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[54] **LOW-TEMPERATURE TRANSFORMATION OF NONCONDUCTIVE SUBSTRATES TO CONDUCTIVE SUBSTRATES**
15 Claims, No Drawings

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ABSTRACT: Substrates, particularly thermoplastic resins and polymers, are plated with metals by pretreatment of the substrate with phosphorus in an organic solvent to deposit phosphorus at the surface of the substrate followed by subjecting the thus treated substrate with a metal salt or complex thereof, in the presence of OH or Br_3H^1 or AlR_3H^1 or mixtures thereof, to form a metal-phosphorus compound, wherein each R is individually selected from the group consisting of alkyl, aryl and hydrogen. The treatment with the metal salt solution can be accomplished at room temperature. The resulting surface is conductive and can be readily electroplated by conventional techniques.

LOW-TEMPERATURE TRANSFORMATION OF NONCONDUCTIVE SUBSTRATES TO CONDUCTIVE 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. The metal plating of plastics and the like has required many process steps and has been limited to either high-temperature operation or the presence of reducing agents for low-temperature operation. Plastics with low melting or softening points were not suited to being plated. A new process for metal plating is described in copending application Ser. No. 614,541, filed Feb. 8, 1967. This process also uses relatively high temperatures for satisfactory results. Not well suited to metal plating were substrates of minimal thickness, such as paints.

It is an object of this invention to provide a safe, economical and reliable low-temperature process for the metal plating of substrates with the phosphorus system described in Ser. No. 614,541. Another object of the invention is to provide a low-temperature bath for employment in the plating of low-heat distortion (below 100° C.) polyolefins such as polyvinylchloride. A further objective is to provide a low-temperature bath suitable for use when the substrate surface is thin. A still further object of the invention is to provide a low-temperature process for making 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 making highway signs, heat exchange components, quick-freezing frozen food containers and plastic pipes which are easy to thaw.

SUMMARY OF THE INVENTION

This invention relates to a low-temperature bath and process for forming a metal-phosphorus compound at the surface of a substrate to render the surface susceptible to conventional electroplating.

More particularly, this invention relates to a process which comprises subjecting a substrate to phosphorus so as to deposit phosphorus at the surface of the substrate and thereafter subjecting the thus treated substrate with low-temperature bath containing a metal salt or complex thereof in the presence of a small amount of OH^1, BR_3H^1, AlR_3H^1, or mixtures thereof, to form a metal-phosphorus compound, wherein each R is individually selected from the group consisting of alkyl, aryl and hydrogen. The resultant surface can be electroplated to deposit an adherent metal coating of desired thickness on the surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of this invention is applicable to substrates, such as plastics and to other substantially nonmetallic substrates. Suitable substrates include, but are not limited to, cellulosic and ceramic materials such as cloth, paper, wood, cork, cardboard, clay, porcelain, leather, porous 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-methylhexene-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 chlorinated polypropylene and methylene; polyindene, indenecoumarone resins; polymers of acrylate esters and polymers of methacrylate esters, acrylate and and methacrylate resins such as ethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, ethyl methacrylate and methyl methacrylate; alkyd 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 furfural ketone); 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-sytrene 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 butyral, vinyl chloride-acetate copolymer, vinyl pyrrolidone and vinylidene chloride copolymer; polyvinylchloride; polyformaldehyde; polyphenylene oxide; polymers of diallylphthalates and phthalates; polycarbonates of phosgene or thiophosgene and dihydroxy compounds such as bisphenols, thermoplastic polymers of bisphenols and epichlorohydrin (tradenamed Phenoxy polymers); graft copolymers of polymers of unsaturated hydrocarbons and an unsaturated monomer, such as graft copolymers of polybutadiene, styrene and acrylonitrile, commonly called ABS resin; ABS-polyvinyl chloride polymers, recently introduced under the trade name of Cycovin; and acrylic polyvinyl chloride polymers, known by the trade name of Kydex 100.

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.

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

In the first step of the preferred process of the invention, the substrate is subjected to elemental white phosphorus, which includes the various impure or commercial grades sometimes referred to as yellow phosphorus. The phosphorus can be utilized in the vapor phase, as a liquid or dissolved in a solvent.

Suitable solvents or diluents for the elemental phosphorus are solvents that dissolve elemental phosphorus and which preferably swell the surface of a plastic without detrimentally affecting the surface of the plastic. Such solvents include the halogenated hydrocarbons and halocarbons such as chloroform, methyl chloroform, phenyl chloroform, dichloroethylene, trichloroethylene, perchloroethylene, trichloroethane, dichloropropane, ethyl dibromide, ethyl chlorobromide, propylene dibromide, monochlorobenzene, monochlorotoluene and the like; aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, naphthalene and the like.

When a solution of phosphorus is employed in the process, the solution concentration is generally in the range from about 0.0001 weight percent of phosphorus based on the weight of the solution up to a saturated solution and preferably from about 1.5 to about 2.5 percent. Prior to subjecting the substrate to the elemental phosphorus, in gaseous, liquid or solution, the surface of the article should be clean. When a solution is used, the solvent generally serves to clean the surface. A solvent wash may be desirable when gaseous or liquid phosphorus is employed. However, it is not necessary to subject the substrate to special treatment such as etching, polishing and the like. The phosphorus treatment is generally conducted at a temperature below the softening point of the substrate, and below the boiling point of the solvent, if a solvent is used. Generally the temperature is in the range of about 10 to about 135 degrees centigrade, but preferably in the range of about 10 to about 40 degrees centigrade. The contact time varies depending on the nature of the substrate, the solvent and temperature, but is generally in the range of about 1 second to 1 hour or more, preferably in the range of about one to ten minutes.

As a result of the first treatment step, the phosphorus is deposited or nucleated at the surface of the substrate. By this is meant that the phosphorus can be located on the surface, embedded in the surface and embedded beneath the surface of the substrate. The location of the phosphorus is somewhat dependent on the action of the solvent and reaction conditions on the surface.

Following the first treatment step, the substrate can be subjected to water and/or aqueous solution of a surfactant, as disclosed in my copending application Ser. No. 671,337, now abandoned filed Sept. 28, 1967, 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 one second to 30 minutes or more, preferably 5 seconds to 10 minutes, more preferably 5 seconds to 20 seconds. The rinsing and drying steps are optional.

In the second treatment step of the process of the invention, the phosphorus-treated substrate is subjected to a bath containing a solution of a metal salt or a complex of a metal salt, which is capable of reacting with the phosphorus to form a metal phosphide, and a stable anion. The term metal phosphide, as used herein, means the metal-phosphorus coating which is formed at the surface of the substrate. Without being limited to theory, the metal phosphide may be an ionic compound or a solution (alloy). 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, dimethylglyoxime, 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, nickel cyanide and nickel chloride.

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 $NiSo_4{\cdot}6NH_3$, $NiC1_2{\cdot}a0NH_3$, $Ni(C_2H_3OO)_2{\cdot}6NH_3$, $CuSO_4{\cdot}6NH_3$, $CuC1_2{\cdot}6NH_3$, $AgNO_3{\cdot}6bNH_3$, $NiSO_4{\cdot}3NH_3$, $CuSO_4{\cdot}4NH_3$, $Ni(NO_3)_2{\cdot}4NH_3$, and the like. Other useful complexing agents include quinoline, amines and pyridine. Useful complexes include compounds of the formula MX_2O_2, wherein M is the metal ion, X is chlorine or bromine and Q is quinoline. Typical examples include: $CoC1_2Q_2$, $CoBr_2Q_2$, $NiC1_2Q_2$, $NiBr_2Q_2$, $Ni1_2Q_2$, $MnC1_2Q_2$, $CuC1_2Q_2$, $CuBr_2Q_2$ and $ZnC1_2Q_2$. Also useful are the corresponding monoquinoline complexes such as $CoC1_2Q$. Useful amine complexes include the mono-(ethylenediamine)-, bis-(ethylenediamine)-, tris-(ethylenediamine)-, bis(1,2-propane diamine)-, and bis-(1,3-propanediamine)- complexes of salts such as copper sulfate. Typical pyridine complexes include $NiC1_2(py)_2$ and $CuC1_2(py)_2$ where py is pyridine.

The foregoing metal salts and their complexes are used in ionic media, preferably in aqueous solutions. However, nonaqueous media can be employed such as alcohols, for example, methyl alcohol, ethyl alcohol, butyl alcohol, hepytl alcohol, decyl alcohol, and the like; cyclic ether, for example, tetrahydrofuran, dioxane, and the like. Mixtures of alcohol and water can be used. Also useful are ionic mixtures of alcohol with other miscible solvents. 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 can range from about 4 to 14 but is generally maintained in the basic range, i.e., greater than 7.0, and preferably from about 10 to about 13.

The stable anion which is added to the metal salt solution is selected from the group consisting of OH^1, BR_3H^1, and $A1R_3H^1$, wherein each R is individually selected from the group consisting of alkyl, aryl and hydrogen. Only a small amount is used because addition of too much stable anion will cause the metal to precipitate. For example, the concentration of OH^1 added is generally in the range of about 0.005 to about 10 percent by volume based on the volume of the solution, preferably from about 0.05 to about 1.0 percent; and the amount of $BH_4{}^1$ added is generally in the range of about 1×10^{14} to about 4×10^{11} moles per liter, preferably from about 2.6×10^{14} to about 0.26 mole per liter. Instead of using these stable anions individually, various combinations of them can be used. The compounds containing these stable anions can contain any cation which will not react with the ingredients of the metal salt bath. The compounds must be soluble in the bath. Suitable cations include sodium; potassium; hetero atom-containing species such as those containing phosphorus, sulfur and quarternary nitrogen; and the metal to be plated. Generally, the sodium and potassium compounds are preferred.

Typical compounds containing the stable anions include: sodium hydroxide, potassium hydroxide, sodium borohydride, potassium borohydride, sodium trimethyl borohydride, sodium triphenyl borohydride, sodium diphenyl methyl borohydride, dimethyl borane, lithium aluminum hydride, sodium trimethyl aluminum hydride, sodium triphenyl aluminum hydride, and the like. When R is a alkyl, the group generally contains 1 to 10 carbon atoms. When R is aryl, the aryl group generally contains 6 to 10 carbon atoms such as in phenyl, toluyl and benzyl.

The step of subjecting the phosphorus-treated substrate to the solution of metal salt and stable anion 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. The addition of the small amount of stable anion allows the treating step to be accomplished efficiently near room temperature, i.e., about 20 degrees centigrade, whereas previously presence of a reducing agent was necessary at this temperature to produce a satisfactory treated article. Generally the temperature is in the range of about 10 to 110 degrees centigrade, preferably from about 20 to 40 degrees centigrade. 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 5 to 10 minutes.

The process of this invention can be carried out in one continuous operation, or the substrate can be stored after removal from the metal salt bath and subjected to electrolytic treatment at some later time. Subjecting the substrate to a bath containing a nickel salt and OH^1 results in a black appearance. If any of the other stable anions, or if a mixture of stable anions is employed, the substrate acquires a metallic appearance. Both metal phosphide coatings are generally conductive and both allow the substrate to be stored. When a black appearance has been obtained and it is desired to have a metallic appearance, the substrate can be subjected to the bath a second time, said bath now containing any of the stable anions besides OH^1 or a mixture of any of stable anions.

The treated substrates of the invention are generally conductive and can be electroplated by the processes known in the art. The treated substrate is generally not subjected to an electroless treatment, as is sometimes the case with the process of Ser. No. 614,541. However, if the substrate is not conductive or if it is desired to increase the conductivity, the article can be subjected to electroless plating prior to electroplating. The treated 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, all temperatures are in degrees centigrade and parts are understood to be expressed in parts by weight.

EXAMPLE 1

A 2 percent solution of phosphorus in trichloroethylene was prepared by adding yellow phosphorus to trichloroethylene at 60 degrees centigrade. A polypropylene sheet was immersed in the resulting solution for 3 minutes and then washed with a 60 percent solution of DMF in water at 50 degrees centigrade for 30 seconds. The sheet was then placed in a two liter nickel bath which contained 1950 cc. of 2 percent $NiCl_2$ in 23 percent NH_4OH and 50 cc. of 20 percent NaOH. After 10 minutes the sheet was withdrawn and was found to have obtained a highly conductive black coating which can be electroplated directly by conventional means. The immersion in the nickel bath was done at room temperature.

EXAMPLE 2

A 1 percent solution of phosphorus in a mixture of trichloroethylene and perchloroethylene was prepared as described in example 1. An ABS plastic sample was treated as in example 1 except that the time of immersion in the phosphorus solution was 2 minutes. An excellent quality black coating was produced on the sample.

EXAMPLE 3

A nickel bath was prepared by dissolving 0.1 gram of solid $NaBH_4$ in 1,000 ml. of 2 percent NiCl in 10 percent NH_4OH. A polypropylene sheet, treated with phosphorus-trichloroethylene as described in example 1, was subjected to this solution at room temperature for 10 minutes. A highly conductive metallic nickel coating was produced and satisfactory results were obtained when this was electroplated with nickel in a conventional manner.

EXAMPLE 4

The black-coated samples of examples 1 and 2 were subjected to the nickel bath of example 3. Upon withdrawal from the bath, the samples had a metallic appearance.

EXAMPLE 5

A nickel bath was prepared by dissolving 8.8 grams of $Ni(C_2H_3B'2)_2$ in 50 cc. of distilled water. The nickel acetate solution was added to 500 cc. of 28 percent NH_4OH followed by 50 cc. of 9 percent NaOH and 1 drop of p-octylphenyl polyethylene glycol (a surfactant). The bath was heated to 30–32 degrees centigrade. A polypropylene sample, treated with phosphorus in trichloroethylene as in example 1, was subjected to this bath for about 20 minutes. An excellent quality, strongly adherent nickel coating was produced on the sample.

EXAMPLE 6

A nickel bath was prepared by dissolving 10 grams of $NiCl_2$ in 500 cc. of distilled water, followed by 50 grams of urea and 150 grams of NH_4OH. Polypropylene sheets and winged shaped knobs were subjected to phosphorus in trichloroethylene, as in example 1, and then to this bath at 40 degrees centigrade for 20 minutes. An adherent coating was formed on the plastic articles.

EXAMPLE 7

Winged-shaped polypropylene knobs were given an adherent nickel phosphide coating by subjecting them to a 2 percent solution of phosphorus in perchloroethylene at about 20 degrees centigrade for about 3 minutes, followed by subjection for 15 minutes to a nickel bath. The bath contained 500 cc. of 28 percent NH_4OH, 50 cc. of distilled water, 10 grams of $NiCl_2$ and 50 cc. of about 10 percent BaOH, and was maintained at 30 to 35 degrees centigrade.

EXAMPLE 8

A bath containing Cr_2O_3, $NiSO_4$, NH_4OH and a small amount of NaOH was maintained at 30 to 37 degrees centigrade. A metal phosphide coating was created on a polypropylene sample by subjecting the sample to phosphorus as in example 7 and then to the above bath for 15 minutes.

EXAMPLE 9

A polypropylene sample was treated with phosphorus as in example 7. It was then subjected to a bath containing 5.21 grams of $NiCl_2 \cdot 6H_2O$, 116 grams of 28 percent NH_4OH, 128 grams of distilled water, 0.8 gram of NaOH and 0.5 gram $NaBH_4$, maintained at 30 degrees centigrade. The resulting sample had a silvery metallic appearance and was electroplated with nickel in the conventional manner.

EXAMPLE 10

A first bath was prepared containing 4.34 grams of $NiSO_4 \cdot 6H_2O$, 115.47 grams of 28 percent NH_4OH, 128.29 grams of distilled water, 0.01 gram of NaOH, and 0.03 gram of a surfactant, and maintained at 30 degrees centigrade. A second bath was prepared containing 5.2 weight percent $NiCl_2$, 94.3 weight percent eater and 0.5 weight percent dimethylamine boran, and maintained at 30 degrees centigrade. A polypropylene sample was treated with phosphorus as in example 7 and then immersed in the first bath for 3 minutes. The resulting black sample was immersed in the second bath for about 2 minutes. The resulting treated sample had a metallic appearance and was electroplated with nickel in the conventional manner.

EXAMPLE 11

A polypropylene sample was treated as in example 10 except that upon withdrawal from the first bath, the black appearing sample was not subjected to the second bath. Instead, the sample was subjected to a bath containing 2.5 weight percent dimethylamine boran, 5.1 weight percent cobalt chloride, 2.5 weight percent H_3BO_3 and 89.9 weight percent water. The bath was maintained at 30 degrees centigrade and a pH of 4.2. The resulting treated sample had a bright cobalt appearing coating.

TABLE I

Example	Polymer	Shape	Metal	Bath temp., ° C.	Time in bath, minutes	Electrodeposition	Adhesion, lbs./inch
12	Polypropylene	Knobs	Ni	20-30	3	Ni(s)/Ni(b)/Cr	----------
13	do	do	Cu	20-30	3	Ni(s)/Ni(b)/Cr	----------
14	do	do	Co	20-30	3	Ni(s)/Ni(b)/Cr	----------
15	do	Plaques	Ni	30	3	Ni(s)/Ni(b)/Cr	15-20
16	do	do	Cu	30	3	Ni(s)/Ni(b)Cr	15-20
17	do	do	Co	30	3	Ni(s)/Ni(b)Cr	15-20
18	Oleoplate	Knobs	Ni	22	2	Ni(s)/Ni(b)/Cr	----------
19	do	do	Cu	22	2	Ni(s)/Ni(b)/Cr	----------
20	Polyethylene	Sheets	Ni	25	2	Ni(s)/Ni(b)	10-15
21	do	do	Cu	25	2	Ni(s)/Ni(b)	10-15
22	do	Plaques	Ni	30	2	Ni(s)/Ni(b)	15-25
23	do	do	Cu	30	2	Ni(s)/Ni(b)	15-25
24	do	do	Co	30	2	Ni(s)/Ni(b)	15-25
25	Polyvinylchloride	Sheets	Ni	26	2	Ni(s)/Ni(b)	10-15
26	do	do	Cu	26	2	Ni(s)/Ni(b)	10-15
27	do	Bottles	Ni	28	2	Ni(s)/Ni(b)/Cr	----------
28	do	do	Cu	28	2	Ni(s)/Ni(b)/Cr	----------
29	do	do	Co	28	2	Ni(s)/Ni(b)/Cr	----------

TABLE II

Example	Polymer	Shape	Metal	Stable anion	Bath temp., ° C.	Time in bath, minutes	Electrodeposition	Adhesion, lbs./inch
30	Polypropylene	Sheets	Ni	OH^- and $(CH_3)_2NHBH_3$	25	4	Ni(s)/Ni(b)/Cr	15-20
31	do	do	Cu	do	25	4	Ni(s)/Ni(b)/Cr	15-20
32	do	do	Co	do	25	4	Ni(s)/Ni(b)/Cr	15-20
33	ABS	Plaques	Ni	do	31	3	Ni(s)/Ni(b)	----------
34	ABS	do	Cu	do	31	3	Ni(s)/Ni(b)	----------
35	ABS	do	Co	do	31	3	Ni(s)/Ni(b)	----------
36	ABS	Knobs	Ni	OH^- and BH^-_4	25	2	Ni(s)/Ni(b)/Cr	----------
37	ABS	do	Cu	do	25	2	Ni(s)/Ni(b)/Cr	----------
38	Polyvinylchloride	do	Ni	do	25	2	Ni(s)/Ni(b)/Cr	----------
39	do	do	Cu	do	25	2	Ni(s)/Ni(b)/Cr	----------
40	do	do	Co	do	25	2	Ni(s)/Ni(b)/Cr	----------

EXAMPLES 12-29

Various polymers in various shapes were subjected to a 2 percent solution of phosphorus in trichloroethylene. Thereafter, the samples were subjected to the low-temperature bath containing a small amount of OH^1 and BH_4^1, introduced into the bath as NaOH and $NaBH_4$, followed by the electroplating of a metal. The variables are reported in table I. The metals in the bath were introduced as the chloride, sulfate or acetate salts. The designation Ni(s) indicates the subjection to a bath of a Harshaw Chemical Company Perflow semibright nickel plating solution, at about 65 degrees centigrade and about 50 amperes per square foot current density for about 30 minutes. The designation Ni(b) indicates subjection to a bath of a Harshaw Chemical Company Airglow bright nickel plating solution, at about 65 degrees centigrade and a current density of about 50 amperes per square foot for about 10 minutes. The designation Cr indicates subjection to a Udylite K2-50 chromic acid plating bath for about 1.5 minutes and a current density of 150 amperes per square foot. Under the heading "Electrodeposition," the metals are listed in the order in which they were plated on the metal phosphide. For example, Ni(s)/Ni(b)/Cr indicate that the sample was first plated with semibright nickel, followed by bright nickel, and finally plated with chrome. The adhesion of the plated metal to the plastic surface is reported in pounds per inch, which represents the quantity of force required to pull an inch wide strip of metal away from the plastic surface. Oleoplate is a type of polypropylene.

The plated articles of each of the above examples were tested for thermal stability by a thermocycling test. Therein, the metal-plated articles were heated in an oven at 180 degrees Fahrenheit for 3 hours, maintained at room temperature for 30 minutes and then placed in a freezer at −40 degrees Fahrenheit for 30 minutes. The same heating and cooling was repeated six times to complete the test. To pass the test, the coating cannot blister, crack or peel. All of the plated articles passed the thermocycling test.

EXAMPLES 30-40

Various polymers in various shapes were subjected to a 3 percent solution of phosphorus in trichloroethylene, the low-temperature bath of this invention, and then electroplated. The variables are reported in table II. All other conditions are as in examples 12-29. All of the plated articles were tested for thermal stability by a thermocycling test, as described in examples 12-29, and all of the plated articles passed the test. Adhesion is reported in pounds per inch.

EXAMPLE 41

A sample of paper was treated with phosphorus and the low-temperature bath as in example 1. Upon withdrawal from the bath, the paper had an adherent nickel phosphide on its surface.

When employing the low-temperature bath of this invention, especially when the pH is in the basic range, it is advantageous to employ a secondary complexing agent to increase the bath life. The secondary agents are selected from the inorganic compounds or alkyl derivatives of Group III A and IV A metals. Examples include the chlorides, fluorides, bromides, iodides, chromates, sulfates, nitrates, acid phosphates, and the like; the methyl, ethyl, isopropyl, and the like, derivatives of gallium, indium, thallium, germanium, silicon, tin and lead.

Various changes and modifications can be made in the process 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 subjecting a substrate to white phosphorus to deposit phosphorus at the surface of the substrate and thereafter subjecting the phosphorus-treated substrate to a bath consisting essentially of a solution of a metal salt or complex thereof which is capable of reacting with the phosphorus to form a metal phosphide and stable anions, wherein said metal is selected from Groups IB, IIB, IVB, VB, VIB, VIIB, and VIII of the Periodic Table, the anion of said metal salt is selected from the group consisting of anions of mineral acids and anions of organic acids, and said stable anions are selected from the group consisting of OH^1 mixed with BR_3H^1 and OH^1 mixed with AlR_3H^1, and mixtures thereof, wherein each R is individually selected from the group consisting of alkyl, aryl, and hydrogen, and said stable

anions are present in such concentration as to avoid precipitation of the metal salts.

2. 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.

3. A process which comprises subjecting a plastic to white phosphorus to deposit phosphorus at the surface of the plastic and thereafter subjecting the phosphorus-treated plastic to a bath consisting essentially of a solution of a metal salt or complex thereof which is capable of reacting with the phosphorus to form a metal phosphide and stable anions, wherein said metal is selected from Groups IB, IIB, IVB, VB, VIB, VIIB, and VIII of the Periodic Table, the anion of said metal salt is selected from the group consisting of anions of mineral acids and anions of organic acids, and wherein said stable anions are selected from the group consisting of OH^1 mixed with BR_3H^1 and OH^1 mixed with AlR_3H^1, and mixtures thereof, wherein each R is individually selected from the group consisting of alkyl, aryl, and hydrogen, and said stable anions are present in such concentration as to avoid precipitation of the metal salts.

4. The process according to claim 3 wherein the plastic is subjected to a solution of phosphorus dissolved in a solvent.

5. A process wherein the treated plastic resulting from the process of claim 3 is electroplated to deposit an adherent metal coating on the treated plastic.

6. The process of claim 3 wherein the BR_3H^1 stable anion is introduced as sodium borohydride.

7. The process of claim 3 wherein the BR_3H^1 stable anion is introduced as dimethylamine borane.

8. The process of claim 3 wherein the bath is maintained at a temperature between about 20 degrees and about 40 degrees centigrade.

9. The process of claim 8 wherein the metal salt complex is an ammoniacal complex of a nickel salt.

10. The process of claim 8 wherein the plastic is polypropylene, the phosphorus is employed as a solution of phosphorus dissolved in trichlornethylene, the metal salt complex is an ammoniacal complex of nickel chloride, and the stable anions are introduced into the bath as sodium hydroxide mixed with sodium bocohydride.

11. The process of claim 8 wherein the plastic is a polyolefin.

12. The process of claim 8 wherein the plastic is polypropylene, the phosphorus is employed as a solution of phosphorus dissolved in trichloroethylene, and the BR_3H^1 stable anion is introduced into the bath as dimethylamine borane.

13. The process of claim 8 wherein the plastic is polyvinylchloride, the phosphorus is employed as a solution of phosphorus dissolved in trichloroethylene, and the BR_3H^1 stable anion is introduced into the bath as sodium borohydride.

14. The process of claim 8 wherein the plastic is a graft copolymer of polybutadiene, styrene and acrylonitrile, the phosphorus is employed as a solution of phosphorus dissolved in trichloroethylene, and the BR_3H^1 stable anion is introduced into the bath as sodium borohydride.

15. The process of claim 8 wherein the plastic is a graft copolymer of polybutadiene, styrene and acrylonitrile, the phosphorus is employed as a solution of phosphorus dissolved in trichloroethylene and the BR_3H^1 stable anion is introduced into the bath as dimethylamine boran.

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PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,295 Dated October 26, 1971

Inventor(s) Sung K. Lee

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

In abstract line 6, "OH" should read ---OH^----; "BR_3H^1" should read ---BR_3H^----; "AlR_3H^1" should read ---AlR_3H^----.

Column 1, line 52, "OH^1, BR_3H^1, AlR_3H^1" should read ---OH^-, BR_3H^-, AlR_3H^----.

Column 4, line 3, "MX_2O_2" should read ---MX_2O_2---; lines 31 and 32, "OH^1, BR_3H^1, and AlR_3H^1" should read ---OH^-, BR_3H^-, and AlR_3H^----; line 36, "OH^1" should read ---OH^----; line 39, "$BH_4{}^1$" should read ---$BH_4{}^-$---; lines 39 and 40, "1×10^{14}" should read ---1×10^{-4}---; line 40, "4×10^{11}" should read ---4×10^{-1}---; "2.6×10^{14}" should read ---2.6×10^{-4}---.

Column 5, line 7, "OH^1" should read ---OH^----; line 15, "OH^1" should read ---OH^----.

Column 6, line 2, "$Ni(C_2H_3B^1{}_2)_2$" should read ---$Ni(C_2H_3O_2)_2$---; line 57, "percent eater" should read ---percent water---.

Column 7, line 37, "OH^1 and $BH_4{}^1$" should read ---OH^- and $BH_4{}^-$---.

Column 8, lines 72 and 73, Claim 1 "OH^1" change to ---OH^----; "BR_3H^1" change to ---BR_3H^----; "OH^1" change to ---OH^----; and "AlR_3H^1" change to ---AlR_3H^----.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,295 Dated October 26, 1971

Inventor(s) Sung K. Lee PAGE - 2

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

Column 9, lines 16 and 17, Claim 3, "OH^1" change to ---OH^----; "BR_3H^1" change to ---BR_3H^----; "OH^1" change to ---OH^----; and "AlR_3H^1" change to ---AlR_3H^----; line 26, Claim 6, "BR_3H^1" change to ---BR_3H^----; line 28, Claim 7, "BR_3H^1" change to ---BR_3H^----;

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Column 10, lines 14 and 15, Claim 12, "BR_3H^1" change to ---BR_3H^----; line 18, Claim 13, "BR_3H^1" change to ---BR_3H^----; line 23, Claim 14, "BR_3H^1" change ---BR_3H^----; line 28, Claim 15, "BR_3H^1" change to ---BR_3H^----. line 30, "boran" should read -- borane --.

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents