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METHOD FOR DEPOSITION OF A COPPER LAYER ON A NON-CONDUCTIVE MATERIAL

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Fig. 1

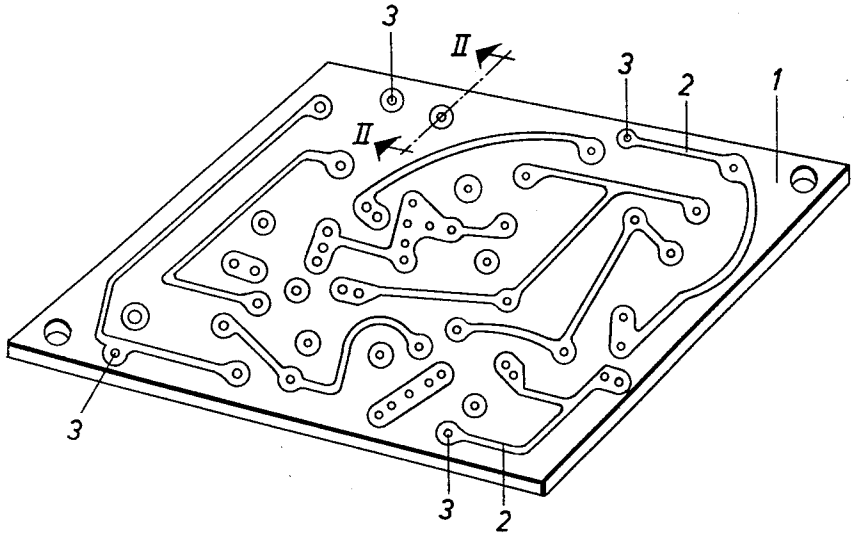


Fig. 2

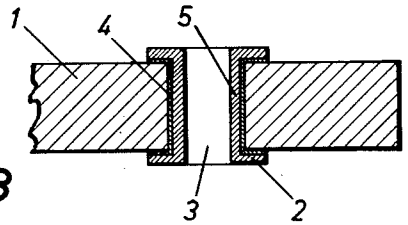
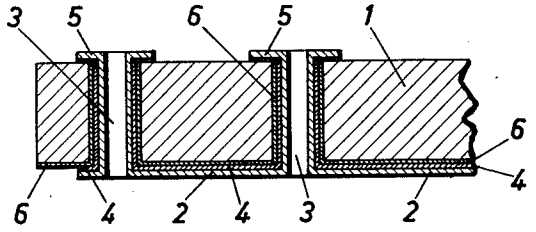


Fig. 3



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METHOD FOR DEPOSITION OF A COPPER LAYER ON A NON-CONDUCTIVE MATERIAL

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The present invention relates to a method of depositing a copper layer on an electrically non-conductive material, e.g. plastic.

In such electric apparatus as radio and television receivers, electronic measuring instruments and similar apparatus so called printed circuits are more and more used. These comprise metal coatings on non-conductive material, e.g. plastic plates. For practical reasons one tries to make these apparatus as small as possible and consequently said plates have to be as small as possible. Therefore, the conductive metal strips have been arranged on either side of the plate. Nowadays, there are no difficulties in shaping the metal strips. Copper coated plastic plates are well known on which it is possible to obtain any pattern by means of different methods, say photographic methods, silk-screen methods etc., and the metal coatings thus obtained can by means of galvanic methods be strengthened to any desired extent.

However, difficulties have arisen in making and the maintenance of the conductive connections between the conductors on each side of the plastic plates. It has turned out to be very difficult to create acceptable connections through the plate for reasons to be related in the following. Attempts have been made to obtain connections of this kind by arranging and attaching metal plugs in bores in the plate but variations in temperature and vibrations which occur when the apparatuses in question are used in vehicles, on engines etc., such plugs are easily loosened and when taken into account that printed circuits are to be used also in aircrafts it is easily understood that such conductors cannot be used.

Attempts have also been made to obtain a sufficiently good connection between the plastic support and the metal coating by precipitation of the metal from salt solutions but until now it has not been possible to solve the problem in an acceptable way.

The present invention is based on the last mentioned method, i.e. a chemical precipitation of a metal, in this case copper, on the plastic support and this is made in such a way that the object to be treated is moistened in a first pre-treatment liquid comprising a water solution of

15–52.5 grams, preferably ca. 43 grams stannic chloride, and
15–52.5 grams, preferably ca. 43 grams hydrochloric acid

in such an amount of water that there is obtained 1000 cm.^{3} of solution, and then in a second pre-treatment liquid, comprising between 1 and 10 grams, preferably ca. 2 grams palladium chloride per American gallon of water and that the actual object finally is immersed into a precipitation bath containing sulphate of copper, formaline or ammonium chloride, nickel chloride, sodium hydroxide, sodium potassium tartrate (Rochelle salt, Seignette salt) and sodium carbonate, all dissolved in water.

In order to obtain a precipitation bath of a suitable composition one could use essentially equal parts of the two following solutions, viz.

(A)

7.5–75 grams, preferably ca. 61 grams of sulphate of copper
50–80 cm.^{3}, preferably ca. 65 cm.^{3} formaline, and
0–40 grams, preferably ca. 17 grams nickel chloride

diluted in such an amount of water that there is obtained 1000 cm.^{3} of solution,

(B)

15–52.5 grams, preferably ca. 40 grams sodium hydroxide,
120–240 grams, preferably ca. 125 grams sodium potassium tartrate (Rochelle or Seignette salt), and
7.5–37.5 grams, preferably ca. 17 grams sodium carbonate

diluted in such an amount of water that there is obtained 1000 cm.^{3} of solution. Instead of formaline it is possible to use a solution of ammonium chloride containing 10 grams salt per litre water.

The invention will now be described with reference to the accompanying drawing. In the drawing:

FIG. 1 shows a printed circuit of the actual kind,

FIG. 2 is a section on the line II—II in FIG. 1 on a larger scale, and

FIG. 3 shows a section as in FIG. 2 of a modified embodiment.

Referring now to FIG. 1 the printed circuit comprises a supporting plate **1** of an electrically non-conducting material, preferably a hard plastic. Conducting connections **2** in the form of metal coatings are arranged on the sides of this plate **1** by means of methods described in the aforegoing. On the side of the plate **1** not shown there are likewise conducting connections of the same kind and shape. Bores **3** are arranged in the plate and in order to obtain conducting connections through the plate in these bores the invention provides the following method.

The surface to be coated with metal deposits, i.e. the inner walls of the bores **3**, are carefully cleaned mechanically, for instance by brushing, and then eventually in a chemical way by treatment with appropriate solutions. The whole plate is immersed into a bath of the kind set forth in the aforegoing and denoted the first pre-treatment liquid. So as to avoid deposits on not desired surfaces, these surfaces are in advance coated with e.g. paint or varnish. Attention is then to be paid so as to ensure that the bores **3** remain clean. The pre-treatment liquids can be stored in containers of rubber, Pyrex glass or plastics or even in metal recipients coated with a suitable material, say plastic or rubber. The plate is left in the container for about one minute whereupon a spongy deposition of tin is obtained in the bores. This precipitation probably develops from both sides by means of ion exchange with the copper. After an eventual rinsing the plate is immersed into the liquid referred to in the aforegoing as the second pre-treatment liquid for about ten seconds whereupon there is obtained a second coating on the material. Said last deposit is, however, very thin. After said last treatment the plate **1** is carefully rinsed in ordinary water. Such a rinsing can be carried out in streaming water and is then carried out in about one minute.

Finally, the plate is immersed in the precipitation bath proper having a composition stated above. There is then obtained a very smooth and continuous deposit **4** (see FIG. 2) of copper on the plastic. This copper deposit is intimately connected with the plastic and there is probably a molecular binding between the plastic and the copper.

Upon the deposit of the copper it is possible to precipitate any desired metal on the same by means of galvanic methods and the thickness of the precipitated metal layer **5** is defined by the treatment time, the current force etc. in usual manner.

Prior to the galvanic treatment, varnish and paint are removed from both sides of the plate by means of so called thinner or solvents, whereupon the remaining parts of the original copper coating is exposed. By means

of the galvanic treatment there is obtained an even and continuous metal deposit on the sides of the plastic plate **1** as well as in its bores **3**. It is also possible to first deposit the copper and then by means of mentioned methods develop the desired pattern on the plate **1**. It is then not necessary to cover the sides of the plate **1** with any paint layer.

A special treatment of printed circuits of this kind is related below. This modification gives an even better adherence between the basic plastic and the precipitated metal layer in comparison with the above method. This special treatment consists in applying a layer of a hardenable plastic after the chemical and/or mechanical cleaning of the surface to be covered with the metal layer. The said layer of plastic is prehardened whereupon the metal coating is deposited in the way described hereinbefore and the hardening of the applied plastic layer finally completed.

The hardenable plastic may be applied by spraying or brushing a mixture of the plastic and a thinner with which "orange peel" effect is produced. The applied layer of, say, 0.03–0.04 mm. in thickness is then partially hardened. On this partially hardened surface layer the metal coatings are deposited in the manner described of FIG. 2. Finally the plastic is substantially completely hardened.

In FIG. 3 on the accompanying drawing there is shown a section through a plate with printed circuits according to last mentioned method. In this figure same reference letters have been used for denoting same details as in FIGS. 1 and 2. The method is the same as described with reference to FIGS. 1 and 2 with the modification that, as already stated, there is applied a plastic coating **6** on the basic plate before the deposit of the metal layer. The plastic layer **6** shall be applied only on the surface of the plastic laminate having no metal film thereon and is hardened in two steps as already described.

The appearance of printed circuits according to the modification now described does not differ from the one of the first embodiment.

It is of course possible before as well as between the special treatments of the plate to perform other special treatments, such as cleaning the remaining copper portions on both sides of the plate **1**, as said portions might have been oxidized by the coating of the plate with the paints and varnishes whereby the binding between the different metal layers could be impaired. Further, it is possible to obtain improved results by special rinsings and by drying and heating the plate. In some cases it might be suitable to perform etchings.

These last mentioned special treatments are independent of the invention and the essential characteristics are to be seen in the composition of the special pre-treatment liquids and of the precipitation bath. The treatment methods proper by these liquids are independent of the invention and could be carried out in many different ways. Besides the above mentioned immersing it is possible to brush or spray etc. the plates with the treatment liquids.

The invention is of course not restricted to the described embodiment for the manufacture of printed circuits and could be used wherever it is desired to deposit a metal coating on an electrically non-conducting material.

Tests have shown when printed circuits manufactured according to previous methods have been tested that after five tests there have been found 14 errors at 518 bores. At corresponding tests with printed circuits manufactured according to present invention it has been possible to carry out 70 tests without any error at the same number of bores. The adhesion between the copper layer and the plastic has proved to have a value which is more than the double of earlier obtained values. So as to further ensure a good resistance and durability of the conduits with regard to vibrations and temperature variations, it is preferable to choose a tenacious metal for the galvanic precipitation.

What I claim is:

1. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.^{3} of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising sulphate of copper, formaline, nickel chloride, sodium hydroxide, sodium potassium tartrate and sodium carbonate, all dissolved in water.

2. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.^{3} of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising sulphate of copper, ammonium chloride, nickel chloride, sodium hydroxide, sodium potassium tartrate and sodium carbonate, all dissolved in water.

3. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 43 grams stannic chloride and 43 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.^{3} of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising sulphate of copper, formaline, nickel chloride, sodium hydroxide, sodium potassium tartrate and sodium carbonate, all dissolved in water.

4. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 43 grams stannic chloride and 43 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.^{3} of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 2 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising sulphate of copper, formaline, nickel chloride, sodium hydroxide, sodium potassium tartrate and sodium carbonate, all dissolved in water.

5. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.^{3} of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising essentially equal parts of the two following solutions, viz.

(A)

7.5–75 grams sulphate of copper
50–80 cm.^{3} formaline, and
0–40 grams nickel chloride

diluted in such an amount of water that there is obtained 1000 cm.^{3} of solution,

(B)

15–52.5 grams sodium hydroxide,

120–240 grams sodium potassium tartrate, and
7.5–37.5 grams sodium carbonate

diluted in such an amount of water that there is obtained 1000 cm.³ of solution.

6. A method for deposition of a copper layer of an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.³ of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising essentially equal parts of the two following solutions, viz.

(A)

61 grams sulphate of copper
65 cm.³ formaline and
17 grams nickel chloride

diluted in such an amount of water that there is obtained 1000 cm.³ of solution,

(B)

40 grams sodium hydroxide,
185 grams sodium potassium tartrate, and
17 grams sodium carbonate

diluted in such an amount of water that there is obtained 1000 cm.³ of solution.

7. A method of deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.³ of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising essentially equal parts of the two following solutions, viz.

(A)

7.5–75 grams sulphate of copper

50–80 cm.³ of an ammonium chloride solution with a concentration of 10 grams per litre, and
0–40 grams nickel chloride

diluted in such an amount of water that there is obtained 1000 cm.³ of solution,

(B)

15–52.5 grams sodium hydroxide,
120–240 grams sodium potassium tartrate, and
7.5–37.5 grams sodium carbonate

diluted in such an amount of water that there is obtained 1000 cm.³ of solution.

8. A method for deposition of a copper layer on an object of an electrically non-conducting plastic material, comprising the steps of moistening the object to be treated with a first pre-treatment liquid, comprising a solution of 15–52.5 grams stannic chloride and 15–52.5 grams hydrochloric acid in such an amount of water that there is obtained 1000 cm.³ of solution, moistening said object with a second pre-treatment liquid, comprising a water solution of 1–10 grams palladium chloride per gallon of water and immersing said object in a precipitation bath comprising essentially equal parts of the two following solutions, viz.

(A)

61 grams sulphate of copper
65 cm.³ of an ammonium chloride solution with a concentration of 10 grams per litre, and
17 grams nickel chloride

diluted in such an amount of water that there is obtained 1000 cm.³ of solution,

(B)

40 grams sodium hydroxide,
185 grams sodium potassium tartrate, and
17 grams sodium carbonate

diluted in such an amount of water that there is obtained 1000 cm.³ of solution.

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