July 5, 1955 J. J. F. GUARDIOLA ARAGONES ET AL 2,712,521

PROCESS OF MAKING BISMUTH RESISTANCES

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Fig. 1

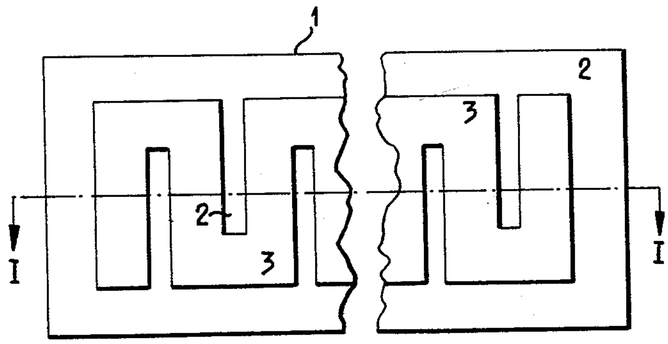


Fig. 2

Fig. 3

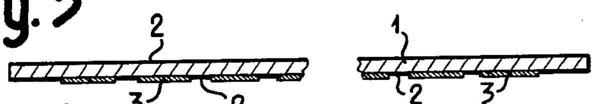


Fig. 4

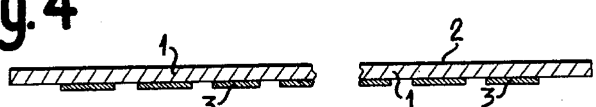


Fig. 5

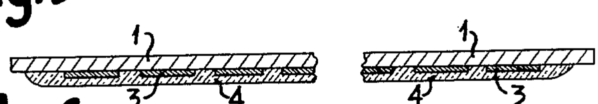


Fig. 6

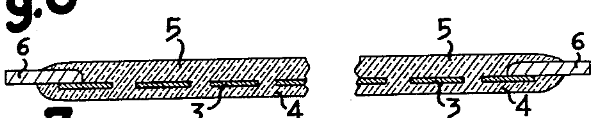
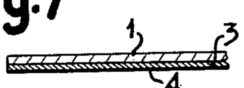


Fig. 7



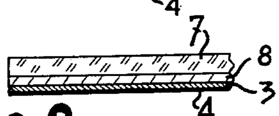


Fig. 8

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Fig. 9

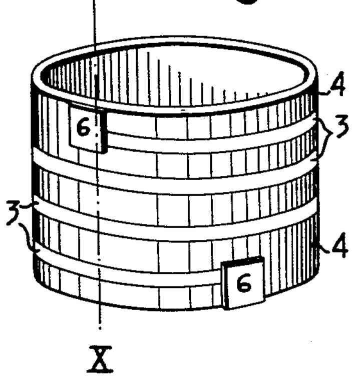


Fig. 10

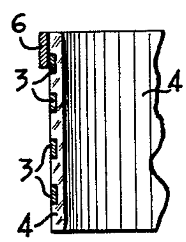
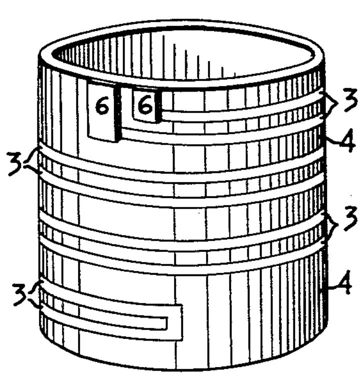


Fig. 11



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United States Patent Office

2,712,521

Patented July 5, 1955

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2,712,521

PROCESS OF MAKING BISMUTH RESISTANCES

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Application May 28, 1951, Serial No. 228,573

Claims priority, application Switzerland July 13, 1950

4 Claims. (Cl. 204—12)

In electric and magnetic circuits, very thin electric resistances are often needed, especially in apparatus where the resistances used are made of a metal whose resistance varies when placed in a magnetic field transversal to the direction in which the resistance is measured.

Among the metals known, it is bismuth which gives the highest resistance variations for a given variation of the magnetic field in which this metal is placed. With the aim of making use of this property, bismuth wire resistances were manufactured up to the present time, but their preparation required considerable time and was expensive and difficult; moreover, the resistances thus obtained were thick and of very low values. It is indeed practically impossible to manufacture bismuth wires of a diameter under 0.08 mm., due to the extreme fragility and practically non-existing mechanical resistance of bismuth. This wire must therefore be set on a rigid support of a certain thickness, the cost of which is moreover very high.

As these resistances are placed in the air-gap of a magnetic field, it is necessary to have this air-gap as small as possible to obtain a magnetic field of a sufficiently high value.

Very thin resistances may be manufactured by effecting a metallic deposit on an insulating support by vacuum evaporation. However, this method only gives a deposit whose thickness is about 1 micron. Due to the fact that this thickness is generally too small for the usual applications, it is necessary to repeat the operation several times until a deposit of the desired thickness is obtained, with the result that the cost of the resistance is greatly increased.

The object of the present invention is a manufacturing process for a bismuth resistance, which avoids the above mentioned inconveniences. This process consists in electrolytically depositing a layer of said metal on a conducting support, applying a thin insulating support to this electrolytic deposit and then dissolving, at least partly, the conducting support by means of at least one chemical agent which does not dissolve either the electrolytic deposit or the insulating support.

The attached drawing shows, schematically and as an example, a resistance obtained according to the process, object of the invention, at various manufacturing stages.

Fig. 1 is a side view of a resistance in the course of manufacture.

Fig. 2 is a sectional view according to II—II on Fig. 1.

Figs. 3 to 6 represent sectional views of a resistance at various manufacturing stages.

Figs. 7 and 8 represent schematically sectional views of two resistances in the course of manufacture, according to two variations of the process, object of the invention.

Fig. 9 represents a perspective view of a cylindrical resistance.

Fig. 10 is a sectional view according to X—X on Fig. 9.

Fig. 11 is a perspective view of a cylindrical resistance with practically no self-induction.

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Figs. 1 and 2 represent, schematically, a copper plate **1**, on a part of which has been applied a layer **2** of an insulating varnish to prevent the electrolytic deposit. As Fig. 1 shows, this layer is applied in such a way as to leave free only a sinuous ribbon surface. Bismuth is electrolytically deposited on that plate, the thickness of the deposit being defined by the time of the electrolysis and the current intensity. Consequently, bismuth only settles on the surface which has not been covered with varnish, and thus forms a continuous ribbon **3** strongly adhering to the copper plate **1** (Fig. 3).

After the electrolysis, the electrolytically deposited side of plate **1** is covered with one or several layers of a varnish **4** which after its hardening constitutes a thin insulating support (Fig. 5).

The protecting layer **2** on the back of the copper plate **1** is then removed, and the latter is dissolved by means of a chemical agent or a mixture of chemical agents which do not corrode bismuth or the insulating support.

During the dissolution, it is advantageous to protect a part of the copper plate at each end of the bismuth ribbon, so that this undissolved metal may be used as contacts **6** when the resistance is connected.

A resistance is thus obtained, which is made of a thin bismuth ribbon strongly adhering to an insulating support and terminated at both ends by a copper contact **6**.

To protect the bismuth ribbon **3** from the air, and to protect it in a mechanical way, one or several layers **5** of insulating varnish may also be applied. In this way, the bismuth ribbon is enclosed between two insulating supports.

Very thin flat resistances, less than 0.1 mm. for instance, may be obtained through this process. The thickness of the bismuth ribbon may be between 0.005 and 0.2 mm., and its width less than 0.1 mm., thus making possible the manufacture of resistances of several tenths of thousand ohms, whose shape, for instance, is that of a rectangle 2 cm. wide by 5 cm. long. When making a rather thick electrolytic deposit of an almost rectangular shape, it is possible to manufacture resistances, the value of which is about 0.1 ohm. In the same way, deposits consisting of bismuth in combination with other metals may be prepared. The process is suitable for the manufacture of resistances of any shape, and is particularly adapted to obtain resistances of cylindric shape, as the electrolytic deposit may be made on the outer or inner wall of a conducting cylinder which is afterwards dissolved.

Fig. 9 shows a completed cylindric resistance. Cylinder **4**, formed by the varnish, constitutes the support of the resisting ribbon **3**. The ends of this ribbon are made of copper contacts, formed by the undissolved parts of the copper cylinder which was used as metallic support for the electrolytic deposit

Fig. 10 is a sectional view according to X—X on Fig. 9 and shows the disposition of one of the copper contacts **6**, of the ribbon **3** and support **4** made of polymerizable varnish.

Fig. 11 represents a cylindric resistance similar to that represented on Fig. 9, but in which the metallic ribbon is disposed in such a way as to form a bifilar winding, thus presenting practically no self-induction.

These cylindric resistances are obtained through the same process as the flat resistances, and it is clear that all variations of this process, which are described for the manufacture of flat resistances, are also valid for the cylindric resistances.

The electrolytic deposit is easily obtained when the dissolution potential of the metal forming the conducting plate is lower than that of bismuth. If, on the contrary, that metal had a higher dissolution potential than that of bismuth, the surface on which the deposit must be made, should be covered with a metal having a lower dissolution potential than bismuth, as, for instance, copper or silver.

A variation of this process consists in first depositing the electrolytic layer on a bare metallic support, then partially removing the deposit by mechanical means (cutter, chisel, tracing machine) or chemical means (for instance, acids) so as to leave on the metallic support only a ribbon of electrolytic deposit of the required shape.

Fig. 4 represents a sectional view of a copper plate, one side of which has however been varnished to prevent the electrolytic deposit and the other side bearing the electrolytic deposit from which certain parts have been mechanically removed to give it the required shape.

In the above mentioned instance of a cylindric resistance, the electrolytic deposit may easily be removed, partially by means of a lathe, or any other adequate machine or tool, cutting a thread into the deposit so as to give it the shape of a helicoidal ribbon.

The varnish applied on the electrolytic deposit and which becomes later on the support of that deposit, is preferably a basic varnish of polymerizable synthetic resin which is then dried in the open air, the polymerization being done at high temperature.

As a variation, the conducting support may also be made with a soluble non-metallic support one part of which at least is metallized. This insulating support might be for instance made of Celluloid, cellulose acetate, polystyrene, and the like. Metallization may also be obtained through various processes, such as spray metallization, chemical reduction metallization, vacuum evaporation metallization, cathodic deposit metallization, and the like.

In the case of spray or vacuum evaporation metallizations, a housing may be used so that the metallized surface may already have the shape to be given to the electrolytic deposit. Consequently, it is no longer necessary to varnish the surface on which no electrolytic deposit is to take place. After the electrolysis, the deposit is covered with a varnish which will later on form the insulating support of the resistance, then the basic non-metallic support is dissolved by means of an appropriate solvent, like acetone, for instance. The metallic layer which was used to make the support a conducting one, is then dissolved by means of chemical products attacking neither bismuth nor the varnish constituting the support.

The metallization may also be made on the entire surface of the insulating support and the desired shape and electrolytic deposit may be obtained by one of the methods previously indicated, i. e. it is possible to either apply a protecting varnish on the parts which are not to receive any deposit, or to produce a uniform deposit, certain parts of which are then removed by chemical or mechanical means.

Fig. 8 is a diagrammatic cross section of such a resistance during its manufacture. On this figure may be seen the non-metallic support **7**, the metallic layer **8** allowing the electrolytic deposit of the layer **3** on which a layer of polymerizable varnish **4** is applied.

Fig. 7 shows, as a comparison, a resistance obtained directly by an electrolytic deposit **3** on a copper plate **1**. This deposit **3** is covered with a layer of polymerizable varnish **4**.

Any kind of metal on which a suitable electrolytic deposit may be made of the metal to form the resistance, can be used to metallize the non-conducting support. For instance, silver which is deposited by chemical reduction, copper deposited by spraying, and the like. When the resistance is to be made of bismuth, it is advantageous to metallize the non-conducting support with bismuth which may be deposited by vacuum evaporation. In this way, it is no longer necessary to dissolve the metal applied on the support, and it is sufficient to dissolve the non-metallic support.

In any case, it is beneficial to choose a bath giving a very fine-grained electrolytic deposit. For instance, a bath of perchloric acid with an addition of colloids is suitable for obtaining a bismuth electrolytic deposit.

As to the insulating support which is to adhere to the electrolytic deposit, it is obvious that it may be made of any material whatsoever, as for instance, mica, porcelain, enamel, cellulose, and the like. However, it is advantageous to choose it among the synthetic plastic materials, such as vinyl, phenolic, acrylic resins, silicone resins, resins based on urea, resins based on styrene, and the like.

Manufacturing example of a bismuth resistance of 1500 ohms

A copper sheet 0.1 mm. thick, 70 mm. long and 30 mm. wide is selected. A design of 25 mm. on one side, such as described above, is printed on that sheet; then the other side of the sheet is completely protected with a varnish.

The support is then carefully cleaned and dipped into an electrolytic bath, of the following composition:

Carbonate of bismuth 40 gr. per litre.
Perchloric acid at 60% 100 gr. per litre.
Glue 0.1 gr. per litre.

The bath has a temperature of 40° C. and the time of electrolysis is 15 minutes for a current density of 2 amp./dm. 2.

The piece is then rinsed, the protecting varnish removed, and the bismuth surface covered with a layer of Araldite varnish. (The trade-name Araldite designates an epoxy resin sold in commerce.) The varnish solvent is evaporated at 80° C. and the polymerization of the Araldite takes place in an oven heated at a temperature of 180° C. during 30 minutes.

This operation completed, the ends of the plate are protected with a varnish and the whole is dipped into a solution at 10% of trichlor-acetic acid of ammonium rendered alkaline through the addition of ammonia.

The dissolution of the copper plate takes an hour at a temperature of 35° C.

I claim:

1. A method of preparing mechanically stable thin bismuth resistances comprising the steps of passing an electric current through an electrolytic cell containing a solution of a bismuth salt and a cathode having at least partially a metallic conducting surface, said surface being of a metal having a lower dissolution potential than bismuth, removing the cathode from the cell after a bismuth containing layer of a thickness not exceeding .2 mm. has been deposited on said metallic cathode surface, coating said layer with a polymerizable resin, curing said resin, and dissolving the metal of the cathode to such an extent as to allow of separating therefrom the bismuth containing layer and the insulating coating as an integral self-sustaining structure, thereby obtaining a bismuth resistance of substantially uniform thickness carried by an insulating support.

2. A method as defined in claim 1 wherein the cathode consists of copper and wherein the cathode is dissolved in an ammoniacal solution of ammonium trichloroacetate.

3. A method as defined in claim 1 comprising the step of finally applying to the bismuth surface of the obtained resin-bismuth structure an insulating coating so as to obtain a bismuth resistance sandwiched between two supporting insulating layers.

4. A method of preparing mechanically stable thin bismuth resistances comprising the steps of providing an electrolytic cell including a cathode having a conducting surface conforming to the shape of the resistance to be obtained and an electrolyte containing about 40 g./1 of bismuth carbonate, about 100 g./1 of 60% perchloric acid, and a protecting colloid, said conducting surface consisting of a metal having a lower dissolution potential than bismuth, passing at a temperature of about 40° C. an electric current through said cell, removing the cathode from the cell after a bismuth layer of a thickness not exceeding 0.2 mm. has been deposited on said conducting

cathode surface, applying an electrically insulating coating to said layer, and dissolving the metal of the cathode to such an extent as to allow of separating therefrom the bismuth containing layer and the insulating coating as an integral self-sustaining structure, thereby obtaining a bismuth resistance of substantially uniform thickness on an insulating support.

References Cited in the file of this patent

UNITED STATES PATENTS

1,352,934	Arntzen et al.	Sept. 14, 1920
1,892,755	Scheppmann	Jan. 3, 1933
1,974,763	Wirth	Sept. 25, 1934
2,133,685	Coughlin	Oct. 18, 1938
2,328,626	Dowling	Sept. 7, 1943
2,441,960	Eisler	May 25, 1948
2,501,322	Ferguson et al.	Mar. 21, 1950
2,521,894	Brown	Sept. 12, 1950
2,564,677	Davis	Aug. 21, 1951