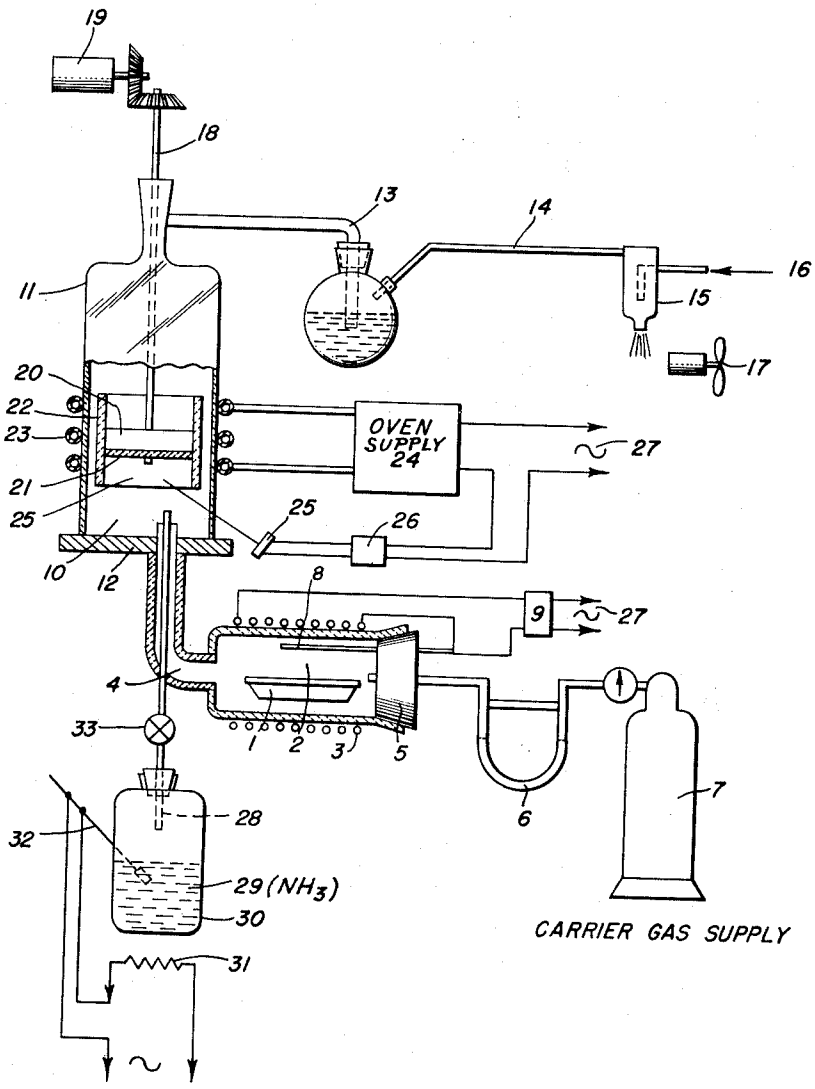
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METHOD OF MANUFACTURING ELECTRICAL RESISTANCES AND ARTICLES RESULTING THEREFROM

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METHOD OF MANUFACTURING ELECTRICAL RESISTANCES AND ARTICLES RESULTING THEREFROM

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The present invention relates to an improved method for manufacturing thin electrically conducting films having a high specific resistivity and a predetermined temperature coefficient, which films are homogeneous and strongly adhere to the surface of an insulating base plate therefor. The meaning intended for the word "thin" throughout the present specification and claims must be understood as relating to films of a thickness less than or at most equal to one micron.

It also relates to such improved resistive films that may result from the said method of manufacturing.

A further object of the invention is to so conduct the said method of manufacturing that the products resulting therefrom present a high quality of surface state, chiefly a very high melting point, a good optical polish and a quite high resistance to mechanical abrasion (the two last points being specially important when such films are intended for sliding contact potentiometer structures.

From a general point of view, a method according to the invention is mainly characterised in that a homogeneous mixture of at least two halides having a predetermined ratio of components is first prepared. The said mixture is then vaporized and brought to a pyrolytic conversion chamber for the formation therein of a film of the products of dissociation of the said halides onto a flat and heated surface, of dielectric material. A chemical conversion of the said elements into a complex of oxides and nitrides is ensured for obtaining the final electro-conductive films constituting the body of the resistance proper.

Referring to the attached drawing, the said method of manufacturing an electroconductive film according to the invention, may be explained as follows:

A homogeneous mixture of halides of the required elements is placed into a carrier **1** within a vessel **2** which is uniformly heated by means of a heating envelope **3**. The temperature is controlled from a thermometer **8** by a heat or temperature regulator **9** fed for instance at **27** by an A.C. current. One end of the vessel **2** is provided with an obturator **5** and at the other end thereof, the said vessel is opened upon an insulated pipe **4** of substantial cross-section in order to avoid losses in the gaseous stream issuing therefrom.

A gas is supplied from a container **7** to the vessel **2** through a regulated feeder **6**. The evaporated halides will be carried therein through the pipe **4** to a vessel **10** constituted by a bell-shaped wall **11** connected by an air-tight joint to a base plate **12**. An outlet **13** is provided for this vessel through which the excess of gas and vapours may pass to a dabbling or moistening equipment and including a water pump **15** which, fed with water through a pipe **16**, sucks through **14** the remaining gas and vapours and evacuates it with the aid of a ventilator **17**.

An axle **18** passes through an air-tight joint into the vessel **10** and is driven at a low speed from a motor **19**. At the end of the said axle **18** is supported a heat-retaining mass **20** subjected to the action of a high frequency heater **23** fed from an electrical oven source **24**. The heating is controlled from an optical pyrometer **25** and a supply regulator **26**. An asbestos screen **22** ensures the protection of the wall **11** against the heating. Mass **20** is supported on a plate **21** of dielectric material such, for

instance as a high melting point glass. This plate **21** constitutes the supporting base for the film to be deposited thereon. The heating mass is thermally matched to the said plate **21** in that the cooling thereof is effected, after the heating current is turned off, during an interval of time which is sufficient to prevent any damaging strain within the plate **21**.

A capillary pipe **28** passes coaxially through the pipe **4** and is provided with a cock **33** for a controlled admission therethrough within the vessel **10**, when required, of a limited quantity of a gas generated within a vessel **30**. This vessel contains for instance a solution of ammonia. The generation of ammoniacal gas is controlled therefrom by means of heating means **31** provided with thermometric regulating means **32**. As it will be herein after explained, an admission of such a gas will be useful when nitridation of the films resulting from pyrolytic reactions of halides within the said vessel **10** is required, either for a surface treatment or for a complete nitridation process. Oxides will be obtained when the carrier gas is made of or comprises oxygen, and nitrides will be obtained by using an inert carrier gas, such as nitrogen, along with NH_3 as the nitridation reagent. In certain cases however, no carrier gas is required. In such a case, the part of the equipment including the container **7** and associated components may be omitted.

The components of the mixture in the evaporator consist of halides (or salts of halogen) of the elements, viz. metals and/or metalloids, the oxides and/or nitrides of which are finally produced, as such components only require quite low temperatures for their fusion and vapour production. In any case however, the decomposition temperatures of the components will always be much higher than the temperature of the plate **21** which is required for the pyrolytic reaction at **10**. Such a pyrolytic reaction is too well known per se to be herein detained. It consists of the dissociation of a volatile complex of an element, in the vapour phase thereof, at a temperature much lower than the melting point of the element, metal or metalloid, included therein. The composite vapours brought into the vessel **10** dissociate and result in the formation upon the surface **21** of a very adherent deposition, which cannot be evaporated even at very high temperatures. The nature of the thus obtained film apparently depends upon the initial components of the evaporated mixture and also upon the atmosphere wherein the pyrolytic reaction is made.

In such a reaction, the control of the temperature of the receiving plate is one of the methods which may be used for controlling the resulting surface state of the film, i.e. the fineness of the film, provided the pressure of the vapour atmosphere is made constant during the said reaction. Varying these two conditions, it is quite possible to obtain a film of very fine structure with a low temperature of operation and conversely a structure of coarse granulometry with a higher temperature of operation, though lower than the temperature of dissociation of the initial mixture. An increase of the density of the vapours or an increase of the pressure within the reaction chamber, or an increase of both these conditions, permits the obtaining of films, the surface structure of which is a crystalline and very fine one. Actually, for practicing the invention, it has been found of advantage to operate the pyrolytic reaction at the highest admissible temperature and to determine the fineness of the film by adjusting the pressure and/or the density of the vapours giving rise to such a film.

But the invention enables the production of thin resistive films having a predetermined temperature coefficients. It is well known that a great many metallic oxides present negative temperature coefficients. Nitrides

generally present positive temperature coefficients. As the films according to the invention are composite ones, wherein the components thereof are quite intimately mixed on a substantially molecular scale, it will be possible to provide therein either oxides of the P type of conduction, having an excess of electrons, such for instance as V_2O_5, ZnO, WO_3, TiO_2, Ta_2O_5, or oxides of the N type of conduction, having a lack in electrons, such for instance as CuO, NiO. It is apparent that associations including oxides of both these types of conduction may easily be provided with predetermined ratios, in films produced according to the present invention.

It is also quite easy to provide associations of oxides and/or nitrides in such a method of processing as herein above defined in order to obtain electroconductive films of predetermined resistivities.

For instance and with a view of illustrating the above, one may consider that the initial mixture comprises stannic bromide and niobium pentabromide. Within an oxidising atmosphere, this mixture will give, through pyrolytic reaction, a composite film of stannic oxide and niobium pentoxide. Bromine will remain in the vapour state, and be evacuated in such a state. Thereafter introducing NH_3 within the vessel **10**, niobium nitride is obtained in the said film. There is no isomorphism between stannic oxide and niobium nitride, but the mechanical hardness of both are similar and the surface hardness of the resulting film thereof will actually be of the same order as that of vanadium. The melting point of the complex constituted by tin oxide and niobium nitride will have a value of about 1700° C. The tetravalent tin oxide has a coefficient of temperature which is highly negative until 700° C. and suddenly reverses at this point. The niobium nitride presents a reverse property in that it becomes superconducting at the neighborhood of 10° K. Their respective resistivities are, at normal temperature, equal to 22.10^3 ohms/cm. for the niobium nitride and to about 10^4 ohms/cm. for the said tin oxide. By regulating the ratio of the components in the initial mixture and consequently in the finally produced film, a predetermined value of coefficient of temperature and electrical resistivity may be obtained.

Instead of tin, other elements from group IV may advantageously also be used, mainly silicon and titanium, and the "impurities" will advantageously be of the third and fifth groups according to the range of resistance and temperature coefficient values which is required for the resulting films.

One example of a resulting complex which will give resistances of a high degree of stability, a high melting point therefor, and also a very good resistance to abrasion, from the mechanical point of view, is that wherein are included titanium and/or tantalum nitrides. Silicon may also be used instead of titanium, sometimes with some advantage due to the isomorphism thereof. But of course, quite a number of other elements may be incorporated in resistive films according to the invention.

Considering for instance two practical cases of utilisation of the equipment which has been herein above described:

In the first case, a homogeneous mixture is made which includes the following proportions by weight of

91% of tin bromide ($SnBr_2$)
3.5% of niobium pentabromide ($NbBr_5$)
5.4% of bismuth tribromide ($BiBr_3$)

and the said mixture is introduced within the vessel **2**, the temperature of which is maintained between 215 and 218° C.

The speed of rotation of the axle **18** is between one and .2 rotation per second at least. The temperature of the plate **21** is established at 500° C. ±20° C.

Through the vessel **2** a flux of carrying gas is established for the halide fumes, which comprise two parts in volume of nitrogen and one part of hydrogen, with a supply rate of .2 litre per minute. Simultaneously a volume of NH_3 is fed at a supply rate of .66 litre per minute through **33**.

With such adjustments, and starting from a mixture weighing 1.8 grams, the film produced over a surface measuring four square centimeters has a total resistance equal to 40,000 ohms ±10%. The temperature coefficient thereof is positive and equal to 5.10^{-6}. The deposition of the film is obtained within three minutes.

The resistance value of a film is approximately a linear and reverse function of the weight of the initial mixture, and consequently of the weight of the film. Starting from a mixture weighting 3.6 grams, the film coating the same surface of 4 square centimeters will have a resistance value of about 20,000 ohms.

In the second case, the following mixture is established within a very dry atmosphere and at a very low temperature:

96% per weight of titanium tetrachloride ($TiCl_4$)
3.5 hafnium tetrachloride ($HfCl_4$)
.5 tantalum pentachloride ($TaCl_5$).

This mixture is placed within the vessel **2** which is first heated to 140° C. in five to six minutes and then up to 221° C. in about one half or one minute, in order to ensure an even diffusion of hafnium and tantalum. No introduction of ammoniac gas is made. The carrier flux is made of or contains oxygen. The result is the formation of a complex film including the oxidies of the above elements on the plate **21**. For the same weight and surface area as above, the resistance value of this film is equal to 200,000 ohms ±20% and the temperature coefficient is negative and equal to 4.10^{-5} up to 200° C.

In the first above case, the carrier gas does not make any part of the pyrolytic reaction process for the formation of nitrides. Nitrides are due to the introduction of ammoniac gas within the vessel **10**. If the addition of NH_3 were cut off, in such a process, the pyrolytic conversion would result in the formation of a film of an alloy of pure tin, niobium and bismuth. Such an alloy might then be submitted to a further operational step for converting the metallic alloy into a nitride complex. The same sequence of steps would be effective for the preparation of oxide films, i.e., first the formation of a film of metallic alloy and then the oxidising thereof.

But the better procedure for applying a further conversion step to a film produced from a pyrolytic conversion appears to be as follows: first the pyrolytic process is made within an oxidising atmosphere, and consequently the film resulting therefrom is an all oxide complex. As an alternative, the process may be carried out to bring a nitridation of at least part of the film. It must be noted that for halides which are strongly hydrometric, the first step will always give an oxidising. In such cases it will be more economical to use moistened air for the carrying of the halide fumes, instead of utilising therefor a specially prepared gas mixture.

If the specific resistivity of the films is determined by an appropriate choice and adjustment of the ratio of the components thereof, the total resistance value of the film depends upon the weight of the material therein and the area thereof, it being understood that the thickness is quite uniform at any point of the said area. The resistance R of a film having a thickness "*s*," a length "L" and a width "T," and having a specific resistivity "*p*" is $R=(p\times L)/(s\times T)$. When the film is made as an annular area, for establishing therefrom a sliding contact potentiometer, the width is equal to the difference of the radii and the length, to that of the arc of circumference of average radius. It is apparent that any law of variation of the resistance along the potentiometer track defined therefrom may be obtained from a variation of the width thereof in function of the angle of the radius along

which is conducted this width with respect to a reference radius.

In order to obtain a shape of resistive film and an area thereof presenting a total resistance value which is predetermined and accurately adjusted, and also a linear change of resistance along the said area which is also accurately adjusted, two ways are possible: first, a mask may be formed over the surface of the base plate **21** through which the deposition of the film is operated; secondly the surface of the base plate may be completely coated with the film and parts of the said film are removed where in excess. The second way may advantageously be used for further adjusting a resistance obtained through a mask according to the first method.

It is apparent that the said mask must be such that it does not impede the process of formation of the resistive film. It may be prepared as follows:

The two following mixtures are separately made:

I. 58% of finely powdered silica, passed through a 325 mesh sieve, 26% of pure alumina, 11% of potassium oxide K_2O, 4% of sodium oxide Na_2O and 1% of sodium borate $Na_2B_4O_7$, weight percentages;

II. 73% of sodium sulfosuccinate, 12% of methanol, 5% of glycerin and 10% of carboxymethylcellulose, weight percentages.

The mixture I is placed into solution into the mixture II until a sirupy mixture is obtained of such a viscosity that it may be applied to the plate 21 by spraying, serigraphy or painting, that is to say to all parts of the said plate which are due to remain free from the film to be established thereon. After deposition of the said film, the mask is easily removed from the base plate.

The removal of parts of a resistive film, on the other hand, cannot be easily made by abrasion or direct mechanical action. Of course diamond tools or electric sparking may be used but it appears preferable to proceed as follows:

A mixture is prepared comprising within 350 cubic centimeters of water and 5 cubic centimeters of glycerin, 1 gram of sodium nitrite and .5 gram of pyrophosphate of sodium to which is added a value of 2.5 grams of bentonite. This mixture may be made as follows: a gel is prepared from the admixture of bentonite with 100 centicubes of water, another mixture is separately prepared containing glycerin and the same volume of water, a third mixture is made containing the pyrophosphate, the nitrite and the remaining water. The two latter mixtures are mixed and the gel is added thereto.

Once the overall mixture is made, an equal volume of methanol is added thereto and in the methanolic solution thus obtained, fine powder of zinc is mixed in the proportion of 1 gram of zinc for 2.5 grams of the said solution. The resulting product is sprayed through a mask over the parts of the film to be removed. After drying, a further spraying is made with a solution in water of hydrochloric acid, the concentration of which is between 1 and 10% per weight of acid. After about ten minutes, a reaction is completed whereby the zinc, of electronegative conductivity, reduces in the presence of the acid all parts of the film sprayed by the above-said solution. Instead of zinc, tin, cadmium, iron or aluminum may be used in the said solution.

The resistances having thus being made and adjusted, electrical connections must be attached thereto. It will be of advantage not to have recourse to mechanical connecting means to such films and, of course, once the adjustments are made it is highly desirable not to alter the resistance of the film, so that the electrical connections must present a much lower electrical resistance than the film.

According to an auxiliary feature of the invention, use is made for the establishment of such connections of the same method as has been herein above described. A mask is set over the film and those parts of the base plate thereof which are due to remain free from any coating. Thereafter, the thus coated base plate and film are placed at the location of the base plate **21** in the shown equipment or plant, and a further pyrolytic reaction is operated with a material in the vessel **2** which now includes boron bromide together with another bromide such as titanium or other material. The resulting connections are thus made as film strips of boron and other oxides which are of a far greater conductibility than the resistive films previously formed, due to the presence of boron, as is well-known per se.

What is claimed is:

1. A method of producing electrical resistor elements having a highly accurate, predetermined resistivity and temperature coefficient and a high degree of surface hardness which comprises mixing into a homogenous stream controlled amounts of vapors of the halides of at least two separate chemical elements, one of the components of said stream constituting at least 90% by weight of the stream and being a halide of an element selected from the group consisting of tin, silicon and titanium, the remainder of said stream being a minor component selected from the group consisting of the halides of niobium, bismuth, hafnium, tantalum, tungsten, zinc, nickel, copper and vanadium, carrying said mixture of vaporized halides into a gaseous stream comprised of an inert carrier gas and a reactive gas selected from the group consisting of water vapor, oxygen and ammonia, and mixtures thereof, contacting the resulting gaseous mixture stream with a dielectric base heated to a temperature high enough pyrolytically to decompose said halides into halogen and the free element and cause said reactive gas to react with the base element forming a compound selected from the group consisting of the oxides and nitrides of said free elemens as a uniform deposit upon said dielectric base in intimate surface cohesion with said base and evacuating excess vapors from the zone surrounding said heated base.

2. A method according to claim 1, and wherein prior to the pyrolytic reaction, applying to predetermined portions of the said receiving plate a layer constituting a mask impeding the deposition of the said film over the said portions, and after the deposition of the said film removing the said mask therefrom.

3. A method according to claim 1 and wherein, after the formation of the said film, the step of coating parts of the film with a layer constituting a mask impeding a deposition of matter over the said parts, and effecting a new pyrolytic reaction in which an halogenated component of boron is the main component of the new mixture the fumes of which enter in the said new pyrolytic process.

4. A method as claimed in claim 1 wherein said gaseous stream at first comprises oxygen with no ammonia causing an oxide deposit to be formed and thereafter said gaseous stream comprises ammonia causing the deposit to comprise, a least in part, a nitride.

5. A method as claimed in claim 1 wherein said reactive gas is oxygen forming a deposit of an oxide and, wherein, thereafter the oxide film deposit is subjected at elevated temperature to an atmosphere containing ammonia whereby the oxide deposit is at least partially converted into nitride.

6. A method as claimed in claim 1 wherein said gaseous mixture stream is contacted with said dielectric base which is supported by a heat-regulating mass and which is slowly rotated within a chamber heated to a temperature high enough pyrolytically to decompose said halides.

7. A method as claimed in claim 1 wherein said halide mixture comprises at least 90% tin halide and at least part of the remainder of the mixture is niobium halide.

8. A method as claimed in claim 1 wherein said halide mixture comprises at least 90% tin halide and at least part of the remainder of the mixture is tantalum halide.

9. A method as claimed in claim 1 wherein said minor component comprises a mixture of two halides.

10. An electrical resistance comprising a dielectric base plate having deposited thereon as a uniform coating, in intimate surface cohesion with the base plate, an electrically conductive layer of a thickness up to one micron consisting of a molecular complex of compounds selected from the group consisting of oxides and nitrides, at least 90% by weight being a compound of an element selected from the group consisting of tin, silicon and titanium and the remainder of the complex being compounds of an element selected from the group consisting of niobium, bismuth, hafnium, tantalum, tungsten, nickel, copper, zinc and vanadium.

11. An electrical resistance as claimed in claim 10 wherein said complex comprises a mixture of oxides and nitrides.

12. An electrical resistance as claimed in claim 10 wherein said complex consists predominantly of a mixture of oxides with said layer thereof being superficially nitridised over its entire exposed area.

13. An electrical resistance according to claim 10 and wherein to the said film and on the same base plate there exists at least one pair of electrical connection films constituted by a complex of oxides including mainly a boron oxide therein.

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