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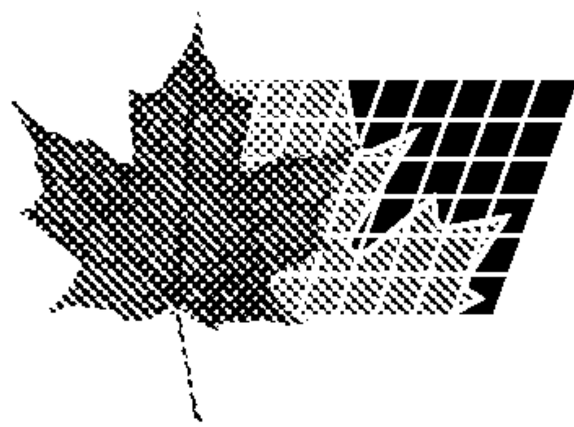

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(72) Mahlkow, Hartmut, DE
(72) Bressel, Burkhard, DE
(73) ATOTECH DEUTSCHLAND GMBH, DE

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(54) **METALLISATION DE MATERIAUX NON CONDUCTEURS**
(54) **METALLIZATION OF NON-CONDUCTORS**

(57) The invention provides a process for enabling direct metallization of nonconductors. Strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution (optionally containing a solubilizer) of initially-nonconductive oligomers, monomer/oligomer mixtures, or monomers or mixtures of monomers of five-membered heterocycles, by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a solution containing permanganates. The electrical conductance of the polymeric products is sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

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ABSTRACT

The invention provides a process for enabling direct metallization of nonconductors. Strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution (optionally containing a solubilizer) of initially-nonconductive oligomers, monomer/oligomer mixtures, or monomers or mixtures of monomers of five-membered heterocycles, by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a solution containing permanganates. The electrical conductance of the polymeric products is sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

The invention concerns a process for the direct metallization of nonconductors. In this process, strongly-adherent, insoluble polymerized products are deposited on the surface of nonconductors from an aqueous solution of initially-nonconductive oligomers, monomers, or various monomer or oligomer-monomer mixtures of five-membered heterocycles through contact with a non-rinsable insoluble coating containing an oxidant which has been adsorbed on the nonconductors, whereby these polymerized products then have
10 sufficient electrical conductance to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

Electrically-conductive heterocyclic polymers as coatings for nonconductors as such are already known (e.g. DE patents 35 20 980, published December 18, 1986, DE 31 32 218, published March 3, 1983 and DE 35 35 709, published April 9, 1987; also, E.P.O. patent 206,133, published December 30, 1986). They describe a process in which polypyrrol can be deposited on nonconductors by means of monomeric pyrrol and a
20 strong oxidant. The utilization of this conductive nonconductor is the basis for other applications.

Another patent (DE 38 06 884, published September 21, 1989) describes the utilization of polymers with intrinsic electrical conductance, formed from the monomer and a strong oxidant, for establishment of through-connections on printed circuit boards.

The above noted patents E.P.O. 206,133 and DE 38 06 884 depend on the use of strong acids and strong oxidants. They

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require a high degree of technical expertise because the working tolerances necessary to achieve the desired result are very narrow.

It is known that use of these heterocycles leads to undesirable side effects; for instance, pyrrol tends to polymerize easily in the presence of light or acids. The acids facilitate rapid formation of polypyrrol from the monomer; this precipitates as a black, insoluble, amorphous deposition that is not amenable to further processing.

10 The present invention provides a process by which soluble, nonconductive derivatives of the group of five-membered heterocycles are converted to electrically-conductive polymers in the presence of mild oxidants in just one processing step and with use of just one solution.

More particularly, the invention provides a process for enabling direct metallization of nonconductors, in which strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution (optionally containing a 20 solubilizer) of initially-nonconductive oligomers (or monomer/oligomer mixtures; or monomers and monomer mixtures) of five-membered heterocycles by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a solution containing permanganates. The electrical conductance of the polymeric products is then sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

Preferably: the formation of soluble oligomers of the group of heterocycles is effected from a solution of the monomer(s) and a weak acid, optionally at low temperatures down to the freezing point of the solutions; pyrrole or substituted derivatives thereof may be used; the concentration of the oligomers, monomers, or mixtures thereof is 0.1 to 200 grams per litre; acids or acidic salts whose dissociation constants in aqueous solution, relative to protons, lie between 0.1 and 0.01, are used; acidic galvanic
10 copper baths are used; and an organic solvent of pronounced polar quality is used as dissolving intermediaries.

The process can be used for the metallization of nonconductive borehole walls in circuit boards. In that case the galvanic metallization is accomplished after preparation of the circuit boards, e.g., by photoprinting, which follows formation of the conductive polymer films; and immediately prior to the galvanic metallization, the conductive polymer film is treated with a solution that contains the acid and/or oxidant.

20 The process may be used in immersion or spraying processes, or in horizontal, continuous passage systems.

According to the invention, the process can be preceded by pretreatment of a printed circuit board. A coating of an oxidant such as pyrolusite (manganese dioxide) is applied to the printed circuit board, which is made of an insulating material. This is accomplished, for instance, by immersing the printed circuit board in a potassium permanganate solution, whereby the printed circuit board material reacts

with the permanganate on the surface of the circuit board. Manganese (VII) is reduced to manganese (IV). The reaction product becomes embedded in the pores of the nonconductive areas of the printed circuit board's surface, or is adsorbed by the surface of the printed circuit board. The degree of oxidation of the manganese, +(IV), ensures that all of the nonconductive areas of the printed circuit board, especially the walls of the borehole, are coated with the mild pyrolusite oxidant. This adsorbed manganese dioxide is not
10 removed in the cleaning process and so constitutes an effective oxidant for the process.

A printed circuit board that is pretreated in this manner then undergoes the process according to the invention.

Through contact with an aqueous, acidic solution (possibly containing a solubilizer) of initially nonconductive oligomers, monomers, or various monomer or monomer-oligomer mixtures of five-membered heterocycles, a printed circuit board, pretreated in said manner, is coated with an electrically-conductive film containing the firmly
20 adherent, insoluble, polymerized product.

The inventive process offers several advantages over the other processes mentioned above.

The conductive polymer film is formed in one procedural step with use of just one solution. This means that one processing stage is eliminated, which reduces the cost of the process (lower investment costs in the metallization plant; smaller expenditures for process control, disposal of used solutions, and storage).

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Moreover, the polymerization reaction takes place immediately after the first contact of the solution of heterocycles with the substrate surface, which permits strict control of the reaction process. One consequence is that the heterocyclic compound need not be carried into subsequent processing solutions in order to be polymerized in later stages of the reaction. In these later stages therefore, use of the inventive process minimizes undesirable formation of sludge from surplus monomer solutions which do not react on
10 the substrate surface. In addition, this process avoids unnecessary use of chemicals and the consequent need to dispose of surplus used chemicals.

In the inventive process, wetting the substrate surface with the solution of heterocycles is not a critical step, as it is with other procedures described in the literature. If a surface film is first applied to the substrate surface, and this film is converted into a conductive polymer by an oxidation reaction in an additional procedural step, then the processing conditions (viscosity of the monomeric solution,
20 roughness of the substrate surface, coating time between the monomer wetting and oxidation steps, etc.) must be determined and adjusted very precisely in order to attain a conductive film with suitable characteristics. This is not necessary with the inventive process, since wetting with the monomer and/or oligomer solution and the oxidation reaction occur in one processing solution.

An additional advantage of the inventive process consists in the utilization of acidic solutions for formation

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of the conductive polymer film. In this way, the oxide films generated on copper surfaces - especially with the technique for printed circuit boards - are removed; as a result, the oxidizing effect of cupric (II) oxide cannot induce a polymerization reaction on the surfaces of the copper.

In the inventive process, furan, thiophene, pyrrol and their derivatives can be utilized as the five-membered heterocycles.

Noteworthy derivatives of these heterocycles are those
10 which have one or two alkyl or alkenyl radicals at positions 3 or 4, or 3 and 4 and/or at the heteroatom, especially such derivatives with one or two methyl, ethyl or propyl groups. Halogen-substituted furans, thiophenes or pyrrols are also suitable. The 3-chloro, 3-bromo, 4-chloro, 4-bromo,-, 3,4-dichloro and 3,4-dibromo derivatives deserve mention. Also suitable are the formyl and carboxyl derivatives that are analogous to the halogen-substituted compounds, as well as those of pyrrol, especially the N-methyl-,N-ethyl -, N-vinyl-pyrrol and the 2,2'-dipyrrol derivatives.

20 It is also possible to convert the heterocycles, especially pyrrol, into their corresponding oligomers with a weak acid. Contact with the weak acid takes place in an aqueous solution of the heterocyclic compound which could contain a solubilizer. This oligomerization reaction can take place at low temperatures, down to the freezing point of the solutions. The reaction can also be carried out at room temperature or 50°C. The temperature of the oligomerization

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reaction influences the conductance of the polymeric material that precipitates and the stability of the solution.

Weak acids such as formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid, fumaric acid, maleic acid, azelaic acid, citric acid, malic acid, ascorbic acid or phosphoric acid can be used for the oligomerization reaction. The corresponding salts can also be utilized; the acids are released through hydrolysis in an aqueous system.

The concentration of oligomers, monomers, or mixtures of
10 various monomers or oligomers & monomers is 0.1 to 200 grams per liter, preferably 0.5 to 50 grams per liter.

In addition to manganese dioxide, the oxidant adsorbed on the printed circuit board to perform the inventive process could be, for instance, the salts of permanganate, manganate, cerium (IV) and/or periodate.

The printed circuit boards are treated in an oxidizing bath at a pH value between 1 and 14. Surfactants or other surface-active substances can also be added to the oxidizing bath.

20 After the printed circuit boards have been treated according to the inventive process, metal can precipitated from the galvanic baths through application of an electrical current by virtue of the electrical conductance of the polymer film. In this context, galvanic copperplating deserves special mention.

Execution of the inventive process can take place by means of the immersion and/or spraying procedure. For instance, the process is especially suitable for use with

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continuous horizontal passage of the printed circuit boards through a processing installation.

The inventive process is also suited to glass fiber metallization. Good metallization results can be achieved when alkaline ions are added to a heterocycle solution. Equally good metallization can be attained through addition of p-phenolsulfonic acid, benzenesulfonic acid and/or benzenedisulfonic acid, or other acids with anions that can be strongly polarized.

10 One way to stabilize an acidic heterocycle solution is to generate hydrogen in the solution. A very good means of doing this is through electrolytic generation on a cathode surface.

One reason for the great significance of the inventive process is its multifunctional nature. This means that when permanganate is used as the oxidant, a manganese dioxide film is deposited which roughens the surface of the nonconductor in an advantageous way, creates a very good adsorption film made of manganese dioxide, and at the same time prepares the

20 oxidant for polymer formation.

The following variants of the inventive process can be carried out to establish through-connections on printed circuit boards:

1. Generation of an oxidizing film on the nonconductive areas of the borehole wall, e.g. by the action of an alkaline potassium permanganate solution. This treatment can be preceded by various preliminary steps, which for example, can

serve to prepare the resinous surface for efficient formation of the oxidant film (e.g. manganese dioxide).

2. Action of the inventive solution containing the heterocyclic compound on the substrate surface with formation of the conductive polymer film in an acidic solution.

3. Galvanic metallization. This processing step can be preceded by pretreatment baths which serve, for example, to clean the copper surfaces.

3a. Galvanic copperplating of the entire printed circuit board to a film thickness of approximately 5 m. Next comes the photo print, using one of the usual techniques, then formation of the conducting pathways (copper and, for instance, an acid resist) in the areas left blank after the photo print; finally, removal of the photo resist, the etching process and, if necessary, removal of the acid resist. This sequence can be modified to meet particular specifications.

3b. Galvanic copperplating of the entire surface of the printed circuit board to a film thickness of approximately 30 m. The photo print follows using one of the usual techniques, then the etching process and removal of the acid resist. This sequence can also be modified to meet particular specifications.

3c. The photo print takes place before the galvanic copperplating. The surface is then metallized galvanically to a film thickness of 30 m and, if necessary, an acid resist coating is deposited. Next

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the metallic acid resist is removed. This sequence can be modified to meet particular specifications.

Immediately before the galvanic copperplating, the surface is treated in a solution which contains acid and/or oxidant in order to achieve a polymer film with sufficient conductance. Sulfuric acid/sodium persulfate or other solutions can be used for this purpose.

Other procedural variants are of course conceivable.
10 The following examples serve to elucidate the invention.

Example 1

Solution I

20 ml pyrrol were dissolved in 110 ml of a mixture of ethylene glycol monobutyl ether and isopropanol and mixed with 70 ml water and 10 grams dichloroacetic acid (K = 0.0332). After a few minutes, the solution changes color from yellow to greenish. No precipitates were observed.

20 An epoxy resin board was treated as follows:

1. Starting materials in a solution with N-methyl pyrrolidone
2. Rinse with water
3. Etch in an alkaline permanganate solution
4. Rinse with water in a standing rinse
5. Rinse with water

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6. Immerse for 5 minutes at 20°C in solution I
7. Rinse with water
8. Dry the board with warm air.

The electrical resistance was 28 kOhms.

Example 2

An epoxy resin board was treated as in Example 1; after rinsing with water (step 7), it was then copperplated in an acidic, galvanic copper electrolyte. The current density was 2 A/qdm. The film was fully copperplated after 5 minutes.

Example 3

Solution II

20 ml pyrrol were dissolved in 70 ml N-methyl pyrrolidone and mixed with 110 ml water and 10 grams oxalic acid (K = 0.059). The solution became a greenish color after several hours. No precipitates were observed.

An epoxy resin board was pretreated as described in Example 1 (1-5) and then (step 6) treated in solution II for 5 minutes, rinsed and dried. Upon drying, the resistance of the polypyrrol film was 35 kOhms.

Example 4

A printed circuit board with boreholes and copper lamination on both sides was pretreated as described in Example 1 (1-5) and then treated in solution II for 5 minutes. After rinsing with water, the board was galvanically copperplated for a short time.

The borehole walls were satisfactorily copperplated after only 5 minutes of the galvanizing process.

Example 5

In a fresh solution consisting of:

25 ml pyrrol,

15 ml phosphoric acid (85%), and

950 ml water,

conductive polypyrrol was deposited on an epoxy resin board
10 that had been pretreated with alkaline potassium permanganate solution.

The resistance of the polymer film was 5-6 kOhms. The film was galvanically copperplated with no defects (4 A/dm).

Example 6

Polypyrrol was deposited on an epoxy resin board that had been pretreated as in Example 5 in a 24-hour old solution consisting of:

25 ml pyrrol,

20 25 ml phosphoric acid (85%), and

950 ml water.

The resistance of the polymer film was 700 kOhms. The film could not be galvanically copperplated any further.

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Example 7

Hydrogen was generated electrolytically on a stainless steel grate in a solution consisting of:

25 ml pyrrol,

25 ml phosphoric acid (85%), and

950 ml water.

(The anode compartment was segregated by an electrolytic key.)

After 48 hours an epoxy resin board pretreated as in
10 Example 1 (up to step 5) was coated with polypyrrol in this solution. The polymer film had a resistance of 105 kOhms. The galvanic copperplating was completed satisfactorily.

Example 8

Conductive polymer was deposited on an epoxy resin board pretreated as in Example 1 (up to step 5) in a solution consisting of:

7.5 g pyrrol,

990 ml water, and

20 phosphoric acid (to pH 2.5).

The resistance of the polymer film was 150-200 kOhms. The film was galvanically reinforced (4 A/dm). The solution was stable; films with equally good conductance were generated even after one week.

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Example 9

Conductive polymer was deposited on an epoxy resin board pretreated as in Example 1 (up to step 5) in a solution consisting of:

7.5 g pyrrol,

990 ml water, and

phosphoric acid (to pH 3.5).

The resistance of the polymer film was 6500 kOhms. The film could not be galvanically reinforced. The solution was
10 stable.

Example 10

Polypyrrol was deposited on an epoxy resin board pretreated as in Example 1 (up to step 5) in a solution consisting of:

7.5 g pyrrol,

5.0 g disodium hydrogen phosphate, crystalline,

5.0 g sodium hydrogen phosphate, crystalline,

980 ml water, and

20 phosphoric acid (to pH 2.5).

The resistance of the polymer film was 30-45 kOhms. The film was galvanically copperplated in a short time (4 A/dm). Conductive polymer was deposited for over one week in this solution without an increase in the resistance of the polypyrrol film.

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Example 11

Polypyrrol was deposited on an epoxy resin board pretreated as in Example 1 (up to step 5) in a solution consisting of:

7.5 g pyrrol,

25.0 g dipotassium hydrogen phosphate,

25.0 g potassium hydrogen phosphate,

960 ml water, and

phosphoric acid (to pH 2.5).

10 The resistance of the polymer film was 10-15 kOhms. The film was galvanically copperplated in a few minutes (4 A/qdm). The solution was stable; polypyrrol films with good conductance were deposited even after the solution had stood for one week.

Example 12

After pretreatment according to Example 1 (up to step 5), polypyrrol and then galvanic copper can be deposited in the boreholes of a printed circuit board at room temperature

20 in a solution consisting of:

7.5 g/l pyrrol.

The results obtained four days after the solution was made were as good, in terms of ability to plate the boreholes walls with copper, as those achieved immediately after the solution was prepared. Another experiment after the solution had stood for six days yielded poorer results in terms of plating.

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Example 13

The same experiment as in Example 12 was conducted with the pyrrol solution at +5$ C. In this case, good metallization was achieved even after twelve days.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for enabling direct metallization of nonconductors, in which strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution of initially-nonconductive oligomers of five-membered heterocycles, optionally containing a solubilizer, by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a solution containing permanganates, whereby the electrical conductance of the polymeric products is sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

2. A process for enabling direct metallization of nonconductors, in which strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution of initially-nonconductive monomers or mixtures of various monomers of five-membered heterocycles, optionally containing a solubilizer, by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a

solution containing permanganates, whereby the electrical conductance of the polymeric products is sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

3. A process for enabling direct metallization of nonconductors, in which strongly-adherent insoluble polymeric products are deposited in one process step on the surface of the nonconductor from an acidic aqueous solution of initially-nonconductive monomer/oligomer mixtures of five-membered heterocycles, optionally containing a solubilizer, by contact with a non-rinsable insoluble coating containing manganese dioxide which has been adsorbed on the surfaces of the nonconductor from a solution containing permanganates, whereby the electrical conductance of the polymeric products is sufficient to permit deposition of metal on the polymer surface from galvanic baths through application of an electrical current.

4. A process as defined in claim 1 or 3, wherein formation of soluble oligomers from the five-membered heterocycles proceeds from a solution of monomers and a weak acid.

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5. A process as defined in any one of claims 1 to 4, characterized by the use of furan, pyrrol, thiophene or their substituted derivatives, as the five-membered heterocycles.

6. A process as defined in any one of claims 1 to 5, wherein the concentration of said monomers or mixtures of monomers, said oligomers or said monomer/oligomer mixtures in the acidic aqueous solution is 0.1 to 200 grams per liter.

7. A process as defined in any one of claims 1 to 6, characterized by the use of acids or acidic salts whose dissociation constants in aqueous solution, relative to protons, lie between 0.1 and 0.01.

8. A process as defined in any one of claims 1 to 7, wherein the adsorbed manganese dioxide forms through the reaction of permanganate with the nonconductor.

9. A process as defined in any one of claims 1 to 8, in which a strongly polar organic solvent is used as a solubilizer.

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10. A process as defined in any one of claims 1 to 9, followed by metallization of the surfaces of the nonconductor.

11. A process as defined in claim 10, for the metallization of nonconductive borehole walls in printed circuit boards.

12. A process as defined in claim 11, wherein galvanic metallization is accomplished after preparation of the circuit board, which follows deposition of the conductive polymeric products, and the conductive polymer products are treated with a solution containing acid and/or oxidant directly before the galvanic metallization.

13. A process as defined in claim 10, 11 or 12, in which metallization is accomplished by use of an acidic galvanic copper bath.

14. A process as defined in any one of claims 1 to 13, characterized by use of an immersion and/or spraying technique for said process.

15. A process as defined in claim 14, wherein said technique is accomplished by horizontal, continuous passage of the nonconductor through a process installation.

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