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㊹ **Coating of polymeric substrates.**

(57) A surface layer of a polymeric material, for instance an epoxy or other polymeric printing substrate, is prepared to receive a metal or other adherent coating by penetrating the surface layer with a first reactant and then with a second reactant that reacts in the surface layer to form pits that extend from the surface into the surface layer. The first reactant may comprise a pyrrole and the second reactant may comprise chromic acid.

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COATING OF POLYMERIC SUBSTRATES

There are many instances where it is desirable to apply a protective layer over a substrate formed of a polymeric material. If the protective layer tends to be incompatible with the substrate it is common practice to apply an organic liquid to the surface of the substrate, before the protective layer, so as to dissolve or swell the substrate with the intention of improving adhesion of the protective layer to it. The dissolution or swelling that occurs is on a gross scale and is generally visible to the naked eye.

Whilst this gives very satisfactory results with many combinations of substrate and protective layer it is unsatisfactory with some, especially when the protective layer is very incompatible with the substrate and exhibits a marked tendency to blister or peel from the substrate. Thus with such combinations it appears that the organic liquid or the residues of swollen or dissolved polymer between the protective layer and the remainder of the substrate provide a region of weakness between the main part of the substrate and the protective layer.

It is also known to chemically etch surfaces of polymeric substrates so as to improve the adhesion of subsequently applied protective layers. However it is very difficult to obtain the right amount of chemical etching, in that with many polymeric compositions either the degree of etching is so small as to make no difference to adhesion or is so high that a weak layer of degradation products is formed between the polymeric substrate and the subsequently applied protective layer. If chemical etching is conducted on a surface that has previously been swollen or swelled on a macro scale then generally the etching will result in the formation of such a thick layer of degradation products that the adhesion between the subsequently applied protective layer and the substrate will be very poor.

The need to secure intimate adhesion between the protective layer and the substrate is particularly serious when the protective layer is a layer of metal or other hard wearing material and is being applied over an engraved gravure or other intaglio printing surface. It is often desirable for such printing surfaces to carry such a protective layer but it is essential that the layer should conform accurately and bond firmly to the polymeric surface and it is also very important that it should not blister away from the surface during use.

In the invention a surface layer of polymeric material is prepared to receive an adherent coating by a process comprising penetrating the surface layer only with a first reactant and then with a second reactant and causing or allowing the second reactant to react with the first reactant within the surface layer to form pits that extend from the surface into the surface layer substantially without chemical degradation of the polymeric material between the pits.

Since the first and second reactants react to form pits that extend to the surface it is possible in the invention to avoid the disadvantage of trapping within the surface layer substantial quantities of a swelling or softening agent. Since the reaction occurs primarily with the first reactant, with the polymeric material between reaction sites being left substantially undegraded, it is possible in the invention to avoid the formation of a surface layer contaminated with large amounts of degraded polymeric material.

The first reactant preferably comprises an organic solvent and penetrates the surface layer during the process substantially without swelling or causing other visible change in the surface appearance when viewed under a magnification of up to 100. Thus preferably the organic solvent does not dissolve or swell the structure of the polymeric material but instead merely penetrates the surface layer while causing substantially no visible change in the surface appearance. Thus it is generally desirable to avoid the use of solvents that one would normally consider to be satisfactory for swelling or softening the polymeric material. For instance when the polymeric material is an epoxy it would normally be expected that solvents such as tetrahydrofuran, dioxan, aliphatic ketones and acetates would be useful for swelling the surface, but in fact it is desirable to avoid such solvents in the method of the invention. If the organic solvent being used has too powerful an effect, and thus either swells the surface or penetrates deeper than is desired, it is possible to moderate this by inclusion in the reactant of an inert cosolvent or by emulsifying it in water or other inert liquid, or by both emulsification and the use of a cosolvent. This is described in more detail below.

The desired depth of the surface layer will depend partly upon the nature of the adherent coating. Generally it is not more than 5 microns and for many purposes is less than 1 micron. However it should normally be at least 0.05 microns in thickness, preferably 0.1 to 0.5 microns. The first reactant preferably penetrates the surface to the depth desired for the surface layer.

The organic solvent in the first reactant will be chosen having regard to the nature of the polymeric material and having regard to the second reactant that is to be used. When, as is preferred, the second reactant is an oxidising agent it is desirable to use as the first reactant an organic liquid that will react with such oxidising agent with a redox reaction that forms gaseous products. Suitable reactants include heterocyclic compounds and in particular derivatives of pyridine or pyrrole. Preferred reactants are keto derivatives of pyrrole, including keto derivatives of partially or fully saturated pyrroles, that is to say pyrrolidones and pyrrolinones. Preferred reactants comprise N-methyl-3-pyrrolin-2-one and N-methyl-2-pyrrolidone. Very satisfactory results can be obtained using Russian White turpentine.

Some solvents used as part or all of the first reactant may have a swelling or dissolving effect on the polymeric material that is too powerful or may attack apparatus in which the process is to be conducted or may have an unpleasant odour. For instance when using the preferred solvents identified above they can give handling difficulties due to their odour and the risk of them attacking the apparatus. It is therefore desirable to use the solvent diluted with an organic diluent or emulsified in water or both. Any inert compatible organic diluent can be used but alkyl ethers of diethylene glycol or ethylene glycol are preferred, especially the mono-n-butyl ether of ethylene glycol.

The proportion of the chosen heterocyclic liquid to any other organic liquid is generally from 0.5:1 to 5:1, most usually about 1:1 to 3:1 (parts by volume). Preferably the organic liquid or liquids are used in the form of an emulsion in water. The concentration of organic liquid or liquids emulsified in water may be, for instance, from 40 to 70% and the emulsion may be stabilised by an appropriate emulsifying agent, such as ethoxylated castor oil.

After application of the first reactant at a temperature and for a duration such that the desired depth of penetration is achieved, excess of the first reactant is generally then removed, for instance by rinsing, and the second reactant may then be applied.

The second reactant generally comprises a chemical etchant for the polymeric material and thus is capable, when used under appropriate conditions (e.g. temperature and duration), of etching and degrading the polymeric material even in the absence of first reactant. Preferably it is applied under conditions such that if it were used alone it would cause substantially no visible change in the surface appearance when viewed under a magnification of up to 100. However under the actual conditions of use as a result of the presence of the first reactant within the surface layer the etchant reacts preferentially with that reactant, and possibly also with the polymeric material in localised positions containing first reactant, to form pits in the surface layer while leaving the polymeric material between the pits substantially unreacted and undegraded. The etchant is preferably one that reacts relatively violently with the first reactant when contacted in bulk. It may be an oxidising agent that will react with the first reactant with a redox reaction that forms gaseous products. The oxidising agent or other etchant is usually an oxidising acid or mixture of acids and may be based on, for instance, nitric acid, sulphuric acid, phosphoric acid or chromic acid. Preferably however it comprises chromic acid both because of the desirable reactions that occur between chromic acid and the preferred first reactants and because of the strong penetrating properties of chromic acid. The chromic acid is preferably introduced as an aqueous solution of from 200 to 600 g/l generally 350 to 500 g/l. The second reactant is normally an aqueous solution. It may include surfactant.

The penetration of the surface layer with the first reactant is achieved by applying the first reactant by immersion, spray, brush or any other convenient technique for an appropriate duration and temperature.

The temperature is generally from ambient to 80°C. Generally excess first reactant is applied to the surface and is left in contact with the surface for from 0.5 to 10 minutes and excess solvent is then removed and the surface rinsed with hot water. Alternatively contact may be achieved by submerging the surface for a shorter period, e.g. up to 1 minute, in the first reactant. After removal of the excess solvent the surface may feel substantially dry to the touch.

Penetration of the second reactant into the surface layer followed by reaction of the reactants may be achieved by application of the second reactant by any convenient application technique, such as those discussed above, and maintaining the reactant in contact with the surface for from 2 to 20 minutes at from 40 to 80°C although shorter times are satisfactory if contact is by prolonged submersion, e.g. for up to 2 minutes. The surface may then be rinsed with water and dried.

The adherent coating may be a metal coating, for instance of copper, nickel or chromium, and is preferably applied in an electroless manner. Thus plating may be conducted by depositing a colloidal palladium based solution, preferably after altering the charge on the surface by subjecting it to a cationic surfactant solution, followed by electroless deposition of copper, nickel, or chromium in conventional manner. Suitable plating methods are described in British Patent Specification No. 1,524,717.

The process of the invention is preferably carried out on a gravure printing surface that has been engraved to form the desired gravure cells, which may be discrete cells or, when the surface is a cylinder, may be a continuous spiral and may be at least 15 microns deep. This engraving is preferably carried out using an electron, ion or laser beam. Accordingly the polymeric material is preferably of a composition that, when struck by an electron, ion or laser beam in an area, is converted to volatile products and volatilises throughout the entire area while remaining as a rigid solid in the zone adjacent the area where it volatilises, as described in our British Patent Specification No. 2034636. Preferably it is of an epoxy material that is substantially unfilled, preferably having a total filler content of below 20% by weight. Preferably the epoxy or other polymeric material includes carbon black and will generally have been mechanically polished, for example by diamond turning, before engraving so as to give it non-print characteristics before being engraved, i.e. between the engraved cells. Other polymeric materials that may be prepared in accordance with the invention for subsequent coating with metal or other coatings include, for instance, polypropylene. The first reactant for this may consist solely of one of the specified pyrrole derivatives and then the second reactant may be chromic acid or a chromic acid-sulphuric acid mixture.

The invention includes not only the described processes but also the novel solvent compositions, and in particular aquoeus emulsions of a mixture of a pyrrole derivative with cosolvent, as described above.

The following are examples of the invention.

Example 1

A cylindrical substrate is coated with an epoxy resin composition containing about 5% to 6% carbon and 1% molybdenum sulphide but free of substantially all other fillers by a powder coating technique followed by fusion of the surface. It is then diamond turned until it is smooth (even when viewed under 100 magnification) and then laser engraved to form the desired gravure cells.

A mixture is formed of one part by volume n-butyl ether of ethylene glycol (n-butyl Cellosolve, Cellosolve being a trade mark) and 2 parts by volume N-methyl-3-

pyrrolin-2-one and this mixture is emulsified in water to form a 60% emulsion of the solvent mixture in water. 10% by weight of ethoxylated castor oil is included in the water as an emulsifying agent.

Excess of this emulsion is then applied to the engraved epoxy resin surface layer and contact is maintained between the emulsion and the surface for from 2 to 6 minutes. The temperature of the surface throughout this time is between 30 and 60°C. The appearance of the surface is unchanged by this treatment.

The surface is then water rinsed and then has applied to it aqueous chromic acid having a concentration of 400 to 480 g/l and containing 5% to 10% by volume surfactant, for 5 to 10 minutes at 55 to 70°C. The surface is then given a hot water rinse at about 65°C. The surface is highly pitted (as viewed under a magnification of 100), with the pits extending less than 0.5 microns deep.

The surface is then contacted for from 5 to 10 minutes at 40 to 60°C with a solution of stannous chloride and 30% hydrochloric acid, in order to neutralise the surface. It is then rinsed and charged transfer is effected by immersing the surface for 2 minutes at 30°C in a 3% by volume aqueous solution of a cationic surfactant.

The surface is then rinsed in water again and is conditioned by contact with a 10% by volume solution of colloidal palladium in hydrochloric acid at 25 to 30°C for from 3 to 5 minutes followed by rinsing and reduction of the colloidal palladium by treatment with a 10% by volume solution of hydrochloric acid containing a small amount of stannous chloride for 3 minutes at 40 to 50°C.

The surface is then again rinsed with water and is then subjected to electroless nickel deposition using an autocatalytic proprietory solution that deposits on the cylinder at 80 to 90°C at a rate of approximately 12 to 14 microns per hour.

Example 2

The process of Example 1 is repeated except that the N-methyl-3-pyrrolin-2-one is replaced by an equal volume of N-methyl-2-pyrrolidone. Similar results are achieved.

Example 3

The process of Example 1 is repeated except that the N-methyl-3-pyrrolin-2-one is replaced with an equal volume of Russian White terpentine.

Example 4

A flat substrate formed of the same epoxy composition as in example 1 is immersed in the same solvent composition for 1 minute at 42°C, while another piece is immersed in the chromic acid solution at 68°C for 30 seconds. Both pieces are washed and dried and examined under 100 magnification. Neither treatment results in any noticeable change in the surface appearance.

The piece that has been solvent treated is then immersed in the same chromic acid solution at 68°C for 30 seconds and then rinsed. When viewed under 100 magnification the surface appears highly pitted. The pits extend to a depth of less than 1 micron. The pitted surface can then be neutralised and plated as described in Example 1.

CLAIMS

1. A process in which a surface layer of a polymeric material is prepared to receive an adherent coating by application of a reactant, characterised in that the process comprises penetrating the surface layer only with a first reactant and then with a second reactant and causing or allowing the second reactant to react with the first reactant within the surface layer to form pits that extend from the surface into the surface layer substantially without chemical degradation of the polymeric material between the pits.

2. A process according to claim 1 characterised in that the first reactant comprises an organic solvent and penetrates the surface layer substanitally without swelling or causing other visible changes in the surface appearance when viewed under a magnification of up to 100.

3. A process according to claim 2 characterised in that the first reactant comprises a keto derivative of a pyrrole that may be partially or fully saturated.

4. A process according to claim 3 characterised in that the first reactant comprises N-methyl-2-pyrrolidone or N-methyl-3-pyrrolin-2-one.

5. A process according to claim 3 characterised in that the first reactant comprises Russian White turpentine.

6. A process according to any preceding claim characterised in that the second reactant comprises a chemical etchant that is applied at a temperature and duration such that, if used without the first reactant,

it causes substantially no visible change in the surface appearance when viewed under a magnification of up to 100.

7. A process according to any preceding claim characterised in that the second reactant comprises an oxidising agent that reacts with the first solvent with a redox reaction to form gaseous products.

8. A process according to any preceding claim characterised in that the second reactant comprises chromic acid.

9. A process according to any preceding claim characterised in that the surface layer is less than 5 microns thick.

10. A process according to claim 9 characterised in that the surface layer is from 0.05 to 0.5 microns thick.

11. A process according to any preceding claim characterised in that the penetration of the first reactant is controlled by providing it in the form of a solution in an inert cosolvent or in an emulsion in water or both.

12. A process according to claim 11 characterised in that the first reactant is provided as a 40 to 70% by volume emulsion in water of a mixture of 0.5 to 5 parts by volume of a keto derivative of a pyrrole that may be partially or fully saturated or Russian White turpentine with one part by volume inert cosolvent.

13. A process according to claim 11 or claim 12 characterised in that the cosolvent is an alkyl ether of ethylene glycol or of diethylene glycol.

14. A process according to any preceding claim characterised in that the polymeric material is an epoxy resin containing less than 20% filler.

15. A process according to any preceding claim characterised in that the surface layer is the surface layer of a printing member that is engraved with gravure cells and that has substantially non-print characteristics between the cells.

16. A process according to any preceding claim characterised in that an adherent coating of metal is subsequently applied to the pitted surface by electroless metal deposition.

17. A composition suitable for use in the process of claim 12 and comprising a reactant that is a keto derivative of a pyrrole that may be partially or fully saturated or is Russian White turpentine characterised in that the reactant is provided as a 40 to 70% by volume emulsion in water of a mixture of 0.5 to 5 parts by volume of the reactant with one part by volume of an inert cosolvent.

18. A composition according to claim 17 characterised in that the cosolvent is an alkyl ether of ethylene glycol or of diethylene glycol.