July 17, 1962 D. A. SKOOG 3,044,903

THIN FILM RESISTORS

Filed Aug. 25, 1958 2 Sheets-Sheet 1

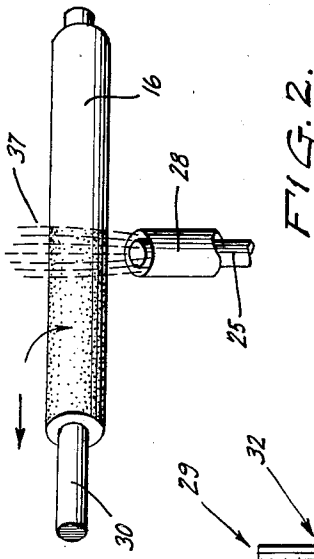


FIG. 2.

FIG. 1.

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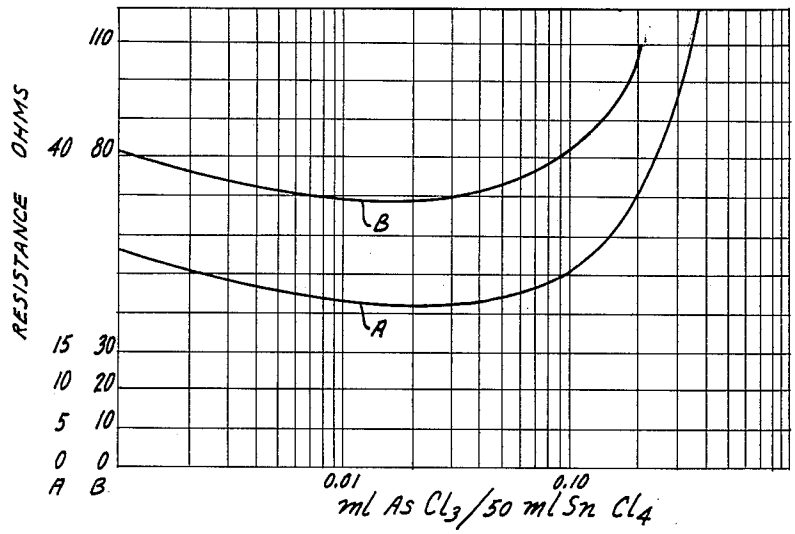


FIG. 3.

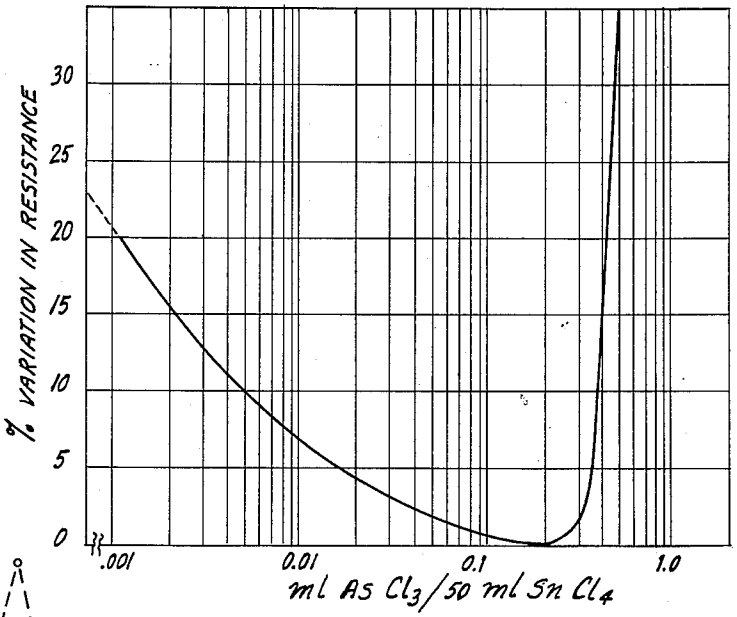
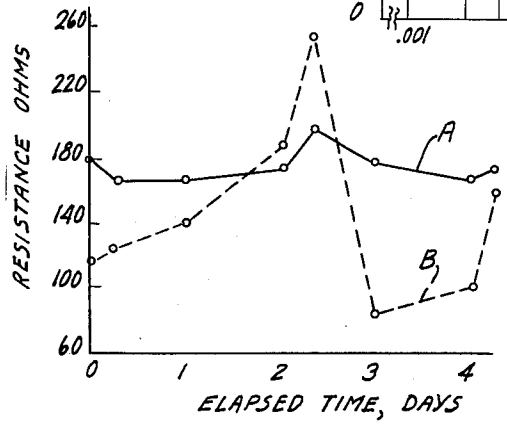


FIG. 4.

FIG. 5.



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THIN FILM RESISTORS

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1 Claim. (Cl. 117—229)

This invention relates generally to the art of fabricating electrically conductive films, and more particularly to a unique and simplified method for manufacturing electrically conductive films of high operational stability and uniformity and to the article of manufacture produced by such a method.

While of broader applicability this invention has particular utility in the manufacture of thin-film, electrically conductive coatings on glass, ceramics and other glass-like materials and it is in this particular field of application that the invention is illustrated and described.

It is well known in the resistor art to produce thin-film resistors by immersing a heated blank of glass, glazed ceramic or the like in a solution of an appropriate metal salt or by exposing the blank to the vapors or atomized spray of such a solution. These techniques, however, while resulting in the formation of a strongly adherent layer of metallic oxide on the supporting surface produce a resistive film lacking electrical stability and one which is acutely sensitive to small deviations from prescribed manufacturing regimen as well as being highly susceptible to post-manufacturing contamination. Moreover, conventional thin-film resistors exhibit a marked variance in resistivity with change in ambient temperature, and while there are processes currently available for producing resistive films of increased stability and constant resistivity, such processes are not easily controllable or productive of a uniform end product.

Accordingly it is a principal object of this invention to provide a readily workable, simplified process for insuring optimum uniformity of mass produced, thin-film resistors, particularly thin-film resistors of the type having constant resistivity over an extended temperature range.

A further object of the invention is to provide a simplified method for manufacturing electrically conductive films having high intrinsic electrical and chemical stability and further to provide a novel process for producing resistive films which are insensitive to post-manufacturing contamination.

A still further object of this invention is to provide a non-critical film forming process for mass producing stable, uniform, thin-film resistors.

These and other objects within contemplation will be more readily understood by reference to the following detailed description and drawings, in which:

FIGURE 1 shows one arrangement for fabricating thin-film resistors in accordance with the present invention;

FIGURE 2 is an enlarged showing of a preferred mode of forming an electrically conductive film;

FIGURE 3 is a graph showing the effect of arsenic on the electrical resistance of tin-oxide films;

FIGURE 4 is a graph showing the effect of varying concentrations of arsenic on the change in resistivity of tin-arsenic films over a temperature span of 600 degrees; and

FIGURE 5 is a graph illustrating the effect of arsenic doping on film stability and reproducibility.

Briefly described, this invention in its preferred aspect, relates to a unique technique for impregnating or doping a vapor-deposited, electrically conductive film, which comprises adding to a liquid solution of a film-forming tin salt a soluble compound of arsenic having a range of vapor pressures permitting the controllable vaporization of a prescribed amount of the arsenic solute along with

the solvent filming vapor. This composite vapor is then transported into impingement with a heated blank of insulating support material and forms a thin electrically conductive film on the surface portions of the insulating substrate. This technique provides optimum and uniform dispersion of the arsenic additive throughout the filming vapor thereby insuring a film of homogeneous composition. Thin-film resistors made by this method accordingly exhibit unprecedented stability and uniformity of electric parameters. The entire process, once the desired composition of the electrically conductive film has been fixed is essentially a one variable system, the concentration of the constituents in the vapor being a function of their vapor pressures which in turn is a function of temperature.

The fundamental concept underlying hte invention is the discovery that arsenic can be used as a film stabilizing element and that when arsenic is found in a form having a vapor pressure conducive to the release of the desired concentration of arsenic when placed in solution with the principal film forming salt it provides a unique method for producing thin-film resistors which method is readily controllable and productive of a more uniform end product, and further, results in minimizing the complexity of vapor filming equipment conventionally required.

One arrangement of apparatus for practicing the method steps of this invention is that shown in FIGURE 1. The preferred, but not exclusive technique, is to provide a temperature-controlled solution or pool of an appropriate filming salt, such as liquid anhydrous stannic chloride into which a measured amount of a soluble arsenic salt, as for example arsenic trichloride has been added. The arsenic solute is so chosen that its range of vapor pressures permits it to coexist with its solvent in the vapor phase at some selected and readily attainable temperature of operation. The concentration of the arsenic in the filming vapor is a function, once having fixed the amount of arsenic in solution, of its vapor pressure which for all practical purposes is exclusively a function of temperature. Accordingly, once the amount of arsenic trichloride in the solution has been fixed, the concentration of arsenic may be maintained at a constant level by merely controlling the temperature of the solution during the filming process.

The amount of arsenic to be placed in solution is determined by the end result desired, as will be discussed more fully hereinafter, the particular arsenic compound to be used being determined in large part by the properties of the filming salt employed insofar as the arsenic compound should, for most satisfactory results, be readily miscible with the main filming constituent. It will be recognized, however, that while the preferred method of forming the electrically conductive film is by vapor deposition, the ordinary techniques such as spray and immersion coating are still available and the use of arsenic in such applications comes within the general purview of the invention.

Referring again to FIGURE 1 the filming reagents are conveniently contained in a closed container or flask **10** provided with a delivery tube **11**. Fumes of the reagent solution are controllably generated by immersing the flask in a temperature controlled water bath **12**. When using a solution comprised of anhydrous stannic chloride and arsenic trichloride as the filming reagent, a temperature of 55° C. was conveniently employed. Accurate control of the temperature was maintained by using conventional thermostatic means, not shown, interposed in a connection between the temperature sensing element or thermocouple **13** and the water-bath heating coils **14**. Arsenic trichloride is readily miscible with anhydrous stannic chloride, the admixture forming a single homogeneous phase. To insure a fixed and unvarying proportion of arsenic in the

vapor emanating from the liquid pool **15** the temperature of the water jacket must, as noted, be carefully controlled, this being satisfactorily accomplished in the embodiment illustrated through the high thermal inertia of the water and surrounding parts which serve to minimize temperature fluctuations induced by transient variations in supply voltage and other extraneous causes.

Substances commonly employed as substrate or foundation material in the fabrication of thin-film resistors include materials such as refractory glass, surface-glazed ceramic and other similar insulating media. The preferred mode of fabrication in order to insure maximum uniformity of the end product is to first clean the surface of the insulating blank on which the coating is to be deposited, as by immersing in hot cleaning solution, followed by several rinses in distilled water. Before initiating vapor flow it is necessary, in order to insure uniform and proper adhesion of the filming material, to preheat the blank to oven temperature. A temperature ranging from 600° C. to 650° C. was found satisfactory when using a refractory type glass such as the pyrex tubing **16** shown in FIGURE 1. When thermal equilibrium is attained, vapor flow is started by opening the main air supply control valve **17** which affords communication with compressed air supplied via the conduit **17'** through pressure reducing valve **18**. The air is passed to manifold **19** and from there is selectively admitted into lines **20** and **21**, the quantity of air passing through these lines being individually regulated by means of individual control valves **22**. The rate of flow in each line is measured by the air flow meters **23**. To exercise optimum control over the moisture content of the air it is necessary to first dehumidify the air by passing it through a dessicant, such as silica gel, contained in flasks **24** placed in each air line. After moisture extraction, the dried air flowing through line **21** is directed over the liquid pool **15** so as to entrain in the air stream the vapors emanating from the pool and to carry the vapors through the insulated conduit **25** into impingement with the heated blank of Pyrex tubing **16**, located, as shown in phantom in FIGURE 1, within the oven **26**. It has been found that the humidity inside the furnace during the filming process is an important determinant of the quality of the surface coating, best results being obtained by introducing some moisture into the film forming vapor stream. Humidity control is effectively maintained by passing a stream of dry air through line **20** over a closed flask **27** of heated water. To produce a confluent stream of entrained moisture and filming vapors, as is preferred, the conduits **25** and **28** are brought into concentric relation, the arrangement being clearly shown in FIGURE 2. The exit ports are arranged to produce a blending of the emerging vapors prior to their impingement on the heated blank **16** thereby insuring a uniform mixture of vapor and salt fumes in the reaction zone. The glass blank **16** is simultaneously rotated and propelled through this vapor stream by the spindle and lead-screw mechanism **29**. The glass sleeve **16** is wedged or otherwise fixedly mounted on the rotatable stainless steel quill or shaft **30** journalled on stanchions **31**, the shaft being powered by the motor-pulley combination **32**. The entire assembly carried by the support **33** is reciprocably translatable into and out of the electric oven **26** by nut means **34** threadedly engaging the motor driven lead-screw **35**.

One illustrative set of operating parameters employed to produce a constant resistivity (16 ohm per square) resistor, utilizing Pyrex glass tubing having an outside diameter of .810 inch, was the following. The reaction zone **36** within the oven **26** was maintained at approximately 625° C. After temperature stabilization air, at the rate of 10 cc. per minute was passed through water flask **27**, the water being heated to 78° C., while 900 cc. of air per minute was passed through flask **10** containing a solution of anhydrous stannic chloride having approximately 0.4% arsenic trichloride by volume heated to 55° C. During maintenance of the above conditions the blank **16** was rotatingly translated through the moisturized vapor stream **37**. To lay down a uniform 16 ohm per square resistive coating in one pass of the blank through the vapor stream under the above operating conditions required the blank to be moved at a traversing speed of 3 inches per minute and a rotative speed of 75 r.p.m.

The vapors, upon emerging from the concentrically disposed vents **25** and **28** mix and impinge on the heated resistor blank **16** where they decompose and immediately react to produce a doped tin oxide coating. The purpose of the water vapor, as mentioned above, is to assist the reaction process, and, in effect, to controllably air condition the reaction zone.

It is not known with certainty whether the final coating is tin oxide doped with arsenic oxide or whether the arsenic goes in as a substitutional metallic impurity in place of the tin in the crystal structure. It is believed, however, that the material is an oxide of tin with metallic arsenic serving as a substantial type of dopant.

The vapors within the oven **25** which have not entered into the reaction are withdrawn through a draft type exhaust port **38** to prevent vapor accumulation.

To tailor a resistor to a specified value of resistance, it is merely necessary to modify the thickness of the resistive coating, this being most readily accomplished by modifying the "residence" time of the blank within the filming vapors.

Numerous tests were run using arsenic as a film stabilizing additive. Some of the more important effects are graphically illustrated in FIGURES 3 through 5. The films were prepared in much the same manner discussed above by exposing the heated blank to gaseous mixtures of air, stannic chloride, and arsenic trichloride. For each set of data, 50 ± 0.5 ml. of stannic chloride was transferred to a flask and heated to 55° C. A few resistors were prepared from the vapor above this solution. A small volume of arsenic trichloride was then introduced into the anhydrous stannic chloride from a microburet. One or more resistors were then prepared from the vapor of this solution. The concentration of arsenic trichloride was then increased by a second addition of the reagent and more resistors were prepared. In this way a series of resistors containing various arsenic concentrations was obtained.

Resistance of the samples was determined by passing a measured D.C. current through the resistor and measuring the potential drop between a pair of pointed contacts held firmly against the resistor at a fixed distance apart. The precision of such measurements is believed to be from 2 to 3%.

The effect of arsenic upon the electrical resistivity of tin oxide films is graphically illustrated in FIGURE 3, the arsenic content being plotted on a logarithmic scale for convenience of illustration. Two series of resistors were prepared in the manner above indicated using identical operating parameters except where specifically noted. In one series a considerably heavier film was imparted to the glass by using a greater flow rate of the vapor and by increasing the oven residence time of the blank. Curve A of FIGURE 3 represents the mean resistance of resistors prepared using an increased flow rate of 902 cc. of air per minute at a traversing speed of 3 inches per minute. Curve B represents the mean resistance of resistors prepared using varying concentrations of arsenic and an intermediate flow rate of 680 cc. per minute at a traversing speed of 6 inches per minute. It will be noted that as little as .003 ml. of arsenic trichloride in 50 ml. of anhydrous stannic chloride results in a 15 to 30% decrease in the electrical resistance of the vapor deposited film. Further increases in arsenic concentration have little effect up to about .03 ml. Beyond this point a rapid rise in the resistance is observed.

The presence of arsenic in the conducting films was found to have a profound effect upon the temperature coefficient of resistance as graphically shown in FIG-

URE 4. In the absence of arsenic the tin oxide films undergo a 20% change in resistance throughout a change in ambient temperature equal to approximately 600° C. It will be seen, however, that with the addition of even trace amounts of arsenic the percentage change becomes smaller and decreases to zero when approximately 0.2 ml. of arsenic trichloride are placed in solution with the main filming constituent. It will be observed that further increase in the arsenic content of the filming solution results in an abrupt reversal of this resistance stabilizing effect producing resistors having increased sensitivity to temperature change. It will be further noted that the zone of stabilization occurs at approximately the same arsenic concentration as that at which the rapid rise in resistance is observed in FIGURE 3.

Another condition which should be noted is that there is a change in sign of the temperature coefficient at about 0.2 ml. of arsenic per 50 ml. of anhydrous stannic chloride, the resistance of the blanks below this point increasing with increasing temperature whereas at greater concentrations their resistance decreases with increasing temperature.

As pointed out earlier, arsenic impregnated films are less sensitive to post-manufacturing contamination. To demonstrate this property numerous thin-film resistors were prepared over a four day interval using a filming solution containing 0.2 ml. or arsenic trichloride per 50 ml. of anhydrous stannic chloride. As a control, films were also prepared from a solution of unadulterated anhydrous stannic chloride. The procedures used were, as far as possible, identical, and the samples and controls were prepared within a few minutes of one another. The results are shown in FIGURE 5. Curve A is representative of films containing arsenic and curve B of films containing no arsenic. With the films containing arsenic the average deviation of the mean resistance as measured using a plurality of similarly made resistors was 10 ohms, while the films containing no arsenic exhibited an average deviation of 40 ohms. The maximum deviation was 40 ohms in one case and 170 ohms in the second. This data indicates clearly that the uncontrollable variables in the process have a considerably smaller effect on films containing arsenic.

The novel use of arsenic in the fabrication of thin-

film resistors results in a simple, readily controllable process for making stable, electrically conductive films having a high degree of reproducibility, and affords an inexpensive and non-critical technique for making films having essentially a zero temperature coefficient of resistance.

While the invention has been described with particular reference to specific practice and embodiments, it will be understood by those skilled in the art that it is susceptible to changes and modifications without departing from the scope thereof, as defined in the appended claim.

We claim:

A method of producing electric resistors of a predetermined temperature coefficient adjacent zero and of a resistivity which is highly stable in the presence of post-manufacturing contamination, said method comprising the steps of: providing a solution consisting of liquid anhydrous stannic chloride and liquid anhydrous arsenic trichloride, the ratio of arsenic trichloride to stannic chloride in said solution ranging from approximately .2% to approximately .4% by volume, and maintaining said solution at a temperature of approximately 55° C. to produce a filming vapor containing tin and arsenic whereby said filming vapor has an arsenic content predetermined by the arsenic vapor pressure which corresponds with said temperature; evolving water vapor; and simultaneously applying said filming and water vapors to exposed surfaces of a refractory body heated to several hundred degrees C. to produce on said body an electrically conductive film of tin, doped with arsenic in proportion with said arsenic content of the filming vapor.

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