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RESEARCH FOR LOW-APPLICATION-TEMPERATURE ELECTRICALLY CONDUCTING, TRANSPARENT COATINGS FOR AIRCRAFT WINDSHIELDS AND RELATED COMPONENTS

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FOREWORD

This report was prepared by Battelle Memorial Institute under Supplemental Agreement No. S4(56-406) to USAF Contract No. AF 33(616)-2467. The contract was initiated under Project No. 7312 "Finishes and Materials Preservation", Task No. 73125 "Transparent Conducting Coatings for Aircraft Materials". This project was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with J. R. Cannon and R. Besancon acting as project engineers.

This report covers a period of work from December 1, 1955, to November 30, 1956.

The present project, aimed at fulfilling the objectives outlined above, is a continuation of the work done at Battelle on Contracts Nos. AF 33(616)-342 and AF 33(616)-2467, and reported in Wright Air Development Center Technical Reports 54-325 and 54-325, Part 2.

ABSTRACT

This report describes a continuation of the studies described in WADC Technical Report 54-325, Part 2.

Transparent, conducting films on glass were prepared by simultaneous evaporation of indium and tin and subsequent thermal oxidation of the metal films in air at 150 to 200°C. Films with resistance as low as 17 ohms/square and transmittance as high as 88 per cent were prepared. Representative specimens had values of 50 to 100 ohms/square and 80 per cent transmittance. Greater reproducibility of film properties was attained as a result of the use of improved techniques and equipment and studies of the effect of varying the process parameters.

Large panels (9 x 9 inches) were filmed, using a rotating substrate and a small source located off the axis of rotation. The transmittance and resistance varied only slightly over the surface. The variation can be reduced by relocation of the source.

A study of magnesium fluoride and silicon oxide overcoatings was made in an attempt to increase the transmittance of the conducting films and to confer mechanical protection. Transmittance increases as high as 13 per cent were obtained. The hardness of the overcoatings approached but did not exceed that of the conducting films.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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RESEARCH FOR LOW-APPLICATION-TEMPERATURE, ELECTRICALLY CONDUCTING, TRANSPARENT COATINGS FOR AIRCRAFT WINDSHIELDS AND RELATED COMPONENTS

INTRODUCTION

In the interest of promoting flight safety, a transparent, high-conductivity coating is required for the removal, by electrical heating, of fog, frost, and ice formations on the interior and exterior areas of glass windshields and side panels of aircraft. This coating must have a resistance no greater than 100 ohms/square. Quarter-inch plate glass coated on one side must have a light transmittance of at least 85 per cent and a haze value no greater than 1 per cent. The coating must be capable of dissipating 1500 watts/square foot to a moving air stream. The coating must be applicable to precision-ground glass at temperatures below the annealing temperature of the glass, to avoid warping.

In previous studies at Battelle on Contract No. AF 33(616)-2467 (Wright Air Development Center Technical Report 54-325, Part 2) transparent, conducting films of indium oxide on glass were prepared by thermal oxidation (at 121 to 204° C) of evaporated and sputtered indium films. Tin was added to the films to decrease their electrical resistance. Tin-doped films were prepared with resistance as low as 50 ohms/square and with optical transmittance of 75 to 80 per cent. The electrical properties of the films under load were found to be within specifications.

The work described in this report is a continuation of the above studies, and was performed under Supplemental Agreement No. S4(56-406) to Contract No. AF 33(616)-2467. The work consisted of three phases, as follows: Phase 1. Further refinement of the coating process to obtain accurate reproducibility and improved optical and electrical properties. Phase 2. Extension of the coating process to accomplish uniform coating of 9-inch-square panels; all knowledge gained under past contracts and under the current studies of Phase 1 was to be utilized. Phase 3. Development of a low-reflectance overcoating to increase the transmittance and to enhance the coating durability.

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SUMMARY AND CONCLUSIONS

Refinement of Deposition Process

Since several months had elapsed since the completion of the work described in WADC Technical Report 54-325, Part 2, a few films were prepared using the same equipment and techniques to insure that the earlier results could be duplicated. The films were found to be similar to those prepared in the course of the previous studies.

Several modifications were made in the equipment and procedure for coating small plates, for the purpose of obtaining greater reproducibility. A new dual evaporation source was designed and constructed. It is similar to the one used previously, but is modified to give more efficient heating and to prevent shorting of electrical leads. Since the molybdenum source oxidizes, forming an oxide on the surface of the molten metal, stainless steel Type 309 (a high-chromium steel) was tried as a source material. It oxidized more heavily than the molybdenum. Subsequently graphite was found to be a suitable source material, since it forms no oxide film. A shutter and monitor plate were installed between the source and the substrate. These additions permit adjustment of the evaporation rate to the desired value, as determined by measurement of the resistance of the monitor plate, before the substrate is exposed to the metal vapor. Controllers were installed to permit accurate control of source temperature. In addition, provision was made for measuring the conductance instead of the resistance of the film during evaporation. Since the conductance is proportional to the thickness (if the resistivity is constant), the evaporation rate can be monitored more accurately than previously.

It was found that elimination of organic contaminants from the vacuum system used for evaporation is extremely important. Decomposition products from diffusion pump oil and from plastic insulation were found to have a deleterious effect on film properties.

It was found that "good" films, that is, films with resistance below 100 ohms/square and with high optical transmittance, could be prepared with tin concentrations ranging from about 3 per cent to about 15 to 20 per cent by weight, based on total metal. Concentrations outside this range were not studied. There is no apparent correlation between tin concentration and final film properties, although the films containing higher tin concentrations convert more easily. Some films containing 3 to 5 per cent tin were not completely converted, even after several days at a temperature of 200°C.

Since the evaporation rate-temperature curves for indium and tin diverge, the tin concentration in the films prepared from concentric-ring

sources is dependent on the source temperature and, therefore, on the evaporation rate. Four films prepared at different rates from one source were found to have tin concentrations ranging from 4.4 to 7.4 per cent.

The best films which have been prepared to date have been those which were evaporated to a resistance below 10 kilohms/square. However, good films have been prepared by evaporating to a resistance as high as 10 megohms/square.

Films were made using oxygen pressures of 0.5, 1, and 2 microns to determine the effect on film properties. Good films were made at all three pressures. One film prepared in air at a pressure of 5 microns had low transmittance and rather high resistance after conversion.

A study of the effect of variation of evaporation rate on the properties of films indicated that rates can be varied over a wide range with little or no apparent effect on final film properties. It was confirmed that the initial evaporation rate must be slow. However, good films were prepared using higher initial rates than was thought feasible previously.

A few films were prepared on Plexiglas II UVA plastic. Conversion at 104° C was very slow, but gave films comparable with companion films on glass. The scatter in the data, as a result of poor deposition control, makes interpretation of the results difficult. Subsequently, several films were prepared on Plexiglas 55. Companion films were made simultaneously on glass. Films on plastic were converted at 100°C, those on glass at 220°C. The films on plastic were not converted completely, even after 34 days. However, those with higher tin concentration (15 to 20 per cent) were more nearly converted than were those with 9 per cent. The best film on plastic had a resistance of 270 ohms/square and an optical transmittance of 66 per cent after 24 days conversion at 100°C. It is probable that use of higher tin concentration would increase ease of conversion on plastics.

Previous studies (WADC Technical Report 54-325, Part 2) showed that conversion of indium films in oxygen at high pressures resulted in films which were extremely transparent, but also of very high resistance. Reconsideration of these studies led to the conclusion that, if the conversion process was greatly accelerated by the increased concentration of oxygen atoms at the surface, possibly complete conversion to the oxide may have occurred, resulting in a decrease in metallic impurity centers and, hence, an increase in resistivity. However, if the concentration of oxygen at the surface were controlled properly, possibly the conversion could be accelerated without the danger of overconversion. Studies were conducted, therefore, on conversion at increased pressures with air and oxygen atmospheres. In oxygen at a pressure of 2 atmospheres, the rate of conversion of indium films at 100°C was increased by a factor of 2 to 3 over the rate in air at 1 atmosphere.

The effect of the angle of incidence was studied to determine whether or not the impinging metal vapor must be directed normal to the substrate to achieve the desired film properties. An angle of incidence up to 45 degrees from the normal had no effect on the conversion rate or on the resultant film properties.

The distribution of metal from a small cup source was measured by coating a 9-inch glass strip mounted so that its center was 15 centimeters above the source. The source was completely filled with indium to minimize directional effects of the source. After conversion, the film varied in resistance from 370 ohms/square at the center to 1600 ohms/square at the ends (4-1/2 inches from the center). The optical transmittance was approximately 80 per cent over the entire strip.

Experiments were conducted on the simultaneous evaporation of indium and tin from an alloy source. Obviously, if a single source could be used much of the complication in a production apparatus for coating large areas would be eliminated. It was found that good films could be prepared from an alloy source. However, the composition of the alloy melt changes during a run, as a result of the difference in the evaporation rate between the two metals. Although this effect may not cause significant changes in the composition and properties of the evaporated film, it presents a serious control problem for production use. Use of a large-volume source would minimize the effect; however, problems would arise with dissipation of heat.

To retain the advantages of the alloy source, a concentric-ring source was constructed which has a single heater, but has the indium and tin in separate compartments. The rate of evaporation of each metal, and hence, the film composition, may be varied by varying the sizes of the compartments, and hence, the evaporation areas of the two metals. The concentric-ring source proved to be satisfactory, and was used for all subsequent work.

A large concentric-ring source, 9 inches in diameter, was constructed for use in filming large panels. The source was unsatisfactory, because excessive substrate temperature resulted from radiation from the large-area source.

Since the large source was unsatisfactory, a study was made to determine the feasibility of coating large panels from a small source, with a rotating mask or sector interposed between the source and substrate to permit uniform deposition. Films prepared in this manner were nonuniform, probably because of temperature gradients on the film. However, it is probable that the method could be developed so that satisfactory films could be produced.

Subsequently, a rotating-substrate technique was employed, with the source located off the axis of rotation. Films with resistance values from 50 to 150 ohms/square and with high transmittance were prepared by this method. The transmittance and resistance varied only slightly from the center to the edge of the substrate. This variation can be reduced by relocation of the source.

Antireflective Coatings

A study of overcoatings was made in an attempt to increase the transmittance of the indium oxide films and to confer mechanical protection to the films.

Overcoatings of magnesium fluoride and silicon oxide were deposited by evaporation. Transmittance increases as great as 13 per cent were obtained. The hardness of the overcoatings approached but did not exceed that of the conducting films.

Three films were sent to American Optical Company for application of their antireflective coating No. 157C-50, which is applied by a wet-chemical technique. After coating, the specimens had "infinite" resistance. Apparently, the conducting film was removed by the process.

Testing

Load Test

More extensive testing of the tin-doped indium-oxide films has been reported previously (see WADC Technical Report 54-325, Part 2). One film prepared recently was load tested. A 4-inch-square section was cut from one of the 9-inch panels for the test. Because of a limitation of the power supply, the plate was operated at a continuous power dissipation of 1300 watts per sq ft for 150 hours (instead of the desired 1500 watts). The plate was cooled during the test by a stream of fast-moving air. The temperature remained below 120°C throughout the test. The resistance increased from 80 to 98 ohms in about 10 hours and remained at this value during the remainder of the test. No other adverse effects were observed.

Abrasion Test

The abrasion resistance of several films was determined by means of an eraser test*. The load on a 3/8-inch diameter eraser was varied from

* Military Specification JAN-F-675.

0.5 to 2.2 lb. Wide variability in the results was noted. Some of the films showed a slight change in reflected color after 20 cycles with the 2.2-lb load. In other cases, it was necessary to decrease the load to 0.5 lb to prevent visual evidence of scratching. Films which were overcoated with silicon oxide, although seemingly as abrasion resistant during the early portion of the test, showed considerably more scratching at the conclusion of the test with 2.2-lb load. It appeared that some of the overcoat material was transferred to the eraser and, subsequently, served to accelerate the wear. With a 0.5-lb load, the overcoated films were satisfactory.

EXPERIMENTAL DETAILS AND DISCUSSION

Refinement of Deposition Process

Orientation Studies

Several months had elapsed since the completion of the studies described in WADC Technical Report 54-325, Part 2. Therefore, a brief orientation study was conducted to insure that the previous work could be duplicated before attempting the refinement of the process and development of techniques for coating large panels.

Films were prepared by evaporating indium from a molybdenum source. The process parameters were those used previously, that is, a source-to-substrate distance of 15 cm and an oxygen pressure of 0.5 micron. The source temperature was raised slowly, to give a very slow initial rate. The total evaporation time was 60 to 90 minutes. The films were converted in air at 177° C, a temperature intermediate between the temperatures 149° C and 204° C used previously. The properties of the films are given in Table 1, along with those of some films prepared previously. It may be seen that the two sets of films are similar.

Equipment and Procedure Modifications

Several modifications were made in the system used for deposition of indium films to improve film uniformity and control of production conditions.

Evaporation Sources. A new dual evaporation source was constructed. It is similar to the one used previously (see WADC Technical Report 54-325, Part 2), but with modified dimensions and method of support. The diameter of the indium (or tin) reservoir was increased from 3/8 inch to 17/32 inch. The greater evaporation area permits preparation of films with greater

TABLE 1. COMPARISON OF PROPERTIES OF In_2O_3 FILMS PREPARED DURING PRESENT AND PREVIOUS WORK

Film	Resistance After Evaporation, kilohms/square	Conversion Temperature, °C	Resistance After Conversion, ohms/square	Transmittance, per cent
		New Films		
097-65A	7.5	177	420	70
097-68A	10.5	177	122	55
097-70A	3.0	177	480	75
		Old Films		
9507-66	4.9	149	370	70
9507A	10.5	149	590	69
9507-70	6.6	149	290	68
9507-95	7.7	204	240	76
9507-90A	15.0	204	195	65

uniformity of thickness, as can be seen from the interference colors of the films. The over-all height of the source was decreased from 1-3/8 inches to 1-5/64 inches, and the over-all diameter was increased from 17/32 inch to 3/4 inch. As a result of the increased height-to-width ratio, the efficiency of heating the reservoir is improved, so that less heat is radiated to the substrate. Measurement of substrate temperature during the preparation of several undoped indium films showed that the temperature remained below 38° C in all cases.

The two sources are supported in wells in a Vycor plate. The plate shields the thermocouple and filament leads from the evaporated metal, thus preventing electrical shorts which were a problem when the steel support was used.

In previous studies, it was observed that an irregular film forms on the surface of the molten metal. Apparently, this film tends to prevent metal evaporation, thereby making control difficult. The film was assumed to be, at least partially, oxides of molybdenum. In an attempt to overcome this difficulty, a source made of Type 309 stainless steel (a high-chromium steel) was tested. The source corroded badly, and formed an even heavier film on the indium. An undoped film prepared with the steel source had a resistance, after conversion, of 1200 ohms/square. Subsequently, graphite was tried as a source material. This change resulted in a decrease in film formation on the molten metal. In addition, since the molten metals do not wet the graphite, there is no tendency for the metals to creep out of the crucible and short out the thermocouples, as is the case with molybdenum crucibles.

Subsequently, a concentric-ring source, in which the indium and tin are in two reservoirs heated by a common filament, was designed. The source is described later in this report. This type of source proved quite satisfactory, and was used for most of the later work.

A source of difficulty in previous work was failure of the tungsten filaments, both by burning out and by embrittlement and consequent breakage. In attempts to alleviate this difficulty, filaments of tantalum and of platinum-10 per cent rhodium were tried. The tantalum embrittles worse than tungsten, and the platinum-rhodium sags so that adjacent turns of the coil touch and fuse together. Consequently, use of tungsten filaments was continued. However, it was found that the greater efficiency of the new source permits operation of the filament at a considerably lower temperature, so that filament failure is less frequent.

Saturable-reactor-type stepless controllers were installed to control the source temperatures. The controllers hold the source temperature within about 1 degree C of the set temperature and permit much more precise control of the evaporation process.

Shutter and Monitor Plate. The properties of indium oxide films are sensitive to the rate of deposition of the metal, particularly during the first few minutes of the deposition. To permit more precise adjustment of the initial rate, a shutter and monitor plate were added to the system. The shutter consists of an aluminum plate, hinged on one edge, which may be held in a horizontal position by a catch or allowed to drop under its own weight to a vertical position by releasing the catch by means of a rotary vacuum seal. When in the horizontal position, the shutter is under the substrate so that the substrate is shielded from the source. The monitor plate (a glass plate similar to that used for the substrate) is attached to the bottom of the shutter. The bus bars on the plate are connected to an external conductance-measuring device. In operation, the deposition rate is adjusted to the desired value, as indicated by the rate of change of conductance of the monitor plate. The shutter is then released, so that the substrate is exposed to the metal vapor.

Conductance-Measuring Device. Previously, the rate of deposition of the film was followed by measuring the film resistance during evaporation. During this contract period, equipment was installed to permit measuring the conductance of the film instead of the resistance. Since the conductance is proportional to the film thickness (if the resistivity is constant) this modification permits more accurate monitoring of the deposition rate. In addition, the equipment is capable of measuring higher resistance (i.e., lower conductance) than the ohmmeter used previously, so that the initial evaporation rate can be controlled more precisely. The apparatus consists of a battery, a Millivac microammeter, and suitable switches, connectors, and shielding. The meter, battery, and the film are connected in series, so that the current through the film, as indicated by the meter, is proportional to the film conductance. A conductance change of 10^{-10} mho (that is, a resistance change of 10,000 megohms) is detectable in the early stages of the deposition.

Elimination of Contamination. The first few films prepared after installation of the conductance-measuring equipment had final resistance values of about 500 ohms to 4 kilohms/square. It was found that the difficulty was caused by contamination from decomposition of plastic insulation in the shielded cable connecting the conductance-measuring equipment. The insulated cable was removed and the system was cleaned thoroughly. Films made subsequently had normal properties. Later in the investigation it was found that a similar difficulty was caused by contaminated diffusion pump oil. Diffusion pump oil oxidizes slowly in service, producing volatile products. Apparently these products have a deleterious effect on film properties, even if the contaminants are in such low concentration that a normal ultimate vacuum can be obtained in the vacuum system. Elimination of contamination from the system resulted in considerably improved reproducibility of film properties.

The Effect of Tin Concentration on Film Properties

To determine the effect of tin concentration on film properties, films were prepared, using concentric-ring sources, with tin concentrations ranging from about 3 to 18 per cent by weight, based on total metal. There appears to be little or no correlation between final film properties and the tin concentration in this range, except that the conversion time is long for films with low tin concentration. Some films containing 3 to 5 per cent tin still had low optical transmittance (25 to 40 per cent) even after several days of conversion at 200 to 220°C (392 to 428°F). On the other hand, films containing 15 to 20 per cent tin converted to high transmittance (in excess of 75 per cent) in a few hours. Resistance values at the same stage of conversion were comparable in both cases.

The Effect of Source Temperature on Tin Concentration

The evaporation rate-temperature curves for indium and tin are divergent; hence, the tin concentration in the films is dependent on the source temperature and, therefore, on the evaporation rate. A study was made to determine the magnitude of this effect. Four films were prepared at different evaporation rates; a concentric-ring source designed to give films containing about 5 per cent tin was used. Analysis of the films showed a range of tin concentrations from 4.4 to 7.4 per cent. The results are shown graphically on Figure 1. On this figure the tin concentration is plotted against the final evaporation temperature (the source temperature at the end of the evaporation run). The source temperature, and therefore the evaporation rate, is increased continually throughout the evaporation period. Since the evaporation rate at the end of the run is 3 to 4 orders of magnitude greater than the initial rate, most of the film is deposited near the end of the run. Hence, the final evaporation temperature is the predominant factor in determining the tin concentration in the film. Although the change in tin concentration with final evaporation temperature is large, as may be seen from Figure 1, the variation probably is not serious, since, as was discussed in the preceding section, the final film properties are not highly sensitive to tin concentration.

The Effect of Evaporation Resistance on Film Properties

A series of films was prepared with a wide range of final evaporation resistance (the resistance at the end of the evaporation period) to determine the effect on film properties. "Good" films were prepared with final evaporation resistance from 2 kilohms to 10 megohms per square. However, the best films were evaporated to a resistance of 10 kilohms per square or less. The results of the studies are presented in Table 2. All films were prepared under essentially the same conditions, using a concentric-ring source designed to give a tin concentration of about 15 to 20 per cent. It

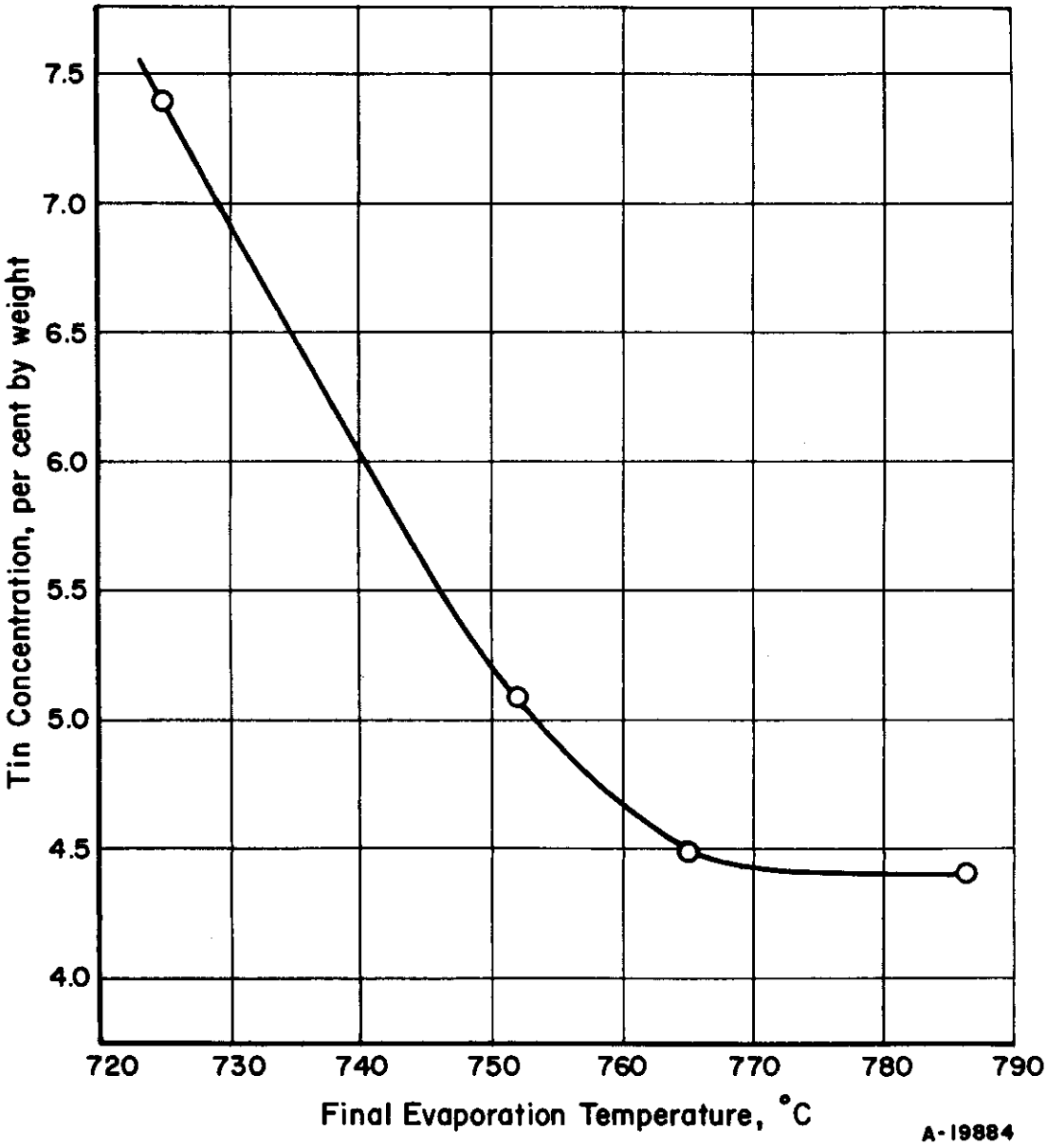

FIGURE 1. TIN CONCENTRATION AS A FUNCTION OF FINAL EVAPORATION TEMPERATURE

may be seen from the table that Film 290-4A, which was evaporated to 10 megohms per square, had a somewhat higher optical transmittance than the films evaporated to lower resistance. Also, this film had a slightly higher resistance after conversion, but not so great as might be expected in view of the high final evaporation resistance. These characteristics were observed for other films as well; films evaporated to high resistance, of the order of 10 megohms, have unusually high optical transmittance, but may have final resistance values below 100 ohms per square.

TABLE 2. PROPERTIES OF FILMS EVAPORATED TO DIFFERENT FINAL EVAPORATION RESISTANCE

Film	Evaporation Resistance, kilohms/square	Resistance After Conversion, ohms/square	Transmittance After Conversion, per cent
290-8A	2	33	80
290-8B	2	19	80
290-7B	10	31	80
290-6A	100	57	80
290-6B	100	83	79
290-5A	1,000	67	80
290-5B	1,000	77	79
290-4A	10,000	93	85

The Effect of Oxygen Pressure on Film Properties

Films were made using oxygen pressures of 0.5, 1, and 2 microns, to determine the effect on film properties. As may be seen from Table 3, good films were made at all three pressures. Higher pressures were not used because the life of the hot-cathode ionization tube is short at higher oxygen pressures. One film prepared in air at a pressure of 5 microns had low transmittance and rather high resistance after conversion.

There is some advantage in using oxygen pressures greater than 0.5 micron. At this pressure, which appears to be in the neighborhood of the lower limit for good film preparation under the conditions which have been studied, a small amount of outgassing or leakage may cause the actual oxygen pressure to be significantly lower than is desirable, since the measured pressure is the total pressure rather than that of the oxygen alone. At higher oxygen pressures (greater than 2 microns), higher source temperatures must be used, because scattering of the metal beam by the oxygen reduces the rate of film formation for a given temperature. Thus, higher substrate temperatures result from the use of higher oxygen pressures. For filming plastics, which must be kept at low temperatures, this factor may be of importance.

TABLE 3. PROPERTIES OF FILMS EVAPORATED AT DIFFERENT OXYGEN PRESSURES

Film	Oxygen Pressure, microns	Resistance After Conversion ohms/square	Transmittance After Conversion, per cent
938-86A	0.5	75	81
938-84A	1	92	82
938-90A	2	79	85
938-100A	5 (air)	140	56

Several films were made for which the oxygen was admitted to the vacuum system after the deposition had been started. There was no apparent difference between the properties of the films and those of films prepared in the usual manner.

The Effect of Evaporation Rate on Film Properties

Several films were prepared with various evaporation-rate schedules to determine the effect on film properties. In general, the evaporation rate is not held constant during the preparation of a film, but is raised continually throughout the run in such a way that the film conductance doubles about every 5 minutes. This procedure is used to shorten the over-all evaporation time. For the rate study reported here, two sets of films were prepared in the usual manner, that is, with continually increasing rate. Thus, for these films, only an instantaneous rate or the time required to reach a given resistance has significance. A third set of films was prepared using constant evaporation rates. The results for the first set of films are presented in Table 4. The films were evaporated to 100 kilohms per square at an oxygen pressure of 1 micron from a source giving 9 per cent tin, except for Film 290-12A which was evaporated at an oxygen pressure of 2 microns from a source giving 15 to 20 per cent tin. With the exception of one film (938-96A) evaporation times to reach 30 megohms per square ranged from 1 to 33 minutes, and total evaporation times (to reach 100 kilohms/square) ranged from 24 to 75 minutes. There is no obvious correlation between the initial or over-all evaporation rate (in these ranges) and the final film properties. Film 938-96A was prepared at an extremely high rate (a total evaporation time of 3 minutes). This film had high resistance, as was expected.

In a further attempt to correlate film resistance with evaporation rate, the data for a second set of films prepared from sources designed to give 5 and 18 per cent tin were examined. For this set of films, instantaneous rates rather than evaporation times were considered. Rates were studied

TABLE 4. PROPERTIES OF FILMS EVAPORATED AT DIFFERENT RATES

Film	Evaporation Time, minutes: To 30 Megohms/Square	Evaporation Time, minutes: To 100 Kilohms/Square	Resistance, ohms/square	Transmittance, per cent
938-90A	33	72	79	85
938-81A	30	75	63	88
938-92A	20	30	82	80
938-88A	20	65	62	81
938-94A	8	29	102	81
290-12A[a]	7	24	92	86
938-97A	1	60	58	80
938-96A	1	3	480	86

(a) Made from source giving about 15 to 20 per cent tin, at oxygen pressure of 2 microns. All others from source giving 9 per cent tin, at oxygen pressure of 1 micron.

for three stages of the deposition, the "initial rate" (the average rate during the period in which the film resistance changed from 100 megohms to 33 megohms per square), an "intermediate" rate (the instantaneous rate at the time the resistance reached 1 megohm per square), and the "final" rate. The results are shown graphically on Figures 2, 3, and 4. For films containing about 5 per cent tin there is no obvious correlation between evaporation rate and final resistance. For films containing about 18 per cent tin, the data indicate that the final resistance increases with increasing initial rate, as may be seen from Figure 2. However, the scatter in the data is large. As may be seen from Figures 3 and 4, there is no apparent correlation of final resistance with "intermediate" or "final" evaporation rate.

The third set of films was prepared from a source giving 15 to 20 per cent tin. Constant evaporation rates were used, such that metal films with resistance of 100,000 ohms/square were achieved in 30, 60, and 120 minutes. In the 30-minute run, a poor film was produced (> 1500 ohms after conversion), whereas in the 60- and 120-minute runs, good films were produced. Although the slow evaporations (60- and 120-minute runs) did show an improvement over the fast evaporation (30-minute run), it is of greater significance that all of these rates are several orders of magnitude faster than was previously considered feasible for the initial rate. Since previous studies indicated that the evaporation rate may be increased after the initial period of the run, the present work suggests that total evaporation time might be shortened appreciably.

Further study of the effects of evaporation rate on film properties is needed, particularly for high initial evaporation rates.

Preparation of Films on Plastics

A few tin-doped films were prepared on Plexiglas II UVA early in this report period. The data for these films are given in Table 5, along with data for films on glass prepared simultaneously. Films with similar numbers were prepared together. Three of the films were evaporated from the separate tin and indium sources described earlier in this report, so that the tin concentration of the films is not known. Also, deposition-rate control was poor for these films, because of difficulty in measurement of source temperatures. Therefore, there is wide scatter in the data. One film was evaporated from an alloy source (to be described in a later section). Conversion was difficult for the films, even at 149° C. This fact suggests that there is little or no tin in the films.

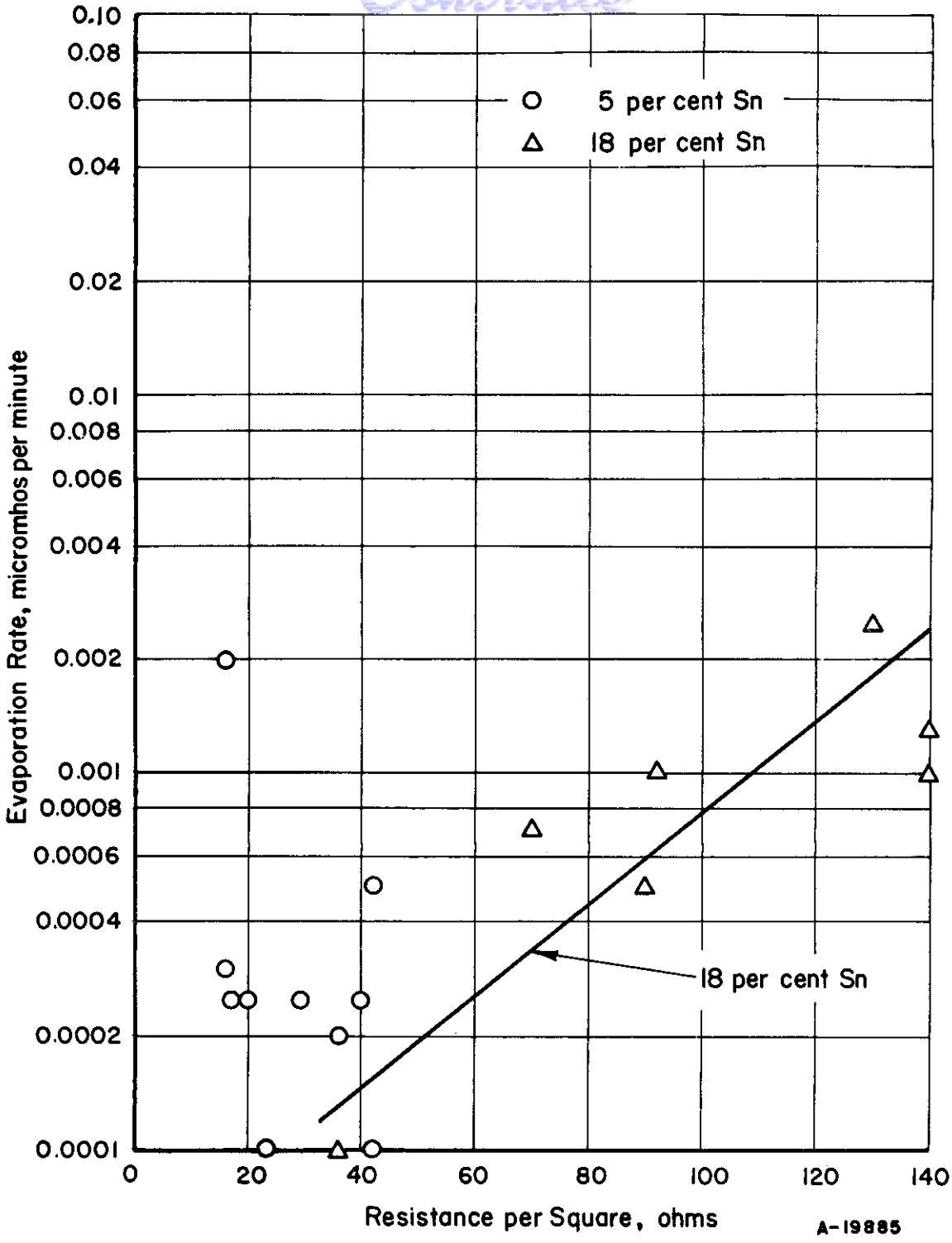

FIGURE 2. FILM RESISTANCE AS A FUNCTION OF INITIAL EVAPORATION RATE

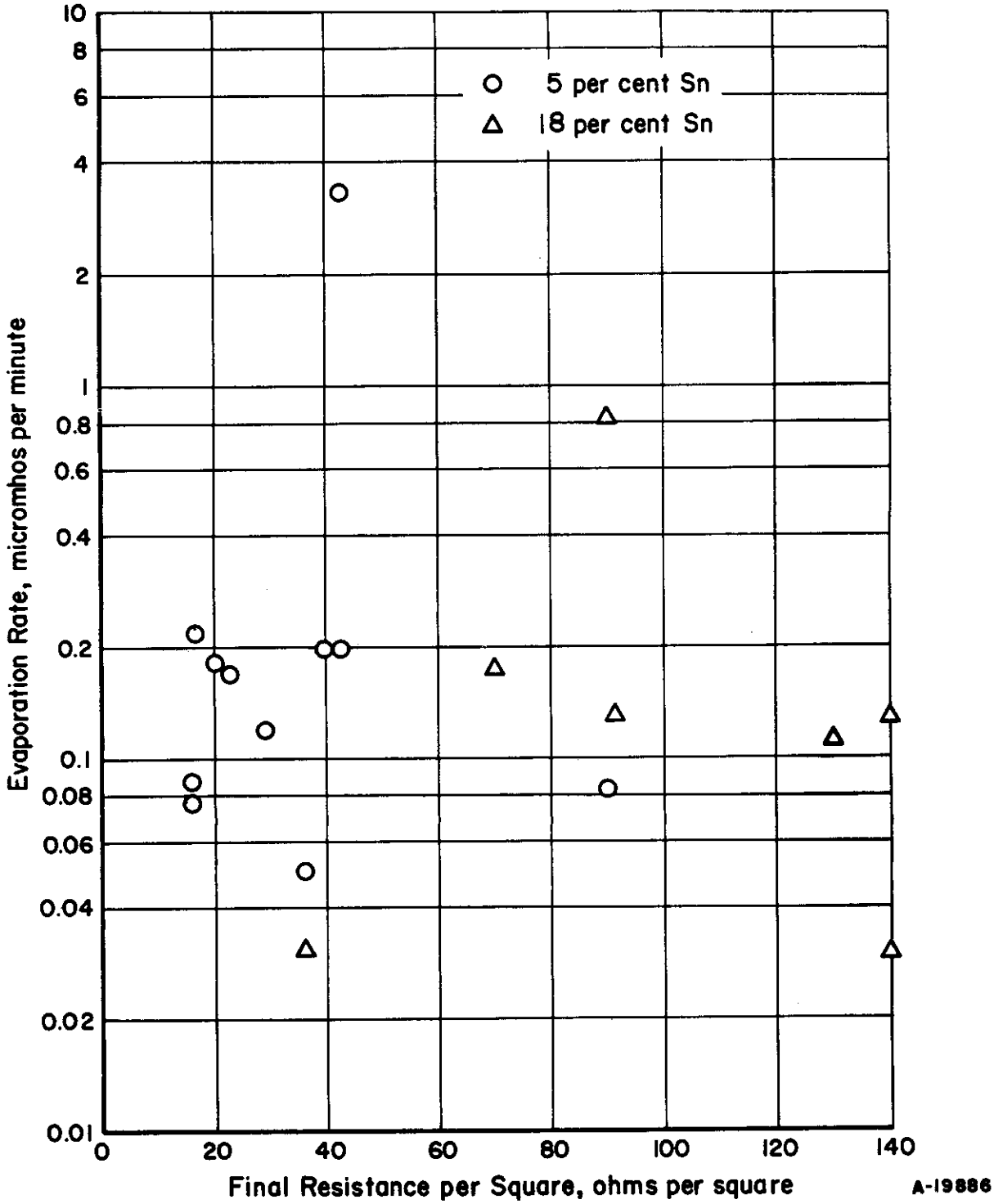

FIGURE 3. FILM RESISTANCE AS A FUNCTION OF EVAPORATION RATE AT 1 MEGOHM PER SQUARE

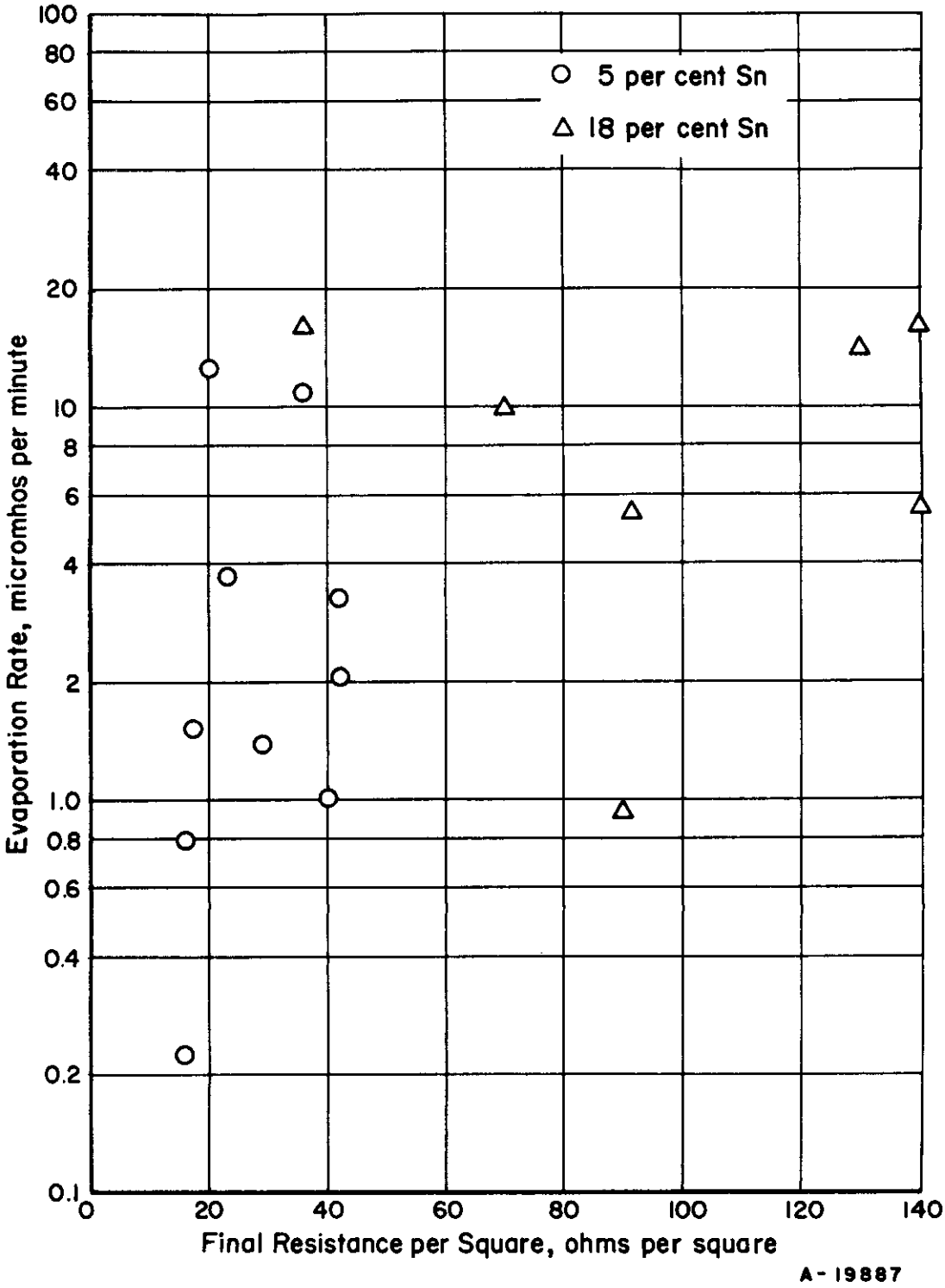

FIGURE 4. FILM RESISTANCE AS A FUNCTION OF FINAL EVAPORATION RATE

TABLE 5. PROPERTIES OF FILMS ON GLASS AND PLEXIGLAS II UVA

Film	Substrate	Evaporation Resistance, kilohms/square	Conversion Temperature, °C	Resistance, ohms/square	Transmittance, per cent	Conversion Time, days
321-86	Glass	5.0	104-204(a)	600	66	13
321-86A	Plastic	--	104	480	53	13
821-89	Glass	5.0	149-204(b)	270	49	11
321-89A	Plastic	--	104	135	40	11
321-91	Glass	2.5	149-204(b)	1350	75	8
321-91A	Plastic	--	104	380	64	8
362-4B	Glass	7.9	104	230	55	3.2
362-4A	Plastic	--	104	220	50	3.2

(a) Raised to 204°C at end of 9 days. Values at this time were 290 ohms per square and 61 per cent. Values for Film 321-86A at same time were 330 ohms per square and 52 per cent.

(b) Started at 149°C; later raised to 204°C.

All the films on plastic were converted at 104°C. Two of the companion films on glass were converted at 104°C, two at higher temperatures. For the pairs converted at 104°C, the resistance and transmittance of the glass and plastic specimens are similar. For the other pairs, the films on glass have higher resistance and transmittance as a result of the additional conversion at the higher temperature. The adherence of the films on plastic appears to be as good as that of films on glass, as indicated by rubbing with a pencil eraser.

Subsequently, a number of films were evaporated simultaneously on Plexiglas 55 and on glass, from concentric-ring sources giving 9 per cent and 15 to 20 per cent tin. All films were evaporated to 100 kilohms per square. The films on plastic were converted at 100°C (212°F), and those on glass at 200°C (392°F). The properties of the films are summarized in Table 6. Films with identical numbers followed by "A" and "B" were prepared simultaneously. No films on plastics were converted completely at 100°C, even after 34 days. At 200°C the companion films on glass were essentially completely converted in a few hours. The best film prepared on plastic to date is Film 290-1B. After 24 days' conversion at 100°C, this film had a resistance of 270 ohms per square and an optical transmittance of 66 per cent. It may be seen from the table that the films containing 15 to 20 per cent tin had higher transmittance (45 and 66 per cent) than did the 9 per cent films (26 to 37 per cent) after conversion. Possibly, a still greater tin concentration would permit complete conversion of films on plastics.

Films 938-60A and B, both on glass, were prepared simultaneously to determine the effect of converting at low temperature. The "B" film, converted at 100°C, had a resistance of 610 ohms and optical transmittance of 29 per cent after 29 days. On the other hand, the "A" film, converted at 200°C, had a resistance of 75 ohms per square and transmittance of 81 per cent after 90 minutes. It is conceivable that the resistance of the "B" film would decrease to below 100 ohms per square if the conversion were continued for sufficient time to reach high transmittance. However, such conversion time would be prohibitive.

Plexiglas 55 was not damaged by conversion at 100°C for more than 30 days. CR 39 crazes and discolors slightly when held at 100°C for 24 hours. Sierracin 611 turns deep yellow after 24 hours at 100°C.

Effect of Air Pressure and Oxygen Concentration on Conversion Rate

Because of the low rate of conversion of films at low temperatures, a study was made to determine the feasibility of increasing the rate by increasing the oxygen concentration in the conversion atmosphere. Previous studies (WADC Technical Report 54-325, Part 2) had shown that conversion

TABLE 6. PROPERTIES OF FILMS ON GLASS AND PLEXIGLAS 55[a]

Film[b]	Substrate	Resistance, ohms/square	Transmittance, per cent	Conversion Time
938-81A	Glass	63	88	5 Hours
938-81B	Plexiglas 55	400	30	34 Days
938-82A	Glass	62	85	3-1/2 Hours
938-82B	Plexiglas 55	330	30	31 Days
938-83A	Glass	40	Dirty	5 Hours
938-83B	Plexiglas 55	850	37	31 Days
938-88A	Glass	62	81	140 Minutes
938-88B	CR 39	4000	26	8 Days
290-1A	Glass	150	68	90 Minutes
290-1B	Plexiglas 55	270	66	24 Days
290-2A	Glass	100	78	100 Minutes
290-2B	Plexiglas 55	470	45	22 Days
938-86A	Glass	75	81	90 Minutes
938-86B	Glass[c]	610	29	29 Days

(a) Films on plastics converted at 100°C, those on glass at 220°C.

(b) Films with 938 numbers prepared from source giving 9 per cent tin; those with 290 numbers from source giving 15 to 20 per cent tin.

(c) Converted at 100°C.

under pressure resulted in high-resistance, high-transmittance films. However, it seems probable that the films were overconverted so that the concentration of excess-indium impurity centers, and therefore of charge carriers, was decreased. Possibly, conversion at high pressure and low temperature would give good films. In the present study, undoped indium films were used to avoid variability in results from variation in tin concentration. The metal films were placed in a small brass pressure chamber which was heated in an oven at about 100°C. The chamber was equipped with electrical lead-throughs to permit continuous measurement of temperature and resistance during conversion. The films were removed from the chamber after they had attained minimum resistance.

In the initial experiments, films were converted in air at pressures of 1 and 2 atmospheres. The scatter in the data is too great to permit drawing conclusions on the effect of increasing the pressure. Subsequently, a comparison was made of the rate of conversion of films prepared simultaneously in air at a pressure of 1 atmosphere and in oxygen at 2 atmospheres (an oxygen-concentration ratio of 1 to 10). The results are shown in Table 7.

TABLE 7. CONVERSION OF INDIUM FILMS IN AIR AND OXYGEN

Film	Evaporation Resistance, kilohms/square	Atmosphere	Pressure, atmospheres	Resistance, ohms/square	Transmittance, per cent	Time to Reach Minimum Resistance, minutes
362-18A	9	O_2	2	850	64	50
362-18B	9	Air	1	1200	69	150
362-22A	5	O_2	2	695	64	50
362-22B	5	Air	1	775	64	102

It may be seen from the table that the time required to attain minimum resistance in oxygen was 1/2 and 1/3 the time in air for the two pairs of films. The differences in final resistance may be significant but are not greater than normal scatter. Although this study was conducted with undoped films and conversion was carried only to minimum resistance rather than to high transmission, it may be anticipated that conversion of tin-doped films to high transmittance also would be accelerated by increasing the oxygen concentration. Accelerated conversion would be of considerable value for preparation of films on plastics.

Preparation of Large Panels

The preparation of panels 9 inches square necessitates changes in the design of the apparatus which has been used to prepare small specimens. One method of coating a large area would be the use of a large source or a number of sources. Another method would involve a tracking technique in which the panel or the source would be moved so as to coat segments of the entire area in sequence, or use of a rotating mask between the source and target.

Advantages and disadvantages lie in both methods, and selection depends on the effects of various relationships in the coating process. Studies, described below, were carried out to determine which methods are most promising.

The Angle of Incidence of the Impinging Metal Vapor

In a coating process employing a small source capable of "seeing" a large area the metal strikes different areas of the substrate at different angles of incidence. This impingement angle has been known to affect the structure of certain metals.*

Experiments were conducted to determine whether the angle of incidence of the impinging indium metal vapor has any large effects on the properties of the resultant In_2O_3 films after conversion. Specimens of glass were supported 15 cm from the source so that the direction of travel of the metal vapor was normal to the glass surface. Companion samples were supported at an equal distance from the source, but at an angle of 45 degrees to the direction of travel. The indium metal was evaporated as described in the orientation studies discussed earlier in this report. The films were then converted in air at 149°C to 166°C.

Typical results of the tests are shown in Table 8. Films with similar numbers were evaporated simultaneously. The thickness of a film is proportional to the sine of the angle of incidence; therefore, the values of resistance for the 45-degree films were corrected (by the factor sin 45°) to the values which would have been obtained if the films were of normal thickness, assuming constant resistivity. The corrected values are given in the fifth column of the table. It may be seen that the resistance values for the normal and 45-degree films are similar. For one pair (Films 097-70A and B), the resistance of the 45-degree film was considerably lower than that of the normal film. This may be a result of scatter. The 45-degree films had higher transmittance than the normal films, probably because they were thinner and, therefore, underwent more nearly complete conversion.

* Holland, L., J. Opt. Soc. Amer., 43, 376 (1953).

TABLE 8. COMPARISON OF In_2O_3 FILMS IN WHICH THE METAL WAS DEPOSITED AT DIFFERENT ANGLES OF INCIDENCE

Film	Orientation of Plate	Evaporation Resistance, kilohms/square	Resistance, ohms/square	Resistance Corrected to Normal Incidence, ohms/square	Transmittance, per cent
097-65A	Normal	4.5	420	--	70
097-65B	45°	7.5	580	410	75
097-68A	Normal	10.5	120	--	55
097-68B	45°	7.3	170	120	65
097-70A	Normal	3.0	480	--	74
097-70B	45°	5.1	420	300	84

Distribution of Metal From a Single Cup Source

A second consideration in a coating process employing a small source which sees a large area is the distribution of metal over this area and the consequent effects of the thickness variation on the resistance of the oxide film.

An experiment was conducted in which a single cup source was completely filled with indium so that the evaporation source had a convex surface, to minimize directional effects of the source. A glass strip 1/2 inch wide by 9 inches long was centered above the source at a distance of 15 cm, normal to the vapor beam at the center. Air-dried silver-paint contact bars were spaced along the strip at intervals so that clear areas of glass 1/2 inch square were located on the strip. Evaporation of the indium was as described in the orientation studies discussed previously.

Figure 5 shows the resistance of the film after evaporation and after conversion. The transmittance of the various sections varied from 75 to 80 per cent. It can be seen from the figure that the resistance increased with distance from the center of the strip. The rate of increase of resistance with distance was greatest in the end sections of the films. The ratio of the resistance at the ends of the strip to that at the center was about 40 to 1 for the metal film. After conversion the ratio was about 4 to 1. The distribution is not that which would be expected from a true point source in a very low-pressure atmosphere; a ratio of two was calculated from the geometry of the system. The directional nature of the source (since it is not a point source) and the short mean free path of electrons in the oxygen evaporation atmosphere (with consequent scattering) may have affected the distribution.

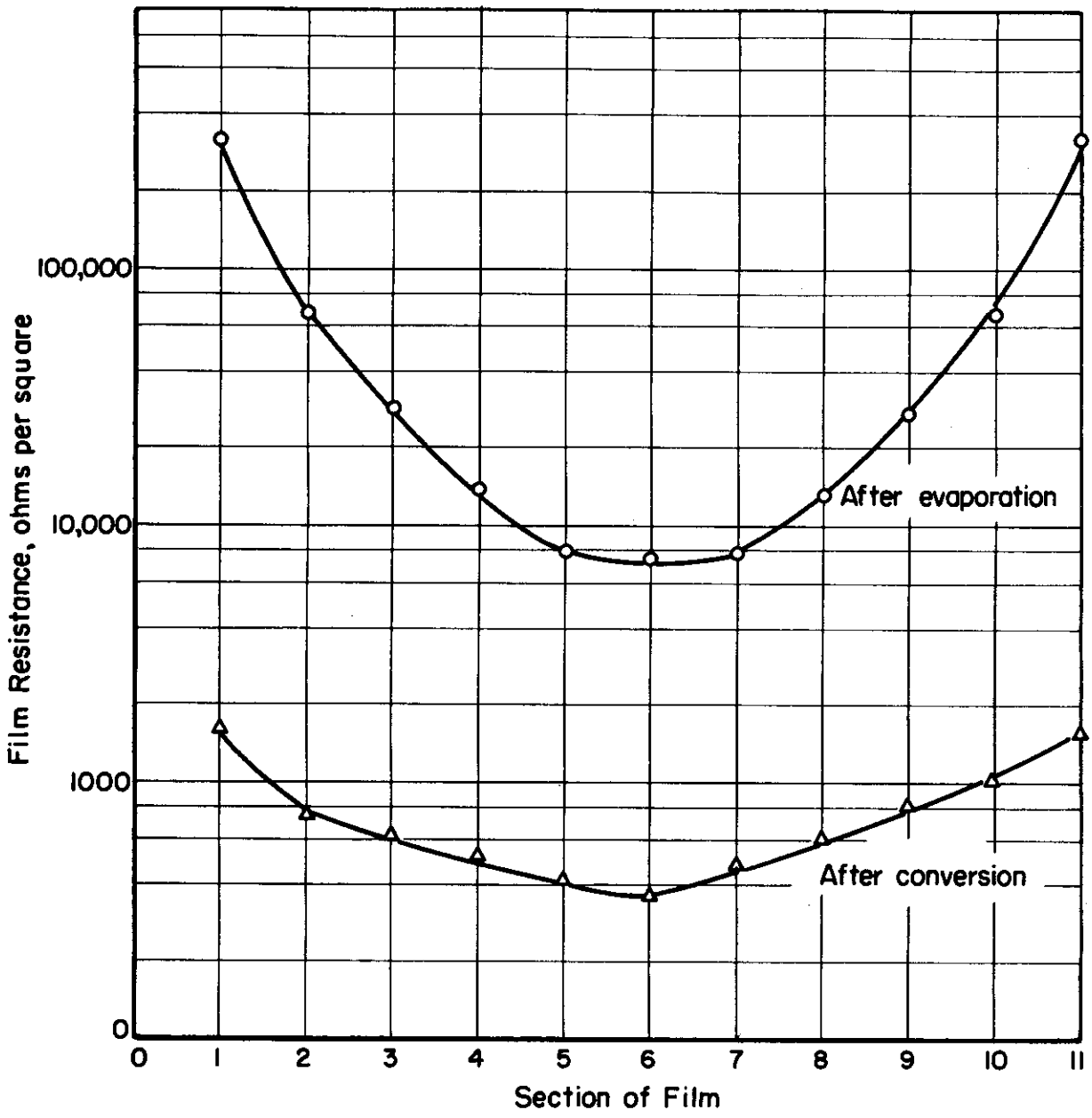

FIGURE 5. DISTRIBUTION OF INDIUM AND In_2O_3 FILM PRODUCED FROM A CENTRALLY LOCATED SINGLE SOURCE

Simultaneous Evaporation of Indium and Tin From an Alloy

The evaporation process would be greatly simplified if the metal could be evaporated from an indium-tin alloy so that the same source could be used for both indium and tin. It was shown previously (WADC Technical Report 54-325, Part 2) that the tin evaporation must not be started before the indium evaporation. The effect of starting simultaneously, as from an alloy, was not known. An investigation was made, therefore, to determine the effects of evaporation from a single source of indium-tin alloy.

Calculations were made on the basis of vapor pressure data and Raoult's Law to determine the probable melt compositions necessary to obtain chosen film compositions, assuming an evaporation temperature of 750°C. The probability that Raoult's Law would apply was unknown. However, the vaporization temperatures used for producing the films are well above the liquidus curve of the indium-tin system.* On the basis of the calculations, alloys of 10 per cent indium-90 per cent tin and of 50 per cent indium-50 per cent tin were chosen as a starting point. Films were evaporated from melts of these alloys.

Films produced from the two alloys were analyzed spectrographically. Two successive evaporations from the 50 per cent indium-50 per cent tin melt gave films with tin concentrations of 2.4 and 1.5 per cent, respectively (calculated 1.4 per cent). Successive evaporations from a 10 per cent indium-90 per cent tin melt gave 16 and 36 per cent tin (calculated 11.5). It will be noted that the tin concentration from the second evaporation from a melt was higher in one case, lower in the other. Another evaporation from a new 10 per cent indium-90 per cent tin melt gave 14 per cent tin. The reason for the scatter in film composition is not known. Possible explanations are that the alloys were not homogeneous, or that the evaporation temperatures varied for the different runs with consequent change in the ratio of the vapor pressures of the two metals.

The films were converted in air at 177°C. The properties of the films are shown in Table 9. The resistance after conversion was abnormally high, particularly for the films from the 90 per cent tin melt.

During an evaporation, and with successive evaporations, the temperature of the source had to be raised to maintain the evaporation rate from the indium-tin alloy melt. It was suspected that the composition of the melt was changing. The rates of evaporation of the two components in the melt are considerably different; therefore, the composition change in the melt may be significant. A cooling curve on a melt, initially 40 per cent indium-60 per cent tin, was made after three evaporations to determine the final composition. The composition was found to be about 30 per cent indium-70 per

* Intermediate Indaloy Solders, The Indium Corporation of America, New York (1954).

cent tin. This change in melt composition produces a change in the concentration of tin in the evaporated film from about 6 per cent to about 8 per cent. However, not only is the melting point of the melt raised, but the evaporation temperature must be raised also to produce an equivalent evaporation rate. The changes in the characteristics of the evaporated film might be small because of the change of composition of the melt, but control of the evaporation becomes difficult under these conditions and would make this technique unsuitable for use as a production method.

TABLE 9. COMPOSITIONS AND PROPERTIES OF FILMS PRODUCED FROM TWO INDIUM-TIN ALLOYS

Film	Alloy Composition(a), per cent by weight	Tin in Film, per cent by weight	Evaporation Resistance, kilohms/square	Final Resistance, kilohms/square	Transmittance, per cent
097-81B	10 In-90 Sn	14	27	6.5	78
097-87B	10 In-90 Sn	16	100	28.0	83
097-92B	10 In-90 Sn	36	41	8.1	86
097-94B	50 In-50 Sn	2.4	11.2	1.5	81
097-96B	50 In-50 Sn	1.5	9	0.62	80

(a) Original composition of melt before evaporation.

Concentric-Ring Source

The common melt or alloy source would have the advantage of simplicity in control if it were not for the change in composition. Since the temperatures for evaporation of tin and indium required to produce a film with the desired tin concentration are approximately the same, both components might be placed in a common crucible with the components separated in a concentric-ring system. This type of source is adaptable for production of large panels*. The composition of the evaporated film could be varied by varying the exposed surface area of each component. A crucible was fabricated which had equal exposed surfaces of tin and indium. This source is shown diagrammatically in Figure 6. Analysis of two films produced from the source showed that the tin concentration was 18 per cent. A second source having an exposed tin area 0.277 times the area of the indium was made. The concentration of tin in the evaporated film was calculated to be about 5 per cent. Analysis of films produced with this source showed a tin concentration of 5.3 per cent. The properties of films prepared from these sources are given in Table 10.

* The use of a ring source for covering large areas uniformly is discussed by many investigators. See, for example, Holland, L., Vacuum, 2, 346 (1952).

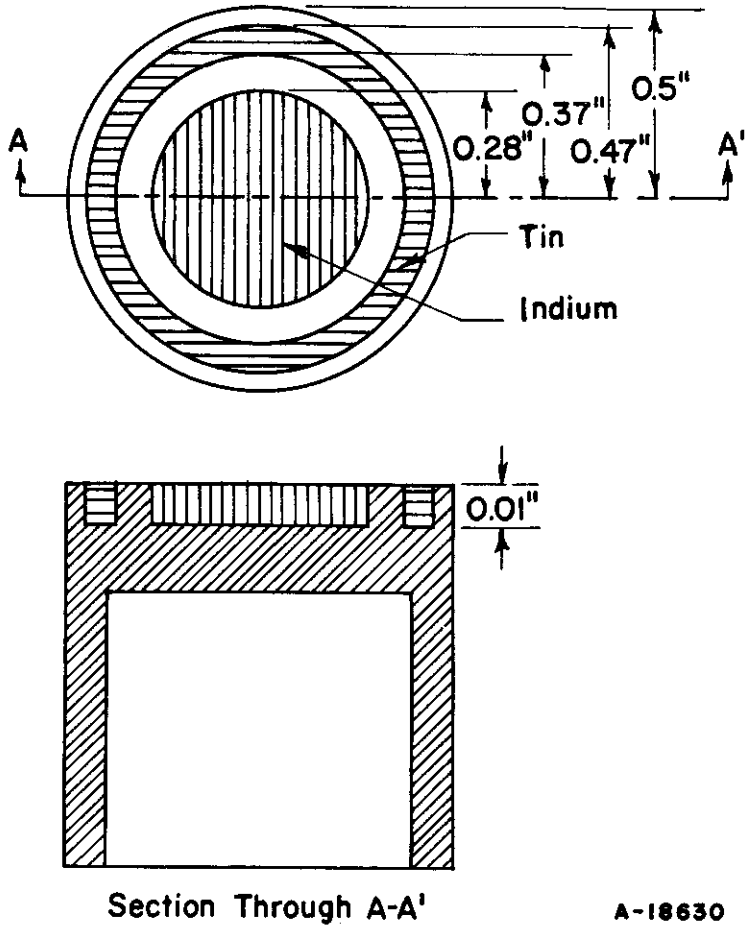

FIGURE 6. CONCENTRIC-RING SOURCE

TABLE 10. PROPERTIES OF FILMS EVAPORATED FROM CONCENTRIC-RING SOURCES

Film	Nominal Tin Concentration, per cent	Evaporation Resistance, kilohms/square	Resistance, ohms/square	Transmittance, per cent
362-63	18	5	202	85
362-65	18+[a]	6	46	77
362-71	18	5	108	87
362-73	18	5	450	87
362-74	18+[a]	5	38	80
362-79	18+[b]	1000	68	87
362-86	5	1000	540	81
362-87	5	10	90	51
362-88	5	5	220	79
362-89	5	10	390	81

(a) Indium agglomerated so that the area of exposed indium was approximately 60 per cent of area of tin. Hence, the tin concentration probably is greater than 18 per cent.

(b) Tin crept from its place in crucible into the indium portion of crucible, thereby reducing the rate of evaporation of indium. Hence, the tin concentration probably is greater than 18 per cent.

Since the indium and tin do not wet the graphite crucibles, it is possible for the metal to agglomerate, as a result of surface tension, and thereby decrease the surface area. The tin is restricted from agglomerating by the geometry of the ring source used, whereas the indium is not so restricted. The indium agglomerated during preparation of Films 362-65 and 362-74. The agglomeration undoubtedly caused an increase in tin concentration in these cases.

Large Concentric-Ring Source

A large concentric-ring source was made, for use in coating 9 by 9-inch panels. The source has a mean diameter of 9 inches and a total evaporation surface area of 21 square inches. The ratio of the tin and indium surface areas was calculated to produce films containing 15 per cent tin by weight.

Use of the large source resulted in excessive radiation to the substrate. In the first attempt to coat a 9 by 9-inch panel, the panel temperature rose to over 300°C, and the panel cracked. Use of the large source was discontinued.

Rotating Mask

Since the large concentric-ring source was unsatisfactory, a study was made to determine the feasibility of coating large panels from a small source, with a rotating sector or mask interposed between the source and substrate to permit uniform deposition.

A small concentric-ring source, designed to produce films containing about 15 per cent tin, was constructed. The source had a hole through the center (along the axis) to accommodate the rotating shaft for the mask. The mask was attached to the top of the shaft, between the source and the substrate. The shape of the mask was designed to give a uniform film distribution over the surface of a 9 by 9-inch plate, on the basis of the results of the study of the distribution of metal from a cup source discussed earlier in this report.

Films produced with the rotating mask were nonuniform. The ratio of the resistance at the edge of a plate to that at the center was as high as 1500 in some cases. Furthermore, on some of the films there was a circular area at the center of the plate having higher optical transmittance before conversion than the rest of the plate. After conversion, this area had a lower transmittance than did the rest of the plate. It was thought that the higher transmittance of this area before conversion might be a result of excessive heating of the area during film preparation, so that some conversion took place during the evaporation process. Since the sector shaft

passed through the source, the top end of the shaft might radiate a large amount of heat to the center of the substrate plate, thereby causing overheating. To test this possibility, several plates were made without the mask and shaft in place. However, the same pattern, that is, the high-transmittance spot in the center, was still observed. In addition, the variation in resistance and optical transmittance from center to edge of the plate was much greater than would be predicted on the basis of the geometry of the system.

Thermocouples were installed to measure the temperature distribution across the filmed surface of the substrate. It was found that the temperature difference from the center to the edge of the plate was about 40°C. In addition, it was found that the temperature at the edge of the center spot on the plate was about 155°C, which is approximately the melting point of indium. This fact suggests that the center spot oxidized in the course of the evaporation process as a result of the high mobility of the indium atoms in the film. The magnitude of the temperature difference between the center and edge of the plate probably is too great to be accounted for by the source-substrate geometry. It seems probable that the interior surface of the bell jar, when coated with indium, is a good infrared reflector. Since the source is in the center of the bell jar, that is, on the vertical axis of the bell jar, heat from the source reaching the bell jar would be reflected back to the axis. Since the center of the substrate also is on the axis, it might be expected that the center of the substrate would be overheated as observed. Possibly, this effect could be avoided if the source and substrate could be placed off-center in the bell jar. However, the bell jar used for the work is too small to permit such relocation.

In an attempt to cool the substrate, a water-cooled copper plate was placed on top of the substrate, that is, on the unfilmed side of the plate. It was found that this modification resulted in an increase rather than a decrease in substrate temperature, probably as a result of reflection of the radiation by the copper plate.

Rotating Substrate

As stated in the previous section, the bell jar is too small to permit relocation of the 9 by 9-inch panels to avoid overheating by reflection of radiation from the jar. Therefore, a rotating-substrate technique was used for subsequent studies. The source was located about 22 cm below the rotating plate and about 17 cm from the axis of rotation. No provision was made for measuring the film conductance during deposition, since construction of the necessary moving-contact system would have been time consuming. Therefore, an attempt was made to simulate the temperature schedule normally employed for the evaporation process.

Several 9 by 9-inch films were prepared by the rotating-plate method. The resistance values of the films ranged from 50 to 150 ohms/square, and optical transmittance values were from 77 to 87 per cent. Some of the films were removed from the conversion oven before maximum transmittance was reached; this accounts for the wide range of transmittance values. Some of the panels were overcoated with silicon monoxide (as discussed in the following section), with resultant increase in transmittance. Panels typical of those prepared are described in Table 11.

TABLE 11. PROPERTIES OF 9-INCH-SQUARE PANELS

Panel	Resistance Per Square, ohms	Transmittance, per cent	Overcoating	Transmittance Before Overcoating, per cent
547-15	150	83	SiO	77
547-16	92	82	SiO	77
547-18	50	86	SiO	84
547-17	100	77	None	--
547-19	105	87	None	--
547-25	80	84	None	--
547-26	135	80	None	--
547-29	125	84	None	--

The uniformity of the films is encouraging. Transmittance and resistance are slightly (a few per cent) higher at the center than at the edges of the plate. This variation can be reduced considerably by moving the source nearer the axis of rotation.

The results of the above studies indicate that it is feasible to coat large panels with the indium oxide film. Additional study is needed to develop the technique to a production stage.

Antireflective Coatings

A study of overcoatings was made in an attempt to increase the transmittance of the indium oxide films and to confer mechanical protection to the films. High-purity magnesium fluoride and silicon monoxide were used*. The composition of films formed by evaporation of SiO is not known. Probably, it is SiO_2. The materials were evaporated at pressures from 4×10^{-5} to 2×10^{-4} mm Hg onto the indium oxide films. Thickness was monitored

* Optical grade MgF_2 was obtained from Optical Films Engineering Company; "Silicote" SiO from National Research Corporation.

by observing the change in reflected color from the target and from a monitor slide, using white light and an angle of reflection of about 30 degrees. The deposition rate was about 100 A/minute.

It can be shown that maximum suppression of reflectance in the neighborhood of a wavelength λ_0 by a double-layer film is attained if the first film has an index of refraction, n_1, greater than that of the glass and an optical thickness $n_1 d_1 = \lambda_0/2$ (where d_1 is the actual thickness) and the second film has a lower index of refraction and an optical thickness $n_2 d_2 = \lambda_0/4$. In the present case, the indium oxide coating serves as the first, high-index film. It is impractical to attempt to form indium oxide films of a given thickness, at least at the present stage of development. Therefore, the investigation of overcoatings was carried out with the objective of reducing the reflectance of indium oxide films of various thicknesses.

Typical results of the studies are shown in Table 12. For most films the maximum transmittance and also the preferred green transmitted color are achieved if the overcoating process is stopped when the reflected color is violet or pink. If the original color is violet or pink, maximum increase in transmittance is achieved by applying sufficient overcoating to produce a green reflected color. However, the transmitted color of such a film is then peaked in the violet. If the original color is violet or pink it appears that no improvement in transmittance can be achieved by applying sufficient overcoating to produce the next order violet. Therefore, as a compromise, films having a violet or pink reflected color prior to overcoating might be coated to a thickness such that the reflected color is yellow-orange. Then the transmitted color would be blue.

The hardness* of the overcoatings depends on the pressure in the vacuum chamber during deposition and also on the heat treatment after deposition. Magnesium fluoride coatings applied at a pressure of about 5×10^{-5} mm H_g are appreciably harder than those produced at pressures of about 2×10^{-4} mm H_g. However, heat treatment in air at 200°C for 2 hours increases the hardness of those produced at the higher pressure, whereas little change occurs in those produced at the lower pressure. The silicon oxide films undergo a greater increase in hardness as a result of heat treatment at 200°C for 2 hours and are considerably harder than the MgF_2 coatings. Further increase in hardness occurs for both types of films after 16 hours of heat treatment. The hardest overcoat, silicon oxide baked for 16 hours, is comparable in hardness to the indium oxide films.

Inquiries were sent to various optical companies and suppliers of coating materials to determine the availability of proprietary materials or processes which might be used for overcoating indium oxide films. Only one of the companies contacted, American Optical Company, suggested a coating other than the usual materials such as MgF_2 and SiO. Three films were sent to American Optical Company for application of their antireflective

* Hardness was compared by rubbing with an eraser under a constant vertical force.

TABLE 12. EFFECT OF OVERCOATINGS

Film	Before Overcoating: Reflected Color and Order	Before Overcoating: Transmittance, per cent	Overcoating Material	After Overcoating: Reflected Color	After Overcoating: Transmitted Color	After Overcoating: Transmittance, per cent	Transmittance Increase, per cent
362-59A	Green 2	81.5	MgF_2	Violet	Green	88.5	7
973-36A	Green 5	80	MgF_2	Pink	Green	87	7
973-35	Green 3	80	MgF_2	Yellow-orange	Blue	85	5
973-24RA	Colorless 1	79	MgF_2	Violet	Green	92	13
362-68A	Violet 1	90	MgF_2	Violet	Green	90	0
973-30A	Pink 4	80	MgF_2	Green	Violet	84	4
362-59B	Green 2	84	SiO	Violet	Green	88	4
973-16RA	Yellow 1	80	SiO	Violet	Green	90	10
973-24BB	Colorless 1	79	SiO	Violet	Green	91	12
973-30B	Pink 4	80	SiO	Green	Violet	81	1

coating (No. 157C-50), which is applied by a wet-chemical process. After coating, the specimens had "infinite" resistance. Apparently, the conducting film had been removed by the coating process.

Testing

Load Test

More extensive testing of the tin-doped indium oxide films has been reported previously (see WADC Technical Report 54-325, Part 2). One film prepared recently was load tested. A 4-inch-square section was cut from one of the 9-inch panels for the test. Because of a limitation of the power supply, the plate was operated at a continuous power dissipation of 1300 watts per sq ft for 150 hours (instead of the desired 1500 watts). The plate was cooled during the test by a stream of fast-moving air. The temperature remained below 120°C throughout the test. The resistance increased from 80 to 98 ohms in about 10 hours and remained at this value during the remainder of the test. No other adverse effects were observed.

Abrasion Test

The abrasion resistance of several films was determined by means of an eraser test*. The load on a 3/8-inch-diameter eraser was varied from 0.5 to 2.2 lb. Wide variability in the results was noted. Some of the films showed a slight change in reflected color after 20 cycles with the 2.2-lb load. In other cases, it was necessary to decrease the load to 0.5 lb to prevent visual evidence of scratching. Films which were overcoated with silicon oxide, although seemingly as abrasion resistant during the early portion of the test, showed considerably more scratching at the conclusion of the test with a 2.2-lb load. It appeared that some of the overcoat material was transferred to the eraser and, subsequently, served to accelerate the wear. With a 0.5-lb load, the overcoated films also were satisfactory.

Transmittance and Reflectance Spectra

The transmittance and reflectance spectra of a portion of one 9-inch-square panel (Film 547-19) were determined by personnel of the Materials Laboratory, Wright Air Development Center. The spectra are presented in Figure 7. The resistance of this panel was 105 ohms/square.

* Military Specification JAN-F-675.

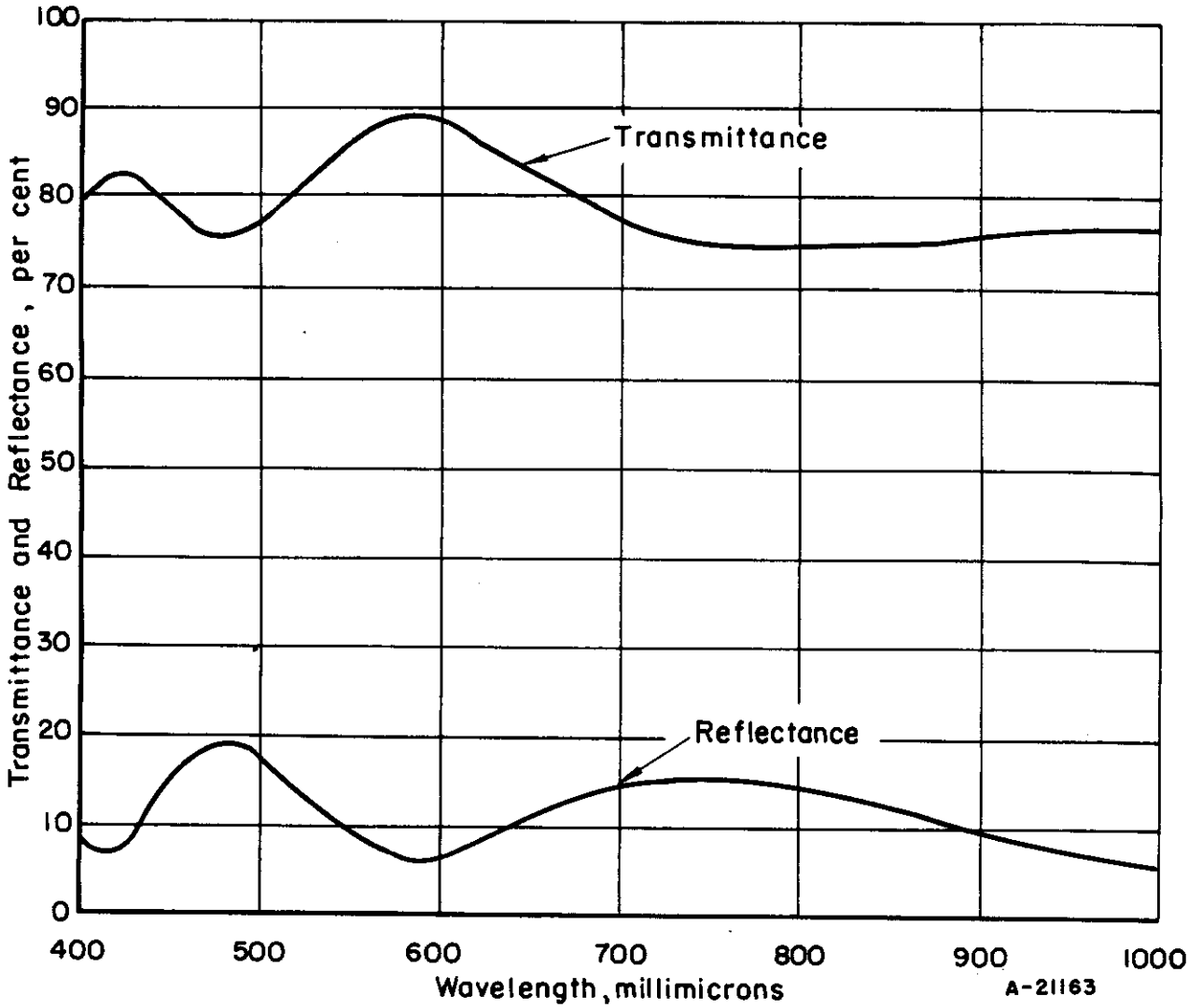

FIGURE 7. TRANSMITTANCE AND REFLECTANCE SPECTRA OF A PORTION OF A 9-INCH-SQUARE PANEL

RECOMMENDATIONS

Although final testing of the characteristics (detailed studies of behavior under load, etc.) of the indium oxide films has not yet been carried out, the tests reported in WADC Technical Report 54-325, Part 2, together with the studies described in this report, indicate that the films have the desired properties and can be applied to large panels for use in aircraft. However, certain studies should be completed before production of coated aircraft panels is attempted. The following additional work is recommended.

(1) Further study is needed to determine the optimum values of evaporation rate and substrate temperature, and to determine the effect, if any, of varying source-to-substrate distance.

(2) Although it is clear that large panels can be coated satisfactorily, further study is needed to develop a coating technique suitable for production use. The rotating mask, rotating plate, and other similar techniques might be used.

(3) Electrodes should be developed for the coatings. Use of electroplating, vacuum metallizing, and conducting paints are possible methods for electroding.

(4) Testing of film characteristics (behavior under load, etc.) should be carried out on large panels.

The indium oxide coating shows promise for use on plastics. Modification of the coating is needed, however, to permit conversion of the films to the oxide at lower temperatures than can be used with the present coating. Possibly the conversion temperature can be reduced by changing process parameters or tin concentration, or by the use of other additives.

APPENDIX

LITERATURE SURVEY SUPPLEMENT

A search of the recent literature was made to supplement the literature survey reported in WADC Technical Report 54-325, Part 2. Only two pertinent articles were found. They are summarized below.

G. Rupprecht* studied the electrical and optical properties of indium oxide films formed by evaporating indium oxide and then oxidizing further in air at 700 to 1000°C. The film thickness ranged from 500 to 2500A, as estimated from interference colors. Conductivity was in the range 10^{-5} to 10^{1} $(ohm\text{-}cm)^{-1}$, depending on the oxidation time**. Measurement of the conductivity as a function of temperature over the range -180 to 200°C in vacuum showed that the conductivity increases reversibly with increasing temperature up to about 100°C, but that further heating causes an additional conductivity increase which cannot be reversed by cooling in vacuum. Introducing oxygen after heating in vacuum decreases the conductivity to its original value. The time required to attain the original conductivity is about 1 day at room temperature and less at higher temperatures. In an oxygen atmosphere (at atmospheric pressure), the temperature dependence of conductivity is similar to that in vacuum up to about 100°C. At higher temperatures, up to about 400 to 500°C, the results are not reproducible; the conductivity increases with temperature up to about 300°C, decreases on further heating to about 500°C, and then increases again as the temperature is raised further. Quenching experiments, designed to minimize the effect of gain or loss of oxygen, indicated that the activation energy of electrons in the films is from 0.07 to 0.13 ev. A study of the dependence of conductivity on oxygen pressure (in the range 0.1 to 760 mm Hg) was made at temperatures of 430, 450, 490, 580, and 750°C. At the highest temperature (730°C), the conductivity is proportional to $P_{O_2}^{-0.19}$, where P_{O_2} is the oxygen pressure. At the two lowest temperatures (430 and 450°C), the conductivity is proportional to $P_{O_2}^{-0.5}$. In the intermediate range (490 and 580°C), the conductivity is proportional to $P_{O_2}^{-0.5}$ from 760 to about 10 mm Hg, and to $P_{O_2}^{-0.19}$ at lower pressures. The $P_{O_2}^{-0.19}$ dependency is compatible with the assumption that the equilibrium may be expressed by the equation $In_2O_3 = 2\ In^{+3} + 6e^- + 3/2\ O_2$, in which the symbols In^{+3} and e^- represent the excess indium ions and electrons, respectively. If the charge carriers are completely dissociated from the excess In^{+3} ions, and if the electron mobility is constant (so that the conductivity is proportional to electron concentration), then application of the mass-action law

* Rupprecht, G., Z. Physik, 139, 504-17 (1954).

** These conductivity values correspond to resistance values of several kilohms per square and higher.

gives a $P_{O_2}^{-3/16} \cong P_{O_2}^{-0.1875}$ dependency of the conductivity, in agreement with experiment. The agreement is evidence that the film consists of In_2O_3. The fact that the conductivity decreases with increasing oxygen pressure indicates that the films are a metal-excess semiconductor, that is, *n*-type.

Study of the photoeffect of the films in vacuum at room temperature showed that the conductivity rises irreversibly when the films are illuminated by a mercury arc lamp. The initial rate of conductivity increase, $d\sigma/dt$, is proportional to $\sigma_D^{2/3}$ where σ_D is the dark conductivity, and also proportional to the intensity of illumination.

L. Holland and G. Sidall* studied the properties of sputtered films of CdO, SnO_2, In_2O_3, and Fe_3O_4. They prepared In_2O_3 films by sputtering indium in a 50-50 mixture of argon and oxygen. The best films had a resistance of 2000 ohms per square and optical transmittance of 80 per cent. Heating the films in air decreased the conductivity. At 400°C, the films became "non-conducting".

* Holland, L., and Sidall, G., Vacuum, 3, 375-391 (1953), Published 1955.