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METHOD OF INCREASING THE ADHESION OF METAL TO A SUBSURFACE

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ABSTRACT OF THE DISCLOSURE

Process for improving the adhesion of metal to a subsurface by applying to the subsurface a resin coating, etching the coated surface, contacting the surface with a reducing bath, sensitizing, contacting the surface with a reducing bath, sensitizing and activating the surface.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to improving the adhesion of metal layers to a base surface, particularly in the formation of conductor plates.

Description of the prior art

It is known to subject base surfaces of, for example, metal or nonmetallic materials, which surfaces are to be coated with a metal, to a pretreatment wherein the surfaces, preferably first roughened by mechanical treatment, are cleaned with relatively strong inorganic acids, such as nitric acid or chromic acid, neutralized by alkali solutions such as aqueous solutions of sodium or potassium hydroxide, metasilicic acid, sodium pyrophosphate or their mixtures, and are then sensitized with a hydrochloric acid solution of tin chloride and/or palladium chloride. On the thus pretreated material surfaces, the metal layers are then chemically or electrolytically deposited (see, for example, French Patents 1,350,613 and 1,408,243).

The cleaning with relatively strong acids requires special corrosion-resistant containers and, in addition, a subsequent neutralization with alkaline neutralizing agents. Therefore, the problem arises of how to avoid this expensive cleaning of the surfaces to be coated with metal and how to improve the adhesion of the metal layers to the base surfaces.

SUMMARY OF THE INVENTION

It is an object of this invention to increase the adhesion of a metal layer to a subsurface formed of a metallic or nonmetallic material. It is an aditional object to avoid the necessity to clean such surfaces with acids and to thereafter neutralize the cleansed surfaces. Further objects of the invention will become apparent as the description proceeds.

According to the invention, a pretreatment process for the subsurface is provided comprising coating the surface, which has been previously roughtened, with a synthetic resin, etching the coated surface with caustic alkali, contacting the etched surface with an alkaline reducing bath containing a strong reducing agent, sensitizing the surface with an aqueous solution of tin chloride, contacting the sensitized surface with a second strong alkaline reducing bath, sensitizing the surface with an aqueous solution of tin chloride and activating the surface with a palladium salt solution.

The pretreatment process can be employed for the preparation of conductor plates or in the application of metal coatings to any subsurface, for example, in the jewelry, furniture, packing and motor vehicle industries.

DETAILED DESCRIPTION OF THE INVENTION

It has been found that, without the previously required cleaning with acids and subsequent neutralizing with alkali, a considerably increased adhesion of applied metal layers to a subsurface is achieved if the material surfaces to be coated with metals are treated in the above manner. The detailed description of the invention is explained below with reference to conductor plates.

After the necessary roughening of the surfaces of the conductor plates, which may be formed of, for example, synthetic resin material, hard rubber, paperboard, wood, ceramic or glass, the plate is coated with a lacquer or adhesive, particularly on a base of synthetic resin material, such as phenolformaldehyde- and/or epoxy resin. After drying or hardening, the coating layer is etched with a caustic base, preferably sodium hydroxide for from 10 minutes to 16 hours, depending on the lacquer or adhesive employed. The temperature of this treatment is between 20–40° C., preferably at 20° C.

The etched layer is then contacted with an alkali-containing first reducing bath containing a strong inorganic and/or organic reducing agent, particularly hydrazine hydrate, as well as a wetting agent for about 2.5 to 10 minutes, preferably 5 minutes, at a temperature between 20 and 90° C., preferably about 50° C. The layer thus treated is then sensitized in a known manner by means of an aqueous tin chloride solution (stannous chloride solution). This procedure is repeated according to the invention by a 2–10 minute treatment at 10 to 30° C. with a second reducing bath containing a strong reducing agent, particularly a sodium hypophosphite solution, followed by sensitization with a tin chloride solution. After this novel two-step sensitization, the coating layer is activated in a manner known per se with the aid of a palladium salt solution, for example, palladium chloride.

The thus pretreated, subsurface usable as the dielectric, can then be completely coated in a known manner with metals by chemical and/or galvanic deposit.

In order to increase the effectiveness of the individual pretreating steps, to the lacquer or adhesive there may be added one or more finely divided filling agents, such as glass dust, calcium carbonate (chalk), aluminum hydroxide, magnesium oxide, etc. This helps achieve in the pretreatment a particularly porous surface.

The first alkaline reducing bath can contain 10–80% hydrazine hydrate; however, 10% hydrazine hydrate is entirely sufficient for the pretreatment. As the alkali in this bath, sodium hydroxide is suitably used in relatively small amounts together with the customary wetting agents. Instead of the hydrazine hydrate, this bath can also contain 10–15%, particularly 10%, of sodium hypophosphite as the reducing agent. Of course, it is also possible to use mixtures of the two reducing agents or even other corresponding reducing agents which have an operating temperature between 20 and 90° C., preferably 50° C.

Between both of the sensitizations with tin chloride carried out in a known manner, there is employed a second reducing bath which suitably consists of a 10–50%,

and preferably 10%, sodium hypophosphite solution having an operating temperature between 10 and 30° C., and preferably about 20° C. (room temperature).

In order to bind the metal layers to be applied to the subsurface, the novel pretreatment can be used on metal carriers or semi-conductors of any type. The nonmetallic carriers to be particularly considered are rubber, glass, ceramic, cardboard, paperboard, paper, wood, wood fiber plates, concrete, cement, lime, graphite artificial stone or similar raw materials or substances.

The following example illustrates but in no way limits the invention.

EXAMPLE

A phenolic resin plate suitable for printed circuits is first roughened on its surface in a known manner, e.g., by fine grinding or sand blasting. After the roughening, the plate is coated with a coating consisting of an epoxy resin to which finely divided calcium carbonate is added as filling material. After drying and hardening of the coating, its surface is etched at about 20–30° C. for one hour in a sodium hydroxide solution containing 5% NaOH.

After this treatment, the surface of the coating applied to the plate has microscopically fine pores. The plate is then dipped for 5 minutes in an aqueous alkaline 10% hydrazine hydrate solution containing a wetting agent and about 5% sodium carbonate and having a temperature of about 50° C.

After the treatment in the alkali bath containing the reducing agent, the lacquer coated phenolic resin plate is washed in clear water. Any remaining sodium carbonate is then neutralized in an aqueous 5% hydrochloric acid and washed again in clear water.

The plate thus prepared is then sensitized in a known manner by contacting it with a stannous chloride solution.

For the purpose of achieving particularly good adhesion, after washing in clear water, the plate is then again dipped for 5 minutes in a reducing aqueous solution, at 20° C., which contains 10% sodium hypophosphite as the reducing agent; and finally it is washed in clear water and sensitized for the second time with the tin chloride solution.

The plate is then activated in a known manner by a palladium chloride solution. It may now be provided, in any desired manner, with metal layers which have an exceptional adhesion.

The plates prepared according to the described process and particularly suitable for printed circuits are provided with a 0.3–2.5μ strong nickel layer which suitably is chemically separated, with a retention of a pH value of 6.5–7.5, from a nickel salt solution, particularly nickel sulfate solution, in the presence of a salt, such as ammonium formate, and a reducing agent, particularly sodium hypophosphite, this dipping bath containing nickel salt and sodium hypophosphite in equivalent amounts.

Upon the thus-obtained nickel layer of the conductor plates, those areas are covered in a known manner by means of screen printing or in photochemical fashion on which no conductor line will be located. The covering lacquer or the body color used here must be stable with respect to the galvanic bath to be used in the subsequent treatment. The conductor lines of the nickel layer not covered are then galvanically coated with a strong copper layer by having the plate as a cathode suspended in a galvanic copper bath.

After the conductor lines have been sufficiently strengthened with a copper layer, the cover lacquer or the photo layer is removed by a suitable organic solvent and thereupon the thus-exposed thin nickel layer is dissolved by means of preferably a 10% sulfuric, nitric or hydrochloric acid, with or without addition of ammonium persulfate, to which copper sulfate, copper nitrate or copper chloride is added according to the conductor lines consisting of copper. After washing the plates in clear water and drying, the conductor plates thus prepared are immediately usable. At their ducts the conductor lines are solderable without any difficulty.

After the novel pretreatment, the metal layers show a tenacity of 5.8–6 boiling point/2.5 cm. which thus is considerably over the recommended DIN (German industrial standards) standard of 2.7 B.P./2.5 cm.

If desired, the prepared conductor plate may be subjected to a temperature treatment at temperatures between 50 and 200° C., particularly at 100–150° C. for a time of at least 2 minutes in order to eliminate eventual tensions between the individual metal layers and so that the adhesion of the applied metal layers is further increased by tempering.

It is obvious that the novel pretreatment can be used on electrically conducting materials, such as any metals. The pretreatment with the lacquer layer to be applied makes superfluous the often not entirely effective purification methods.

Instead of nickel for the base layer, any other metal can of course be used which has a sufficient conductivity, as also instead of copper on the base layer another metal can be chemically or galvanically deposited, e.g., aluminum, magnesium, chromium, cobalt, silver, gold, platinum or palladium.

The inventive pretreatment process is not only usable in the preparation of conductor plates, but can of course be carried out prior to the application of the metals with respect to any type of metal coating, particularly in the jewelry, furniture, structure coating, packing and motor vehicle industries.

What is claimed is:

1. A process for increasing the adhesion of a subsurface to metal comprising (A) roughening the subsurface, (B) coating the subsurface with a synthetic resin selected from the group consisting of phenolformaldehyde resin, epoxy resin and mixtures thereof, (C) etching the coated surface for from 10 minutes to 16 hours with caustic alkali at 20–40° C., (D) contacting the etched subsurface with a first alkaline reducing bath containing a strong reducing agent selected from the group consisting of hydrazine hydrate, sodium hypophosphite and mixtures thereof and small amounts of a wetting agent for 2.5 to 10 minutes, (E) sensitizing the so treated surface by contacting it with a tin II chloride solution, (F) contacting the so treated surface for from 2 to 5 minutes with a second alkaline reducing bath containing a strong reducing agent selected from the group consisting of hydrazine hydrate, sodium hypophosphite and mixtures thereof, (G) sensitizing the so treated surface by contacting with a tin II chloride solution and (H) activating the surface by contacting it with a palladium salt solution.

2. A process according to claim **1** wherein the caustic alkali in step (C) is sodium hydroxide.

3. A process according to claim **1** wherein there is added to synthetic resin employed in step (B) at least one filling agent selected from the group consisting of glass dust, calcium carbonate, aluminum hydroxide and magnesium oxide.

4. A process according to claim **1** wherein the first alkaline reducing bath contains 10–80% hydrazine hydrate, and the second alkaline reducing bath contains 10–50% sodium hypophosphite as the reducing agent.

5. A process according to claim **1** wherein the first and second alkaline reducing baths contain a mixture of hydrazine hydrate and sodium hypophosphite as the reducing agent.

6. A process according to claim **1** wherein the reducing baths contain sodium carbonate as the alkali.

7. A process according to claim **1** wherein the first alkaline reducing bath is employed at a temperature of 20–90° C., while the second alkaline reducing bath is employed at a temperature of about 10–30° C.

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