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(57)

**ABSTRACT**

The invention relates to a device for the electrolytic coating of a structured or full-surface base layer (9) on a surface of a substrate (7), which comprises at least one electrolyte bath (3) having at least one rotatably mounted roller (2) connectable as a cathode, which contacts the base layer (9) during the electrolytic coating, the base layer (9) being covered by an electrolyte solution (5) contained in the electrolyte bath (3) and being moved relative to the at least one roller (2) during the coating. The at least one roller (2) connectable as a cathode is connected cathodically during the contact with the base layer (9) and is connected neutrally or anodically as soon as there is no contact with the base layer (9). The invention furthermore relates to a method for the electrolytic coating of a structured or full-surface base layer (9) on a surface of a substrate (7), the base layer (9) being surrounded by an electrolyte solution (5) and being contacted by at least one roller (2) connectable as a cathode. The roller (2) connectable as a cathode is connected cathodically when it contacts the base layer (9) and is connected neutrally or anodically as soon as there is no contact with the base layer (9).

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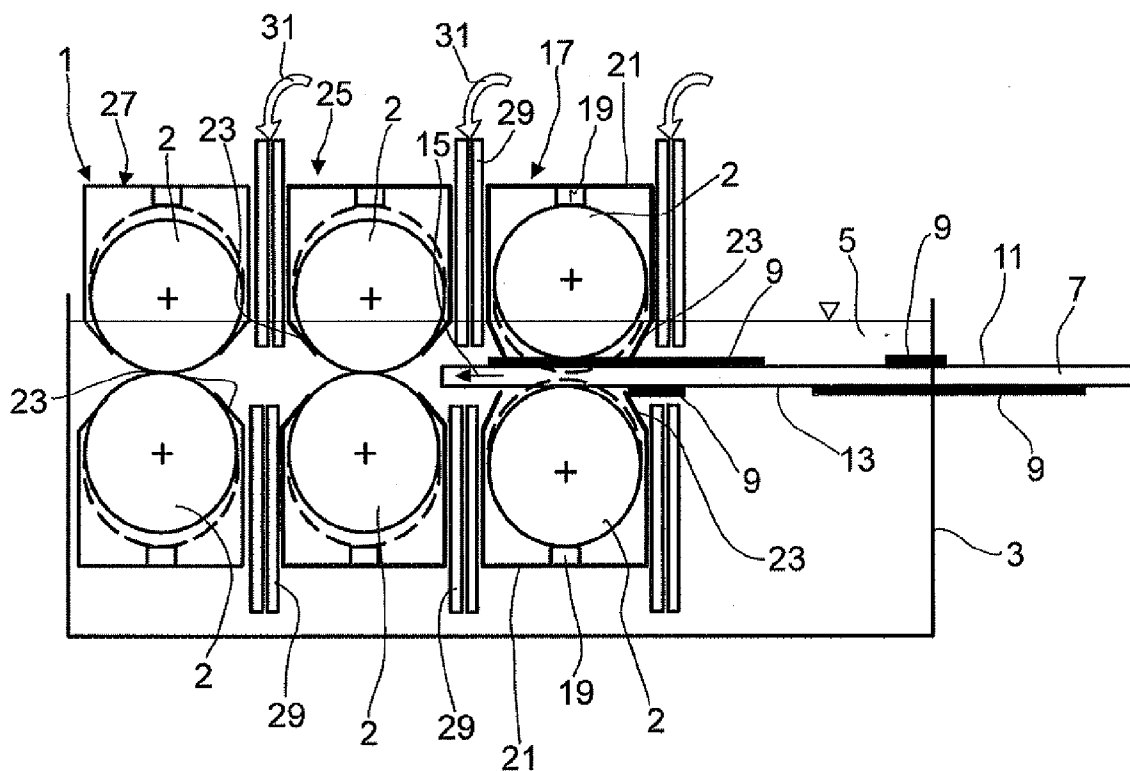


FIG.1

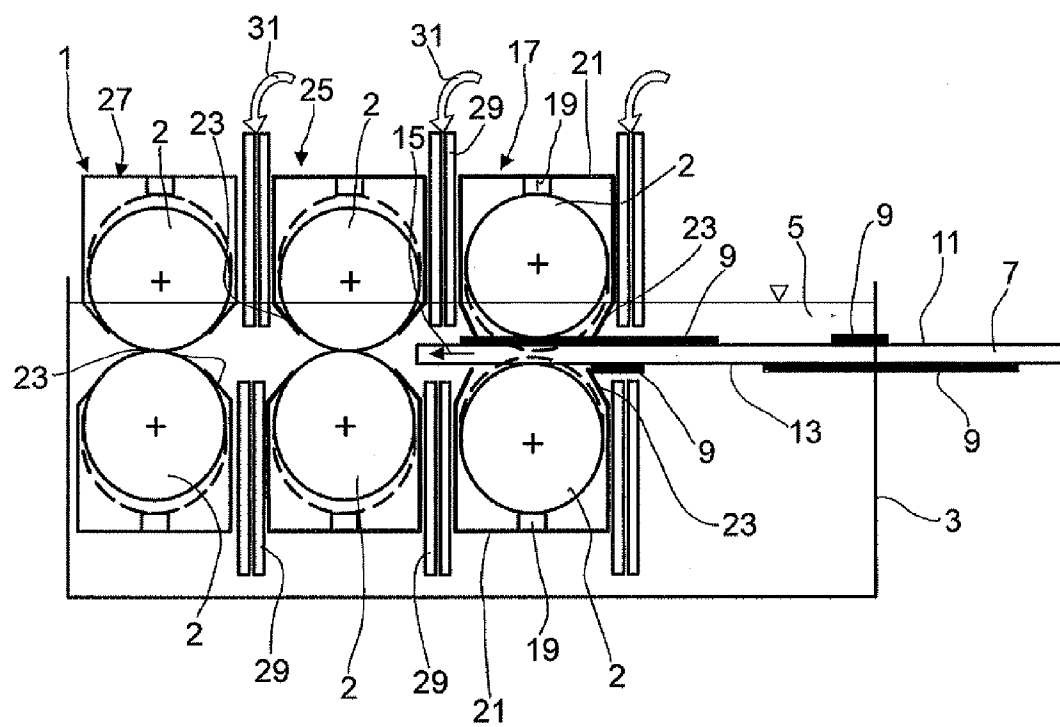
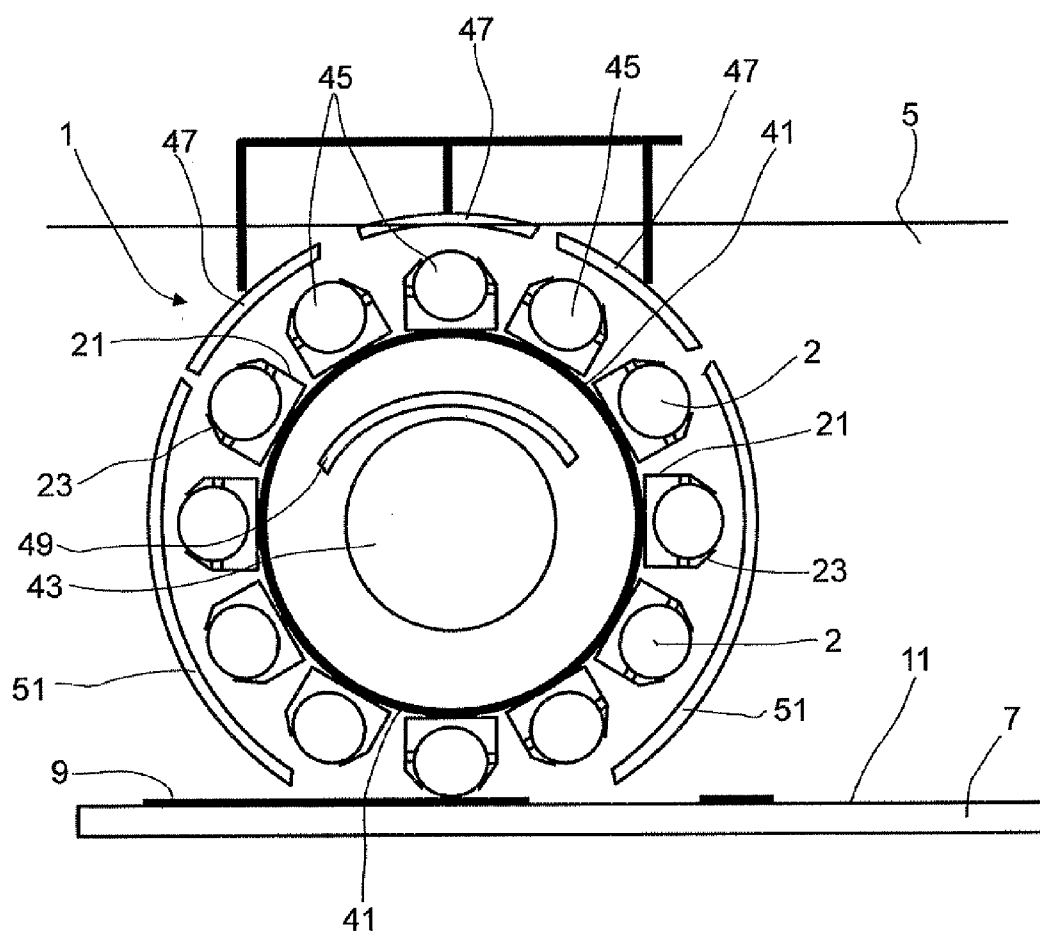


FIG.2



## DEVICE AND METHOD FOR ELECTROPLATING

[0001] The invention relates to a device and to a method for the electrolytic coating of a structured or full-surface base layer on a surface of a substrate, which comprises at least one electrolyte bath having at least one rotatably mounted roller connectable as a cathode, which contacts the base layer during the electrolytic coating, the base layer being covered by an electrolyte solution contained in the electrolyte bath and being moved relative to the at least one roller during the coating.

[0002] The device according to the invention and the method according to the invention are suitable, for example, for producing conductor tracks on printed circuit boards, RFID antennas, transponder antennas or other antenna structures, chip card modules, flat cables, seat heaters, foil conductors, conductor tracks in solar cells or in LCD/plasma screens or electrolytically coated products in any form. The device is also suitable for producing decorative or functional surfaces on products, which are used for example for shielding electromagnetic radiation, for thermal conduction or as packaging.

[0003] A method and a device for electrolytically amplifying the thickness of an electrically conductive structure on a dielectric substrate is known, for example, from WO-A 2005/076680. The device described here is suitable for coating flexible supports. These are fed around a roller, on the outer circumference of which cylindrical electrodes rotatable about their longitudinal axis are held. The electrodes are respectively enclosed by shielding elements. Electrodes which are in contact with the foil, on which the structure to be coated is applied, are connected cathodically. Electrodes which are not in contact with the foil to be coated may, for example, be replaced. The roller is preferably only half-immersed in an electrolyte solution. This prevents metal from being deposited on electrodes which are not in contact with the foil. The shielding elements, which enclose the cylindrical electrodes, are made of a dielectric material, for example rubber or plastic.

[0004] A disadvantage of the embodiment according to WO-A 2005/076680 is that it is suitable only for coating flexible circuit supports. Rigid circuit supports cannot be coated by the device. Another disadvantage is that a voltage is constantly applied to the electrodes, so that metal can also deposit on electrodes which are not in contact with the flexible supports to be coated.

[0005] It is an object of the invention to provide a device for electrolytic coating, with which it is possible to coat structured or full-surface base layers on a surface of a substrate, which may be rigid or flexible, and in which metal deposition on the electrode is reduced or prevented.

[0006] The object is achieved by a device for the electrolytic coating of a structured or full-surface base layer on a surface of a substrate, which comprises at least one electrolyte bath having at least one rotatably mounted roller connectable as a cathode, which contacts the base layer during the electrolyte coating. The base layer is covered by an electrolyte solution contained in the electrolytic bath and is moved relative to the one roller during the coating. The roller is connected cathodically during the contact with the base layer and is connected neutrally or anodically as soon as there is no contact with the base layer.

[0007] The fact that the base layer is moved relative to the roller during the coating means that either the substrate with the base layer is held statically and the roller is moved past it, or the roller is held statically and the substrate with the base layer is moved along the roller.

[0008] The advantage of connecting the roller neutrally, while there is no contact with the base layer, is that no deposition takes place on the roller during this time. The advantage of connecting the roller anodically, while there is no contact with the base layer, is that metal which may have been deposited on the roller surface during the cathodic connection is removed again during this time.

[0009] Electrolytically coatable structured or full-surface base layers on a surface of a substrate may, for example, be produced by printed circuit board fabrication methods known to the person skilled in the art. In this case, for example, a substrate clad with copper on one or two sides is processed by etching and resist methods known to the person skilled in the art, so that a structured electrolytically coatable base layer of copper is produced. It is nevertheless also possible to use all other methods known to the person skilled in the art.

[0010] Electrolytically coatable structured or full-surface base layers on a surface of a substrate may furthermore be produced, for example, by applying a dispersion which contains at least galvanizable particles and a matrix material onto a structured or full-surface base layer, at least partially drying and/or at least partially curing the applied dispersion, and optionally exposing the electrically conductive particles on the surface of the remaining base layer by at least partial chemical, physical or mechanical removal of the matrix.

[0011] Rigid or flexible supports, for example, are suitable as supports onto which the structured or full-surface base layer to be electrolytically coated can be applied. The support is preferably electrically nonconductive. This means that the resistivity is more than  $10^9$  ohm $\times$ cm. Suitable supports are for example reinforced or unreinforced polymers, such as those conventionally used for printed circuit boards. Suitable polymers are epoxy resins or modified epoxy resins, for example bifunctional or polyfunctional Bisphenol A or Bisphenol F resins, epoxy-novolak resins, brominated epoxy resins, aramid-reinforced or glass fiber-reinforced or paper-reinforced epoxy resins (for example FR4), glass fiber-reinforced plastics, liquid-crystal polymers (LCP), polyphenylene sulfides (PPS), polyoxymethylenes (POM), polyaryl ether ketones (PAEK), polyether ether ketones (PEEK), polyamides (PA), polycarbonates (PC), polybutylene terephthalates (PBT), polyethylene terephthalates (PET), polyimides (PI), polyimide resins, cyanate esters, bismaleimide-triazene resins, nylon, vinyl ester resins, polyesters, polyester resins, polyamides, polyanilines, phenol resins, polypyrroles, polyethylene naphthalate (PEN), polymethyl methacrylate, polyethylene dioxithiophenes, phenolic resin-coated aramid paper, polytetrafluoroethylene (PTFE), melamine resins, silicone resins, fluorine resins, allylated polyphenylene ethers (APPE), polyether imides (PEI), polyphenylene oxides (PPO), polypropylenes (PP), polyethylenes (PE), polysulfones (PSU), polyether sulfones (PES), polyaryl amides (PAA), polyvinyl chlorides (PVC), polystyrenes (PS), acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene acrylate (ASA), styrene acrylonitrile (SAN) and mixtures (blends) of two or more of the aforementioned polymers, which may be present in a wide variety of forms. The substrates may comprise additives known to the person skilled in the art, for example flame retardants.

**[0012]** Other substrates conventional in the printed circuit board industry are also suitable.

**[0013]** Composite materials, foam-like polymers, Styropor®, Styrodur®, polyurethanes (PU), ceramic surfaces, textiles, pulp, board, paper, polymer-coated paper, wood, mineral materials, silicon, glass, vegetable tissue and animal tissue are furthermore suitable substrates.

**[0014]** The substrate may be either rigid or flexible.

**[0015]** The base layer preferably contains electrolytically coatable particles in a matrix material. In order to produce the base layer, for example, a dispersion which contains the electrolytically coatable particles in the matrix material is applied. The electrically conductive particles may be particles of any geometry made of any electrically conductive material, mixtures of different electrically conductive materials or mixtures of electrically conductive materials and materials which are not electrically conductive. Suitable electrically conductive materials are for example carbon, electrically conductive metal complexes, conductive organic compounds or conductive polymers or metals, preferably zinc, nickel, copper, tin, cobalt, manganese, iron, magnesium, lead, chromium, bismuth, silver, gold, aluminum, titanium, palladium, platinum, tantalum and alloys thereof or metal mixtures which contain at least one of these metals. Suitable alloys are for example CuZn, CuSn, CuNi, SnPb, SnBi, SnCo, NiPb, ZnFe, ZnNi, ZnCo and ZnMn. Aluminum, iron, copper, nickel, zinc, carbon and mixtures thereof are particularly preferred.

**[0016]** The electrolytically coatable particles preferably have an average particle diameter of from 0.001 to 100  $\mu\text{m}$ , preferably from 0.005 to 50  $\mu\text{m}$  and particularly preferably from 0.01 to 10  $\mu\text{m}$ . The average particle diameter may be determined by means of laser diffraction measurement, for example using a Microtrac X100 device. The distribution of the particle diameters depends on their production method. The diameter distribution typically comprises only one maximum, although a plurality of maxima are also possible.

**[0017]** The surface of the electrolytically coatable particles may be provided at least partially with a coating. Suitable coatings may be inorganic (for example  $\text{SiO}_2$ , phosphates) or organic in nature. The electrolytically coatable particles may of course also be coated with a metal or metal oxide. The metal may likewise be present in an at least partially oxidized form.

**[0018]** If two or more different metals are intended to form the electrolytically coatable particles, then this may be done using a mixture of these metals. It is particularly preferable for the metals to be selected from the group consisting of aluminum, iron, copper, nickel and zinc.

**[0019]** The electrolytically coatable particles may nevertheless also contain a first metal and a second metal, in which the first metal is present in the form of an alloy (with the first metal or one or more other metals), or the electrolytically coatable particles may contain two different alloys.

**[0020]** Besides the choice of electrolytically coatable particles, the shape of the electrolytically coatable particles also has an effect on the properties of the dispersion after coating. In respect of the shape, numerous variants known to the person skilled in the art are possible. The shape of the electrolytically coatable particles may, for example, be needle-shaped, cylindrical, plate-shaped or spherical. These particle shapes represent idealized shapes and the actual shape may differ more or less strongly therefrom, for example owing to

production. For example, teardrop-shaped particles are a real deviation from the idealized spherical shape in the scope of the present invention.

**[0021]** Electrolytically coatable particles with various particle shapes are commercially available.

**[0022]** When mixtures of electrolytically coatable particles are used, the individual mixing partners may also have different particle shapes and/or particle sizes. It is also possible to use mixtures of one type of electrolytically coatable particles with different particle sizes and/or particle shapes. In the case of different particle shapes and/or particle sizes, the metals aluminum, iron, copper, nickel and zinc as well as carbon are likewise preferred.

**[0023]** As already mentioned, the electrolytically coatable particles may be added to the dispersion in the form of their powder. Such powders, for example metal powders, are commercially available goods or can be readily produced by means of known methods, for instance by electrolytic deposition or chemical reduction from solutions of metal salts or by reduction of an oxidic powder, for example by means of hydrogen, by spraying or atomizing a metal melt, particularly into coolants, for example gases or water. Gas and water atomization and the reduction of metal oxides are preferred. Metal powders with the preferred particle size may also be produced by grinding coarser metal powders. A ball mill, for example, is suitable for this.

**[0024]** Besides gas and water atomization, the carbonyl-iron powder process for producing carbonyl-iron powder is preferred in the case of iron. This is done by thermal decomposition of iron pentacarbonyl. This is described, for example, in Ullman's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A14, p. 599. The decomposition of iron pentacarbonyl may, for example, take place at elevated temperatures and elevated pressures in a heatable decomposer that comprises a tube of a refractory material such as quartz glass or V2A steel in a preferably vertical position, which is enclosed by a heating instrument, for example consisting of heating baths, heating wires or a heating jacket through which a heating medium flows.

**[0025]** Platelet-shaped electrolytically coatable particles can be controlled by optimized conditions in the production process or obtained afterwards by mechanical treatment, for example by treatment in an agitator ball mill.

**[0026]** Expressed in terms of the total weight of the dried base layer, the proportion of electrolytically coatable particles preferably lies in the range of from 20 to 98 wt. %. A preferred range for the proportion of the electrolytically coatable particles is from 30 to 95 wt. % expressed in terms of the total weight of the dried base layer.

**[0027]** For example, binders with a pigment-affine anchor group, natural and synthetic polymers and derivatives thereof, natural resins as well as synthetic resins and derivatives thereof, natural rubber, synthetic rubber, proteins, cellulose derivatives, drying and non-drying oils etc. are suitable as a matrix material. They may—but need not—be chemically or physically curing, for example air-curing, radiation-curing or temperature-curing.

**[0028]** The matrix material is preferably a polymer or polymer blend.

**[0029]** Polymers preferred as a matrix material are, for example, ABS (acrylonitrile-butadiene-styrene); ASA (acrylonitrile-styrene acrylate); acrylic acrylates; alkyd resins; alkyl vinyl acetates; alkyl vinyl acetate copolymers, in particular methylene vinyl acetate, ethylene vinyl acetate, buty-

lene vinyl acetate; alkylene vinyl chloride copolymers; amino resins; aldehyde and ketone resins; celluloses and cellulose derivatives, in particular hydroxyalkyl celluloses, cellulose esters such as acetates, propionates, butyrates, carboxyalkyl celluloses, cellulose nitrate; epoxy acrylate; epoxy resins; modified epoxy resins, for example bifunctional or polyfunctional Bisphenol A or Bisphenol F resins, epoxy-novolak resins, brominated epoxy resins, cycloaliphatic epoxy resins; aliphatic epoxy resins, glycidyl ethers, vinyl ethers, ethylene-acrylic acid copolymers; hydrocarbon resins; MABS (transparent ABS also containing acrylate units); melamine resins, maleic acid anhydride copolymers; methacrylates; natural rubber; synthetic rubber; chlorine rubber; natural resins; colophonium resins; shellac; phenolic resins; polyesters; polyester resins such as phenyl ester resins; polysulfones; polyether sulfones; polyamides; polyimides; polyanilines; polypyrroles; polybutylene terephthalate (PBT); polycarbonate (for example Makrolon® from Bayer AG); polyester acrylates; polyether acrylates; polyethylene; polyethylene thiophene; polyethylene naphthalates; polyethylene terephthalate (PET); polyethylene terephthalate glycol (PETG); polypropylene; polymethyl methacrylate (PMMA); polyphenylene oxide (PPO); polystyrenes (PS), polytetrafluoroethylene (PTFE); polytetrahydrofuran; polyethers (for example polyethylene glycol, polypropylene glycol); polyvinyl compounds, in particular polyvinyl chloride (PVC), PVC copolymers, PVdC, polyvinyl acetate as well as copolymers thereof, optionally partially hydrolyzed polyvinyl alcohol, polyvinyl acetals, polyvinyl acetates, polyvinyl pyrrolidone, polyvinyl ethers, polyvinyl acrylates and methacrylates in solution and as a dispersion as well as copolymers thereof, polyacrylates and polystyrene copolymers; polystyrene (modified or not to be shockproof); polyurethanes, uncrosslinked or crosslinked with isocyanates; polyurethane acrylate; styrene acrylic copolymers; styrene butadiene block copolymers (for example Styroflex® or Styrolux® from BASF AG, K-Resin™ from CPC); proteins, for example casein; SIS; triazine resin, bismaleimide triazine resin (BT), cyanate ester resin (CE), allylated polyphenylene ethers (APPE). Mixtures of two or more polymers may also form the matrix material.

**[0030]** Polymers particularly preferred as a matrix material are acrylates, acrylic resins, cellulose derivatives, methacrylates, methacrylic resins, melamine and amino resins, polyalkylenes, polyimides, epoxy resins, modified epoxy resins, for example bifunctional or polyfunctional Bisphenol A or Bisphenol F resins, epoxy-novolak resins, brominated epoxy resins, cycloaliphatic epoxy resins; aliphatic epoxy resins, glycidyl ethers, vinyl ethers and phenolic resins, polyurethanes, polyesters, polyvinyl acetals, polyvinyl acetates, polystyrenes, polystyrene copolymers, polystyrene acrylates, styrene butadiene block copolymers, alkenyl vinyl acetates and vinyl chloride copolymers, polyamides and copolymers thereof.

**[0031]** As a matrix material for the dispersion in the production of printed circuit boards, it is preferable to use thermally or radiation-curing resins, for example modified epoxy resins such as bifunctional or polyfunctional Bisphenol A or Bisphenol F resins, epoxy-novolak resins, brominated epoxy resins, cycloaliphatic epoxy resins; aliphatic epoxy resins, glycidyl ethers, cyanate esters, vinyl ethers, phenolic resins, polyimides, melamine resins and amino resins, polyurethanes, polyesters and cellulose derivatives.

**[0032]** Expressed in terms of the total weight of the dry coating, the proportion of the organic binder component is

preferably from 0.01 to 60 wt. %. The proportion is preferably from 0.1 to 45 wt. %, more preferably from 0.5 to 35 wt. %.

**[0033]** In order to be able to apply the dispersion containing the electrically conductive particles and the matrix material onto the support, a solvent or a solvent mixture may furthermore be added to the dispersion in order to adjust the viscosity of the dispersion suitable for the respective application method. Suitable solvents are, for example, aliphatic and aromatic hydrocarbons (for example n-octane, cyclohexane, toluene, xylene), alcohols (for example methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, amyl alcohol), polyvalent alcohols such as glycerol, ethylene glycol, propylene glycol, neopentyl glycol, alkyl esters (for example methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, isopropyl acetate, 3-methyl butanol), alkoxy alcohols (for example methoxypropanol, methoxybutanol, ethoxypropanol), alkyl benzenes (for example ethyl benzene, isopropyl benzene), butyl glycol, dibutyl glycol, alkyl glycol acetates (for example butyl glycol acetate, dibutyl glycol acetate), diacetone alcohol, diglycol dialkyl ethers, diglycol monoalkyl ethers, dipropylene glycol dialkyl ethers, dipropylene glycol monoalkyl ethers, diglycol alkyl ether acetates, dipropylene glycol alkyl ether acetate, dioxane, dipropylene glycol and ethers, diethylene glycol and ethers, DBE (dibasic esters), ethers (for example diethyl ether, tetrahydrofuran), ethylene chloride, ethylene glycol, ethylene glycol acetate, ethylene glycol dimethyl ester, cresol, lactones (for example butyrolactone), ketones (for example acetone, 2-butanone, cyclohexanone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK)), dimethyl glycol, methylene chloride, methylene glycol, methylene glycol acetate, methyl phenol (ortho-, meta-, para-cresol), pyrrolidones (for example N-methyl-2-pyrrolidone), propylene glycol, propylene carbonate, carbon tetrachloride, toluene, trimethylol propane (TMP), aromatic hydrocarbons and mixtures, aliphatic hydrocarbons and mixtures, alcoholic monoterpenes (for example terpinol), water and mixtures of two or more of these solvents.

**[0034]** Preferred solvents are alcohols (for example ethanol, 1-propanol, 2-propanol, 1-butanol), alkoxyalcohols (for example methoxy propanol, ethoxy propanol, butyl glycol, dibutyl glycol), butyrolactone, diglycol dialkyl ethers, diglycol monoalkyl ethers, dipropylene glycol dialkyl ethers, dipropylene glycol monoalkyl ethers, esters (for example ethyl acetate, butyl acetate, butyl glycol acetate, dibutyl glycol acetate, diglycol alkyl ether acetates, dipropylene glycol alkyl ether acetates, DBE), ethers (for example tetrahydrofuran), polyvalent alcohols such as glycerol, ethylene glycol, propylene glycol, neopentyl glycol, ketones (for example acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone), hydrocarbons (for example cyclohexane, ethyl benzene, toluene, xylene), N-methyl-2-pyrrolidone, water and mixtures thereof.

**[0035]** When the dispersion is applied onto the support using an inkjet method, alkoxy alcohols (for example ethoxy propanol, butyl glycol, dibutyl glycol) and polyvalent alcohols such as glycerol, esters (for example dibutyl glycol acetate, butyl glycol acetate, dipropylene glycol methyl ether acetates), water, cyclohexanone, butyrolactone, N-methylpyrrolidone, DBE and mixtures thereof are particularly preferred as solvents.

**[0036]** In the case of liquid matrix materials (for example liquid epoxy resins, acrylic esters), the respective viscosity

may alternatively be adjusted via the temperature during application, or via a combination of a solvent and temperature.

**[0037]** The dispersion may furthermore contain a dispersant component. This consists of one or more dispersants.

**[0038]** In principle, all dispersants known to the person skilled in the art for application in dispersions and described in the prior art are suitable. Preferred dispersants are surfactants or surfactant mixtures, for example anionic, cationic, amphoteric or non-ionic surfactants.

**[0039]** The dispersant may be used in the range of from 0.01 to 50 wt. %, expressed in terms of the total weight of the dispersion. The proportion is preferably from 0.1 to 25 wt. %, particularly preferably from 0.2 to 10 wt. %.

**[0040]** The dispersion according to the invention may furthermore contain a filler component. This may consist of one or more fillers. For instance, the filler component of the metallizable mass may contain fillers in fiber, layer or particle form, or mixtures thereof. These are preferably commercially available products, for example carbon and mineral fillers.

**[0041]** It is furthermore possible to use fillers or reinforcers such as glass powder, mineral fibers, whiskers, aluminum hydroxide, metal oxides such as aluminum oxide or iron oxide, mica, quartz powder, calcium carbonate, barium sulfate, titanium dioxide or wollastonite.

**[0042]** Other additives may furthermore be used, such as thixotropic agents, for example silica, silicates, for example aerosils or bentonites, or organic thixotropic agents and thickeners, for example polyacrylic acid, polyurethanes, hydrated castor oil, dyes, fatty acids, fatty acid amides, plasticizers, networking agents, defoaming agents, lubricants, desiccants, crosslinkers, photoinitiators, sequestrants, waxes, pigments, conductive polymer particles.

**[0043]** The proportion of the filler component is preferably from 0.01 to 50 wt. %, expressed in terms of the total weight of the dry coating. From 0.1 to 30 wt. % are further preferred, and from 0.3 to 20 wt. % are particularly preferred.

**[0044]** There may furthermore be processing auxiliaries and stabilizers in the dispersion according to the invention, such as UV stabilizers, lubricating agents, corrosion inhibitors and flame retardants. Their proportion is usually from 0.01 to 5 wt. %, expressed in terms of the total weight of the dispersion. The proportion is preferably from 0.05 to 3 wt. %.

**[0045]** The structured or full-surface base layer is preferably printed onto the support with any printing method by using the dispersion. The printing method with which it is possible to print on the structured surface is, for example, a roll or a sheet printing method such as for example screen printing, intaglio printing, flexographic printing, typography, pad printing, inkjet printing, the Lasersonic® method as described in DE10051850, or offset printing. Any other printing method known to the person skilled in the art may, however, also be used. It is also possible to apply the surface using another conventional and widely known coating method. Such coating methods are, for example, casting, painting, doctor blading, brushing, spraying, immersion, rolling, powdering, fluidized bed or the like. Thickness of the structured or full-area surface produced by printing or the coating method preferably varies between 0.01 and 50  $\mu\text{m}$ , more preferably between 0.05 and 25  $\mu\text{m}$  and particularly preferably between 0.1 and 15  $\mu\text{m}$ . The layers may be applied either surface-wide or in a structured way.

**[0046]** Differently fine structures can be printed, depending on the printing method.

**[0047]** As an alternative, it is also possible to apply the base layer by applying an adhesive layer and subsequently transferring the electrolytically coatable particles. The material of the adhesive layer in this case preferably corresponds to the matrix material of the dispersion as described above. The adhesive layer is preferably applied by a printing method. The printing method may be the same as described above for applying the dispersion.

**[0048]** The electrolytically coatable particles may, for example, be transferred onto the adhesive layer from a transfer medium. For example any rigid or flexible support, on which the electrolytically coatable particles can be applied, is suitable as the transfer medium. Suitable materials for the transfer medium are for example metals, glass, ceramic, plastics or any composite materials.

**[0049]** After applying the base layer, it is possible for the electrolytically coatable particles contained therein to be at least partially exposed so that electrolytically coatable nucleation sites are directly obtained, onto which the metal ions can be deposited to form a metal layer during the subsequent electrolytic coating. If the particles consist of materials which can readily oxidize, it is sometimes also necessary to remove the oxide layer at least partially beforehand. Depending on the way in which the method is carried out, for example by using acidic electrolyte solutions, the removal of the oxide layer may already take place simultaneously as the electrolytic coating is carried out, without an additional process step being necessary.

**[0050]** An advantage of exposing the electrolytically coatable particles is that in order to obtain a continuous electrically conductive surface, by exposing the particles the base layer only needs to contain a proportion of electrolytically coatable particles which is about 5 to 10 wt. % lower than is the case when the particles are not exposed. Further advantages are the homogeneity and continuity of the coatings being produced and the high process reliability.

**[0051]** The electrolytically coatable particles may be exposed either mechanically, for example by brushing, grinding, milling, sandblasting or blasting with supercritical carbon dioxide, physically, for example by heating, laser, UV light corona or plasma discharge, or chemically. In the case of chemical exposure, it is preferable to use a chemical or chemical mixture which is compatible with the matrix material. In the case of chemical exposure, either the matrix material may be at least partially dissolved on the surface and washed away, for example by a solvent, or the chemical structure of the matrix material may be at least partially disrupted by means of suitable reagents so that the electrolytically coatable particles are exposed. Reagents which make the matrix material tumesce are also suitable for exposing the electrolytically coatable particles. The tumescence creates cavities which the metal ions to be deposited can enter from the electrolyte solution, so that a larger number of electrolytically coatable particles can be metallized. The bonding, homogeneity and continuity of the metal layer subsequently deposited electrolytically is significantly better than in the methods described in the prior art. The process rate of the metallization is also higher because of the larger number of exposed electrolytically coatable particles, so that additional cost advantages can be achieved.

**[0052]** If the matrix material is for example an epoxy resin, a modified epoxy resin, an epoxy-novolak, a polyacrylate,

ABS, a styrene-butadiene copolymer or a polyether, the electrolytically and/or electrolytically coatable particles are preferably exposed by using an oxidant. The oxidant breaks bonds of the matrix material, so that the binder can be dissolved and the particles can thereby be exposed. Suitable oxidants are, for example, manganates such as for example potassium permanganate, potassium manganate, sodium permanganate, sodium manganate, hydrogen peroxide, oxygen, oxygen in the presence of catalysts such as for example manganese salts, molybdenum salts, bismuth salts, tungsten salts and cobalt salts, ozone, vanadium pentoxide, selenium dioxide, ammonium polysulfide solution, sulfur in the presence of ammonia or amines, manganese dioxide, potassium ferrate, dichromatesulfuric acid, chromic acid in sulfuric acid or in acetic acid or in acetic anhydride, nitric acid, hydroiodic acid, hydrobromic acid, pyridinium dichromate, chromic acid-pyridine complex, chromic acid anhydride, chromium(VI) oxide, periodic acid, lead tetraacetate, quinone, methylquinone, anthraquinone, bromine, chlorine, fluorine, iron (III) salt solutions, disulfate solutions, sodium percarbonate, salts of oxohalic acids such as for example chlorates or bromates or iodates, salts of perhalic acids such as for example sodium periodate or sodium perchlorate, sodium perborate, dichromates such as for example sodium dichromate, salts of persulfuric acids such as potassium peroxodisulfate, potassium peroxomonosulfate, pyridinium chlorochromate, salts of hypohalic acids, for example sodium hypochloride, dimethyl sulfoxide in the presence of electrophilic reagents, tert-butyl hydroperoxide, 3-chloroperbenzoate, 2,2-dimethylpropanal, Des-Martin periodinane, oxalyl chloride, urea hydrogen peroxide adduct, urea hydrogen peroxide, 2-iodoxybenzoic acid, potassium peroxomonosulfate, m-chloroperbenzoic acid, N-methylmorpholine-N-oxide, 2-methylprop-2-yl hydroperoxide, peracetic acid, pivaldehyde, osmium tetroxide, oxone, ruthenium(III) and (IV) salts, oxygen in the presence of 2,2,6,6-tetramethylpiperidinyl-N-oxide, triacetoxiperiodinane, trifluoroperacetic acid, trimethyl acetaldehyde, ammonium nitrate. The temperature during the process may optionally be increased in order to improve the exposure process.

**[0053]** It is preferable to use manganates, for example potassium permanganate, potassium manganate, sodium permanganate; sodium manganate, hydrogen peroxide, N-methylmorpholine-N-oxide, percarbonates, for example sodium or potassium percarbonate, perborates, for example sodium or potassium perborate; persulfates, for example sodium or potassium persulfate; sodium, potassium and ammonium peroxodiand monosulfates, sodium hypochloride, urea hydrogen peroxide adducts, salts of oxohalic acids such as for example chlorates or bromates or iodates, salts of perhalic acids such as for example sodium periodate or sodium perchlorate, tetrabutylammonium peroxodisulfate, quinone, iron (III) salt solutions, vanadium pentoxide, pyridinium dichromate, hydrochloric acid, bromine, chlorine, dichromates.

**[0054]** It is particularly preferable to use potassium permanganate, potassium manganate, sodium permanganate, sodium manganate, hydrogen peroxide and its adducts, perborates, percarbonates, persulfates, peroxodisulfates, sodium hypochloride and perchlorates.

**[0055]** In order to expose the electrolytically coatable particles in a matrix material which contains for example ester structures such as polyester resins, polyester acrylates, polyether acrylates, polyester urethanes, it is preferable for example to use acidic or alkaline chemicals and/or chemical

mixtures. Preferred acidic chemicals and/or chemical mixtures are, for example, concentrated or dilute acids such as hydrochloric acid, sulfuric acid, phosphoric acid or nitric acid. Organic acids such as formic acid or acetic acid may also be suitable, depending on the matrix material. Suitable alkaline chemicals and/or chemical mixtures are, for example, bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide or carbonates, for example sodium carbonate or calcium carbonate. The temperature during the process may optionally be increased in order to improve the exposure process.

**[0056]** Solvents may also be used to expose the electrolytically coatable particles in the matrix material. The solvent must be adapted to the matrix material, since the matrix material must dissolve in the solvent or be tumesced by the solvent. When using a solvent in which the matrix material dissolves, the base layer is brought in contact with the solvent only for a short time so that the upper layer of the matrix material is solvated and thereby dissolved. Preferred solvents are xylene, toluene, halogenated hydrocarbons, acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), diethylene glycol monobutyl ether. The temperature during the dissolving process may optionally be increased in order to improve the dissolving behavior.

**[0057]** Furthermore, it is also possible to expose the electrolytically coatable particles by using a mechanical method. Suitable mechanical methods are, for example, brushing, grinding, polishing with an abrasive or pressure blasting with a water jet, sandblasting or blasting with supercritical carbon dioxide. The top layer of the cured, printed, structured base layer is respectively removed by such a mechanical method. The electrolytically coatable particles contained in the matrix material are thereby exposed.

**[0058]** All abrasives known to the person skilled in the art may be used as abrasives for polishing. A suitable abrasive is, for example, pumice powder. In order to remove the top layer of the cured dispersion by pressure blasting with a water jet, the water jet preferably contains small solid particles, for example pumice powder ( $\text{Al}_2\text{O}_3$ ) with an average particle size distribution of from 40 to 120  $\mu\text{m}$ , preferably from 60 to 80  $\mu\text{m}$ , as well as quartz powder ( $\text{SiO}_2$ ) with a particle size >3  $\mu\text{m}$ .

**[0059]** If the electrolytically coatable particles contain a material which can readily oxidize, in a preferred method variant the oxide layer is at least partially removed before the metal layer is formed on the structured or full-surface base layer. The oxide layer may in this case be removed chemically and/or mechanically, for example. Suitable substances with which the base layer can be treated in order to chemically remove an oxide layer from the electrolytically coatable particles are, for example, acids such as concentrated or dilute sulfuric acid or concentrated or dilute hydrochloric acid, citric acid, phosphoric acid, amidosulfonic acid, formic acid, acetic acid.

**[0060]** Suitable mechanical methods for removing the oxide layer from the electrolytically coatable particles are generally the same as the mechanical methods for exposing the particles.

**[0061]** The composition of the electrolyte solution, which is used for the coating, depends on the metal with which the base layer on the substrate is intended to be coated. In principle, all metals which are nobler or equally noble as the least noble metal of the base layer may be used for the electrolytic coating. Conventional metals which are deposited by electro-



lytic coating are, for example, gold, nickel, palladium, platinum, silver, tin, copper or chromium. The thicknesses of the one or more deposited layers lie in the conventional range known to the person skilled in the art, and are not essential to the invention.

**[0062]** Suitable electrolyte solutions, which are used for coating electrically conductive structures, are known to the person skilled in the art for example from Werner Jillek, Gustl Keller, *Handbuch der Leiterplattentechnik* [Handbook of printed circuit technology], Eugen G. Leuze Verlag, 2003, volume 4, pages 332-352

**[0063]** In one embodiment the at least one roller, which is mounted so that it can be connected cathodically and rotated, is held statically in the electrolyte bath while the substrate with the base layer is transported through the electrolyte bath. During the transport of the substrate with the base layer, the roller moves over the base layer. The base layer is thereby contacted. So long as the roller is in contact with the base layer and is connected cathodically, metal is deposited on the base layer from the electrolyte solution. A continuous metal layer is formed.

**[0064]** In order to produce a thicker metal layer on the base layer, it is preferable for at least two cathodically connectable rollers to be connected in series in the electrolyte bath. The contact time of the base layer with the cathode is increased by the cathodically connectable rollers connected in series. Owing to the longer contact time, more metal is deposited on the base layer. This leads to a thicker metal coating of the base layer. In order to reduce or even entirely prevent metal deposition on the surface of the rollers, it is preferable for the rollers to be enclosed by shielding which prevents electrolyte solution from being delivered onto the surface of the rollers. The shielding per se is preferably made of an electrically nonconductive material, in order to prevent the shieldings from becoming negatively charged so that metal can deposit on them. Suitable materials for the shieldings are, for example, plastics such as PVC, EPDM, silicone rubber.

**[0065]** The shieldings are open toward the substrate with the base layer, so that the roller can contact the base layer on this side. In order that the substrate can be fed along the roller enclosed by the shielding, without damaging the base layer or a metallic coating already produced on the base layer, it is preferable for a gap to be formed between the shielding and the surface of the substrate. So that as little electrolyte solution as possible enters the space between the shielding and the roller along the gap, it is preferable for the gap between the shielding and the surface of the substrate to be closed by a resilient lip. A suitable material for the resilient lip is any elastomer which has a lower hardness than the surface of the base layer or of the metallic coating. This prevents the latter from being damaged. Suitable materials for the resilient lip are, for example, EPDM, silicone rubber.

**[0066]** When electrolyte solution enters between the shielding and the roller, it becomes depleted by depositing the metal ions on the roller. The resilient lip substantially prevents fresh electrolyte solution from flowing in. The decreasing concentration of the metal ions also reduces the deposition of metal on the roller or even, when a correspondingly low concentration is reached, entirely prevents it.

**[0067]** As an alternative, it is also possible for the resilient lip to close a gap between the shielding and the roller. By closing the gap between the roller and the shielding, it is still possible for the roller to move. If the gap between the shielding and the roller is closed by a resilient lip, then this also

substantially prevents electrolyte solution from entering the space between the shielding and the roller when there is no substrate in the region of the roller.

**[0068]** Furthermore, it is also possible for the gap between the shielding and the surface of the substrate to be substantially sealed by a roller with a resilient surface. To this end, the roller with a resilient surface bears on the one hand on the substrate's surface provided with the base layer and, on the other hand, on the cathodically connectable roller. As an alternative, it is also possible for the roller with a resilient surface to bear on the one hand on the substrate's surface provided with the base layer and, on the other hand, on the shielding. In a third variant, the gap between the shielding and the cathodically connectable roller may also be substantially sealed by the roller with a resilient surface. To this end, the roller with a resilient surface bears on the one hand on the shielding and, on the other hand, on the cathodically connectable roller.

**[0069]** If the gap between the shielding and the cathodically connectable roller is substantially sealed respectively by the resilient lip or the roller with a resilient surface, then only that part of the cathodically connectable roller which lies outside the shielding is respectively in contact with electrolyte solution. In this region, however, metal can deposit on the surface of the cathodically connectable roller.

**[0070]** Closing the gap between the surface of the substrate and the cathodically connectable roller substantially prevents electrolyte solution from being able to flow to the surface of the cathodically connectable roller. This substantially prevents metal from depositing on the cathodically connectable roller.

**[0071]** The resilient lip or the roller with a resilient surface are preferably arranged so that the gap between the substrate and the roller is sealed whenever a substrate with a structured or full-surface base layer to be coated contacts the cathodically connectable roller, so that no electrolyte solution can flow onto the roller and at the same time the space between the cathodically connectable roller and the shielding is also substantially sealed by the resilient lip of the roller with a resilient surface. As soon as there is no substrate in the region of the cathodically connectable roller and the roller is therefore connected neutrally, it is preferable for the space surrounding the cathodically connectable roller, between the shielding and the cathodically connectable roller, to be substantially sealed by the resilient lip or the roller with a resilient surface so that as little electrolyte solution as possible can flow into this space. In this way the electrolyte solution is always kept away from the surface of the cathodically connectable roller, and metal deposition on the cathodically connectable roller is thus substantially prevented. The advantage of this is that the operating times of the rollers are extended, since the rollers do not have to be replaced so often.

**[0072]** The roller with a resilient surface, by which the gap between the substrate and the shielding or between the cathodically connectable roller and the shielding can be sealed, may for example comprise a nonresilient core for example of metal, for example steel or aluminum, and a resilient coating. The resilient coating is, for example, a coating of EPDM or silicone rubber. As an alternative, it is of course also possible for the roller with a resilient surface to be made entirely of resilient material. This, however, then needs to have a sufficiently high strength so as to prevent the roller with a resilient surface from being compressed at least partially and being drawn through between the cathodically con-

nectable roller and the substrate. The same materials as for seals, for example, are suitable as a material for the roller with a resilient surface when it is made entirely of resilient material. For example, the roller may then be made of EPDM or silicone rubber.

**[0073]** In order to generate a flow of current in the electrolyte solution and thereby permit deposition on the structured or full-surface base layer, it is preferable for an anode to be held respectively between the shieldings of two rollers. The anode is preferably designed as a grid anode. This offers the advantage that electrolyte solution can be delivered along the anode. Particularly when the individual cathodically connectable rollers are sealed by the resilient lip or the roller with a resilient surface, then delivering electrolyte solution along the anodes ensures that there is respectively an electrolyte solution with enough metal ions between two rollers, since the resilient lips or rollers with a resilient surface impede or even prevent liquid exchange between various regions inside the electrolyte bath, respectively between two cathodically connectable rollers.

**[0074]** As an alternative to the option of electrolyte delivery, it is also possible to use soluble anodes. The soluble anodes then preferably contain the metal with which the structured or full-surface base layer is electrolytically coated. During the flow of current, in this case the metal from the soluble anode enters into solution and subsequently deposits on the cathodically connected base layer.

**[0075]** The electricity supply to the individual cathodically connectable rollers takes place, for example, through sliding contacts. The sliding contacts are preferably formed inside the shielding. Pressing the cathodically connectable rollers onto the sliding contacts produces a flow of current, and the rollers become connected cathodically. For example, the rollers are pressed against the sliding contacts by the substrate on which the structured or full-surface base layer to be coated lies. To this end, the cathodically connectable rollers are displaceable perpendicularly to the surface of the substrate. As soon as there is no substrate in contact with the cathodically connectable rollers, a force acts on the roller so as to remove it from the sliding contact. By the substrate, the cathodically connectable roller is lifted in opposition to this force and pressed against the sliding contact. If the substrate is moved in a horizontal direction and the rollers lie above the substrate, then it is generally sufficient to use the force of gravity by which the rollers are removed from the sliding contact when there is no substrate in the region of the rollers. When the positioning and transport direction of the substrate are different from this, the required force which removes the roller from the sliding contact may, for example, be applied by spring elements.

**[0076]** As an alternative to electrifying the cathodically connectable rollers by sliding contacts, it is also possible for example to use sensors which detect whether the roller is in contact with a base layer to be coated. As soon as it is detected that the cathodically connectable roller is contacting a base layer to be coated, a voltage is applied to the cathodically connectable roller. As soon as the sensors detect that there is no contact with a base layer to be coated, the flow of current is interrupted again. The sensors, which detect whether the roller is in contact with a substrate having a structured or full-surface base layer to be coated, are for example optical or mechanical. When using sensors in order to detect whether the cathodically connectable roller is in contact with a base layer to be coated, it is also possible to produce the current

supply from outside the electrolyte bath. Then, for example, the current supply may take place via slip rings on the roller axles. Regulating the current supply using an optical or mechanical sensor is preferable, in particular, when the substrate has only a very small thickness. In this case, the thickness of the substrate would not be sufficient to induce a sufficiently large travel in order to press the roller against a sliding contact, so as to produce the current supply. This is the case, for example, when the base layer to be coated lies on a thin foil carrier.

**[0077]** In the case of thin foil carriers, the at least one roller may naturally also be permanently connected cathodically. As before, metal depositions resulting therefrom are significantly reduced by the shielding precautions in comparison with systems as are known from the prior art. This offers corresponding cost advantages, since the rollers have longer operating times and shorter maintenance intervals.

**[0078]** In order to simultaneously coat the upper side and the lower side of a substrate with structured or full-surface base layers formed thereon, in one embodiment two rollers respectively face one another and the substrate is fed through between them. In this way, the base layer on the upper side and the base layer on the lower side of the substrate can be coated simultaneously. Another advantage of the mutually opposing rollers is that they can simultaneously be used for transporting the substrate through the electrolyte bath. To this end, at least some of the rollers are driven.

**[0079]** As an alternative, the substrate may also be transported by having a transport device which faces the rollers. The transport device may for example comprise individually driven rollers, on which the substrate is conveyed. Furthermore, it is also possible for the conveyor device to comprise a conveyor belt, for example, on which the substrate lies. If there is a conveyor device facing the rollers, however, then only one side of the substrate can be coated. In order to coat a base layer possibly existing on the lower side of the substrate in this case, it is necessary to turn the substrate around and feed it through the electrolytic coating device for a second time, or to provide a second device through which the substrate is fed.

**[0080]** After having fed the substrate through the electrolytic coating device, it is preferable for the substrate to be rotated. The rotation axis, about which the substrate is rotated, is in this case arranged perpendicularly to the substrate's base layer to be coated. Structures which are initially wide and short, as seen in the transport direction of the substrate, are aligned by the rotation so that they are narrow and long as seen in the transport direction after the rotation. This extends the contact time for which an individual cathodically connectable roller contacts the structure. This increases the amount of metal deposited on the structure, and therefore of the layer thickness. After rotating the substrate, it may be fed either through the same device for a second time or through a second device downstream.

**[0081]** In another embodiment, the cathodically connectable rollers are arranged on the outer circumference of a rotating roller. In this embodiment, for example, it is possible to arrange the anode inside the rotating roller. To this end, the rotating roller, on which the cathodically connectable rollers are arranged, is designed as a hollow shaft. Those rollers which are not in contact with the substrate may, for example, be covered by shielding.

**[0082]** These shieldings are used to concentrate the profile of the primary current on the path from the central anode to

the substrate, and to restrict the current profile of the secondary current from the anodically connected contact rollers to the auxiliary cathodes. The electrical efficiency for metallizing the substrate can thereby be improved. Nevertheless, these shieldings are not categorically necessary.

**[0083]** In order to remove metal which may have deposited on the cathodically connected rollers, in all embodiments it is preferable for those rollers which are not in contact with the structured or full-surface base layer on the substrate to be connected anodically. By this anodic connection, the metal previously deposited on the roller is removed from it again. As an alternative, it is also possible for material deposited on the rollers to be cleaned off from them, for example during operating pauses. The cathodically connectable rollers may also be cleaned by taking the rollers out of the electrolyte bath. With an arrangement of the rollers in series, however, this is possible only when no substrate is being coated. If the cathodically connectable rollers are arranged on a rotating shaft, it is possible for those cathodically connectable rollers which do not contact the base layer to be removed and cleaned.

**[0084]** The method according to the invention and the device according to the invention for electrolytically coating structured or full-surface base layers on a substrate are suitable, for example, for producing conductor tracks on printed circuit boards. Such printed circuit boards are, for example, those with multilayer inner levels and multilayer outer levels, micro-via chips-on-boards, flexible and rigid printed circuit boards, and are for example installed in products such as computers, telephones, televisions, electrical automobile components, keyboards, radios, video, CD, CD-ROM and DVD players, game consoles, measuring and regulating equipment, sensors, electrical kitchen appliances, electrical toys etc.

**[0085]** Electrically conductive structures on flexible circuit supports may also be coated by the method according to the invention. Such flexible circuit supports are, for example, plastic films made of the materials mentioned above for the supports, onto which electrically conductive structures are printed. The method according to the invention and the device according to the invention are furthermore suitable for producing RFID antennas, transponder antennas or other antenna structures, chip card modules, flat cables, seat heaters, foil conductors, conductor tracks in solar cells or in LCD/plasma screens, capacitors, foil capacitors, resistors, convectors or electrical fuses. For example, two- or three-dimensional molded interconnected devices may also be produced by the method according to the invention.

**[0086]** It is furthermore possible to produce antennas with contacts for organic electronic components, as well as coatings on surfaces consisting of electrically nonconductive material for electromagnetic shielding.

**[0087]** Use is furthermore possible in the context of flow fields of bipolar plates for application in fuel cells. The application range of the method according to the invention and the device according to the invention allows inexpensive production of metallized, even nonconductive substrates, particularly for use as switches and sensors, absorbers for electromagnetic radiation or gas barriers or decorative parts, in particular decorative parts for the motor vehicle, sanitary, toy, household and office sectors, and packaging as well as foils. The invention may also be applied in the field of security printing for banknotes, credit cards, identity documents etc. Textiles may be electrically and magnetically functionalized

with the aid of the method according to the invention (antennas, transmitters, RFID and transponder antennas, sensors, heating elements, antistatic (even for plastics), shielding etc.).

**[0088]** It is furthermore possible to produce contact points or contact pads or interconnections on an integrated electronic component.

**[0089]** The method according to the invention and the device according to the invention may likewise be used for the metallization of holes, vias, blind holes etc., for example in printed circuit boards, RFID antennas or transponder antennas, flat cables, foil conductors with a view to through-contacting the upper and lower printed circuit board sides. This also applies when other substrates are used.

**[0090]** The metallized articles produced in the device designed according to the invention or by the method according to the invention—if they comprise magnetizable metals—may also be employed in the field of magnetizable functional parts such as magnetic tables, magnetic games, magnetic surfaces for example on refrigerator doors. They may also be employed in fields in which good thermal conductivity is advantageous, for example in foils for seat heaters, floor heating and insulating materials.

**[0091]** Preferred uses of the surfaces electrolytically coated according to the invention are those in which the products produced in this way are used as printed circuit boards, RFID antennas, transponder antennas, seat heaters, flat cables, contactless chip cards, thin metal foils or polymer supports clad on one or two sides, foil conductors, conductor tracks in solar cells or in LCD/plasma screens or as decorative application, for example for packaging materials.

**[0092]** In particular, the method according to the invention and the device according to the invention may be used for electrolytically coating individualized boards, for example the printed circuit boards.

**[0093]** The dimensions of the cathodically connectable rollers and the distance from roller to roller are dictated by the smallest structure length to be galvanized uniformly. The smaller the smallest structure length to be galvanized is, the smaller the distance between two rollers should be selected, and therefore also the roller diameter.

**[0094]** The invention will be explained in more detail below with the aid of the drawings. The figures respectively show only one possible embodiment by way of example. Other than in the embodiments mentioned, the invention may naturally also be implemented in further embodiments or in a combination of these embodiments.

**[0095]** FIG. 1 shows a device designed according to the invention with mutually opposing rollers connected in series,

**[0096]** FIG. 2 shows a device designed according to the invention, in which the cathodically connectable rollers are arranged on a rotatable shaft.

**[0097]** FIG. 1 shows a device designed according to the invention with mutually opposing rollers connected in series.

**[0098]** An electrolytic coating device 1 designed according to the invention comprises rollers 2 which are cathodically connectable. In the embodiment represented here, three rollers 2 are respectively connected in series and two rollers 2 respectively face one other.

**[0099]** The rollers 2 lie in a bath 3. The bath 3 contains an electrolyte solution 5. The composition of the electrolyte solution depends on the material with which coating is intended to take place. Usually, a metallic coating is applied by electrolytic methods. Conventional metals, which can be deposited by electrolytic coating, are for example gold,

nickel, palladium, platinum, silver, tin, copper or chromium. In principle, however, all metals which are nobler or equally noble as the least noble metal of the base layer may be used for the electrolytic coating. If need be, the substrate to be coated may also pass through a plurality of devices in succession. If necessary, the base layer on the substrate may even be coated successively with different metals in this case.

**[0100]** The electrolytic coating device **1** is supplied with the substrate **7** that comprises a base layer **9**, which is electrolytically coatable. The base layer **9** may be configured so that it is either structured or full-surface. In the embodiment represented in FIG. 1, the base layer **9** is structured. There is furthermore a base layer **9**, which is electrolytically coated, both on the upper side **11** of the substrate **7** and on the lower side **13** of the substrate **7**. The substrate **7** with the electrolytically coatable base layer **9** is respectively fed through between two opposing rollers **2**. By feeding the substrate **7** through, the movement direction of which is represented by an arrow **15**, the rollers **2** are displaced perpendicularly to the movement direction **15** of the substrate **7**. In the case of a first roller pair **17**, which contacts the substrate **7** with the base layer **9**, the starting position is represented by the dashed lines and the position after contacting by a solid line.

**[0101]** Owing to the thickness of the substrate **7**, the upper roller of the first roller pair **17** is lifted and the lower roller of the first roller pair **17** is depressed. As a result of this movement, the rollers **2** of the first roller pair **17** are respectively contacted by a sliding contact **19**. Via the sliding contact **19**, the rollers **2** of the first roller pair **17** are connected cathodically. As a result of the contact of the rollers **2** with the base layer **9** on the substrate **7**, the base layer **9** is also connected cathodically. Metal is deposited on the base layer **9** from the electrolyte solution **5**.

**[0102]** So that only little or preferably no metal is deposited on the rollers **2** which are connected cathodically, the rollers **2** are respectively enclosed by shielding **21**. The shielding **21** substantially prevents electrolyte solution from reaching the surface of the rollers **2**. So that the rollers remain both rotatable and radially displaceable, preferably resilient lips **23** are formed on the shieldings. When there is no substrate between two rollers of a roller pair, as is the case for example with the second roller pair **25** or the third roller pair **27**, the resilient lips **23** preferably bear on the roller **2**. As soon as the substrate **7** with the base layer **9** has been fed through between two opposing rollers **2** of a roller pair **17**—as represented for the first roller pair **17** in FIG. 1—the resilient lips **23** preferably bear on the upper side **11** or lower side **13** of the substrate **7**, respectively. A gap between the substrate **7** and the shielding **21** is thereby closed. No electrolyte solution can reach the roller **2**. Therefore, no metal can likewise be deposited on the roller **2** from the electrolyte solution.

**[0103]** As an alternative to the resilient lips **23**, it is also possible to provide a roller having a resilient surface, which contacts on the one hand the surface of the rollers **2** and on the other hand the shielding **27**, or the substrate **7**.

**[0104]** In the embodiment represented here, an anode **29** is respectively held between two shieldings **21**. The anode **29** is preferably designed as a grid anode.

**[0105]** Since the concentration of metal ions in the electrolyte solution **5** is reduced by the deposition of metal on the electrolytically coatable base layer **9**, it is preferably possible to supply fresh electrolyte solution. If the anodes **29** are designed as grid anodes, for example, then it is possible to supply the electrolyte solution via the anodes **29** as repre-

sented by the arrows **31** in FIG. 1. Supplying the electrolyte solution along the anodes **29** has the advantage that fresh electrolyte solution is delivered into the intermediate regions between the rollers **2**. Owing to the positioning of the rollers which, for example as represented in FIG. 1, touch one another when no substrate **7** is being fed through between them and which otherwise contact the substrate **7**, it is possible only with great difficulty to exchange electrolyte solution in the intermediate spaces between two respectively neighboring rollers.

**[0106]** As an alternative, it is also possible to form channels in the anodes **29**, through which the electrolyte solution is delivered. In this case, it is not necessary to design the anodes **29** as grid electrodes.

**[0107]** By moving the substrate **7** in the direction **15**, the individual roller pairs **17**, **25**, **27** are contacted successively by the base layer **9** on the substrate **7**. The roller pairs **17**, **25**, **27**, between which the substrate **7** is fed through, are respectively contacted by the corresponding sliding contacts **19**. The fact that the rollers **2** are connected in series increases the contact time of the base layer **9** to be coated with a cathodically connected electrode, which is designed here as roller **2**. A thicker layer can be deposited.

**[0108]** The substrate **7** is transported through between the roller pairs **17**, **25**, **27**, for example, by providing the individual rollers **2** of the roller pairs **17**, **25**, **27** with a drive. As an alternative, all rollers **2** of the roller pairs **17**, **25**, **27** may be driven. Preferably, however, the rollers **2** which lie on the same side of the substrate **7** are respectively driven. Thus, for example, either the rollers **2** on the lower side **13** of the substrate **7** or the rollers **2** on the upper side **11** of the substrate **7** may be driven.

**[0109]** If small amounts of metal are deposited on the rollers **2** despite the shieldings described above, the rollers **2** may either be removed or connected anodically for cleaning. Anodic connection of the rollers may, for example, be carried out by connecting the sliding contacts **19** anodically and feeding a substrate without a base layer through the device, so that the rollers **2** then contact the anodically connected sliding contacts **19**.

**[0110]** FIG. 2 represents a second embodiment of the device according to the invention.

**[0111]** In the embodiment represented in FIG. 2, the cathodically connectable rollers **2** are arranged on a rotatable shaft **41**. Unlike in the embodiment represented in FIG. 1, however, a substrate **7** with a base layer **9** formed thereon can be coated only on one side with the embodiment represented in FIG. 2. As in the embodiment represented in FIG. 1, the rollers **2** are enclosed by shielding **21** with resilient lips **23** formed thereon. The substrate **7** with the base layer **9** to be coated electrolytically is fed along the device **1**. At least one roller **2** thereby contacts the base layer **9**. As a result of the contact of the roller **2** with the base layer **9**, the base layer **9** becomes connected cathodically. Metal is deposited on the base layer **9**. As in the embodiment represented in FIG. 1, in the embodiment represented in FIG. 2 as well only the roller **2** which contacts the surface **11** with the base layer **9** is connected cathodically.

**[0112]** The rotatable shaft **41**, on which the rollers **2** are arranged, is preferably designed as a hollow shaft. Inside the shaft **41**, there is an anode **43**.

**[0113]** In order to remove metal which may have deposited on the rollers **2**, those rollers **2** which are not in contact with the base layer **9** can be connected anodically. Preferably,

those rollers 2 which lie furthest away from the base layer 9 to be coated are connected anodically. The anodically connected rollers are provided with references 45 in FIG. 2.

[0114] The anodically connected rollers 45 preferably face cathodes 47, which make it possible for a current to flow.

[0115] In order to avoid a short circuit, there is preferably shielding 49 between the anode 43 and the anodically connected rollers 45.

[0116] Those rollers 2 which are not contacting the base layer 9 and are not connected cathodically are preferably neutral. These rollers may be covered by shielding 51.

[0117] As an alternative to the embodiment variants in which anodically connected rollers 45 are provided for cleaning, it is also possible for rollers 2 which are not in contact with the base layer 9 to be removed and cleaned outside the device 1. If it is proposed to use anodically connected rollers 45 for cleaning, however, then preferably the entire device 1 is covered by the electrolyte solution 5. In the embodiment in which rollers 2 are removed for cleaning, it is sufficient for the surface 11 of the substrate 7 to be covered by electrolyte solution. Those rollers 2 which do not contact the base layer 9 on the upper side 11 of the substrate 7 may lie outside the electrolyte solution. It is nevertheless necessary for the anode 43 likewise to lie in the electrolyte solution 5. In this case, however, it is also possible for the anode 43 to lie outside the shaft 41, instead of inside the shaft 41 designed as a hollow shaft as represented in FIG. 2.

#### LIST OF REFERENCES

|        |                                |
|--------|--------------------------------|
| [0118] | 1 Electrolytic coating device  |
| [0119] | 2 Roller                       |
| [0120] | 3 Bath                         |
| [0121] | 5 Electrolyte solution         |
| [0122] | 7 Substrate                    |
| [0123] | 9 Base layer                   |
| [0124] | 11 Upper side                  |
| [0125] | 13 Lower side                  |
| [0126] | 15 Movement direction          |
| [0127] | 17 First roller pair           |
| [0128] | 19 Sliding contact             |
| [0129] | 21 Shielding                   |
| [0130] | 23 Resilient lip               |
| [0131] | 25 Second roller pair          |
| [0132] | 27 Third roller pair           |
| [0133] | 29 Anode                       |
| [0134] | 31 Electrolyte supply          |
| [0135] | 41 Shaft                       |
| [0136] | 43 Anode                       |
| [0137] | 45 Anodically connected roller |
| [0138] | 47 Cathode                     |
| [0139] | 49 Shielding                   |
| [0140] | 51 Shielding                   |

1.-15. (canceled)

16. A device for the electrolytic coating of a structured or full-surface base layer (9) on a surface of a substrate (7), which comprises at least one electrolyte bath (3) having at least one rotatably mounted roller (2) connectable as a cathode, which contacts the base layer (9) during the electrolytic coating, the base layer (9) being covered by an electrolyte solution (5) contained in the electrolyte bath (3) and being moved relative to the at least one roller (2) during the coating, wherein the at least one roller (2) connectable as a cathode is connectable cathodically during the contact with the base layer (9) and is connectable neutrally or anodically as soon as

there is no contact with the base layer (9), wherein the rollers (2) are enclosed by shielding (21) which substantially prevents electrolyte solution (5) from being delivered onto the surface of the rollers (2), wherein a gap is formed between the shielding (21) and the surface of the substrate (7), and wherein the gap between the shielding (21) and the surface of the substrate (7) is sealed by a roller having a resilient surface.

17. The device as claimed in claim 16, wherein the at least one roller (2) connectable as a cathode is held statically in the electrolyte bath (3), while the substrate (7) with the base layer (9) is transported through the electrolyte bath (3).

18. The device as claimed in claim 16, wherein at least two rollers (2) connectable as a cathode are connected in series in the electrolyte bath (3).

19. The device as claimed in claim 16, wherein an anode (29) is held between the shieldings (21) of two rollers (2) connectable as a cathode.

20. The device as claimed in claim 19, wherein the anode (29) is designed as a grid anode.

21. The device as claimed in claim 19, wherein electrolyte solution can be delivered between two shieldings (21) in the region of the anode (29).

22. The device as claimed in claim 16, wherein the electricity supply to the rollers (2) connectable as a cathode takes place through sliding contacts (19).

23. The device as claimed in claim 22, wherein the rollers (2) connectable as a cathode are pressed against the sliding contacts (19) by the substrate (7).

24. The device as claimed in claim 16, wherein two rollers (2) respectively face one another, and the substrate (7) is fed through between them so that a base layer (9) on the upper side (11) and on the lower side (13) of the substrate (7) can be coated simultaneously.

25. The device as claimed in claim 16, wherein a transport device, by which the substrate (7) is transported along the rollers (2), faces the rollers (2).

26. The device as claimed in claim 16, wherein the rollers (2) connectable as a cathode are arranged on the circumference of a rotating shaft (41).

27. The device as claimed in claim 26, wherein the rotating shaft (41) is designed as a hollow shaft, in which at least one anode (43) is arranged.

28. A method for the electrolytic coating of a structured or full-surface base layer (9) on a surface of a substrate (7), the base layer (9) being surrounded by an electrolyte solution (5) and being contacted by at least one roller (2) connectable as a cathode, wherein the roller (2) connectable as a cathode is connected cathodically when it contacts the base layer (9) and/or the substrate (7) and is connected neutrally or anodically in order to remove material deposited thereon as soon as there is no contact with the base layer (9) and/or the substrate (7).

29. The method as claimed in claim 28, wherein after a first electrolytic coating process, the substrate (7) is rotated about an axis perpendicular to the surface to be coated, and subsequently passes through an electrolytic coating process again.

30. The device as claimed in claim 16 for producing conductor tracks on printed circuit boards, RFID antennas, transponder antennas or other antenna structures, chip card modules, flat cables, seat heaters, foil conductors, conductor tracks in solar cells or in LCD/plasma screens, for producing decorative or functional surfaces on products, which are used

for shielding electromagnetic radiation, for thermal conduction or as packaging, or for producing electrolytically coated products in any form.

**31.** The method as claimed in claim **28** for producing conductor tracks on printed circuit boards, RFID antennas, transponder antennas or other antenna structures, chip card modules, flat cables, seat heaters, foil conductors, conductor

tracks in solar cells or in LCD/plasma screens, for producing decorative or functional surfaces on products, which are used for shielding electromagnetic radiation, for thermal conduction or as packaging, or for producing electrolytically coated products in any form.

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