Jan. 5, 1960

J. DEARDEN

2,920,005

ELECTRICAL RESISTORS

Filed Dec. 3, 1956

2 Sheets-Sheet 1

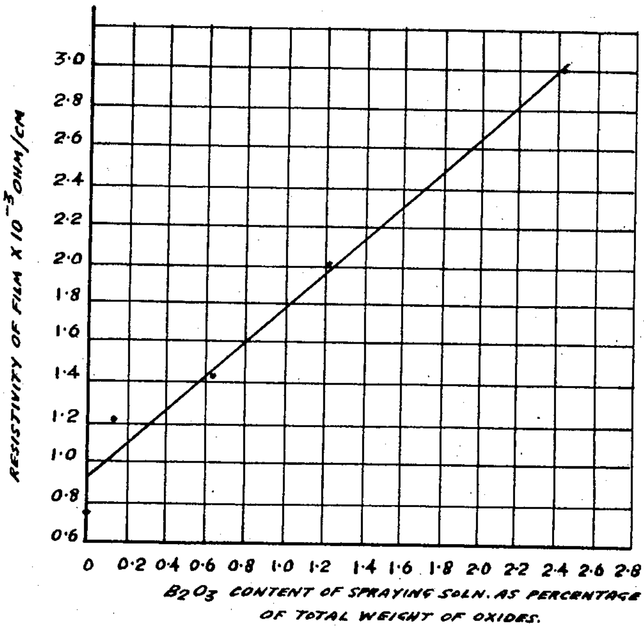

Fig. 1.

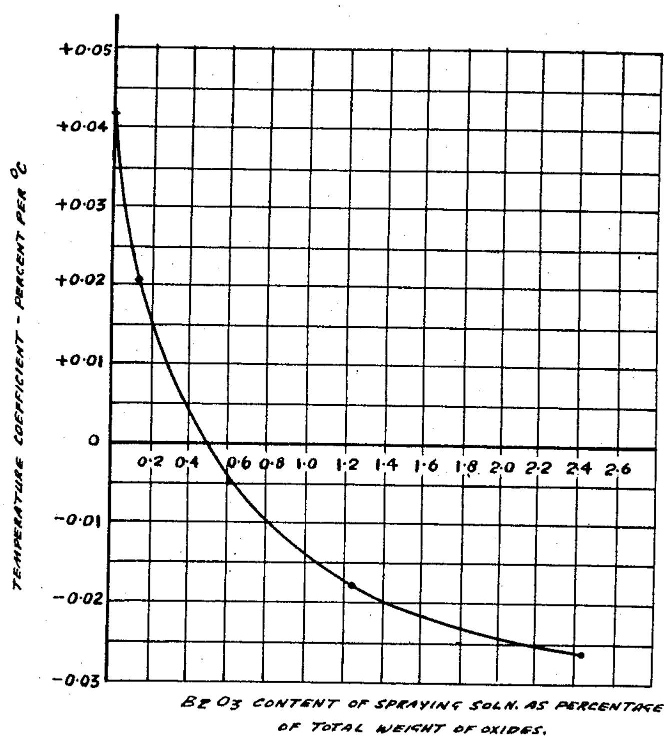

Fig. 2.

Inventor:
Jack Dearden
by Albert L. Jacobs
Attorney

Jan. 5, 1960 J. DEARDEN 2,920,005

ELECTRICAL RESISTORS

Filed Dec. 3, 1956 2 Sheets-Sheet 2

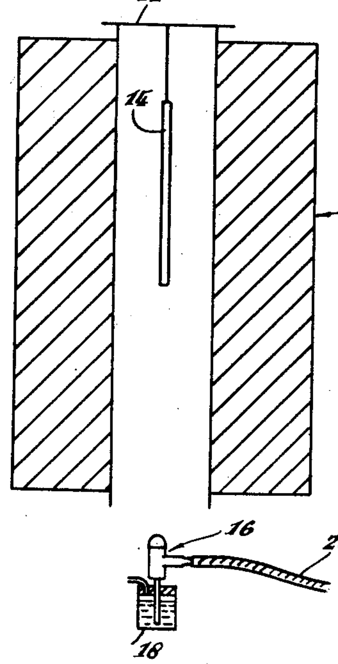

Fig. 3.

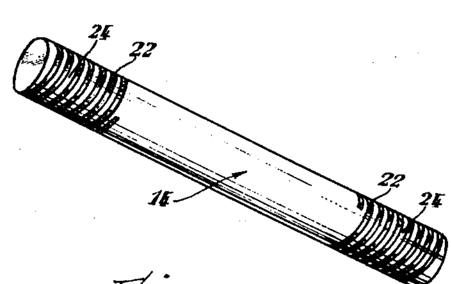

Fig. 4.

Inventor:
Jack Dearden
by Albert L. Jacobs
Attorney

United States Patent Office

2,920,005

Patented Jan. 5, 1960

2,920,005

ELECTRICAL RESISTORS

Jack Dearden, Whitley Bay, England, assignor to Welwyn Electrical Laboratories Limited, Bedlington, England, a company of Great Britain and Northern Ireland

Application December 3, 1956, Serial No. 625,811

Claims priority, application Great Britain December 9, 1955

16 Claims. (Cl. 117—229)

This invention relates to electrical resistors provided with an electrically conductive coating consisting of oxides and having a core or body of glass, porcelain, vitreous ceramic or similar insulating material; these resistors are referred to herein as resistors of the kind described.

It is known to provide glass or other vitreous bodies with a coating of tin and antimony oxides. The resulting elements are used for electrical heating elements, for example as vehicle wind screens or for heating food. The heating elements provided with an antimony and tin oxide layer which have hitherto been known have all been iridescent. The production of iridescent coatings on glass and similar vitreous bodies has been practiced for a very long time for the purpose of producing visual effects appealing to the eye. However, the use of such iridescent coatings of tin and antimony oxides for the purpose of providing heating elements is a comparatively recent development.

Electrical resistors which are suitable for use in precision components often require a high electrical resistance coupled with other properties required of resistors for use in precision instruments, e.g. low or constant temperature coefficient of resistance.

As already mentioned above, the coating of glass or other vitreous bodies with tin and antimony oxides is known. Further investigation has now shown that good electrical properties in resistors of the kind described are obtained when they are coated with a coating medium of tin and antimony compounds in which the percentage of antimony, calculated as antimony pentoxide is from 1½ to 10% by weight of total metal compounds. Hereinafter all percentages referring to constituents of the coating, or of the coating medium for producing it, are by weight. The last mentioned resistors of the kind described have a temperature coefficient of resistance of 0.05% or less which figure is considered satisfactory for electrical resistors in general. The lowest temperature coefficient of resistance is obtained by resistors of the kind described which have been coated with a coating medium in which there is present tin and antimony compounds, expressed as SnO_2 and Sb_2O_5, in the ratio of 92:8 parts by weight.

It has also been found that the presence of antimony in the above mentioned quantities in the coating medium for resistors of the kind described gives a minimum of resistivity in the antimony-tin oxide coating of the finished resistors of the kind described, although such resistors have otherwise desirable electrical properties; the use of such resistors is limited as a result of their low resistivity. For example rods having a diameter of ¼" and a length of 1" have been made with such films, but the resistance values have not been greater than 100 ohms/square centimetre and the process of increasing the effective length and reducing the width of the conductive path by cutting a fine pitch helix through the film, a technique well known in the manufacture of so-called pyrolitic carbon resistors, cannot increase the effective resistance to much greater than 100,000 ohms. However, electrical and electronic

resistors are often required with a resistance value up to several megohms.

The present invention is based on the discovery that the resistivity of resistors of the kind described which have been coated with a coating medium of tin and antimony compounds in the proportions stated above, can be increased considerably by the presence in the final coating of a small amount of boric oxide; however, the presence of the boric oxide in the antimony and tin oxide coating alters the temperature coefficient of resistance and best results are obtained with a coating containing less antimony than would be the case without boric oxide. For example, a resistor having a coating of stannic oxide and antimony pentoxide in the ratio of 14.9:1 and containing 1.0% of boric oxide or less, all parts being by weight, has a temerature coefficient of resistance which can be regarded as zero for practical purposes, i.e. 0.05% per ° C. or less, and, as will be shown, has a much greater resistivity than a similar resistor having a coating of the stannic oxide and antimony pentoxide only, the antimony pentoxide being replaced by boric oxide.

It is an object of the present invention to provide resistors of the kind described which have a high electrical resistance coupled with other properties required of resistors for use in precision instruments, such as for example low or constant temperature coefficient of resistance.

It is a further object of the present invention to provide resistors of the kind described which are very stable electrically when subject to high temperatures.

Further objects of the invention will become apparent hereinafter.

Thus the present invention consists in an electrical resistor having a body of a material selected from glass, vitreous material, porcelain and similar insulating material and provided with an electrically conductive coating consisting of oxides, characterized in that said coating comprises tin, antimony and boron in the form of oxides, the amount of antimony expressed as antimony pentoxide being at most 10% and the amount of boron expressed as boric oxide being at most 2.5%, both percentages being based on the total weight of the electrically conductive coating, said resistance coating being in the form of a film of which the surface resistivity is 1 to 10,000 ohms per square centimetre; it must be understood that the resistance of the resistor will depend on, inter alia, its dimensions, film thickness and specific resistance. The film thickness may vary from 200–10,000 Angstrom units and the resistivity may vary from 0.5 to 10 milli-ohms/cm.^{3}.

The electrically conductive coating of the resistors of the invention may contain, in addition to the oxides of tin, antimony and boron, one or more further oxides selected from titanium oxide, aluminum oxide, beryllium oxide, magnesium oxide, silicon oxide, zinc oxide, manganese oxide and cobalt oxide.

The resistors in accordance with the invention are preferably provided with an electrically conductive coating which has an antimony content expressed as antimony pentoxide of from 1½ to 9% and a boron content expressed as boric oxide of from $\frac{1}{20}$ to 1% (preferably 0.1 to 0.5%), both percentages being calculated on the total weight of the said coating.

Suitably the resistors in accordance with the invention have the electrically conductive coating solely consisting of the oxides of tin, antimony and boron.

Further in accordance with the invention a process for the production of the above resistors comprises depositing under oxidizing conditions a fluid coating medium comprising a volatile tin compound, antimony compound and boron compound on the resistor body in a furnace, the furnace temperature being 600 to 1000° C.

Said tin compound and said antimony compound are preferably salts (e.g. chlorides) of tin and antimony respectively and said boron compound is preferably boric acid. The said compounds are preferably dissolved in a solvent therefor, for example hydrochloric acid.

The process of the present invention may be effected by directing intermittent blasts of the coating medium in the form of a solution from an atomizing spray gun on to the resistor bodies whereby the electrically conductive coating is deposited on said bodies. Alternatively, the deposit may be effected by vaporization of the coating medium in known manner.

The above coating has a rather higher resistivity when it is applied to resistor cores made of porcelain. This material has a rougher surface than has glass, and porcelain resistors will, of course, not exhibit any iridescence. Better electrical performance is obtained when the said coating is applied to porcelain, glass or similar vitreous cores having a roughened surface than when their coating is applied to a similar core having a smooth surface. The reason why improved properties are obtained with a core having a roughened surface than with a core having a smooth surface is thought to be due to the fact that an equivalent surface resistivity is achieved by using thicker coatings in the case of roughened cores.

It should be noted that porcelain used as the resistor body may be sand blasted before the oxide coating is deposited thereon.

The surface of the porcelain or any other vitreous material which may be used must be clean; a suitable cleaning solution for removing serious contamination is a concentrated solution of chromic acid and the resistor bodies should be left in contact with this solution for approximately a week. This cleaning process may be accelerated by heating.

For less serious contamination a milder cleaning agent such as a detergent or an acid other than chromic acid may be employed.

The coatings of tin, antimony and boron oxides, and any other oxides present, may be produced on the resistors by contacting at an elevated temperature the resistor bodies with fumes or atomized solutions of volatile compounds of the said elements, said compounds being of such a nature as to form the oxides of the elements at the temperature of contact, if necessary in the presence of oxygen or water vapour. It should be noted that the compounds of the elements of which the oxides are required in the electrically conductive coating should be volatile under the particular conditions used for deposition, e.g. a tin halide, preferably a chloride, and on decomposition give the oxide of the elements.

For example a solution of tin chloride, antimony chloride and boric acid (H_3BO_3) in hydrochloric acid may be applied from a known type of atomizing spray gun to the resistor bodies which have been preheated to a temperature of 500° C. or higher, preferably 600–650° C., in a furnace. The strength of the hydrochloric acid may be from 10% by weight to concentrated acid, the strength being determined by the solubility of H_3BO_3 in HCl. In all cases the maximum strength of HCl possible, having regard to the solubility of H_3BO_3 should be employed. The proportions of the said compounds in the solutions should be such that an oxide coating is produced on the resistor bodies containing the desired proportion of tin and boron oxides. It should be noted that a solvent is not essential and need only be used when the volatile compound is a solid or liquid of low vapour pressure. The thickness of the oxide coating will be one of the most important factors determining the resistance value of the final resistor. By using the atomizing spray gun with spraying times of 5–30 seconds coatings may be produced having a thickness of 1000 to 10,000 Angstrom units. In some instances coatings having a thickness less than 1000 Angstrom units are desirable and coatings as thin as 200 or even 100 Angstrom units can be produced but such very thin coatings are less stable than 0.5%, which is generally the desirable stability for electronic and radio equipment, and they are less homogeneous than is desirable for said equipment. For some purposes a thickness of 1000 to 5000 Angstrom units is desirable.

Deposition should take place in a furnace at a wall temperature of 600–1000° C. The time of spraying varies inversely with the wall temperature. It is preferable to spray with several short blasts rather than one long blast to minimize cooling of the resistor body. For example, at a wall temperature of 800° C. (resistor body temperature 650° C.+) satisfactory spraying times are 2–3 seconds, one single spray giving satisfactory results.

The criterion governing the choice of any solvent for spraying is that, at a temperature below 600° C., it should prevent hydrolysis or decomposition of the compounds being sprayed.

In the case of compounds which are vaporized directly into the furnace, the compounds should not decompose into oxides or combine with oxygen or water vapour to form oxides at temperatures below 600° C.; if this is not the case then it is necessary to introduce, with the vapours, compounds which will prevent such decomposition. For example, if tin chloride were evaporated directly into the furnace it would decompose below 600° C. in the presence of oxygen and water vapour to form tin oxide, and it is necessary, therefore to evaporate tin chloride in the presence of HCl gas and it must remain in the presence of this gas until the surface of the resistor body is reached, where decomposition to the oxide occurs due to oxygen and water vapour from the atmosphere intermingling with the vapour on or near the surface of the resistor body.

It must be understood that the ratio of stannic oxide (SnO_2), antimony pentoxide (Sb_2O_5) and boric oxide (B_2O_3) in the final coating on the resistors according to the invention is different from the ratio of the corresponding tin, antimony and boron compounds (expressed as their said oxides) in the coating medium. For example, analysis has shown that an amount of boric acid (H_3BO_3), corresponding to 0.6% of B_2O_3, in the coating medium produces 0.2% of B_2O_3 (this depends to some extent on the conditions of deposition) in the final coating on the finished resistors of the kind described. There is also a reduction in the proportion of antimony oxide, but unless the total amount of antimony oxide in the coating approaches 10% the diminution is small enough to be unimportant.

In order to demonstrate the relationship between the proportions of tin, antimony and boron compounds contained in the coating medium and those of the resulting coating on the resistors, there is given hereinafter tables showing numerical values. Table I, column 1 shows the antimony content, expressed as antimony pentoxide, as a weight percentage of total tin, antimony and boron compounds in the coating medium; column 2 shows the value corresponding to column 1 in the electrically conductive coating of the finished resistor. In Table II, column 1 indicates the amount of boric acid in the coating solution, expressed as a percentage of boric oxide, while column 2 gives the corresponding value in the electrically conductive coating of the finished resistor. The tin content is not shown as this may be determined from the antimony and boron values.

TABLE I

Resistor coated with the oxides of tin, antimony and boron only	1	2
A	2.0	2.0
B	4.0	3.2
C	6.0	4.9
D	10.0	8.7

TABLE II

Resistor coated with the oxides of tin, antimony and boron only	1	2
A	0.6	0.22
B	2.5	0.86

Reference will now be made to the accompanying drawings in which Figure 1 is a graph showing the variation in resistivity caused by the presence of varying amounts of boric acid expressed as boric oxide (B_2O_3) in a resistor coating solution containing tin chloride (expressed as stannic oxide) and antimony chloride (expressed as antimony pentoxide) in the proportion of 14.9:1. Figure 2 of said drawings is a graph showing the variation in temperature coefficient of resistance corresponding to the amounts of boric oxide in the coating solution corresponding to that shown in Figure 1. Figure 3 is a diagrammatic cross sectional view of a furnace and spray device for applying the electrically conductive coatings in accordance with the invention. Figure 4 is a perspective view of a resistor in accordance with the invention.

The presence of boric oxide in a tin and antimony oxide coating results in a marked increase in resistivity and the graph shown in Figure 1 of the said drawings indicates this quite clearly. It will be seen that with a ratio of tin chloride (expressed as SnO_2) to antimony chloride (expressed as Sb_2O_5) in the coating solution of 14.9:1 up to 2.5% by weight of boric acid (expressed as B_2O_3) will increase the resistivity from that corresponding to a zero boric oxide content by a factor of 4. By the nature of the curve it will be seen that there is good reason to expect a progressive increase which would increase the resistivity available even further. Corresponding to this increase in resistivity the value of the temperature coefficient of resistance changes from positive to negative with increasing boric acid content so that, while the temperature coefficient of resistance of the coating consisting of tin and antimony oxides only but in the same proportions is +0.04% per ° C., with 2½% of boric acid (expressed as B_2O_3) present in the coating solution the temperature coefficient is −0.025% per ° C., as may be seen from the graph shown in Figure 2 of the said drawings. The presence of boric acid in the solution produces a negative trend in the temperature coefficient value and it has been found that over the range of 4–25% of antimony compound (expressed as Sb_2O_5) this can be compensated by a reduction in the antimony compound content. It is thus possible to apply this principle to a film containing boric oxide so that it is possible to reduce the antimony oxide content so that the temperature coefficient can be brought closer to zero than would be the case without boric oxide present. At the same time, the resistivity of the resultant film material improves.

Electrical resistors of the invention are very stable electrically when subject to high temperatures. In the case of the thinner films or where the boric oxide content is high their stability is decreased when subject to moist conditions and it is therefore of great importance that such metal oxide resistors should be protected with a film of moisture impervious lacquer or other moisture imprevious non-conducting material.

In order to illustrate the invention the following description of the manufacture of one specific embodiment in accordance with the present invention is given below.

Example

A solution was produced of the following constituents:

$SnCl_4.5H_2O$	g	100
$SbCl_3$	g	4
H_3BO_3	g	0.5
and		
Concentrated hydrochloric acid	cc	60

A previously sand blasted and cleaned porcelain rod, 4.4 mm. in diameter and 25 cm. long, was hung in a vertical furnace, similar to that shown in Figure 3 of the accompanying drawings, the walls of which furnace were at a temperature of 800° C. In Figure 3 reference numeral **10** generally indicates a vertical furnace, **12** is a wire support for the above porcelain rod **14**, and reference numeral **16** generally indicates an acid resistant spray gun of known kind which is fed from a reservoir **18** containing the above spraying solution and operated by compressed air via pressure tube **20**. The rod **14** was allowed to remain in the furnace **10** for about five minutes in order to attain equilibrium temperature. Three 3-second blasts produced a coating having a thickness of 3,100 Angstrom units. The ratio in the coating of stannic oxide and antimony pentoxide was 12.2 to 1 and the boric oxide percentage in the oxide coating was .2%. The resulting resistors had a resistivity of 56 ohms per square centimetre and the load stability at 1.5 watts/inch² was better than 0.2%. Loading up to 4.5 watts/inch² gives stabilities of 1% or better. After the oxide coating had been applied a varnish coating of known composition was applied to the resistors.

In order to produce resistors having a very high resistance the oxide coating produced as above may be formed into a fine pitch helix by known methods prior to the application of the varnish coating. By means of the formation of a fine pitch helix resistors can be produced whose resistance is up to 10 megohms. Figure 4 diagrammatically illustrates such a resistor in perspective, **14** designating generally the resistor body, **22** designating the oxide film formed into a fine pitch helix and **24** designating the spaces between the turns of the helix.

From what has been said above it will be seen that the proportions of the materials in the spraying solution stated in the example may be varied and an example of ranges of these proportions is as follows:

	Parts by weight
$SnCl_4.5H_2O$	80 to 120
$SbCl_3$	3 to 5
H_3BO_3	0.2 to 1.5

And at least sufficient concentrated hydrochloric acid to dissolve the solid constituents.

It must also be appreciated that the coating of oxides need not be as in the example, but may have a composition such that, for example, stannic oxide and antimony pentoxide are present in the ratio of 9–15:1 together with an amount of boric oxide of from 0.1 to 0.5%.

Although the present invention has been described with particular reference to specific details, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

I claim:

1. An electrical resistor comprising a non-conducting vitreous body and an electrically conductive coating thereon of tin, antimony and boron oxides, the amount of antimony expressed as antimony pentoxide being from about 1.5 to 10% and the amount of boron expressed as boric oxide being from about 0.05 to 2.5%, both percentages being based on the total weight of the electrically conductive coating, said coating being in the form of a film of which the surface resistivity is 1 ohm to 10,000 ohms per square centimetre.

2. A resistor according to claim 1, in which there is present in the electrically conductive coating at least one further oxide selected from the group consisting of titanium oxide, aluminum oxide, beryllium oxide, magnesium oxide, silicon oxide, zinc oxide, manganese oxide and cobalt oxide.

3. A resistor according to claim 1, in which the body of the resistor has a roughened surface.

4. A resistor according to claim 1, in which the electrically conductive coating has a thickness of from 200 to 10,000 Angstrom units.

5. A resistor according to claim 1, in which the electrically conductive coating has a thickness of from 1000 to 5000 Angstrom units.

6. An electrical resistor comprising a non-conducting vitreous body and an electrically conductive coating of oxides of tin, antimony and boron, the amount of antimony expressed as antimony pentoxide being from 1½ to 9% and the amount of boron present expressed as boric oxide being from $\frac{1}{20}$ to 1%, both percentages being calculated on the total weight of the said coating, said coating being in the form of a film having a thickness of from 200 to 10,000 Angstrom units and having a surface resistivity of 1 ohm to 10,000 ohms per square centimetre.

7. An electrical resistor comprising a non-conducting vitreous body and an electrically conductive coating of oxides of tin, antimony and boron, the amount of antimony expressed as antimony pentoxide being from 1½ to 9% and the amount of boron present expressed as boric oxide being from 0.1 to 0.5%, both percentages being calculated on the total weight of said coating, said coating being in the form of a film having a thickness of from 1000 to 5000 Angstrom units and having a surface resistivity of 1 ohm to 10,000 ohms per square centimetre.

8. An electrical resistor comprising a non-conducting roughened vitreous body and an electrically conductive coating of stannic oxide and antimony pentoxide in the ratio of 9–15:1 together with an amount of boric oxide of from 0.1 to 0.5%, based on the total weight of stannic oxide and antimony pentoxide, said coating being in the form of a film having a thickness of from 1000 to 5000 Angstrom units, the load stability of said resistor being better than 0.5%.

9. A process for the production of an electrical resistor having a non-conducting vitreous body and an electrically conductive coating of oxides, which comprises depositing under oxidizing conditions a fluid coating medium comprising a volatile tin compound, antimony compound and boron compound on the resistor body in a heated zone, the temperature of the heated zone being 600 to 1000° C., to form coating as a film of which the surface resistivity is from 1 ohm to 10,000 ohms per square centimetre.

10. A process according to claim 9, in which the said tin and antimony compounds are salts.

11. A process according to claim 9, in which the said tin and antimony compounds are chlorides and the said boron compound is boric acid.

12. A process according to claim 9, in which the said fluid coating medium comprises tin chloride, antimony chloride and boric acid dissolved in hydrochloric acid.

13. A process according to claim 12, in which, in the presence of air, the said fluid coating medium is sprayed on to the said resistor body, which has been previously roughened, by a plurality of intermittent short blasts from an atomizing spray gun.

14. A process according to claim 9, in which the said volatile tin compound, antimony compound and boron compound are vaporized on to the said resistor body, which has been previously roughened, in the presence of a substance inhibiting formation of oxides at a temperature below 600° C., said volatile tin and antimony compounds being salts.

15. A process for the production of an electrical resistor having a non-conducting porcelain body and an electrically conductive coating of oxides thereon, which comprises roughening a porcelain body, cleaning it, placing it into a heated zone, said zone being at a temperature of from 600 to 1500° C., depositing on said rod an oxide coating by spraying on to said rod a solution in concentrated hydrochloric acid of tin chloride, antimony chloride and boric acid by means of a plurality of intermittent short blasts from an atomizing spray gun, said solution being composed of the following constituents in the amounts specified:

	Parts by weight
$SnCl_4.5H_2O$	80 to 120
$SbCl_3$	3 to 5
H_3BO_3	0.2 to 1.5

And at least sufficient concentrated hydrochloric acid to dissolve the solid constituents,

the spraying being effected for a sufficient length of time for the film to have a thickness of from 200 to 1000 Angstrom units.

16. A process according to claim 15, in which the film resulting by the deposition is cut into a fine pitch helix and the resistor is then coated with a moisture impervious non-conducting protective material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,118,795	Littleton	May 24, 1938
2,440,691	Jira	May 4, 1948
2,564,677	Davis	Aug. 21, 1951
2,564,706	Mochel	Aug. 21, 1951
2,564,707	Mochel	Aug. 21, 1951
2,617,741	Lytle	Nov. 11, 1952
2,624,823	Lytle	Jan. 6, 1953
2,671,735	Grisdale et al.	Mar. 9, 1954
2,717,946	Peck	Sept. 13, 1955
2,720,471	Suchet et al.	Oct. 11, 1955
2,818,354	Pritikin et al.	Dec. 31, 1957

OTHER REFERENCES

Holland: Vacuum Deposition of This Film, John Wiley & Sons, Inc., N.Y., page 496.