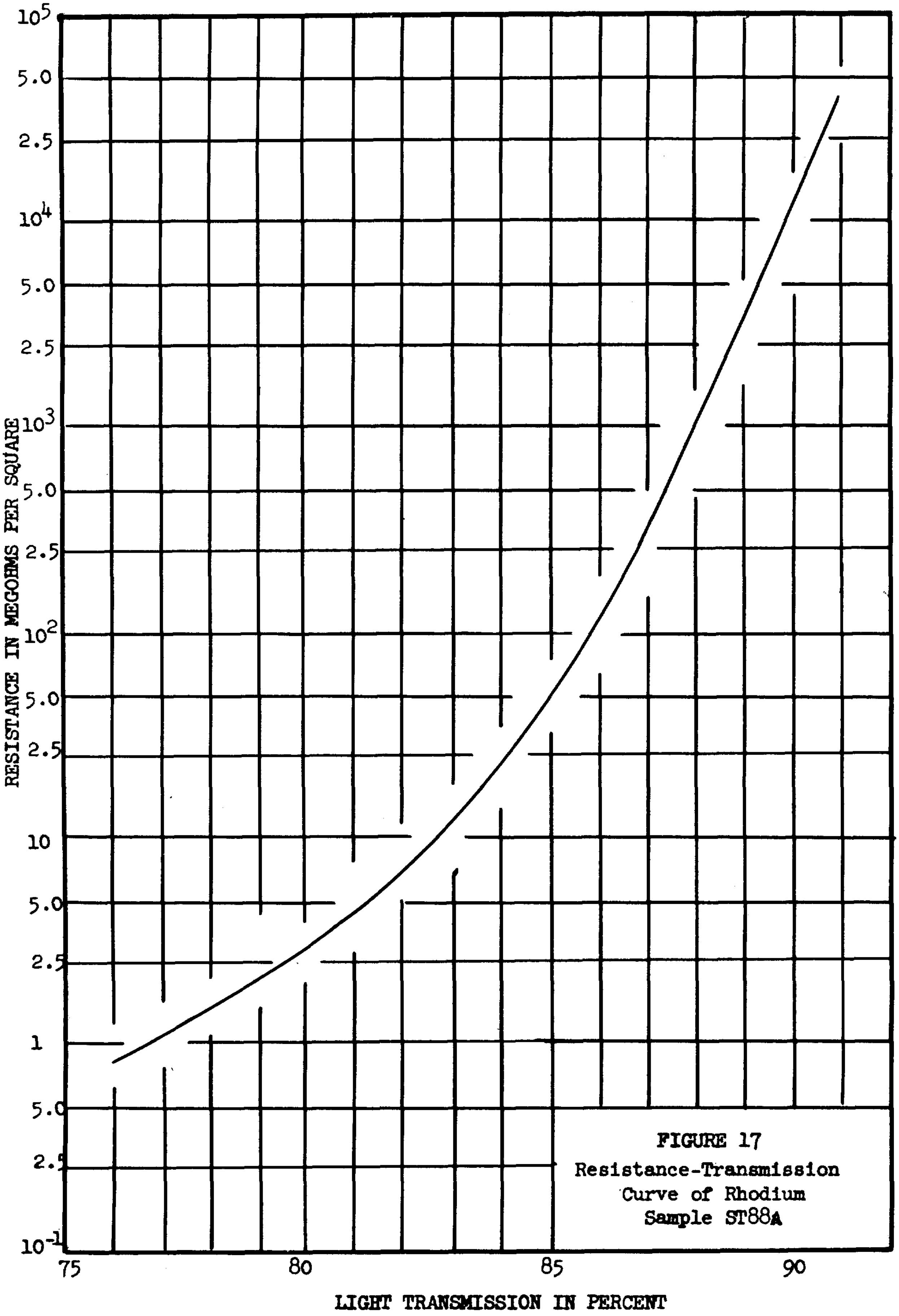


FIGURE 17
Resistance-Transmission
Curve of Rhodium
Sample ST88A

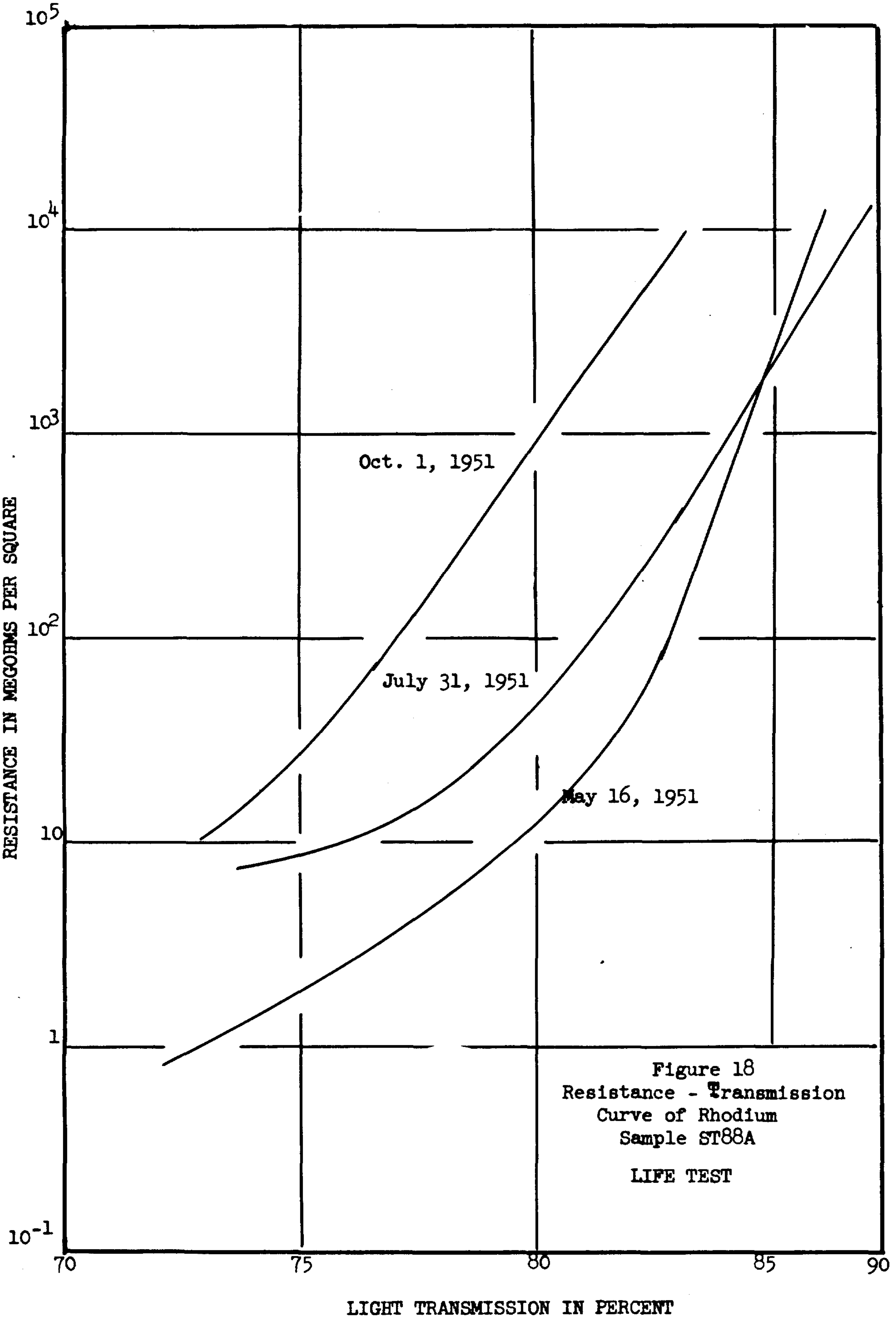


Figure 18
Resistance - Transmission
Curve of Rhodium
Sample ST88A

LIFE TEST

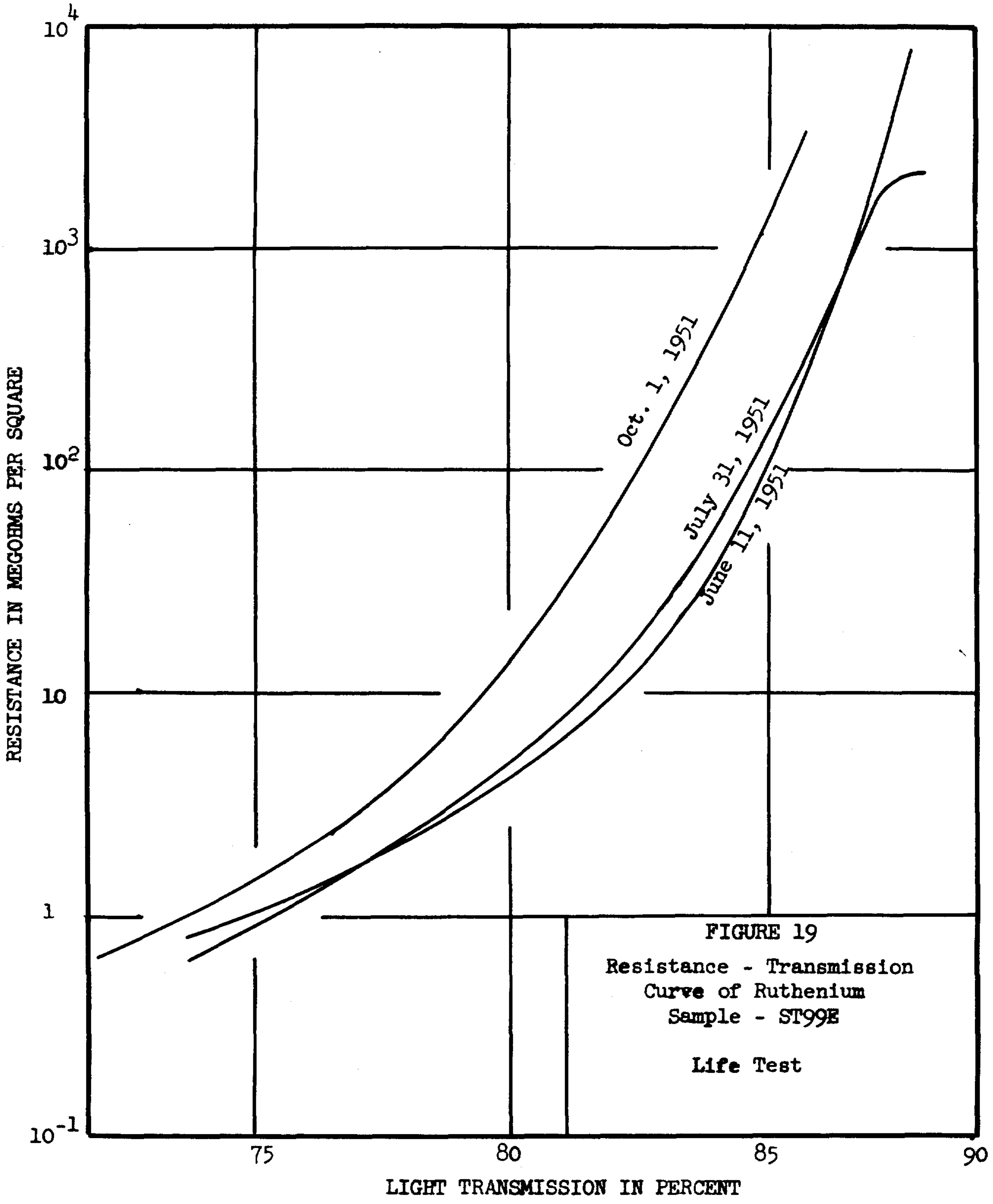


FIGURE 19
Resistance - Transmission
Curve of Ruthenium
Sample - ST99E

Life Test

3.5 THE EVAPORATION OF METALLOIDS SELENIUM AND GERMANIUM

A sample of pure selenium (99.99+) was evaporated to form a wedge on lucite. During the vaporization, resistances of the order of 50 meg/square were noted, but the resistance jumped as soon as the heating current in the boat was cut off. Evidently the light from the incandescent boat gave rise to enough photo-conductivity to account for the measured conductivity. However, no conductivity was apparent when the light source was removed, even though the deposit was quite heavy.

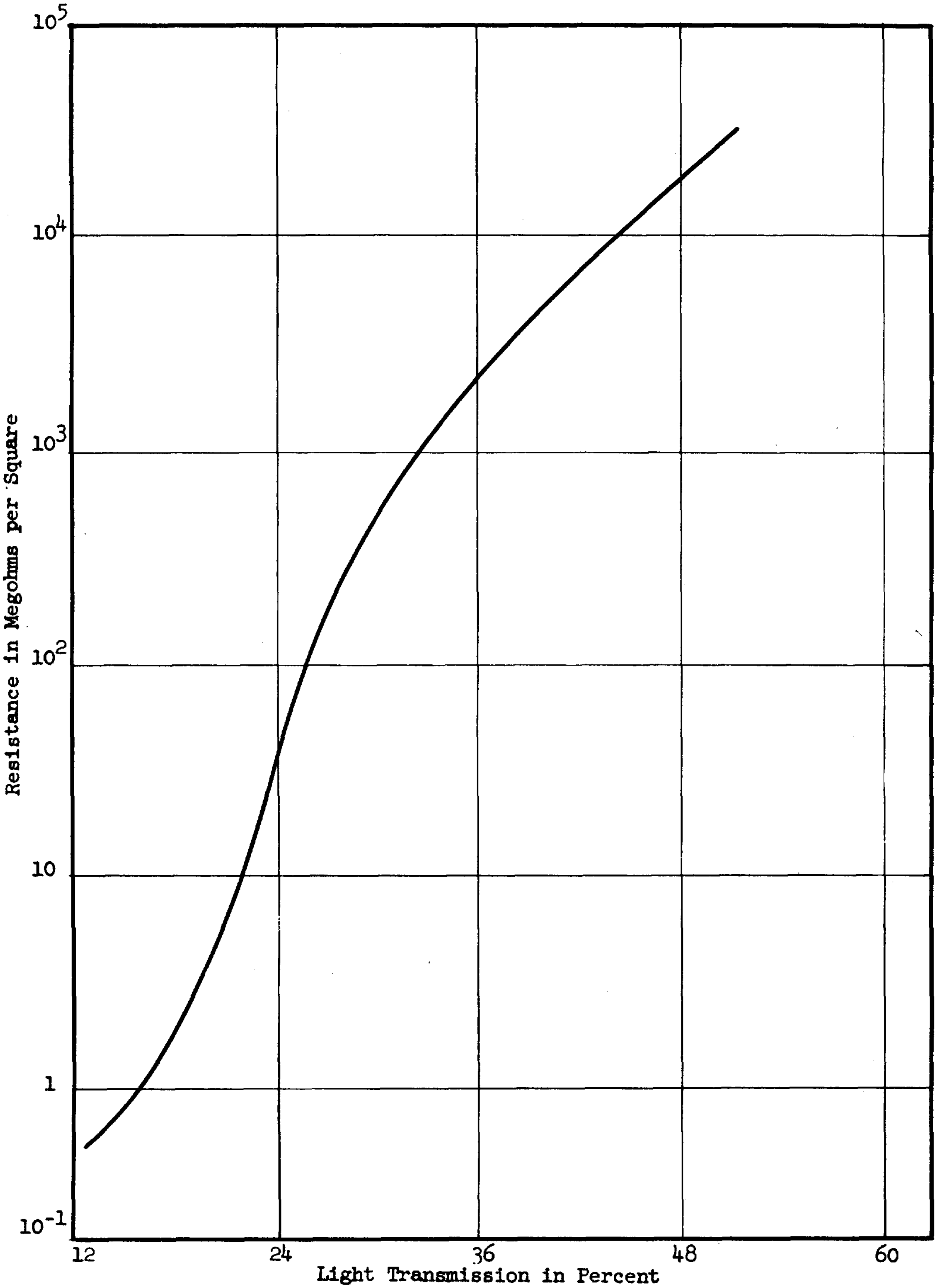
The literature on selenium is extensive so that the semi-conductivity of selenium is well known. The absence of conductivity in our films is therefore probably due to the form of the deposit. The adherence of the selenium deposit to the lucite substrate was poor.

Germanium was also evaporated in wedge form on lucite. Like selenium, germanium also showed photo-conductivity during the evaporations. Unlike selenium, appreciable conductivity was evident after removal from the evaporator. Again, unlike selenium, the adhesion to the lucite was good.

Figure 20 shows the relationship between resistivity and light transmission for the germanium deposit. As can be seen, the transmission is low in the desired resistivity range. Even at 10 megohms per square which is the upper end of the range, the transmission is only 25%. It should be noted that relaxing the resistivity specification by two or three orders of magnitude will not solve the problem, since even at 10,000 megohms per square the transmission is only 48%. Only a significant improvement in the conductivity of the deposit will overcome the difficulty. To this end compositions of the type used in germanium diodes were studied, since these compositions are already select with regard to semi-conductivity.

The crystals from six 1N34 germanium diodes were removed. The total weight of the six crystals was inadequate for an evaporation so an approximately equal weight of pure germanium was added. The mixture was evaporated on 9" x 2" wedges. The product was very low in conductivity -- about 1,000 megohms per square -- at 10% transmission.

The particular diode used for this test was selected because its conductivity rating is fairly high, but the results were nevertheless negative.



RESISTANCE-TRANSMISSION CURVE OF GERMANIUM
SAMPLES ST87B, C, AND D

In a literature search, we found considerable theoretical discussion of defect structures (4,13,27,28), but relatively little specific information on the most effective impurities, particularly for the modification of germanium.

Some data on silicon are available. The resistivity of silicon containing boron and phosphorus in amounts up to 1% has been given by Pearson and Bardeen (42). The resistivity falls off by several orders of magnitude as the impurity is introduced and is a function of temperature, decreasing with increasing temperature, as is to be expected.

The lowest resistivity values given in Pearson's paper are for the highest concentration of impurity. At room temperature, the resistivities are 3×10^{-4} ohm cm for 1% boron in silicon, and 6×10^{-4} ohm cm for 1% phosphorus in silicon. The curves for the various alloys do not indicate any conductivity maximum with respect to concentration of impurity. Also, at the 1% impurity level, the conductivity is relatively independent of temperature.

Evaporated films of pure germanium should be sufficiently defective in structure to be much more conductive than the bulk metal, which accounts for the relatively high values we found. This prediction has been substantiated by a radiation technique (10). Germanium (n-type) was bombarded with alpha particles and with deuterons. In both cases, the conductivity was transformed to p-type. It was established that the conductivity was due to the creation of disorder, and not to transmutation of metal atoms into other elements.

The addition of antimony to germanium has been studied (28), but the only data given cover the retention of the impurity in the alloy during the crystallization process. It was found that even at concentrations as low as 0.054% some separation occurs. Shockley, in one of the problems in his book (6) p. 26, discusses an alloy containing 3.22×10^{-8} grams of antimony per gram of germanium, and estimates that the conductivity of the alloy would be 0.50 per ohm cm.

We have previously reported the reluctance of germanium manufacturers and processers concerning the transmission of specific information about germanium alloys. Dr. Willy van Roosbroeck, one of the Bell Telephone transistor specialists, was however kind enough to discuss the germanium composition problem with us. Dr. van Roosbroeck's information should augment that given above. We note, however, that his statements are not completely consistent with those given above.

According to Dr. van Roosbroeck, the optimum concentration of impurity for n-type materials is $1.73 \times 10^{15}/R$ atoms/cm ^{3}, where R is the resistance of germanium in ohm cm. The resistance refers to that of the bulk metal, of course, but it will be assumed that the formulae also applies to evaporated films.

The optimum concentration then will be -

$1.73 \times 10^{15}/89 \times 10^3 = 1.94 \times 10^{12}$ atoms/cm ^{3}.
A mol contains 6.02×10^{23} atoms.

The required concentration of impurity is therefore 3.20×10^{-12} moles per cm ^{3}. The optimum for p-type impurities is 6.81×10^{-12}. These quantities are manifestly so small as to make the method of addition a serious problem. Furthermore, the fact that the formulae apply only when the additive decreases the resistance by a factor of three or more, must be taken into account. As yet, we have no information that this is the case for evaporated films.

The impurities most frequently added are arsenic, antimony, phosphorus, gallium, and boron. The first three, with germanium, give n-type structures, the last two, p-type. For evaporation purposes, gallium can be neglected because its vapor pressure is inconveniently low.

3.6 THE EVAPORATION OF MISCELLANEOUS DEFECT-STRUCTURE MATERIALS

3.6.1 Phthalocyanine

Phthalocyanine, both metal-free and in complexes with copper and with magnesium has been reported to be conductive (50). To make the measurement, the material was rubbed on a quartz surface between two gold electrodes. The apparent specific conductivity was found to be 5×10^{-8} (ohm-cm)$^{-1}$. The conductivity increased with temperature, which would indicate the presence of true semi-conductivity.

We evaporated copper phthalocyanine in the form of wedges to a density great enough so that the transparency was much reduced. No conductivity was apparent with our instruments. The adherence was also poor.

3.6.2 Phosphors

Zinc sulphide, C.P., was evaporated from a molybdenum boat. The evaporation was difficult because the powder was thrown about in the boat during vaporization. The vibration was sufficiently vigorous to throw much of the powder out of the vessel. Enough was evaporated, however, to form a dense wedge on lucite. The film produced was non-conductive and non-adherent.

Zinc sulphide containing a trace of silver was obtained from the New Jersey Zinc Company, as composition number 2205, and evaporated to form a wedge on lucite. The difficulty described above was again encountered. The deposit was photo-conductive, but the dark conductivity was below the range of our instruments.

A second zinc sulphide composition supplied by the New Jersey Zinc Company under the number 2330 and containing

100	parts Zinc sulphide
0.0093	parts Copper
0.020	parts Lead acetate
2.0	parts Sodium chloride

was evaporated as above. The deposit was non-conductive though dense, as well as non-adherent.

We had been informed that zinc sulfide-tin oxide compositions were reported to be conductive. Mixtures of the following compositions were prepared and evaporated for examination.

Experiment Number	$ZnS : SnO_2$ by weight
ST 69	100:0
ST 109	50:50
ST 110	10:90
ST 111	4:96
ST 112	96:4
ST 113	0:100

None of the deposits was conductive, although all were thick enough to cut the light transmission by more than 50%.

The pure tin oxide films were particularly interesting. In the first place, they were definitely non-metallic, which is contrary to our previous experience. It is possible that this was due to the fact that the pressure at which this latest evaporation was carried out was somewhat higher than in our earlier work.

In the second place, the film thickness approached that of the tin oxide films on glass which are commercially available as resistance heaters. The commercial films are approximately one-half wave-length in thickness. Our tin-oxide films showed interference colors, and therefore were at least one-quarter wave-length thick.

Along with this series, a ZnO-ZnS mixture of 50-50 composition was evaporated. This deposit was also nonconductive.

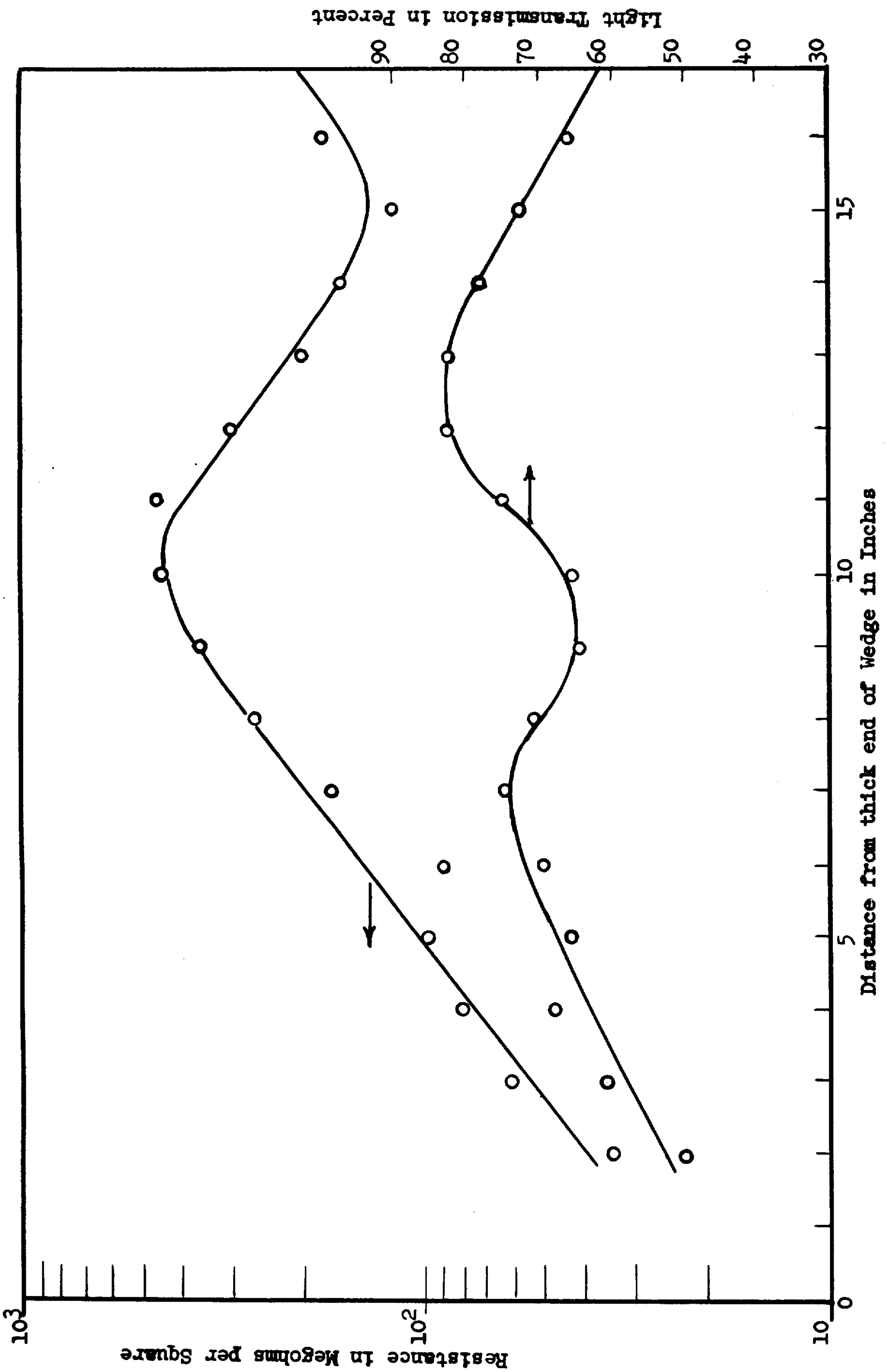
A number of special phosphors were obtained from a variety of sources, commercial and otherwise. Eight of these were evaporated, of which the film of the phosphor No. 6178A from New Jersey Zinc Company was found to be conductive. The resistance and transmission curves are shown in Figure 21. The peaks in the transmission curve are due to corresponding variations in the reflectivity with thickness, due to interference.

The peak in the resistance curve was noted on all six wedges made during the evaporation. Starting at the thick end of the wedge, which is the end nearer the boat, the resistance first rises with increase in distance, as expected. The decrease in resistance which follows may be due to decrease in the angle of impingement. Possibly, the phosphor deposit is laid down in the form of rods or scales which at low angles of impingement tend to lie on each other like roof-shingles, thus making better contact. As the distance from the boat increases, the decrease in density of deposit again becomes paramount, and the resistance therefore rises once more.

Other phosphors evaporated were L302A-1 from U.S. Radium; L2150, CT-5109, 0024 Fluorescent-2210, 0016 Fluorescent-2500 and 1150 Phosphorescent-2330, all from New Jersey Zinc; and 33-2-20A from R.C.A.

3.7 ADHERENCE - UNDERCOATING AND OVERCOATING

Although we found it possible to prepare by chemical methods films which adhere well to methacrylate, a number of the films deposited by evaporation, though otherwise fairly satisfactory, are fragile and easily abraded. This lack of



RESISTANCE AND TRANSMISSION CURVES
OF N. J. ZINC CO. 6178A PHOSPHOR WEDGE
IMMEDIATELY AFTER EVAPORATION

adhesion comprises a serious difficulty. We attacked the problem in accordance with the more or less standard methods; for instance, we solution-coated methacrylate with silica which adheres well and then washed with stannous chloride before evaporation-coating with silver. As is well known, washing glass with stannous chloride greatly improves the adherence of chemically deposited silver to the surface.

In general, we found that the metals yield the best products -- the metal oxides dissociate appreciably during the process and the sulfides and the organic compounds showed high resistivities. The difficulty is thus narrowed down to the problem of rendering metal deposits adherent.

A number of patents have been issued describing various means of improving metal film adherence (61,62,63). These patents claim the use of specific materials deposited as interlayers for the purpose of improving the adhesion of evaporated metallic films. The interlayer materials described consist of metallic oxides, sulfides, sulfates, etc., of which lead oxide is the most highly recommended.

We had already attempted to improve the adherence of platinum to methacrylate by depositing on both silica and titania as interlayers; these materials had been laid down from solution. In both cases, no improvement in adherence was perceptible. In accordance with the patent description we evaporated two milligrams of lead oxide (PbO) onto lucite. The deposit was invisible. A somewhat heavier deposit was evaporated onto lucite, previously coated with silica to simulate a glass surface. The heavier coating was applied in order to render it visible. It was found that the visible coating could easily be rubbed off, and that platinum deposited on this type of interlayer was also non-adherent.

As was pointed out above, these patents mentioned other metal oxides besides lead oxide. Also, the formation of an adherent interlayer by first depositing a metal and then oxidizing in the glow discharge was claimed. This procedure is similar to the interrupted evaporation of nickel which we described.

It is to be anticipated that adhesion to methacrylate and to glass should present different problems. Glass is comprised of groups which give rise to much stronger force fields than occur at the surface of the plastics. Consequently, almost any deposit should adhere more strongly to glass.

That this is not the whole story is evident from the fact that both silica and titania adhere very well to methacrylate. However, these films must age before they reach their maximum resistance to abrasion. It is likely that the strength of the film itself, in a direction parallel to the surface, is an important factor. If this is the case, then an evaporated film cannot be expected to be abrasion-resistant unless bonds between the deposited atoms are formed; in other words, unless the deposit crystallizes. Evidence for such crystallization comes from the observed increase in the abrasion resistance of silver films after heating.

The above does not account for the greater adherence shown by germanium than by selenium. However, the fact that germanium adheres well indicates that other films with desirable properties may also be found.

As a second line of approach to this problem, the possibility of modifying the methacrylate surface by means of chemical reagents was considered. This is the approach which has been used commercially in the so-called metallizing of plastics. Washing with stannous chloride solution, which we mentioned above, is a carry-over from mirror manufacture. Plastics of the phenol-formaldehyde, urea-formaldehyde, and cellulose ester types can be treated in a "bright dip" solution (a sulphuric-nitric-hydrochloric acid mixture) followed immediately by neutralization with 10% sodium carbonate. Treatment of cellulose esters with 5-10% caustic for 1-5 minutes has also been recommended -- also a short exposure to organic solvents such as 10% acetone.

Methylmethacrylate is an ester, so it is reasonable to infer that some of these reagents might, without impairing the transparency, modify the surface sufficiently to increase the surface field and improve adherence. The possibility of hydrolysis is particularly interesting since metal atoms such as sodium, or even silver might be incorporated into the molecular structure.

The principal difficulty with this approach stems from the fact that the carbon to which the ester group is attacked is quarternary. Under these conditions the ester group is split only with great difficulty and it would therefore be necessary to use very strong hydrolytic agents. The subject will be discussed in more detail in the section on polyelectrolytes.

The possibility of depositing transparent coatings over the evaporated metal films was considered as a means of protecting the metal films from abrasion. However, for an overcoating to be useful, it must not interfere with the discharge of static by the conductive film beneath.

To determine whether overcoatings oppose any appreciable resistance to the flow of current, a piece of copper-clad bakelite was first partially coated with titania and the resistance was measured. One flat metal contact was placed against the film and a second contact was placed against the bare metal. The measured resistance was found to be essentially equal to the resistance of the copper itself. It would seem that the titania film is so porous that the film interposes no resistance, or that the voltage applied in the measurement is great enough to cause dielectric breakdown. The resistance was measured with a vacuum tube voltmeter.

In a second experiment, the copper was coated with a transparent lacquer. The film was approximately one mil thick. When tested with metallic contacts, no current flowed until the applied potential was raised to 350 volts.

Measurements were then made with Acheson-Graphite Alkadag and with salt solution electrodes. With the Alkadag electrodes the measured resistance was approximately 300 ohms more than that of the copper sheet. With the salt solution, no additional resistance was observed. Evidently the lacquer overcoat is porous.

Several evaporated platinum films were lacquered. The abrasion resistance was markedly improved.

SECTION IV

POLYELECTROLYTES

4.1 INTRODUCTION

In preliminary tests, a transparent film of the ammonium salt of the co-polymer of maleic anhydride and styrene was found to be conductive. Again, the surface of a sheet of co-polymerized styrene and divinyl benzene became conductive when treated with concentrated sulfuric acid. These findings served as the stimulus for the initiation of a program of research into the properties of polyelectrolyte films.

The program activity, of course, included a study of the literature and discussions with manufacturers' representatives. In addition, we engaged as consultant Professor Charles Overberger, of the Polytechnic Institute of Brooklyn, a recognized expert in this field. Professor Overberger is Assistant Director of the High Polymer Institute, and has published some 35 papers in the fields of high polymers and organic synthesis.

We visited the laboratories of a number of companies engaged in the manufacture of polyelectrolytes, where we discussed our problem directly with the laboratory men working in the subject field. Dr. Raymond Fuoss, of Yale University, supplied us with important data concerning anionic-exchange materials. Based on the information obtained from these sources and from the literature (9,14, 26,38,41,55) we formulated a number of principles which served as the point of departure for the experimental program. These are:

1. Polyelectrolyte films, in order to be conductive must contain water (or some other effective ionizing medium).

2. The approach to conductive, permanent (that is, insoluble) films lies through one of the following paths:

    (a) Deposition of a soluble polyelectrolyte film followed by cross-linking to confer insolubility.

    (b) Deposition of a low-molecular weight nonpolar film which is first polymerized and cross-linked, and subsequently reacted to introduce ionizable groups.

    (c) Modification of the surface of the polymethyl-methacrylate as by hydrolysis of ester groups.

    (d) Deposition of a film of a solution of monomers on the surface, followed by co-polymerization. One of the monomers, or the solvent, should exhibit superficial attack on the acrylic substrate in order to confer adhesion.

3. As the degree of cross-linking is increased, first the solubility and then the tendency to swell in water will decrease. As the tendency to absorb water decreases, the conductivity will decrease.

4. The water absorption capacity can be augmented by the introduction of hydrophilic compounds into the film. Polyhydric alcohols are examples of such compounds.

5. The nub of the problem as set by statements 3 and 4 is to determine whether the range of cross-linking in which the resin is water absorptive, plasticizable and conductive, overlaps the range in which it is water-insoluble, so that a product may be obtained which is conductive and yet permanent.

6. Conductivity is expected to be a function of the concentration of ionizable groups, the concentration of water in the film, and the nature of the ionizable groups. This last condition refers to the "ionization constant" of the groups, and to the transport number of the ion or ions produced.

In addition, the following considerations apply:

1. A semi-permanent film which can be very easily applied and removed, should be useful, and should also be valuable for study. Waxy compositions which can be wiped on, and are relatively water-insoluble, are of particular interest.

2. Compounds which oxidize or decompose to give highly colored products must be avoided.

3. It will be necessary to devote special attention to the problem of securing adhesion without visible attack on the substrate.

This point turned out to be the most critical in the whole program. It appears that while excellent conductivity and transparency can be obtained with films of water-soluble materials, the adhesion of such films is poor. Within the limited period devoted to the study of polyelectrolytes, good adherence was obtained only with non-aqueous systems. The work on aqueous polyelectrolyte systems is therefore presented, primarily, so that the record will be complete.

4.2 MODIFICATION OF THE PLASTIC SURFACE

The ester grouping in polymethyl-methacrylate represents a region which theoretically is susceptible of alteration. If the ester linkage can be broken by hydrolysis, the resultant acid group should be ionizable. Furthermore, since it is anticipated that only the surface layer would be reacted, then only a relatively small part of each polymer chain would be modified, and the chain as a whole would still be water-insoluble.

To investigate this possibility, pieces of DuPont HC-202 (polymethyl-methacrylate) sheet were immersed in concentrated hydrochloric acid for varying periods of time, and then washed and dried. This treatment rendered the surface conductive; the conductivity was a fairly smooth function of the duration of the treatment. Although resistivities in the range of 1 to 0.01 megohms per square can be thus obtained, the effect is transitory; the conductivity disappears after several hours, and the surface is marred with a non-adherent white powdery thin film. In addition, interference colors are apparent on pieces which are immersed for 20 minutes or longer.

A number of the hydrochloric-acid treated samples were coated with lacquer, but the conductivity nevertheless disappeared after about the same length of time.

Alkaline hydrolysis is frequently more effective with esters than is acid hydrolysis. If the methyl groups are successfully replaced by sodium, the sodium can ionize to conduct. Also, a subsequent treatment with acid should remove the sodium and convert the resin to the acid form. This would also be expected to take place on contacting the sodium resin with water, in analogy with the behavior of cationic exchange resins.

Experimentally, we found that treatment of the plastic surface with concentrated caustic at room temperature and with 15% caustic at 80°C for several hours produced no effect, either visibly or as measured by the resistance meter. However, it is known that ester groups attached to quarternary carbons, as in methyl-methacrylate, are difficult to hydrolyze.

4.3 INTRODUCTION OF IONIZABLE GROUPS INTO INSOLUBLE RESINS

The sulphonated styrene-divinyl benzene ion-exchange resins represent possibly the best example of the introduction of ionizable groups into an insoluble resin. These resins are now in commercial production, and a great deal of study has been devoted both to the polymerization process and to the method of introducing the sulphonic acid group.

Styrene and divinyl benzene co-polymerize in all proportions and at the same rate, so that the degree of cross-linking achieved corresponds closely to the original composition. It is known that the surface of the sample, when polymerized in air, is generally not so completely polymerized as the interior, due to the effect of oxygen upon the reaction mechanism. As a result, there was some question as to whether films of satisfactory properties could be prepared, since the bulk of the material is so close to the surface.

We found that films ranging in thickness from a few tenths of a mil up to several mils could be prepared by pre-polymerizing in bulk before casting on the substrate. The films were cast only after the viscosity of the liquid had visibly increased. Some difficulty was noted during the curing of the films, that is, the rate of cure was low, even with one per cent benzoyl peroxide catalyst, and cloudiness in the film was occasionally noted. The use of ultra-violet light to catalyze the polymerization was of some assistance in eliminating the cloudiness. At the conclusion of the cure, the films were resistant to toluene, indicating that at least some cross-linking had taken place.

From our experimental work, it appears that sulfonation of the film takes place readily either with concentrated sulfuric acid or with the acid plus 0.1% of silver sulfate as catalyst. However, two undesirable side effects occur. In the first place, the acrylic substrate is attacked, and becomes opaque. Treatment of uncoated acrylic gives exactly the same result, so that there is no question but that the opacity is a result of attack on the acrylic surface. It seemed possible that an increase in the extent of cross-linking would decrease the porosity of the film, and thus protect the substrate. This was not our finding.

Secondly, some depolymerization evidently takes place during the sulfonation, since the sulfonated film is removed by the water wash which follows the immersion in the sulfuric acid bath. It is possible that gentler sulfonation methods might eliminate both of these difficulties; a particularly interesting possibility is the use of sulfur trioxide in dioxane as the sulfonating agent.

Some consideration must also be given to the possibility that the film is not so well polymerized as we have assumed. Our polymerizations were carried out in air, under which condition oxygen can function as an inhibitor (13). However, in the one polymerization carried out in nitrogen, no perceptible improvement was noted.

4.4 POLYACRYLIC ACID FILMS

A solution of polyacrylic acid when cast on polymethylmethacrylate and oven dried at 100°C yielded a film which was non-conductive, even in humid atmosphere. However, when two to five percent of a number of materials such as glycerol, propylene glycol or lactic acid were added to the solution and the deposits were dried under controlled conditions, the resultant films were found to be conductive and relatively tack-free. The resistivities were, of course, dependent on thickness and humidity, but in general ranged from two to thirty megohms per square. Where the film was dried too intensively, exposure to the air for a short while brought the conductivity to the range described.

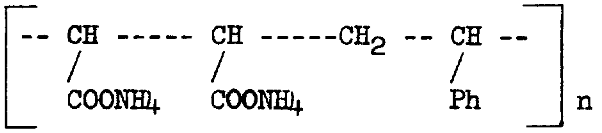
Wetting of the substrate during casting, and adhesion after drying, were extremely poor, even when substantial amounts of a wetting agent, Carbide and Carbon Tergitol 08, were included in the composition. In fact, dip-coated films could not have been prepared if one side of the plastic had not first been roughened. We should be inclined to regard this difficulty as a subsidiary problem, except that it is likely to crop up with all strongly polar materials. Deposition from non-aqueous solutions will probably be necessary. This obviously cannot be done unless the polyelectrolyte is soluble in non-aqueous solvent.

In an attempt to circumvent this requirement, acrylic acid was polymerized on the surface of the sheet. Two types of acrylic acid were used, Rohm & Haas 60% solution in water, and Goodrich Chemical glacial. The acid was also co-polymerized with ethylene di-maleate. Only a slight improvement in adhesion was obtained.

4.5 FILMS OF THE AMMONIUM SALT
OF STYRENE-MALEIC ACID COPOLYMER

We described above our first work with the ammonium salt of the styrene-maleic acid copolymer. We had been informed that this material, originally water-soluble, becomes insoluble by imide formation, upon heating. We therefore considered the possible mechanism of this reaction.

The resin, initially, is of the form:



$$\left[\;--\underset{\displaystyle COONH_4}{\underset{/}{CH}}-----\underset{\displaystyle COONH_4}{\underset{/}{CH}}-----CH_2--\underset{\displaystyle Ph}{\underset{/}{CH}}--\;\right]_n$$

and the ionizing group is - $COONH_4$. On heating, this group should lose water and go over to the amide - $CONH_2$. The amide group does not ionize, but is hydrophilic. The resin in this stage should be non-conductive, and should absorb water with consequent swelling.

On further heating, two amide groups should lose ammonia and imidize as follows:

$$- CONH_2 + - CONH_2 \rightarrow - CONHCO - + NH_3$$

This reaction is not reversible, since the ammonia goes off as a gas.

Experimentally, we found that the ammonia salt of the copolymer, when cast from water solution and dried at 60°C, is not conductive. The addition of a few percent of glycerol, propylene glycol or lactic acid, renders the dried film conductive. Thus, 7% of glycerol gave a film with a resistivity of 8 megohms per square, after 15 minutes drying. In the drying process, at this stage, only the water of solution is removed. The added alcohol undoubtedly functions as a humectant, so that the film, although apparently dry, nevertheless holds some water; this water is the ionizing medium.

The film, at this stage, swells in water, and eventually goes into solution. When heated for fifteen minutes at 80°C, the resistivity rises to 200 megohms per square, although the extent of swelling, when in contact with water, is still severe.

Baking for 15 minutes at 100°C increases the resistivity beyond the range of the meter; the film nevertheless swells strongly. Treatment at 125°C eliminates the sensitivity to water completely. Also, the film cracks up and peels away from the substrate during the bake.

These experimental results correlate closely with the theory. The film after drying at 60°C is evidently still in the ammonium salt stage. After drying at 80°C, the fall in conductivity is probably due only to removal of the dissolved water. The properties of the film after treatment at 100°C correspond to the amide stage, and after treatment at 125°C, to the imide form. Complete confirmation of this theory can be established by determining whether the conductivity phenomena are reversible at each stage by treatment with water. However, we have found that exposing the film of the last stage to a humid atmosphere does not restore conductivity.

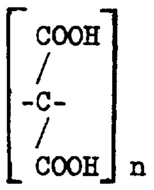
Evidently, the completely imidized film is useless for our purposes, but the imidization reaction is of potential value since it takes place at moderate temperatures, and since it can render the resin insoluble. A possible approach to the utilization of the reaction would be to start with the partially neutralized resin, ammonia again constituting the base. Half-neutralization would be excessive since all of the groups would once more be involved in imide formation by the following mechanism:

$$2\ RCOOH + NH_4OH \rightarrow RCOOH + RCOONH_4$$
$$RCOONH_4 + heat \rightarrow RCONH_2$$
$$RCONH_2 + RCOOH + heat \rightarrow RCONHCOR$$

The required degree of neutralization must then be less than half. What this would be in terms of free acid groups per unit weight is derived in the following paragraphs.

Workers in the resin field, particularly those manufacturing condensation resins, customarily measure the free acid content in terms of the acid value or acid number. This is defined as the number of milligrams of potassium hydroxide required to neutralize one gram of resin. Now, one equivalent of acid will neutralize 56.1 g of KOH. If b is the number of equivalents of acid in one gram of resin, then the acid number will be a.n. = b x 56.1 x 1,000 = 56,100 b.

Restricting ourselves for the present to carboxyl compounds, the polymer with the highest conceivable acid number is

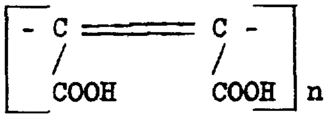


$$\left[\begin{array}{c} COOH \\ / \\ -C- \\ / \\ COOH \end{array}\right]_n$$

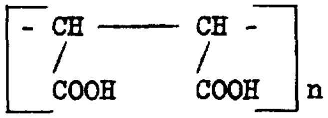
The acid number for this material is

$$\frac{2}{102} \times 56{,}100 = 1{,}100$$

Two more hypothetical compounds of high acid number are



a.n. = 984



a.n. = 966

The following table shows the acid numbers of some available compounds:

Polymer	Acid Number
Polyacrylic acid	780
Polymethacrylic acid	653
1:1 Styrene-maleic acid copolymer	510
Commercially available condensation resins	5-50
Specially formulated condensation resins	260-290

We have already established that polyacrylic acid with an acid number of 780 is conductive. If the conductivity is, as we expect, a function of the acid number, then the styrene - maleic acid copolymer should not be seriously inferior. To find the effect of the addition of ammonia, consider an n-mer, (that is, a polymer consisting of n units of the simplest repeating structure) of the above composition. The mer weight is 220, the n-mer molecular weight is 220 n, and the number of equivalents of acid is 2 n, since maleic acid is dibasic. Assume this n-mer is reacted with m molecules of ammonia to form m imide groups.

Each ammonia reacts with two carboxyls to cause a net weight loss of 2 x 45 - 71 = 19 units.

The acid number then becomes

$$\frac{2n - 2m}{220n - 19m} \times 56{,}100 = \frac{2 - 2m/n}{220 - 19m/n} \times 56{,}100$$

The quantity, m/n, is the moles of ammonia per mole of mer. Also, it is twice the fraction of neutralization. The following table shows the effect of the fraction of neutralization on the acid number as calculated from the above formula.

Fraction of Neutralization	Acid Number
0	510
0.05	464
0.10	415
0.15	366
0.20	316
0.25	267

The table has not been extended to greater degrees of neutralization, since it is unlikely that a greater degree of cross-linking will be necessary to render the resin water-resistant.

A batch was treated with dilute ammonium hydroxide to neutralize 10% of the acid groups. When heated to effect the imidization, the film cracked and peeled from the substrate. This approach was therefore abandoned. Nevertheless, the method could be useful if an adherent, water-soluble polyacid is found.

It should be noted that the pure acid form of the copolymer is relatively insoluble in water. Otherwise, a series of these resins at various degrees of neutralization would constitute an excellent test group for the study of the relationship between acid number and conductivity. Possible methods of avoiding the solubility difficulty are discussed below.

We have confined ourselves to carboxyl groups in this discussion because the available materials of greatest promise at the present time are carboxylic. Making allowance for the variation in acid strength in passing to sulfonic or phenolic groups, the same principles can be applied.

4.6 IMIDIZATION

We have already pointed out that the imidization reaction can be used to insolubilize the styrene-maleic acid copolymer. This reaction could theoretically serve for any linear polymer with more than two carboxyl groups per chain. The resin would be partially neutralized with ammonia and then heated as described above.

So far as the styrene-maleic anhydride resin, in the acid form, is concerned, it is possible that the solubility difficulty referred to could be avoided as follows:

Start with the half-sodium salt of the resin; this material is water-soluble. Add the desired quantity of ammonia. Cast the film and heat to imidize and thus insolubilize. Then wash the sodium out of the product exactly as if it were an ion-exchange resin. It remains to be seen whether the dimensional changes which take place during these operations will destroy the film.

A second, and much simpler, possibility is that the acid form of the resin may go into solution when only partially neutralized with ammonia.

4.7 VINYL ADDITION

The addition of divinyl benzene to styrene to form a cross-linked resin has already been described. The addition of mono-olefinic compound to chains containing more than one vinyl group can also be used to insolubilize the composition, provided some means of forming the chains without consuming olefin groups is available.

This technique is exemplified in the styrenated alkyds. The chains are formed by condensation of dihydric alcohols with dibasic acids. The dibasic acids consist partially of olefinic compounds such as maleic or fumaric acid. Although unsaturated, neither of these acids can polymerize alone. However, they do form so-called hetero-polymers with styrene. To make use of this property, the alcohol-acid mixture is heated until the condensation has progressed as far as desired, and styrene is then added to cross-link the chains.

A commercial formulation of this type was disclosed to us during a conference with one of the large resin manufacturers, with the suggestion that it be used as a starting point for research in this field.

Propylene glycol, to the extent of 6.3 moles, 4 moles of phthalic anhydride and 2 moles of maleic acid are heated to 190°C under nitrogen. Condensation is continued until the acid number falls to 45. The resin is cooled to 120°C, at which point 0.02% of tertiary butyl catechol is added. At 80°C, 1 part of styrene, for each two parts of the above, is added rapidly with stirring. To polymerize, the mixture is heated to 80° - 100°C with 1% of benzoylperoxide.

We had planned to control the acid number by limiting the degree of condensation. However, we found that the initial condensation proceeds so rapidly that it is difficult to obtain a useful degree of control of the acid number by this means. This result is in agreement with published work (4,7,27,28) in which curves are presented which show that the initial stages of the reaction are completed in a short time. It is possible that some control can be achieved by lowering the temperature at which the condensation is carried out, but it seems to us that modification of the reaction mixture seems more likely to give the desired result.

In line with this view, suppose that 2 moles of maleic acid are first condensed with ethylene glycol. The average composition of the mixture would correspond to ethylene dimaleate. Assuming this were copolymerized with styrene in the ratio of 1:2, the resultant acid number would be 310. The resin produced would be cross-linked, since the ethylene dimaleate is tetrafunctional, and would therefore be insoluble. Since it would be polymerized after casting, whatever additives would be considered desirable would have to be introduced into the composition before casting. It should be noted that the temperature at which polymerization by vinyl addition takes place is much lower than that required for condensation by esterification. Consequently, a glycol added to the mixture just before vinyl polymerization would not be esterified, and would subsequently function as a humectant. Also, the temperature of addition polymerization is within the upper limit which the plastic substrate can tolerate, whereas the temperature of rapid esterification is not. As a result, cross-linking by esterification is not likely to be a useful method of insolubilization.

Again, a small quantity of ethylene dimaleate, or EDM, could be copolymerized with maleic anhydride and styrene to cross-link the product and render it insoluble by the same mechanism. If EDM is insoluble in the reaction mixture, then a condensation-product of glycol and maleic acid of somewhat higher molecular weight could be used. The average size of the condensate molecule could be controlled by fixing the ratio of acid to glycol.

It is expected that the amount of EDM or homologue needed would be small enough so that the acid number of the copolymer would not fall materially below 510, which is the value for the straight styrene-maleic anhydride adduct when converted to the acid form.

As still another approach to the problem of preparing an insoluble styrene-maleic anhydride, divinyl benzene could be used as the cross-linker. The problem of mutual solubility during the polymerization would be eliminated, since styrene and divinyl benzene are miscible in all proprotions. Furthermore, the polymerization rates of these compounds are equal (3,10); consequently, it should be easy to control the composition of the product.

These various possibilities were tested with results given below.

It was found that as the fraction of unesterified carboxyl groups was increased that incompatibility with styrene or divinyl benzene appeared before any measurable conductivity was developed. Also, when citric acid was used as part of the total acid, the resultant resin was non-conductive and brittle. However, these resins, when clear, were also adherent to the acrylic sheet.

Although ethylene dimaleate has proved to be too polar for use in styrene resins, it may be valuable for other applications. EDM should have an appreciable water solubility and therefore might be useful as a cross-linker for polymerizations in aqueous solutions. A particularly interesting application would be for use with vinyl sulfonic acid. The product should be much more acidic than acrylic acid hetero-polymers.

4.8 WAXES

The polyethylene diamines, insofar as they are water soluble, fall within the category of polyelectrolytes. The polyethylene glycols, while not exactly polyelectrolytes, still can function as humectants and thus possess conductivity. Both materials add hydrogen chloride, the amine to form salt and the glycol to form a coordination complex. The products are in both cases conductive. However, in order to reach the desired level of conductivity, the film must be thick enough to be visible; at such a thickness, the waxy character of the product interferes with optical clarity.

A considerable number of derivatives were examined, in the hope that blends of the waxes might be sufficiently free of crystallinity to afford unimpaired transparency. Materials investigated included mono- and di-oleates and mono- and di-stearates of polyethylene glycols, the glycols ranging in molecular weight from 400 to 4,000. Similar amine products were also blended. Films were applied by brushing, from hot-melt and from solution. Sal and a variety of low-molecular weight organic acids, as well as mineral acids, were added as electrolytes.

The degree of conductivity obtainable, particularly with hydrochloric acid as the adduct was very satisfactory, but in no case was the transparency adequate.

4.9 CONDUCTIVE INCLUSIONS

Polymethyl-methacrylate potentially could serve as the carrier "solvent" for an electrolyte provided that a soluble electrolyte can be found. In the first experiment, an attempt was made to dissolve a small quantity of sulfuric acid in a solution of polymethyl-methacrylate in acetone. Precipitation occurred immediately upon adding the first drop.

Sulfuric acid was then dissolved in acetone before addition to the acrylate solution. The sulfuric acid solution darkened rapidly, but could be added to the acrylate solution without causing precipitation. The acrylate solution was then cast on acrylic sheet. After drying, the film was found to be conductive, but the conductivity disappeared after washing the film. It therefore appears that the acid migrates to the surface during the drying process and does not remain in the acrylic to any useful extent.

Similar results were obtained with phosphoric acid, mono- and dichloroacetic acid, and toluenesulfonic acid. Inclusion of trichloroethylene in the formulation, and pre-softening of the acrylic in trichloroethylene, were also of no use. Isophorone was added in two separate experiments in the attempt to hold toluenesulfonic acid and sulfuric acid in solution. Washing in these cases did not so rapidly eliminate the conductivity, but the films produced were dark in color.

The final group of experiments in this series consisted of addition of the various acids to monomeric methyl methacrylate, followed by polymerization with benzoyl peroxide as catalyst. Polymerization generally took place, at least to some extent, but in all cases the acid was rejected and could easily be removed by washing. The lack of conductivity in the film, following the washing operation, was the basis for this conclusion.

The first important step forward was taken with the discovery that considerable quantities of the compound, monobutyl acid ortho-phosphate, $C_4H_9OP(OH)_2O$, were miscible with monomethyl-methacrylate over a wide range of proportions. However, the polymerized film was found to be tacky.

Polymerizations were then carried out at temperatures from 60°C up to 110°C in nitrogen and in air with the same results. It was suspected that the tackiness was due to loss of monomer by evaporation during the cure, as a result of which the phosphate concentration increased to excessive values. To test this, a slide was weighed, coated with a film of catalyzed monomer and phosphate, rapidly reweighed and then placed in a 60°C oven. After 30 minutes, the slide was removed and weighed once more. The weight loss indicated that 90% of the monomer had evaporated.

In order to decrease the loss, the cure was carried out at 30 C, using a redox system consisting of tertiary butyl hydroperoxide and thiourea. A second redox system consisting of dimethyl aniline and benzoyl peroxide was also investigated. In both cases the improvement was negligible.

The addition of cobalt naphthenate, a standard paint dryer, also failed to effect any improvement.

The furnace used for the polymerizations consisted of a metal can 9" long by 3" in diameter, wound with nichrome resistance wire on a layer of asbestos. The furnace was also fitted with thermometer and nitrogen inlets, a nitrogen outlet and a removable lid. With such a small furnace, it seemed that it might be feasible to saturate the atmosphere with monomer and so decrease the rate of evaporation from the slide. To effect this, an open container of monomer was placed in the furnace and allowed to come up to temperature before inserting the coated slide.

Some increase in retention of monomer on the slide was noted, but rather than try to improve the degree of saturation of the atmosphere and tightness of the furnace, etc., a conclusive step was taken, namely, polymerization in a sealed tube.

This variation in technique demonstrated immediately that even with one per cent of peroxide the rate of polymerization is low at 60°C. At this temperature, approximately 3 hours are required for conversion to a solid. Even at 80°C, 2 hours and 20 minutes are needed. Twenty-two minutes are required at 98°C.

A series of sealed-tube polymerizations showed that up to 60 parts of phosphate could be included with 40 parts of methyl-methacrylate monomer without retarding the polymerization or causing separation. At this composition, the product is soft, rubbery, and completely transparent, and permanently conductive.

The tubes used for the test were 6 mm i.d. The tubes were only about half-filled and were heated in a horizontal position. As a result, the cross section of the final pieces was approximately a semi-circle. Electrode points placed 1 cm apart on the flat surface gave a resistance reading of about 1 megohm. After washing in running water for several minutes, the resistance dropped to 0.2 megohms, but quickly returned to 1 megohm as the piece dried by evaporation. It therefore appears that the phosphate is uniformly distributed in the polymer and cannot be removed by washing. This is substantiated by the mechanical properties of the polymer referred to above.

The resistivity of the piece was measured at progressively lower temperatures. The following table shows the values obtained.

Table 9.1

Resistivity of 60% Phosphate Polymer vs Temperature

Temperature in °C	Resistivity in Megohms
24	1.05
0	1.3
-35	8.9
-45	20
-65	60

These data show that as the temperature is lowered, the resistance rises very slowly at first, and even at -65°C is not prohibitively great.

A few experiments were run to get some indication of the relations among phosphate content, resistance, and flexibility.

Table 9.2

Resistivity as a Function
of Butyl Acid Ortho-Phosphate Content

Percent Butyl Acid Ortho-Phosphate	Resistivity in Megohms	Mechanical Condition
10	High	Strong
20	High	Brittle
35	17	Fairly flexible
40	3.5	Flexible
43	3.5	Flexible
47	1.5	Flexible
54	1.5	Very flexible

According to Table 9.2, a content of about 40% best meets the requirements. The values measured are apparently bulk resistivities; actually, most of the resistance is at the electrodes, so that the measured resistivity of a film would probably not be very different. Also, it is to be expected that adherence would be good, since both components are good solvents for the acrylic sheet.

A number of materials related in structure to the phosphate were also tested, but were found to be insufficiently compatible with the methacrylate monomer. The compounds examined were dimethyl acid pyrophosphate, benzene phosphinic acid, and benzene phosphoric acid. It need hardly be pointed out that this list is far short of comprehensive.

Within the subject of conductive inclusions can be included powdered conductive solids in a matrix. The commonest conductive powder used is graphite. We dispersed graphite in a lacquer and cast a film which was then dried. The transparency was inadequate at the desired conductivity. It has now become apparent that the principal fault with the technique was the vertical separation of the graphite particles. This separation decreased the conductivity without affecting the opacity.

A second possibility is the use of powdered tin oxide in a transparent matrix. We laid down a film of this oxide in a plastisol. The film was definitely conductive, but, of course, was opaque. This was due not only to the absorption of the plastisol, but to the fact that the indices of refraction of the two materials are different.

A better matrix would be a mixture of silica and titania in a ratio such as to have the same index of refraction as the tin oxide. Such mixtures have been prepared, and close control of the index is possible. One method of preparing the composite film might be to disperse the tin oxide in a solution of the tetra-alcoholates of silicon and titanium, cast, hydrolyze and cure as described above.

We have also considered the possibility of flame-spraying the tin oxide and then filling in any residual porosity with the silica-titania solution.

CONCLUSIONS

Metallic films on polymethyl methacrylate sheet with the requisite conductivity and with light transmittances of approximately 80% can be prepared by vacuum evaporation. Ruthenium and platinum yield the most stable films. Resistance to abrasion is poor, but can be greatly improved by overcoating with lacquer. The combination has a resistance, as measured with probes, which is only slightly greater than that of the metallic film itself.

Silver films become more abrasion-resistant with age and with moderate heating.

Films of metals such as titanium and nickel, although usually considered resistant to oxidation, nevertheless show a rapid increase in resistance on exposure to air.

Pure germanium films show fair conductivity at relatively low light-transmissions. It is possible that the introduction of selected impurities into the film might result in a substantial increase in conductivity.

The deposition of metal oxide films by vacuum-evaporation is difficult because of thermal decomposition of most oxides at the temperatures and pressures used in the evaporation process. As a result, the metal, rather than the metal oxide, is deposited.

Films of silica and titania which are hard, abrasion-resistant and transparent, can be laid down on acrylic sheet from alcohol solution of the metal alcoholates. Although the films are non-conductive, the finding is of importance because it indicates that films of stannic oxide similar to those used commercially on glass for conduction should also be producible in this way. Transparent films of the tin alcoholate and the hydrated tin oxide have been prepared but thus far no low temperature method of converting them to the electrically conductive oxide form has been found.

Only thermal and liquid phase methods of effecting the conversion have been investigated in this study. In view of the known conductivity and transparency of tin oxide films, the extension of the investigation to include other methods would appear to be one of the most desirable lines along which to extend the study.

Satisfactory optical and electrical properties are exhibited by films of polyelectrolytes deposited from water solution. Lacquer coatings can be used to protect the polyelectrolyte film from atmospheric water. However, it appears to be a general rule that films laid down from water solution do not adhere well to the acrylic substrate.

In general, films laid down from solutions which contain components which attack the acrylic substrate superficially will exhibit good adherence. The ionizable groups upon which conductivity depends can be introduced into the film as part of the polymer comprising the film-forming constituent or as part of a plasticizer in the film. The monobutyl ester of ortho-phosphoric acid has been found to possess desirable characteristics in the role of plasticizer.

Based on the results obtained in the severely limited period which could be allocated to this phase of the investigation, it is our opinion that the field of ionizable materials, soluble in solvents which attack polymethyl methacrylate, constitutes the most promising area for further investigation. We wish further to emphasize that the excellent optical properties and adhesion of solution-deposited silica and titania films should make them very useful for optical purposes, such as reflectance-reduction, and beam-splitter applications.

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APPENDIX I

MEASUREMENT OF SURFACE RESISTIVITY

I.1 ASTM METHOD

The ASTM gives a standard test for measuring the resistance of electrical insulating materials. The test is designated D-25746. In this method, the surface resistivity is defined as the ratio of the potential gradient in volts per unit distance parallel to the current flow along the surface, to the current in amperes per unit width of surface. It is numerically equal to the surface resistance between two electrodes forming opposite sides of a square. The size of the square is immaterial.

Although the size of the square is itself irrelevant, it is nevertheless necessary that the dimensions of the enclosed area be known. A number of methods have been devised for the purpose of insuring good contact over a known length. The method prescribed in the ASTM procedure calls for the use of guard rings enclosing mercury pools. Another method occasionally used involves clamping the test piece between pieces of soft metal which conform to the surface of the specimen. Good contact can seemingly be made by these methods, but there are objections to both. The mercury technique is both laborious and hazardous (mercury vapor is toxic). The contact between a metal and a semi-conductor frequently has so high a resistance due to so-called "barrier layer" effects (40) that the resistance as measured is essentially the resistance of the contact rather than that of the semi-conductor. Furthermore, these methods are difficult to use on curved surfaces, such as plastic canopies.

I.2 BALCO METHOD

Two stripes of conductive silver paint are applied one inch apart on the surface of the test specimen, and allowed to dry. A jig has been prepared to receive the coated and silver striped test piece and to hold it in an atmosphere of controlled humidity while the surface resistivity is measured. Figure 22 shows the apparatus.

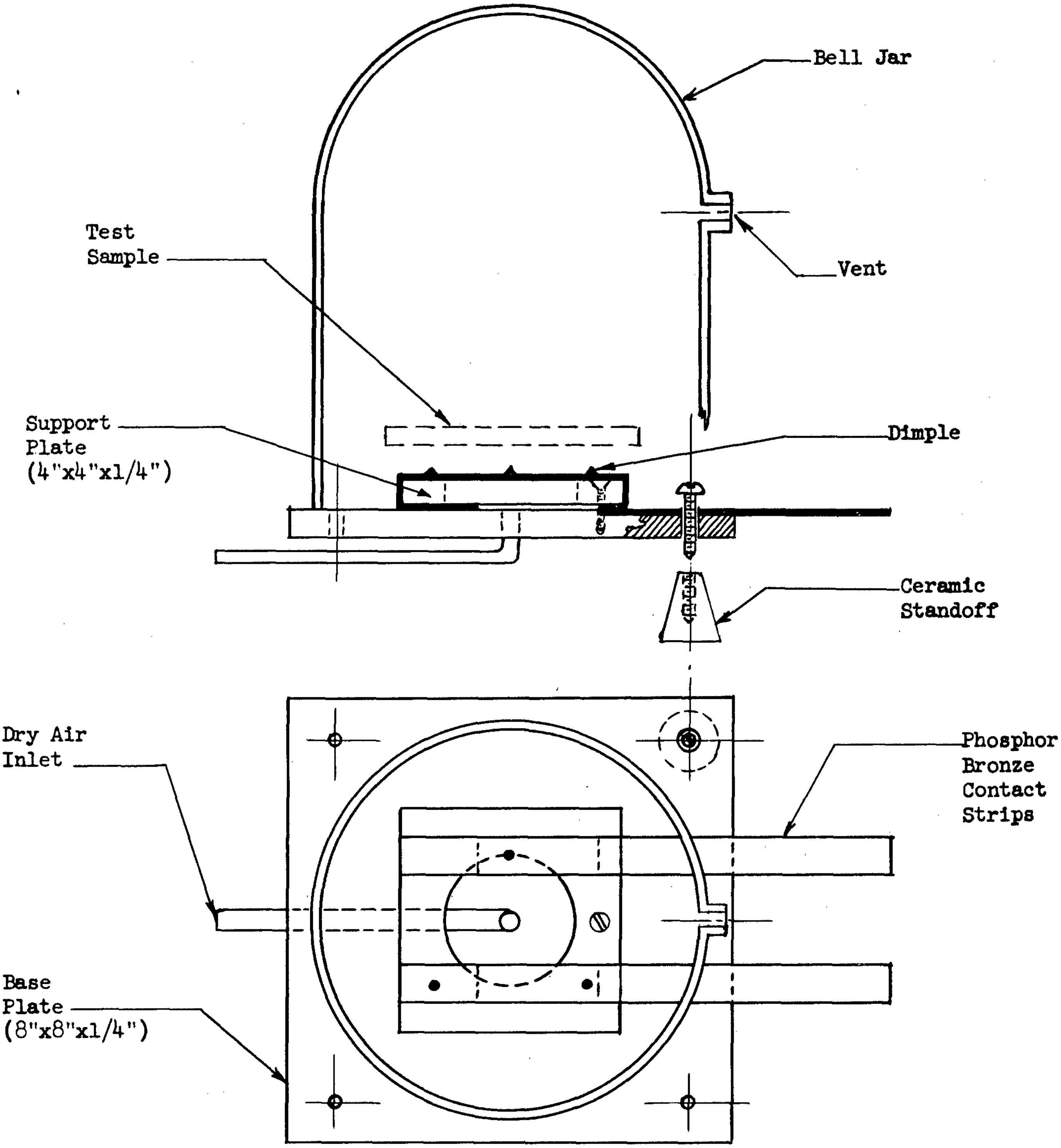

FIGURE 22

JIG FOR MEASURING SURFACE RESISTANCE
OF A SILVER ELECTRODED SAMPLE

The bottom plate is supported by three legs approximately one inch high. Through a hole bored in the bottom is inserted a copper tube carrying air, the humidity of which can be adjusted. The support plate which is centered directly over the air inlet is four inches square and has a center hole two inches in diameter. Fastened to the support plate are two phosphor-bronze strips into which are punched three dimples, (two dimples in one strip and one in the other). The test specimen is then placed coated side downwards on the phosphor strips so that the dimples form a three-point support for the test piece, and make good contact with the silver stripes. A bell jar with a small vent near the top is placed over the specimen and conditioned air is then passed through the jar.

Leads from the strip contacts pass under the edge of the bell jar and are so arranged that they can be brought either to an electronic voltmeter or to a Leeds and Northrup galvanometer, both of which possess ample sensitivity so that resistances in the range of 0.2 to 500 megohms can be measured.

Since the test pieces are 2 inches square and the silver stripes are only one inch apart, the enclosed area is 2 x 1. The silver contact lengths are thus twice as long as the distance through which the current must travel. To convert the result to resistance per square, the instrument reading must therefore be multiplied by two.

In a later modification, described in the text, strips of foam rubber coated with conductive silver paint are substituted for the phosphor bronze strips. The painted silver stripes on the sample are then unnecessary.

The onset of conduction, in general, could be determined by painting silver electrodes on one of the samples and attaching clips before dropping the bell jar over the assembly. The clips, in turn, were attached through "lead-outs" to a vacuum-tube-voltmeter outside the jar. Where the temperature of vaporization was sufficiently high, electron emission from the boat or the charge resulted in erratic readings. For the more easily volatilized metals, the conductivity could readily be followed during the evaporation.