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PROCESS OF METALLIZING POLYMERIC MATERIALS

Filed Jan. 27, 1972 2 Sheets-Sheet 1

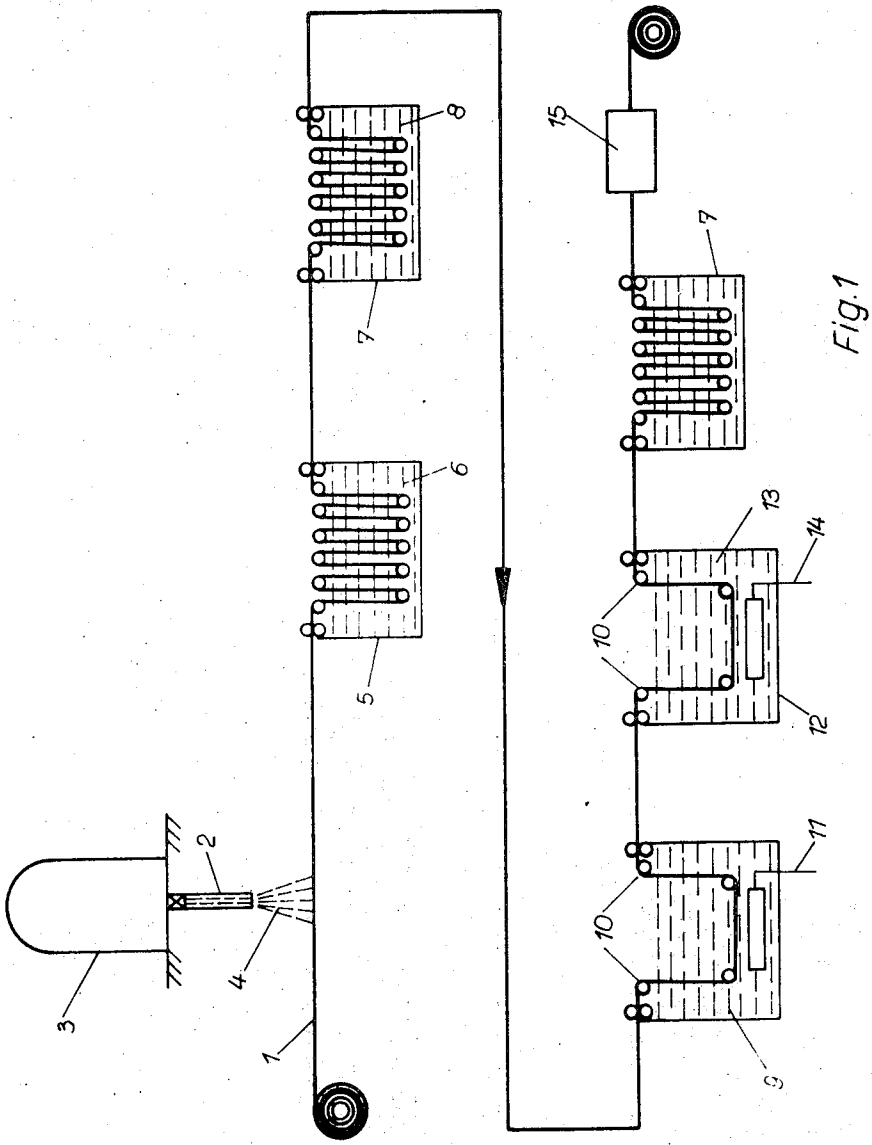


Fig. 1

PROCESS OF METALLIZING POLYMERIC MATERIALS

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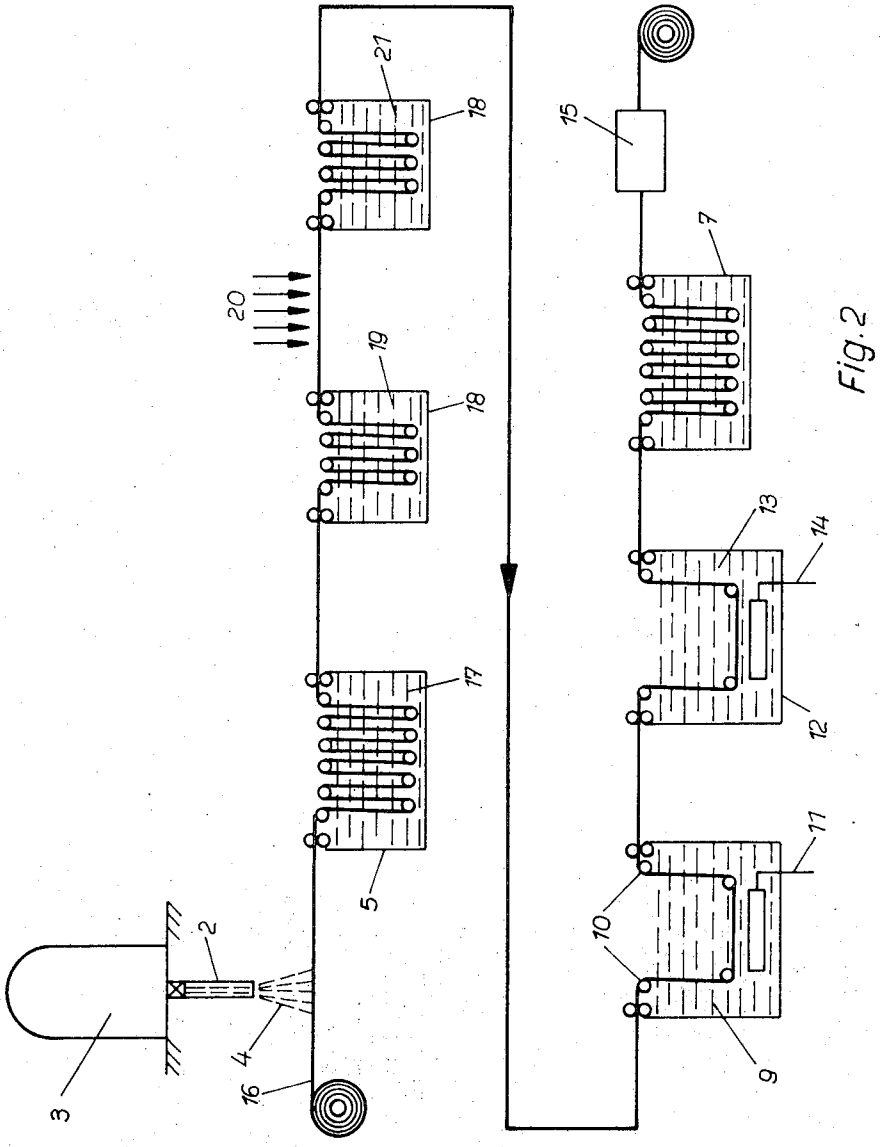


Fig. 2

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PROCESS OF METALLIZING POLYMERIC MATERIALS

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ABSTRACT OF THE DISCLOSURE

The surface of organic or inorganic polymeric substrates, particularly textile materials, is metallized by applying a firmly adhering surface coating to the polymeric substrate, for instance by a graft process, and then making the surface coating thus applied conductive, and finally superimposing a metallic or non-metallic coating or reinforcement by a galvanic process on the said surface.

BACKGROUND OF THE INVENTION

The present invention relates to a process for metallizing the surface of organic and inorganic polymers, particularly of textile materials made of such polymers.

The surface of organic and inorganic materials can be modified, according to the prior art, by vapor application of metals in a vacuum. The shortcoming of this process is that the vapor-applied metal coating has only insufficient mechanical resistance, particularly against abrasion and sharp bending.

Methods are also known to metallize copolymers which consist of at least two phases. One of the two phases in this case has a cotton plug structure of colloidal dimensions. This phase does dissolve more rapidly in an etching agent than the other phase or phases. Thus, a firmly adhering surface is formed. Simultaneously with the etching step or thereafter, noble metal nuclei are formed on the surface of the synthetic material. These nuclei permit causing a chemical deposition, for instance of copper or nickel. Thus, the surface of the material is made conductive. The metal surface can be then be reinforced galvanically, particularly by a copper deposit. Subsequently, any desired galvanically applicable substances may be deposited on the surface.

The disadvantage of this process is that the synthetic material must always consist of at least two phases.

In another process it has been proposed to apply a coating of a conductive lacquer to the surface of a synthetic material. On the lacquer metals can then be deposited galvanically. The shortcoming of this process is that the coating thus formed has little abrasion-resistance. The process for this reason finds little use.

The object of the present invention is to provide a process for metallizing the surface of organic and inorganic polymeric materials, particularly textile materials, which avoids the shortcomings of the prior-art processes and enlarges the range of metallizable organic and inorganic polymers.

SUMMARY OF THE INVENTION

The invention resides in a process wherein a firmly adhering surface coating is applied to the polymer, for instance by a graft process, whereupon the thus formed surface coating is made conductive, followed by superimposing a metallic or non-metallic coating or reinforcement by galvanic process on the conductive surface.

The novel features which are considered as characteristic of the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its mode of operation, together with additional objects and advantages thereof, will be best

understood from the following description of specific embodiments when read in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 2 are schematic illustrations of two different embodiments of the present invention.

DETAILED DECRIPTION OF THE INVENTION AND SPECIFIC EMBODIMENTS

The initial surface coating may be formed on the substrate by polymerization or cross-linking or a combination of both steps of monomeric or polymeric substances. Preferably the polymerization and/or cross-linking are initiated by radiation. There is thus obtained a firmly adhering surface film which is chemically attached to the polymeric material. This film can then be made conductive, for instance, by an exchange of acidic hydrogen with cations.

However, it is also possible to form the initial coating by a graft process in which a salt of an unsaturated acid, for instance sodium acrylate, is grafted upon the polymer. Preferably, this step is again initiated by radiation. If the degree of grafting is not sufficient, that is, if only a small electric conductivity is obtained, it is possible to add a conductive electrolyte, for instance during the grafting process, in order to increase the electric conductivity. The surface coating then becomes grafted with preferably hydrophilic substances, and thus becomes swellable.

The thus treated polymeric material is then employed as the electrode for a galvanic step.

A firmly adhering metallic coating can also be obtained by grafting noble metal salts of unsaturated acids, for instance silver salts and preferably silver acrylate, onto the polymer. The grafting should again, preferably, be initiated by radiation. The noble metal salt, for instance silver salt, may also be formed by an exchange reaction with acid hydrogen of a grafted unsaturated compound such as acrylic acid, whereupon the thus treated organic or inorganic polymer may be subjected to radiation, for instance exposure to light. The thus formed noble metal nuclei, particularly silver nuclei, then form the nuclei for the chemical metal deposition of, for instance, copper or nickel. The thus formed surface film may finally be reinforced galvanically.

The following examples will further illustrate the invention. Reference is made in these examples to the attached drawings.

EXAMPLE 1

With reference to FIG. 1, it will be seen that a smooth-warp-knitted polyamide ("nylon 6") textile **1** was subjected to radiation by electron rays **4** under the scanner **2** of an electron accelerator **3** until a dose of 3.10^6 rad. had been obtained. The textile was then moved through a grafting vessel **6** containing a 20%-conc. sodium acrylate solution at a temperature of 50° C. remained in the vessel for 10 minutes until a graft copolymer had formed resulting in a mass increase by 20%. The material was then passed to a washing device **7** where, by means of a washing agent **8**, the unreacted monomer of the sodium acrylate solution **6** was washed out of the polyamide textile. The textile material, following the washing step, was then passed across a roller **10** into the galvanizing bath **9**, the roller serving as the cathode. In this step a coating of dull copper was deposited galvanically on the textile. The deposited copper was supplied, in conventional manner,

through a copper anode **11**. The bath had the following composition:

226.5 g. $CuSO_4 \cdot 5H_2O$ per liter of electrolyte
65.8 g. H_2SO_4 per liter of electrolyte
current density: 1 a./dm.^{2} of surface
temperature: 20° C.
current yield: 97%
exposure time: 15 min.

The textile then passed into the galvanizing bath **12**, where the copper deposit served as the base for a subsequent chromium deposit from the solution **13**. The anode **14** was a lead anode. The composition and conditions of the bath in this case were as follows:

250 g. chromic acid per liter of electrolyte
25 g. sulfuric acid per liter of electrolyte
current density: 10–20 a./dm.^{2} of surface
temperature: 40–45° C.
current yield: 100%
exposure time: 5 min. 1μ of coating

The textile was finally washed in the washing device **7***a* and dried in the drier **15**, followed by collection of the material on a roller.

EXAMPLE 2

With reference to FIG. 2, it will be seen that a polyester fiber textile **16** (polyethylene glycolterephthalate) was subjected to radiation with electron rays **4** on the scanner **2** of an electron accelerator **3** until a dose of 10^7 rad. was obtained. The textile was subsequently passed through the grafting vessel **5** where a 20%-conc. acrylic acid solution **17** was applied at 100° C. for a time of 30 min. after which a graft copolymer had formed causing the mass to become increased by 10%.

In the reaction vessel **18** a silver nitrate solution **19** was then applied. The solution had an $AgNO_3$ concentration of 1 to 5%. The time of treatment was 10 min., the temperature was 20–40° C.

The textile was thereafter exposed to light at 20, which caused silver nuclei to form. There was thus formed a silver polyacrylate on the polyacrylic acid chains of the graft polymer.

In the reaction vessel **18***a* a dull copper coat was then deposited on the silver nuclei from a formaldehyde-copper salt solution **21**. The thus obtained conductivity made it possible to reinforce the copper coating in a galvanic bath **9** of the same composition and conditions as in Example 1. In a subsequent galvanic bath **12** a chromium deposit was formed from the solution **24** on the copper coating in the same manner as in Example 1. The anode **14** again consisted of lead. The textile was then finally washed in the washing machine **7***b*, and thereafter dried in drier **15** and collected on a roller.

EXAMPLE 3

A low pressure polyethylene foil was subjected to radiation with electron rays under a scanner of an electron accelerator similar to the arrangement of FIG. 1. The material was passed through a graft vessel, wherein it was treated for 120 min. at a temperature of 100° C. with a 20%-conc. sodium acrylate solution. There was thus formed a graft copolymer causing a mass increase by 28%. Thereafter, non-reacted monomers of the sodium acrylate solution were washed out in a washing machine. Subsequently, the polyethylene foil was passed into an electrophoresis bath at 20° C. The bath contained a lacquer in the form of a plastic resin lacquer dispersion.

Between the roller used in this bath, which was similar to the roller **10** employed in FIG. 1, and the outer container of the vessel a current was applied. The polyethylene foil was thus provided with a lacquer coat and was subsequently passed through a drier and rolled up on a spool.

EXAMPLE 4

This process was similar to the process illustrated in Example 2.

A high pressure polyethylene foil of a thickness of 1.5 mm. was passed under a scanner of an electron accelerator. By means of a stencil or face plate placed on the foil, a specific area was exposed to radiation. The radiation was effected until a dose of 2.10^7 rad. was obtained. The foil was subsequently passed through a graft vessel which contained a 20%-conc. acrylic acid. It was treated in this vessel until an increase of the mass by 32% had been obtained.

In a subsequent reaction vessel a silver nitrate solution was applied to the textile, which caused a silver salt to form on the grafted acrylic acid surface of the polyethylene foil. The foil was then exposed to light, which caused formation of silver nuclei on the foil. In a subsequent reaction vessel, a high gloss copper coat was deposited on the silver nuclei from a formaldehyde-copper sulfate solution. The copper thus formed the conductive outer coating. The conductivity of the surface thus permitted reinforcement of the copper coating in a subsequent galvanic bath. The electrolyte in this case was a so-called high gloss copper electrolyte GTL–"Cu 70" (made by VEB Galvanotechnik of Leipzig, Germany). The conditions of the treatment were:

current density: 4 a./dm.^{2} of surface
temperature: 20° C.
exposure time: 45 min. 40μ m.

It will be understood that the metal coating in this case was formed at the places only which were exposed to the electron radiation.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, readily adapt it was various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be protected by Letters Patent is set forth in the appended claims:

1. Method of metallizing the surface of an organic polymeric substrate which comprises exposing an organic polymeric substrate to high-energy ionizing radiation, thereafter immersing the irradiated substrate in a solution of an electrically conductive metal salt of acrylic acid, thereby producing a grafting of the said metal salt of acrylic acid onto the polymeric substrate and forming a firmly adhering surface coating of the grafted metal salt of acrylic acid on the polymeric substrate, thereafter immersing the organic polymeric substrate upon which a surface coating of the electrically conductive metal salt of acrylic acid has thus been formed in a metal electroplating bath and passing an electric current between an anode in the bath and the electrically conductive surface of the organic polymeric substrate as cathode, and thereafter plating out metal from the bath onto the surface of the polymeric substrate.

2. A process as defined in claim **1** in which the electrically conductive metal salt of acrylic acid is sodium acrylate.

3. A process as defined in claim **1** in which the metal electroplating bath is a copper electroplating bath.

4. A process as defined in claim **1** in which the metal electroplating bath is a copper electroplating bath and the organic polymeric substrate on which a copper layer has thus been plated is thereafter immersed in an electroplating bath of another metal and an electric current is passed between an anode in the bath and the copper surface of the organic polymer substrate as cathode, thereby superimposing a coating of the other metal thereupon.

5. A process as defined in claim 4 in which the electroplating bath of another metal is a chromium electroplating bath.

6. The process of claim 1, wherein the substrate is a textile material.

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