

[54] METALLIZING SUBSTRATES

[72] Inventor: Kingso Chingtsung Lin, Niagara Falls, N.Y.
[73] Assignee: Hooker Chemical Corporation, Niagara Falls, N.Y.
[22] Filed: Aug. 6, 1968
[21] Appl. No.: 750,476

[52] U.S. Cl. 204/30, 117/47 A, 117/47 R, 117/71, 117/160, 106/1
[51] Int. Cl. C23b 5/60, B44d 1/092
[58] Field of Search 117/47, 47 R, 71, 160; 106/1; 204/30

[56] References Cited

UNITED STATES PATENTS

3,394,023 7/1968 Wilhelm 117/47

3,423,226 1/1969 Jensen 117/47
3,438,805 4/1969 Potrafke 117/160

Primary Examiner—Ralph S. Kendall
Assistant Examiner—Janyce A. Bell
Attorney—Peter F. Casella, Donald C. Studley, James F. Mudd, Richard P. Mueller and William J. Crossetta

[57] ABSTRACT

Substrates particularly thermoplastic resins and polymers, are plated with metals by pre-treatment of the substrate with a metallic coating by contacting said substrate with a basic solution of a metal salt to which is being introduced continuously or portionwise a phosphorus compound wherein the phosphorus has an oxidation number of less than 5. The resulting treated surface is conductive. Such conductive surfaces are readily electroplated by conventional techniques.

16 Claims, No Drawings

METALLIZING SUBSTRATES

BACKGROUND OF THE INVENTION

There is a rapidly increasing demand for metal plated articles, for example, in the production of low cost plastic articles that have a simulated metal appearance. Such articles are in demand in such industries as automotive, home appliance, radio and television and for use in decorative containers and the like. Heretofore, the metal plating of plastics and the like has required many process steps, and generally such processes have been applicable to only one or a few related substrates.

It is an object of this invention to provide a simple process for the metal plating of plastics. Another object of the invention is to provide a process that is applicable to the plating of many different substrates, particularly the thermoplastic polymers. A further object of the invention is to provide articles having an adherent metal coating that is resistant to peeling, temperature cycling, and corrosion. Such coatings are electrically conductive whereby static charges are readily dissipated from the surfaces. The metal coatings further serve to protect the articles from abrasion, scratching and marring, reduce their porosity and improve their thermal conductivity. The process of this invention can be used for unidirectional mirrors and the like; water and liquid collecting devices and the like; protective coatings on houses, cars, boats, power line poles, street lights and the like; in thermal control of clothing, houses and the like.

SUMMARY OF THE INVENTION

This invention provides a process which comprises forming a metallic coating at the surface of a substrate to render the surface susceptible to conventional electroless plating and/or electrolytic plating.

More particularly, this invention provides a process which comprises intimately contacting a substrate with a basic solution of a metal salt or complex thereof in the presence of a phosphorus compound wherein the phosphorus has an oxidation number of 3 or less. In one aspect of the invention, the resultant surface is electroplated to deposit an adherent metal coating on the surface. In another aspect of the invention, the treated surface is subjected to electroless metal plating to deposit an electroless conductive coating on the surface. Thereafter, the article can be electroplated so as to deposit an adherent metal coating of the desired thickness on the electroless conductive coating.

Also in accordance with the invention, there is provided a article having a metallic coating adherently formed at the surface of the substrate as a result of the process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of this invention is applicable to substrates, such as plastics and to other substantially non-metallic substrates. Suitable substrates include, but are not limited to, cellulosic and ceramic materials such as cloth, paper, wood, cork, card board, clay, porcelain, leather, glass, asbestos cement, and the like.

Typical plastics to which the process of this invention is applicable include the homopolymers and copolymers of ethylenically unsaturated aliphatic, alicyclic and aromatic hydrocarbons such as polyethylene, polypropylene, polybutene, ethylenepropylene copolymers; copolymers of ethylene or propylene with other olefins, polybutadiene; polymers of butadiene, polyisoprene, both natural and synthetic, polystyrene and polymers of pentene, hexene, heptene, octene, 2-methylpropene, 4-methyl-hexene-1, bicyclo-(2.2.1)-2-heptene, pentadiene, hexadiene, 2,3-dimethylbutadiene-1,3,4-vinylcyclohexene, cyclopentadiene, methylstyrene, and the like. Other polymers useful in the invention include polyindene, indenecoumarones; polymers of acrylate esters and polymers of methacrylate esters, acrylate and methacrylate resins such as ethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, ethyl methacrylate and methyl methacrylate; alkyl resins; cellulose derivatives such as cellulose acetate, cellulose acetate butyrate, cellulose nitrate, ethyl cellulose, hydroxyethyl cellulose, methyl cellulose and sodium carboxymethyl cellulose; epoxy resins; furan resins (furfuryl alcohol or furfuraldehyde); hydrocarbon resins from petroleum; isobutylene resins (polyisobutylene); isocyanate resins (polyurethanes); melamine resins such as melamine-formaldehyde and melamine-urea-formaldehyde; oleo-resins; phenolic resins such as phenol-formaldehyde, phenolic-elastomer, phenolic-epoxy, phenolic-polyamide, and phenolic-vinyl acetals; polyamide polymers, such as polyamides, polyamide-epoxy and particularly long chain synthetic polymeric amides containing recurring carbonamide groups as an integral part of the main polymer chain; polyester resins such as unsaturated polyesters of dibasic acids and dihydroxy compounds, and polyester elastomer and resorcinol resins such as resorcinol-formaldehyde, resorcinol-furfural, resorcinol-phenol-formaldehyde, resorcinol-polyamide and resorcinol-urea; rubbers such as natural rubber, synthetic polyisoprene, reclaimed rubber, chlorinated rubber, polybutadiene, cyclized rubber, butadiene-acrylonitrile rubber, butadiene-styrene rubber, and butyl rubber; neoprene rubber (polychloroprene); polysulfides (Thiokol); terpene resins; urea resins; vinyl resins such as polymers of vinyl acetal, vinyl acetate or vinyl alcohol-acetate copolymer, vinyl alcohol, vinyl chloride, vinyl butyl, vinyl chloride-acetate copolymer, vinyl pyrrolidone and vinylidene chloride copolymer; polyformaldehyde; polyphenylene oxide; polymers of diallyl phthalates and phthalates; polycarbonates of phosgene or thiophosgene and dihydroxy compounds such as bisphenols, thermoplastic polymers of bisphenols and epichlorohydrin (tradenamed Phenoxy polymers); graft copolymers and polymers of unsaturated hydrocarbon and an unsaturated monomer, such as graft copolymers of polybutadiene, styrene and acrylonitrile, commonly called ABS resins; ABS-polyvinyl chloride polymers, recently introduced under the tradename of Cycovin; acrylic polyvinyl chloride polymers, known by the tradename of Kydex 100; polytetrafluoroethylene and poly(monochlorotrifluoroethylene).

The polymers of the invention can be used in the unfilled condition, or with fillers such as glass fiber, glass powder, glass beads, asbestos, talc and other mineral fillers, wood flour and other vegetable fillers, carbon in its various forms, dyes, pigments, waxes and the like. If a wax is used as a filler, it has been found that the harder the wax, the more adherent the metal will be bound to the substrate.

The substrates of the invention can be in various physical forms, such as shaped articles, for example, moldings, sheets, rods, beads, and the like; fibers, films and fabrics, and the like.

As a result of the treatment step of the invention, a metallic coating is deposited at the surface of the substrate. The metallic coating is primarily elemental metal but can also include phosphorus from the phosphorus in the reducing agent. Without being limited to theory, the metal-phosphorus portion of the coating can be an alloy or compound.

In the treatment step of the process of the invention, the substrate is contacted with a solution of a metal salt or a complex of a metal salt, which is capable of being reduced by a phosphorus compound of the invention to form a metallic coating. The metals generally employed are those of Groups IB, IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table appearing on pages 60-61 of Lange's Handbook of Chemistry (Revised Tenth Edition). The preferred metals are copper, silver, gold, chromium, manganese, cobalt, nickel, palladium, titanium, zirconium, vanadium, tantalum, cadmium, tungsten, molybdenum, and the like.

The metal salts that are used in the invention can contain a wide variety of anions. Suitable anions include the anions of mineral acids such as sulfate, chloride, bromide, iodide, fluoride, nitrate, phosphate, chlorate, perchlorate, borate, carbonate, cyanide, and the like. Also useful are the anions of organic acids such as formate, acetate, citrate, butyrate, valerate, caproate, heptylate, caprylate, naphthenate, 2-ethyl caproate, cinnamate, stearate, oleate, palmitate, dimethyl-

glyoxime, and the like. Generally the anions of organic acids contain one to 18 carbon atoms.

Some useful metal salts include copper sulfate, copper chloride, silver nitrate and nickel cyanide.

The metal salts can be complexed with a complexing agent that produces a solution having a basic pH (>7). Particularly useful are the ammoniacal complexes of the metal salts, in which one to six ammonia molecules are complexed with the foregoing metal salts. Typical examples include $\text{NiSO}_4 \cdot 6\text{NH}_3$, $\text{NiCl}_2 \cdot 6\text{NH}_3$, $\text{Ni}(\text{C}_2\text{H}_5\text{OO})_2 \cdot 6\text{NH}_3$, $\text{CuSO}_4 \cdot 6\text{NH}_3$, $\text{CuCl}_2 \cdot 6\text{NH}_3$, $\text{AgNO}_3 \cdot 6\text{NH}_3$, $\text{NiSO}_4 \cdot 3\text{NH}_3$, $\text{CuSO}_4 \cdot 4\text{NH}_3$, $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3$, and the like. Other useful complexing agents include quinoline, amines and pyridine. Useful complexes include compounds of the formula MX_2Q_2 wherein M is the metal ion, X is chlorine or bromine and Q is quinoline. Typical examples include: CoCl_2Q_2 , CoBr_2Q_2 , NiCl_2Q_2 , NiBr_2Q_2 , NiI_2Q_2 , MnCl_2Q_2 , CuCl_2Q_2 , CuBr_2Q_2 and ZnCl_2Q_2 . Also useful are the corresponding monoquinoline complexes such as CoCl_2Q . Useful amine complexes include the mono-(ethylenediamine)-, bis-(ethylenediamine)-, tris-(ethylenediamine)-, bis-(1,2-propanediamine)-, and bis-(1,3-propanediamine)- complexes of salts such as copper sulfate. Typical pyridine complexes include $\text{NiCl}_2(\text{py})_2$ and $\text{CuCl}_2(\text{py})_2$ where py is pyridine.

The foregoing metal salts and their complexes are used in ionic media, preferably in aqueous solutions. However, non-aqueous media can be employed such as alcohols, for example, methyl alcohol, ethyl alcohol, butyl alcohol, heptyl alcohol, decyl alcohol, and the like. Mixtures of alcohol and water can be used. Also, useful are ionic mixtures of alcohol with other miscible solvents of the types disclosed hereinbefore. The solution concentration is generally in the range from about 0.1 weight percent metal salt or complex based on the total weight of the solution up to a saturated solution, preferably from about 1 to about 10 weight percent metal salt or complex. The pH of the metal salt or complex solution is generally maintained in the basic range, i.e., greater than 7, and preferably from about 10 to about 13.

The step of contacting the substrate with the solution of metal salt is generally conducted at a temperature below the softening point of the substrate, and below the boiling point of the solvent, if one is used. Generally the temperature is in the range of about 0° to 110° centigrade, preferably from about 25° – 100°C . The time of contact can vary considerably, depending on the nature of the substrate, the characteristics of the metal salts employed and the contact temperature. However, the time of contact is generally in the range of about 0.1 to 30 minutes, preferably about 1 to 10 minutes.

The metallic coating is applied to the surface of the substrate by introducing a phosphorus component continuously or portionwise into the metal salt solution while the substrate is in contact therewith. The metallic species generated by the reaction of the phosphorus compound and the metal cations have a strong tendency to adhere to the substrate surface. This tendency is enhanced when the metal in its nascent form is rapidly brought into intimate contact with the substrate. The coincidental reduction of the metal and its impingement on the substrate can be effected by suitable agitation. For example, the substrate can be placed in a flowing stream composed of the metal salt solution, into which the phosphorous compound is passed. The phosphorus compound can be ejected from a nozzle against a substrate suspended in a rapidly stirred metal salt solution. Suitable phosphorus compounds or phosphorus components are those wherein the phosphorus has low oxidation; the phosphorus has an oxidation number of less than 5, more particularly the oxidation number can be -3 , -2 , 0 , $+1$ or $+3$.

Typical phosphorus compounds that can be employed are phosphine, diphosphine, hypophosphorous acid and the salts thereof of the metals of Groups I, II and IIIA; phosphorous acid and the salts thereof of the metals of Groups I, II and IIIA; and the phosphides of the metals of Groups IA, IIA, and IIIA. The preferred salts of the acids include the sodium, potassium

and lithium salts. The preferred phosphides are calcium and aluminum phosphides. Less preferred are the compounds of copper, magnesium, calcium, strontium, cesium, zinc, cadmium, aluminum and gallium. Particles of elemental phosphorus can be used.

As a result of the treatment step of the invention, a metallic coating is deposited at the surface of the substrate. The metallic coating is primarily elemental metal but can also include phosphorus from the phosphorus in the reducing agent. Without being limited to theory, the metal-phosphorus portion of the coating can be an alloy or compound.

Following the foregoing treatment step, the substrate can be rinsed with water or a solvent, and then can be dried by merely exposing the substrate to the atmosphere or to inert atmospheres such as nitrogen, carbon dioxide, and the like, or by drying the surface with radiant heaters or in a conventional oven. Drying times can vary considerably, for example, from 1 second to 30 minutes, or more, preferably 5 seconds to 10 minutes, more preferably 5 to 120 seconds. The rinsing and drying steps are optional.

The treated substrates that result from the foregoing process can be subjected to a process that has become known in the art as electroless plating or chemical plating. In a typical electroless plating process, a catalytic or metallic surface is contacted with a solution of a metal salt under conditions in which the metallic ion of the metal salt is reduced to the metallic state and deposited on the catalytic or metallic surface. The use of this process with the products of this invention relies upon the electroconductive coating deposited on the surface as a result of the treatment with the solution of metal salt or complex and phosphorus compound of this invention. A suitable chemical treating bath for the deposition of a nickel coating on the electroconductive surface produced in accordance with the process of the invention can comprise, for example, a solution of a nickel salt in an aqueous hypophosphite solution. Suitable hypophosphites include the alkali metal hypophosphite such as sodium hypophosphite and potassium hypophosphite, and the alkaline earth metal hypophosphites such as calcium hypophosphite and barium hypophosphite. Other suitable metal salts for use in the chemical treating bath include the metal salts described hereinbefore with respect to the metal salt treatment of the phosphorus-treated substrate of the invention. Other reducing media include formaldehyde, hydroquinone and hydrazine. Other agents, such as buffering agents, complexing agents, and other additives are included in the chemical plating solutions or baths.

The treated substrates of the invention can be electroplated by the processes known in the art. The article is generally used as the cathode. The metal desired to be plated is generally dissolved in an aqueous plating bath, although other media can be employed. Generally, a soluble metal anode of the metal to be plated can be employed. In some instances, however, a carbon anode or other inert anode is used. Suitable metals, solutions and condition for electroplating are described in Metal Finishing Guidebook Directory for 1967, published by Metals and Plastics Publications, Inc., Westwood, N.J.

The following examples serve to illustrate the invention but are not intended to limit it. Unless specified otherwise in this specification and claims, all temperatures are in degrees centigrade and parts are understood to be expressed in parts by weight.

EXAMPLE 1

(a) A solution was prepared by mixing 90 grams of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1,800 milliliters of water and 600 milliliters of concentrated ammonium hydroxide (28–30 percent NH_3). Phosphine was introduced to the solution at a rate of 0.79 grams per minute, while vigorously agitating the solution. A plastic article comprised of a graft copolymer of polybutadiene, styrene and acrylonitrile was introduced into the vigorously agitated solution, which was at a temperature of 26° – 27° centigrade,

for a total period of 2 minutes, 25 seconds. A portion of the plastic article had been abraded with steel wool, the remainder of the plastic article had been treated with concentrated nitric acid for 2 minutes. At the end of the treatment, it was observed that an adherent conductive metal surface had been formed on both portions of the plastic article.

Another ABS copolymer article was abraded with steel wool and treated in accordance with the above-described process of the invention. As a result, an adherent metal conductive surface was formed on the plastic surface.

Still another ABS copolymer article was contacted with concentrated nitric acid for one minute and thereafter subjected to the process of the above-described process. Again, an adherent metallic conductive surface was formed on the surface of the plastic article.

The above-described metal coated articles were then subjected to a MacDermid electroless nickel plating bath whereby an electroless nickel adherent coating was applied to the surfaces of the plastic articles. The thus treated articles were then copper plated in a Udylyte bright acid copper plating bath at a current density of 40 amperes per square foot to produce and adherent copper plate on the outer surface of the plastic articles.

The foregoing process is repeated utilizing other ammoniacal metal salts as follows to form metallic coating on the surface of ABS articles.

- b. nickel sulfate
- c. copper chloride
- d. silver nitrate
- e. cobalt chloride
- f. nickel acetate

EXAMPLE 2

A solution was prepared by mixing 15 grams of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 100 milliliters of concentrated ammonium hydroxide (28–30% NH_3) and 300 milliliters of water. The resulting solution was vigorously agitated at about 30° centigrade in a glass container. Thereafter, phosphine was introduced to the solution and a metallic coating was deposited on the inside surface of the glass container. The foregoing process was repeated in a polyethylene container, and the inside surface of the polyethylene container was similarly metal coated. Both containers were emptied and dried and the metallic coatings formed on the inside surface of the container were tested for conductivity by applying a pair of electrodes to the metallic surfaces. The electrodes were spaced 0.75 centimeters apart. The metal coated glass surface exhibited a resistance of 33 ohms, while the metal coated polypropylene surface was found to have a resistance of about 200 ohms.

EXAMPLE 3

The process of Example 1 was repeated at several temperatures utilizing a polytetrafluoroethylene substrate. The temperature and phosphine rate was varied as follows:

Polymer Sample	Temperature	Phosphine Rate Grams Per Minute
A	25	0.66
B	39	0.88
C	4	0.5

In all cases, the polymer samples were nickel-coated, and the sample that had been treated at 25° centigrade had the most adherent metallic coating.

EXAMPLE 4

A solution was prepared by mixing 15 grams of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 100 milliliters of concentrated ammonium hydroxide (28–30% NH_3) and 300 milliliters of water. Phosphine was introduced beneath the surface of the metal salt solution, which

was vigorously agitated. Various substrates were subjected to treatment in the metal salt bath as follows.

a. A polypropylene article that had been washed with a detergent, acetone and water and dried, was introduced into the coating bath for 159 seconds at 26°–27° centigrade at an agitator speed of 5,095 revolutions per minute. The resulting treated polypropylene surface was tested and found to have a conductive metal coating adherently deposited thereon.

b. An article made from ABS (graft copolymer of polybutadiene, styrene and acrylonitrile) was subjected to the above-described metal coating bath for 2 minutes, 18 seconds at 25°–26 centigrade, while being agitated at 5,635 revolutions per minute. The resulting treated article was found to have a homogeneous, metallic coating that was conductive.

The above-described process is applied to the following additional substrates to deposit conductive metallic coatings on the surfaces of the substrates.

- c. Phenol-formaldehyde novolac resin.
- d. Polyethylene terephthalate.
- e. Glass plate.
- f. Wood.
- g. Porcelain.
- h. Cork.
- i. Asbestos cement.

The process of the invention can be conducted by introducing elemental phosphorus, particularly white or yellow phosphorus into the metal salt bath instead of the phosphine of the foregoing examples. Finely divided phosphorus particles are introduced to the aqueous solution and phosphine is formed in situ to provide the low oxidation state phosphorus compound.

Various changes and modifications can be made in the process and products of this invention without departing from the spirit and scope of the invention. The various embodiments of the invention disclosed herein serve to further illustrate the invention but are not intended to limit it.

I claim:

1. A process which comprises forming a metallic coating at the surface of a substantially non-metallic substrate by intimately contacting the substrate with a basic, aqueous solution of a metal salt or complex thereof in the presence of a phosphorus compound wherein the phosphorus has an oxidation number of less than 5; wherein the metal is selected from groups IB, IIB, IVB, VB, VIB, VIIB and VIII of the periodic table.

2. A process which comprises forming a metallic coating at the surface of a substantially non-metallic substrate by intimately contacting the substrate with a basic, aqueous solution of a metal salt or complex thereof, which solution also contains a phosphorus compound wherein the phosphorus has an oxidation number of less than 5, wherein the metal is selected from groups IB, IIB, IVB, VB, VIB, VIIB and VIII of the periodic table.

3. A process which comprises forming a metallic coating at the surface of a substantially non-metallic substrate by contacting the substrate with a basic, aqueous solution of a metal salt or complex thereof, and simultaneously agitating the solution and introducing therein continuously or portionwise a phosphorus component, wherein the metal is selected from groups IB, IIB, IVB, VB, VIB, VIIB and VIII of the periodic table, and wherein the phosphorus component is selected from the group consisting of elemental phosphorus, phosphine, diphosphine, hypophosphorous acid and the salts thereof of the metals of groups I, II and IIIA, phosphorous acid and the salts thereof of the metals of groups I, II and IIIA, and the phosphides of the metals of groups IA, IIA and IIIA.

4. The process of claim 3 wherein the phosphorus component is phosphine.

5. The process of claim 3 wherein the phosphorus component is sodium hypophosphite.

6. The process of claim 3 wherein the metal salt complex is an ammoniacal complex of a nickel salt.

7. The process of claim 6 wherein the nickel salt is nickel chloride.

7

8

8. The process wherein the treated substrate resulting from the process of claim 1 is subjected to electroless metal plating to deposit an electroless conductive coating on the treated substrate.

9. A process wherein the substrate resulting from the process of claim 8 is electroplated to deposit an adherent metal coating on the electroless conductive coating.

10. A process wherein the treated substrate resulting from the process of claim 1 is electroplated to deposit an adherent metal coating on the treated substrate.

11. The process of claim 1 wherein the substrate is a plastic.

12. The process of claim 3 wherein the substrate is polypropylene.

13. The process of claim 3 wherein the substrate is a graft copolymer of polybutadiene, styrene and acrylonitrile.

14. The process of claim 3 wherein the substrate is a polycarbonate.

15. The process of claim 3 wherein the substrate is polytetrafluoroethylene.

16. The process of claim 3 wherein the substrate is glass.

* * * * *

15

20

25

30

35

40

45

50

55

60

65

70

75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,650,911 Dated March 21, 1972

Inventor(s) Kingso Chingtsung Lin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 43, "100bL" should read --- 100° ---.
Column 6, line 74, "precess" should read --- process ---.
Column 7, line 11, "precess" should read --- process ---.

Signed and sealed this 18th day of July 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents