

- [54] **PROCESS FOR THE MANUFACTURE OF METALLIZED SHAPED BODIES OF MACROMOLECULAR MATERIAL**
- [75] Inventors: **Wilhelm Brandt**, Wertach; **Irmgard Bindrum**, Wiesbaden-Biebrich, both of Germany
- [73] Assignee: **Hoechst Aktiengesellschaft**, Germany
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- [58] **Field of Search** 117/47 A, 138.8 UF, 138.8 UA, 117/138.8 PV, 143 B, 130 E, 160 R, 213; 428/421, 422

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Primary Examiner—P. E. Willis, Jr.
Attorney, Agent, or Firm—James E. Bryan

- [57] **ABSTRACT**
- This invention relates to a process for the deposition of a metal coating on the surface of a shaped body of macromolecular material which comprises forming a layer of a noble metal salt solution or dispersion of a film-forming macromolecular material on the surface of a solid support material,
- heating the coated support to remove the liquid and form a film,
- treating the film with a metallization liquid, and drying.

3 Claims, 2 Drawing Figures

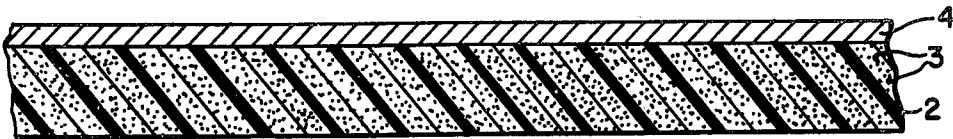


FIG. 1

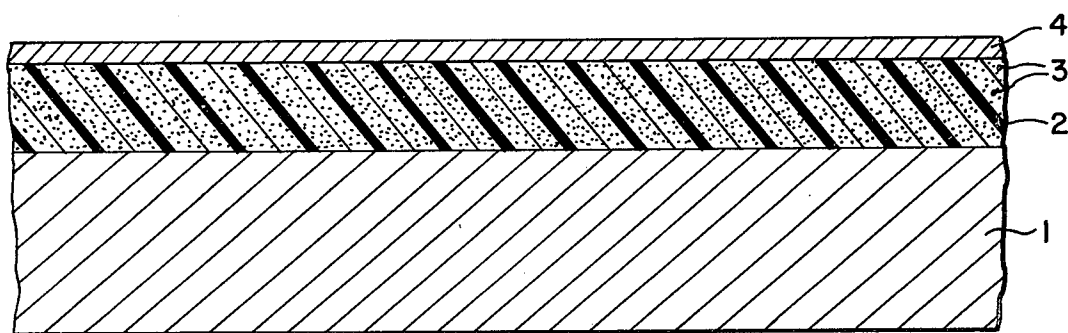
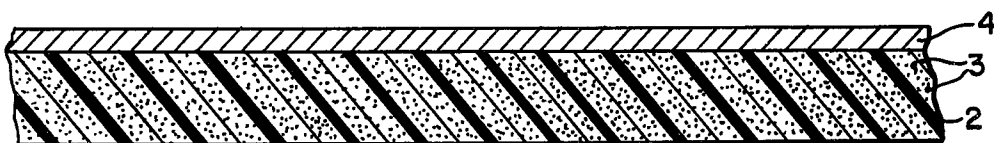


FIG. 2



PROCESS FOR THE MANUFACTURE OF METALLIZED SHAPED BODIES OF MACROMOLECULAR MATERIAL

This is a division of application Ser. No. 231,825, filed Mar. 6, 1972.

The present invention relates to a process for the deposition of a metal coating on the surface of a shaped body, particularly a sheet, of macromolecular material. The invention also relates to shaped bodies of macromolecular material with metallized surfaces, particularly to sheet materials.

It is known to provide shaped bodies of non-electroconductive plastics, e.g. of polystyrene, acrylonitrile/butadiene/styrene copolymers, polyolefins, and polyesters, if desired after suitable pretreatment, with thin metal coatings either by electroplating or electroless plating.

In this connection, a process has proved particularly suitable in which a very thin layer of noble metal nuclei is deposited on the plastic surface. In this process, the surface is sensitized and a noble metal salt solution and activated with a solution of a reducing agent. By means of electroplating or electroless plating baths, continuous metal layers are deposited at the noble metal nuclei.

In such a pretreatment, for example, the surface is first treated with a palladium salt solution, e.g. PdCl_2 , and then with a hydrazine hydrate solution, or first with a stannous chloride solution and then with a silver nitrate solution. In each case, small quantities of elemental noble metal are deposited on the surface.

The present invention provides a process by which it is possible to deposit, by electroless plating on the surface of a shaped body, a metal coating firmly adhering to the polymer surface of the shaped body and which eliminates the disadvantages of known processes.

In the present process for the deposition of a metal coating on the surface of a shaped body of synthetic or natural macromolecular material, a noble metal salt solution or dispersion of a film-forming macromolecular material, which optionally may contain a wetting agent, is spread on the surface of a solid support material to form a layer and, for removing the liquid component of the layer and for forming a continuous film on the support, sufficient heat is caused to act on the coated support. Then, optionally, an activating solution is caused to act thereon and, in a further process step, metallization liquid is caused to act on the film-carrying support. Optionally, the film then is stripped from the support.

A shaped body of macromolecular material means in particular a sheet material of macromolecular material which is self-supporting, as well as a composite material comprising a mechanically stable support sheet material and a film of macromolecular material firmly adhering thereto.

A film capable of being stripped from the solid support without leaving any residue is self-supporting.

The self-supporting film has two free surfaces and the film adhering to the substrate one free surface accessible to metallization.

The support material may have a continuous structured or structureless surface.

It is also possible to use textile sheet materials as supports.

The layer of a liquid polymer dispersion or solution which is first to be applied to the support according to

the process of the invention is applied by known processes to the surface of the support material, e.g. by doctor devices, and levelled. The liquid component of the layer is then removed, e.g. by subjecting the coated support material to heat at a temperature sufficient to remove the liquid component. This may be performed, for example, by means of a drying cabinet operated with warm air or in a drying channel.

For the production of a sintered film of polytetrafluoroethylene, a liquid layer of an aqueous tetrafluoroethylene dispersion spread on a sufficiently heat-resistant solid support is exposed in known manner to heat at a temperature of about 100°C ; after vaporizing the liquid component of the layer, heat in the temperature range above 300°C , preferably in the range between 380° and 400°C , is applied to the coated support material in order to form a sintered film of polytetrafluoroethylene on the surface of the support. The time of the heat action is not critical.

The invention further provides a modification of the said process including, when using a polymer dispersion and a discontinuous layer is produced on the surface of the support after vaporization of the dispersing agent, heating the metallized layer sufficiently to form a sintered film of the polymer.

In the following, the liquid containing the noble metal salt and the film-forming macromolecular substances in dispersed or dissolved form is called the "sensitized liquid containing film-forming macromolecular material." The liquid used for metallization of the shaped bodies, which contains ions reducible to yield free metal and a reducing agent in an aqueous solution, is called the "metallization liquid." Furthermore, the metal baths generally contain substances forming complexes with the metal ions, which complexes provide for the necessary stability of the bath and which act on the structure of the metal layer to be formed, e.g. as glossing agents.

The metallization liquid contains no dissolved noble metal salt.

An aqueous solution of a chemical reducing agent is called the "activating liquid".

Suitable aqueous noble metal salt solutions have a content of noble metal salt in the range from 0.001 to 10 per cent by weight, calculated on the total weight of the solution.

Suitable noble metal salts for the production of the sensitized liquid containing film-forming macromolecular material are palladium chloride, gold chloride, platinum chloride, and silver nitrate.

Aqueous noble metal salt solutions may be ammoniacal or acidic.

Since the described noble metal salts dissolve in acidic media as well as in ammoniacal aqueous media, the aqueous noble metal salt solutions may be incorporated into ammoniacal as well as into acidic aqueous polymer dispersions or solutions.

If permanent adhesion of the film of polymer material to the support is desired, it is necessary to add to the polymer dispersion or solution a suitable wetting agent, e.g. dodecyl benzene sulfonate, in a quantity of at least 0.1 per cent by weight, calculated on the total weight of the dispersion.

Polymer solutions or dispersions are those which contain natural or synthetic film-forming macromolecular substances, particularly those with a thermoplastic character, in a dissolved or dispersed form.

The solvent or dispersing agent may be water or an organic liquid.

Suitable macromolecular substances are: vinyl polymers and the copolymers thereof, e.g. polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate, vinylidene chloride copolymers, polytetrafluoroethylene, polystyrene, synthetic elastomers, e.g. polyurethane or polyacrylates, polymethacrylates, as well as the copolymers thereof, natural rubbers and synthetic rubbers, polyolefins, cellulose derivatives, polycarbonates, epoxides, polyesters, melamine condensates, urea condensation products, phenol-formaldehyde condensation products, polyamides, and polyphenyls.

If the liquid component of the sensitized liquid containing film-forming macromolecular material is an organic liquid, the noble metal salt is incorporated into the liquid in a manner such that it is dissolved in a suitable solvent, e.g. in acetone or butanone, and this solution is then added to the liquid containing the polymer.

The metallization liquid has a solids content of metal salt in the range from 5 to 20 g, preferably from 7 to 10 g, per liter of copper salt-containing metallization liquid, and 10 to 50 g, preferably from 20 to 30 g, per liter of nickel salt-containing metallization liquid.

Suitable salts are CuSO_4 and NiSO_4 .

It is particularly advantageous to use metallization liquids which contain a chemical medium capable of complex formation with the metal salt; these complex-forming agents maintain the concentration of the metal ions in the metallization liquid low.

Chemical reducing agents in the metallization liquid are, for example, sodium hypophosphite, sodium hydride or nitrogen diethyl borane; formaldehyde, hydrazine hydrate as well as sodium bisulfite are suitable for copper salt-containing liquids.

Particularly suitable for the production of the aqueous activating liquid are stannous chloride combined with hydrochloric acid dissolved in water and hydrazine hydrate in an alkaline solution.

In some cases, it is advantageous to activate the palladium chloride-containing plastic layers, prior to their metallization, with hydrazine hydrate solution. It may be ascertained by simple preliminary tests whether deposition of the metal salt from the metallization liquid takes place sufficiently rapidly without previous activation of the layer by the action of hydrazine hydrate solution.

It is advantageous to use metallization liquids which contain a stabilizer for the reducing agent, e.g. telluric acid in nickel salt baths.

The stabilizer for the chemical reducing agent generally is employed in a concentration in the range from 0.001 to 2 per cent by weight, calculated on the total weight of the liquid. In special cases, it is advantageous when copper-containing metallization liquids contain a gloss-imparting additive, e.g. saccharin, in a concentration of 0.01 g/l.

The ratio by weight of metal salt to chemical reducing agent in the metallization liquid advantageously is so selected that the reducing agent is in excess.

The metallization liquid in accordance with the process has a temperature in the range from 30° to 100°C, in the case of a nickel salt-containing liquid, and a temperature in the range from 20° to 50°C in the case of a copper salt-containing liquid.

The time of action of the metallization liquid upon the shaped body depends upon the metal quantity to be deposited per unit area.

For depositing, for example, a 0.2 mm thick metal layer, a time in the range from 1 to 10 minutes is required, depending on the chemical composition of the metallization liquid or the metal salt concentration thereof.

The metallized shaped bodies produced according to the process of the invention have metal coatings of a thickness in the range between 0.02 and 0.25 μ .

The metal coatings are abrasion-resistant and firmly adherent to the polymer surfaces of the shaped bodies.

A firmly adherent coating means a coating which cannot be separated from its contact surface of polymer material by the adhesive tape test.

The adhesive tape test is performed as follows:

A crisscross pattern is scratched into the surface of the metal coating on the shaped body, which pattern is then covered with an adhesive tape having a pressure-sensitive layer. The adhesive tape is then stripped with a pull. The metal coating is firmly adherent to its contact surface when the metal coating cannot be separated from its contact surface under the aforementioned conditions.

The process of the invention is performed in a manner such that first the solution of a noble metal salt is added to a polymer dispersion or to a polymer solution. The solids content of the polymer dispersion or of the polymer solution is not critical in the usual viscosity range of easily spreadable or castable solutions.

When preferably using as the aqueous polymer dispersion a dispersion of polytetrafluoroethylene, this dispersion advantageously has a polymer portion in the range from 1 to 10 per cent by weight, calculated on the total weight of the dispersion, particularly preferably, however, in the range from 5 to 8 per cent by weight.

The ratio by weight of the polymer to the noble metal salt in the liquid obtained after the mixing of the polymer dispersion or solution with the noble metal salt solution is in the range between 2 : 1 and 100 : 1, preferably in the range between 5 : 1 and 25 : 1.

The liquid obtained by mixing the polymer dispersion or the polymer solution with the noble metal salt solution is then applied in the form of a layer to a self-supporting planar support of sufficient inherent rigidity and sufficient strength. The material forming the support must be chemically resistant to the liquid components of the liquid layer applied to the support.

The support must be chemically resistant as well as sufficiently mechanically stable in the temperature range in which vaporization of the liquid component of the layer applied to the support takes place.

Suitable supports are those of synthetic or natural organic material as well as of inorganic material which fulfill the above-mentioned conditions. For the production of preferable shaped bodies of polytetrafluoroethylene with metallized surfaces, supports particularly suitable are those of glass, steel, aluminum, unglazed porous clay, unglazed ceramic material or roughened polyimide film. All these supports are well wetted by aqueous polytetrafluoroethylene dispersions containing wetting agents. The support for a shaped body of polytetrafluoroethylene must be thermally resistant in the range between 250° and 400°C.

After the application of the liquid layer to the support, the coated support is exposed to heat sufficient to

vaporize the liquid components of the applied layer; the temperature to be maintained during heating depends upon the boiling point of the liquid component of the layer which must be vaporized.

The heating of the coated support may take place, for example, in a drying cabinet operated with warm air.

If a copper layer is to be applied, it is advantageous, prior to the action of the copper salt-containing metallization liquid, to treat the surface of the polymer film with activating liquid.

Metallization liquid is then caused to act upon the support provided with a polymer film. This may be performed by immersing the support provided with a polymer film into a tank filled with metallization liquid. After removal of the film-carrying support from the tank, the shaped body with the metallized surface of the polymer film is treated in a rinsing liquid, preferably water, and liberated from the rinsing liquid by drying.

In accordance with the invention, the production of a self-supporting film from polymer material, the surface of which is metallized, is performed by using a planar sheet material as the support, to the surface of which is applied the above-mentioned liquid layer in the manner described above and, after the formation of a metal layer on the film of polymer material, this film is stripped as a self-supporting film from the support.

If the film to be metallized and united with a support or the self-supporting film to be metallized is of polytetrafluoroethylene, film formation must be performed by a sintering process on a support. In this case, after the application of the aqueous palladium chloride-containing polytetrafluoroethylene dispersion to the support, first the liquid component of the layer is removed by heating sufficient to vaporize this component, and the coated support is then exposed to heat sufficient to produce a sintered film of polytetrafluoroethylene on the surface of the support.

A sintered film is a continuous voidless film in which, by the action of heat, the plurality of discrete particles of polytetrafluoroethylene on the surface of the support fuse to form a continuous film.

Film formation on the support also may be performed continuously by applying a liquid layer in known manner, for example by means of a doctor knife, to the surface of a web support moving at a constant speed, levelled, and then converted in the described manner into a polymer film. In connection with the preferred production of metallized shaped bodies of polytetrafluoroethylene, the following should be borne in mind:

When the solid support has a rough surface, the film produced by sintering the polytetrafluoroethylene particles on the support adheres thereto in any case. The film, for example, adheres inseparably to a surface of a glass plate roughened with silicon carbide paste (depth of roughness $11\ \mu$), independently of whether sintering of the film has occurred prior to or after the action of the metallization liquid.

When the support has a surface of a smaller depth of roughness, adhesion of the metallized polytetrafluoroethylene film depends upon whether the layer has been sintered prior to or after metallization.

When, for example, a palladium chloride-containing aqueous polytetrafluoroethylene dispersion is applied to a grease-free roughened surface of a steel plate (depth of roughness $3.5\ \mu$), the dispersion is dried, the layer of a plurality of discrete particles is metallized by

the action of the metallization liquid and the layer is then sintered, the metallized film cannot be stripped from the steel plate surface. When, however, the aqueous polytetrafluoroethylene dispersion is applied to the polished surface of the steel plate and the polytetrafluoroethylene layer is dried, sintered and only then metallized by the action of the metallization liquid, the metallized polytetrafluoroethylene film can be stripped from the support without leaving any residue. In this manner, it is possible to produce self-supporting films with metallized surfaces.

When the palladium chloride-containing aqueous polytetrafluoroethylene dispersion is coated onto a grease-free polished surface of a glass plate or of a high-luster polished steel plate (depth of roughness $< 0.1\ \mu$) and then dried, the metallized film can be stripped from the support in the form of a self-supporting film independently of whether the action of the metallization liquid has taken place prior to or after sintering.

If the production of self-supporting metallized films of polytetrafluoroethylene is desired, the support to which the polytetrafluoroethylene dispersion is applied must be so selected that easy separation of the sintered metallized film therefrom without any residue is guaranteed.

It is possible, for example, to apply the dispersion continuously to the polished surface of a drum. At the periphery of the drum, is a device for the application of the aqueous dispersion, a device for drying the applied layer, a device by means of which it is possible to cause the metallization liquid to act upon the dry polytetrafluoroethylene layer, and a heating device for effecting sintering of the layer to give a film. In this manner, it is possible to continuously strip from the surface of the rotating drum a self-supporting metallized film of polytetrafluoroethylene in the form of a self-supporting web.

The metal coating applied to the polytetrafluoroethylene film, self-supporting or not, may serve as an adhesive for substances which, without the adhesive metal coating on the polytetrafluoroethylene film, cannot be firmly united with a shaped body of polytetrafluoroethylene.

Plastics adhering to the metal coating, for example, may be sufficiently deposited from solutions, dispersions or melts in the form of self-supporting sheet materials, e.g. by laminating while hot, to the metallized surface of the polytetrafluoroethylene layer.

For these cases, it is sufficient if the metal layer imparting adhesion is very thin, e.g. has a thickness of $0.1\ \mu$.

In this manner, it is also possible to produce sandwiches constructed from a plurality of alternately superimposed layers of polytetrafluoroethylene and metal. The individual metal layers may be similar or different.

The quantity of noble metal salt in the aqueous polytetrafluoroethylene dispersion which is necessary to form a continuous metal coating deposited by electroless plating on the surface of the polytetrafluoroethylene layer determines:

1. the flocculation of the dispersed plastic material or the stability of the dispersion during drying of the layer on the support,
2. the speed of deposition of the metal from the metallization liquid on the layer of polytetrafluoroethylene,

and

3. the continuity of the metal coating deposited on the surface of the polytetrafluoroethylene layer.

The shaped bodies metallized according to the process of the invention may be used as electrical resistance elements. When using a shaped body of a metallized film of macromolecular material which adheres to a support, the support must be an electrically insulating material.

The invention will be further illustrated by reference to the accompanying drawing, in which:

FIG. 1 shows a sheet material with a metallized surface (which consists of a substrate with a continuous surface) of a noble metal salt-containing layer of macromolecular material thereon and a coating of metal on the surface and firmly adhering thereto, and

FIG. 2 shows a noble metal salt-containing self-supporting film of macromolecular material on the surface of which there is a firmly adhering metal coating.

The self-supporting film with the metallized surface according to FIG. 2 is obtained by stripping the film 2 with the metallized surface from the substrate 1 according to FIG. 1.

Referring to FIG. 1, numeral 1 identifies the substrate, numeral 2 identifies the noble metal salt-containing film of macromolecular material, numeral 3 the noble metal salt uniformly distributed over the cross-section of the film, and numeral 4 identifies the metal coating.

Referring to FIG. 2, numerals 2, 3, and 4 have the same meanings as in FIG. 1.

The following examples further illustrate the invention:

EXAMPLE 1

A 60 percent by weight aqueous polytetrafluoroethylene dispersion (e.g. Hostafon TF 32, registered trade mark of Farbwerke Hoechst AG, Frankfurt, Germany), which contains 5 percent by weight of a non-ionic wetting agent, i.e. a reaction product of ethylene oxide and nonyl phenol (Hostapal, a registered trade mark of Farbwerke Hoechst AG, Frankfurt, Germany) and 0.04 percent by weight of ammonia is diluted with water in a ratio of 1 : 12.

A 5 percent by weight aqueous polytetrafluoroethylene dispersion is obtained thereby. To 86 ml of this diluted aqueous polytetrafluoroethylene dispersion, there is added a solution of 0.2 g of palladium chloride dissolved in 10 ml of concentrated ammonia and 0.8 g of the sodium salt of dodecylphenyl sulfonic acid dissolved in 4 ml of water. The liquid thus prepared has a content of 4.3 per cent by weight of polytetrafluoroethylene and 0.2 per cent by weight of palladium chloride: the ratio of palladium chloride to polytetrafluoroethylene in the dispersion is 1 : 21.5.

The pH value of the liquid is 8.0.

One support used for the liquid layer of the above-described composition is an aluminum plate of a depth of roughness of 4.8 μ , and another one a glass plate of a depth of roughness of 11 μ .

A liquid layer of the above-described palladium chloride-containing aqueous polytetrafluoroethylene dispersion is applied to each of the two plates. The application is performed by casting the liquid onto the surface of the support and levelling the layer thickness. The coated plate is dried for 2 minutes in a drying cabinet at 90°C. After removal from the drying cabinet,

the plates are placed into a liquid bath of the metallization liquid which is prepared as follows: 25 g of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ are dissolved in 200 ml of distilled water. A second solution is prepared containing 24.4 g of $\text{Na}_2\text{H}_2\text{PO}_4$ dissolved in 200 ml of distilled water. Both salt solutions are combined and 27 g of d,l-lactic acid and 16.8 g of succinic acid, dissolved in 200 ml of distilled water, are added to the aqueous solution containing the metal salt and the chemical reducing agent. The solution is adjusted to a pH value of 6 by addition of caustic soda. A small quantity of telluric acid is added to the solution, which is then diluted with distilled water to 1,000 ml. The metallization liquid has a temperature of 70°C. The time of action of the metallization liquid onto the supporting plates coated with polytetrafluoroethylene is 1 minute. After this time of action, the plates are removed from the bath and placed in a drying cabinet heated to 380°C. The plates remain in this drying cabinet for 15 minutes. The sintered polytetrafluoroethylene layer has a thickness of 1.1 μ ; the nickel coating deposited by electroless plating on its surface has a thickness of 0.2 μ .

A crisscross pattern is scratched into the nickel coating by means of a razor blade. A pressure-sensitive adhesive tape (e.g. a Tesa tape marketed by Messrs. Beiersdorf, Hamburg, Germany) is bonded over the crisscross pattern and then stripped again with a pull. The adhesive tape can be separated from the metal coating without leaving any residue, i.e. the metal coating firmly adheres to the polytetrafluoroethylene film.

Even after repeated sharp bending of the coated aluminum plate, the plastic layer does not break; the nickel coating cannot be separated.

EXAMPLE 2

A liquid layer of a palladium chloride-containing aqueous polytetrafluoroethylene dispersion, as described in Example 1, is applied to the surface of an unglazed porous clay plate and dried. In contradistinction to Example 1, the plate is then placed for 5 minutes into a metallization liquid containing, instead of a nickel salt, a 0.6 percent aqueous copper sulfate solution containing 1.5 percent of formaldehyde and 1.9 per cent of sodium hydrogen sulfite (e.g. chemical copper deposition bath CP 70 of Messrs. Shipley). Sintering takes place during 15 minutes at a temperature of 380°C in a drying cabinet.

The metallization liquid has a temperature of 50°C. The copper coating on the film of polytetrafluoroethylene has a thickness of 0.2 to 0.3 μ . Result of the adhesive tape test: firm adhesion.

The polytetrafluoroethylene film provided with a copper coating adheres firmly to the supporting plate. The thickness of the copper coating applied to the polytetrafluoroethylene film by electroless plating is then increased by electroplating to 10 μ .

The 10 μ thick coating is subjected to the adhesive tape test. Result: firm adhesion.

EXAMPLE 3

This example is similar to Example 1 with the exception that the supporting plate used is a steel plate with a degreased high-luster polished surface (depth of roughness 0.1 μ). The thickness of the nickel coating deposited by electroless plating on the surface of the polytetrafluoroethylene film is then increased to 10 μ by electroplating with a further nickel layer. The film of polytetrafluoroethylene has a thickness of 1 μ .

The nickel-plated polytetrafluoroethylene layer can be easily stripped from the support without leaving any residue.

The adhesion of the metal coating to the self-supporting nickel-plated polytetrafluoroethylene layer is tested according to the adhesive tape test. Result: firm adhesion.

EXAMPLE 4

An 8 percent aqueous solution of polyvinyl alcohol (e.g. Mowiol N 70-98 of Farbwerke Hoechst AG, Frankfurt, Germany) is prepared which contains 0.1 percent of palladium chloride, calculated on the solution weight, or 1.2 percent of palladium chloride, calculated on the polyvinyl alcohol weight. A liquid layer of this solution is applied to the roughened surface of a glass plate and dried for 5 minutes at 200°C in a drying cabinet operated with warm air. The dried polymer film has a thickness of 10 μ . The film-carrying glass plate is then placed into a metallization liquid of the composition described in Example 1. Duration: 1 minute. The plate is then removed from the bath and rinsed with water. The nickel coating firmly adhering to the surface of the polymer film has a thickness of about 0.2 μ . The thickness of the applied nickel layer is then increased in known manner by electroplating to 5 μ , the time of action in the electroplating bath is 20 minutes at a current density of 1 A/dm², and the electroplating bath has a temperature of 60°C.

EXAMPLE 5

A 10 percent aqueous dispersion of a copolymer based on vinylidene chloride/methyl methacrylate/methyl acrylate/itaconic acid which contains an addition of 0.05 percent of palladium chloride, calculated on the dispersion weight, or of 0.5 percent of palladium chloride, calculated on the polymer component weight, is applied to the surface of a textile fabric (cotton/nettle fabric) and dried for 3 minutes at 130°C. The layer thickness of the polymer film formed on the support material is 10 μ . The polymer film-carrying support material is then treated for 6 minutes in a metallization liquid according to the procedure of Example 1. After this treatment, a continuous nickel coating of a thickness of about 0.2 μ has formed on the surface of the polymer film to which it firmly adheres.

EXAMPLE 6

The example is similar to Example 5 with the exception that the coated textile material, after drying at 130°C, is immersed for 1 minute into a 0.6 percent aqueous hydrazine hydrate solution containing 1.2 percent of NaOH. The coated textile material is then placed for 8 minutes into a metallization bath according to example 2. A 0.2 μ thick copper coating is formed on the surface of the polymer film on the support material.

EXAMPLE 7

A 10 percent aqueous dispersion of a copolymer based on acrylic acid butyl ester is prepared which contains 0.1 per cent of palladium chloride, calculated on the dispersion weight, or 1 per cent of palladium chloride, calculated on the polymer component weight. A layer of the liquid is applied to the surface of a polyester film (e.g. Hostaphan, registered trade mark of Farbwerke Hoechst AG, Frankfurt, Germany). The coated polyester film is dried for 2 minutes at 130°C in

a drying cabinet operated with warm air; the thickness of the dry layer of the copolymer film on the surface of the polyester film is 7 μ . The coated polyester film is bathed for 1 minute in a 0.6 percent aqueous hydrazine hydrate solution containing 1.2 percent of NaOH and then rinsed under running water.

- One half of the coated polyester film is placed for 1 minute into a metallization liquid of the composition described in Example 1. After treatment, a continuous, about 0.2 μ thick, nickel coating has formed on the surface of the film of the copolymer.
- The other half of the polyester supporting film coating with a polymer is placed for 5 minutes into a metallization liquid according to Example 2. After the indicated time of action, a 0.2 μ thick copper coating has formed on the surface of the film of the polyacrylic ester copolymer.

The metal coatings produced are firmly adherent to the plastic film surfaces.

The shaped body is suitable for use as an electrical resistance element.

EXAMPLE 8

A 10 percent solution of polyvinyl acetate (e.g. Mowilith 50 of Farbwerke Hoechst AG, Frankfurt, Germany) in acetone is prepared, which contains 0.04 percent of palladium chloride, calculated on the solution weight, or 0.4 percent of palladium chloride, calculated on the polymer component weight, and applied to the surface of a supporting film of cellulose acetate. The supporting film coated with the liquid, is placed for 2 minutes into a drying cabinet operated with warm air of 130°C. After heat treatment, the thickness of the polymer film on the supporting film is 10 μ .

The coated supporting film is divided into two parts of equal size:

- One part of the coated film is placed for 1 minute into a metallization liquid according to the procedure of Example 1. A continuous 0.2 μ thick nickel coating is formed on the surface of the polyvinyl acetate film.
- The other half of the coated film is bathed in a 0.5 per cent aqueous stannous chloride solution and then rinsed under running water. The thus treated film is then placed for 5 minutes into a metallization liquid according to the procedure of Example 2. A 0.2 μ thick continuous copper coating is formed on the surface of the polyvinyl acetate film.

In both cases, the metal coatings are firmly adherent to the plastic film surfaces.

EXAMPLE 9

A 10 percent by weight solution of cellulose acetate in acetone is prepared which contains 0.04 percent of palladium chloride, calculated on the solution weight. For the preparation of this acetone solution of cellulose acetate and palladium chloride, 0.2 g of palladium chloride are dissolved in 1 ml of concentrated hydrochloric acid at 70°C. After cooling this solution to room temperature, 15 ml of acetone are carefully added with continuous stirring. With further stirring, the solution prepared is heated to 40° to 50°C, whereby the total quantity of palladium chloride is dissolved. This acetic palladium chloride solution is added to the ace-

11

tonic cellulose acetate solution.

The cellulose acetate has a fatty acid content of 72 percent, a K value of 70 (e.g. Cello 700 of Farbenfabriken Bayer, Leverkusen, Germany, may be used). This solution is spread on the surface of a cellulose acetate supporting film to produce a layer. The coated cellulose acetate film is dried for 2 minutes at 130°C. The thickness of the film on the supporting film is 2 μ . The coated film is bathed for 1 minute in a 0.6 percent aqueous hydrazine solution and then rinsed for 1 minute in running water.

The pretreated coated film is then placed for 2 minutes into a metallization liquid according to Example 2. After the time of action, an about 0.2 μ thick continuous copper coating has formed on the surface of the applied cellulose acetate film.

The metal coating is firmly adherent to its support.

EXAMPLE 10

A 10 percent by weight acetic solution of a copolymer based on polyvinyl chloride/acrylonitrile/itaconic acid, e.g. F 220 of Messrs. Dow Chemical Company, Midland, U. S. A., having a content of 0.04 percent of palladium chloride, calculated on the solution weight, or of 0.4 percent of palladium chloride, calculated on the copolymer component weight. The addition of the palladium chloride is always performed in the manner described in Example 8. This solution is spread in the form of a liquid layer on the surface of a polyester film (e.g. Hostaphan, registered trade mark of Farbwerke Hoechst AG, Frankfurt, Germany). The coated Hostaphan film is dried for 2 minutes at 140°C by placing it into a drying cabinet operated with warm air. After drying, the applied copolymer film has a layer thickness of 10 μ . The film sample is divided into two pieces of equal size.

One half of the film is placed for 1 minute into a metallization liquid according to the procedure of Ex-

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ample 1. After the time of action, an about 0.2 μ thick coating of nickel has formed on the surface of the copolymer film. The coating is firmly adherent to its contact surface.

The second half of the film sample is bathed for 1 minute in 0.6 per cent aqueous hydrazine hydrate solution. The coated film is then rinse for 1 minute in running water. The film is then placed for 5 minutes into a metallization liquid according to the procedure of Example 2. After the time of action of the metallization bath, an about 0.2 μ thick continuous copper coating has formed on the surface of the copolymer film on the supporting film. The coating is firmly adherent to its contact surface.

Shaped bodies produced in accordance with the invention may be used as electrical resistance elements provided the metallized film has a substrate of non-electroconductive material.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A self-supporting film of polytetrafluoroethylene having a noble metal salt dispersed therein and a metal coating selected from the group consisting of copper and nickel on the surface of said film.

2. A self-supporting film according to claim 1 in which the noble metal salt is selected from the group consisting of palladium chloride, platinum chloride or silver nitrate.

3. A self-supporting film according to claim 1 in which the weight ratio of polytetrafluoroethylene to noble metal salt disposed therein is in the range of about 5 : 1 to 25 : 1.

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