SPECIFICATION

Accelerating solution and its use in a process for treating polymeric substrates prior to plating

The invention relates to an accelerating solution and its use in a process for treating polymeric substrates prior to plating.

A variety of methods have been used or proposed for use in applying metallic platings to the whole or portions of the surfaces of polymeric plastics parts. Such processes conventionally comprise a plurality of sequential pre-treatment steps to render the plastics substrate receptive to the application of an electroless plating whereafter the plated part can be processed through conventional electroplating operations to apply one or a plurality of supplemental metallic platings over all or selected portions of the plastics substrate. Conventionally, the pre-treatment steps employed include a cleaning or series of cleaning steps, if necessary, to remove surface films or contaminating substances. This is followed by an aqueous acidic etching step employing a hexavalent chromium solution to achieve a desired surface roughness or texture, which enhances a mechanical interlock between the substrate and the metallic plating to be applied thereover. The etched substrate is subjected to one or a plurality of rinse treatments to extract and remove residual hexavalent chromium ions on the surfaces of the substrate. There may also be a neutralization step including reducing agents to substantially convert any residual hexavalent chromium ions to the trivalent state. The etched substrate is thereafter subjected to an activation treatment in an aqueous acidic solution containing a tin-palladium complex to form active sites on the surface of the substrate. This is followed by one or more rinsing steps after which the activated surface is subjected to an accelerating treatment in an aqueous solution to extract residual tin constituents or compounds on the surface of the substrate. The accelerated plastics part is again rinsed with water and thereafter is subjected to an electroless plating operation of any of the types known in the art to apply a metallic plating such as copper, nickel or cobalt over all or certain selected areas of the plastics part. The part is then rinsed and subjected to conventional electroplating operations.

Typical of such plastics plating processes are those described in United States Patent No. 3,622,370. 3,961,109; and 3,962,497.

A continuing problem associated with the electroplating of polymeric substrates has been in the careful control of the activation and accelerating steps to achieve a plastics substrate which is receptive to the subsequent electroless plating solution to provide 100% coverage of a conductive metal layer which is adherent to the substrate and which is devoid of any lack of continuity of coverage or "skipping". The presence of such discontinuities or skips results in plastics parts which upon subsequent electroplating contain non-plated areas or non-uniformity in the metallic plating deposit rendering them unsuitable for the intended end use.

It has been observed that etched and activated plastics substrates employing a tin-palladium complex activator which have not been accelerated or which have been subjected to an accelerating treatment in a weak accelerator will not become plated or will only become partially plated in the subsequent electroless plating step. Such parts are ordinarily referred to as being "under accelerated". On the other hand, when such parts are accelerated in an accelerating solution that is too strong or too aggressive, electroless plating is also adversely effected as evidenced by discontinuity or skips and in some instances no plating deposit at all. In such instances, the parts are referred to as being "over-accelerated". Accordingly it is important that the accelerating solution employed be carefully controlled so as to provide the requisite degree of acceleration in order to achieve uniform continuous electroless plating deposits on a consistent basis.

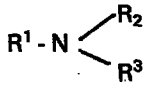
Known accelerating solutions are extremely sensitive to the presence of contaminating metal ions carried over from other processing steps or inherently present in the accelerating solution. For example, hexavalent chromium ions in spite of vigorous rinsing and neutralization steps nevertheless are carried over into the subsequent accelerating solution by entrapment in the plastics parts being processed as well as by bleed-through from cracks or openings in the protective plastisol coating conventionally employed over portions of the work racks. Tin compounds similarly are carried over from the prior activation step and these adversely affect the accelerating treatment. The presence of ferric and cupric ions in relatively low concentrations such as only 10 ppm and 20 ppm, respectively, have been found to significantly alter the aggressiveness of the accelerating solution rendering the accelerating solution unsuitable for further use. Ferric ions constitute a normal contaminant in the water employed for preparing the several aqueous solutions and are further introduced by the dissolution of the stainless steel components of the work rack on which the plastics parts are suspended. Additionally, ferric ions are introduced into the solution by oxidative attack of the steel tanks through imperfections in the protective plastics coating and also by conventional rust present in the plating environment. Copper ions similarly are introduced through the water system including copper pipeline, the copper bus bars adjoining the treating receptacles, dissolution of the rack splines and from carryover and bleed-out from the racks as a result of the presence of residual copper on the racks from copper plating operations. Such residual contamination of the racks can not be completely eliminated in spite of vigorous stripping of the racks at the conclusion of each plating cycle. In many instances, ferric and cupric ion contamination is also introduced as inherent impurities in the chemicals employed to make up the several solutions including the accelerator solution.

In any event, the presence of such ferric, cupric, and hexavalent chromium ions in only very small amounts

has adversely affected the accelerating treatment and previously has occasioned a discarding and replacement of the aqueous accelerating solution after only a short period of operation.

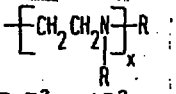
The present invention helps overcome the problems and disadvantages associated with processes for the plating of plastics articles, and particularly the acceleration thereof, by providing an accelerating solution which is stable, which is easy to control, which is tolerant to such conventional metallic impurities present, which will further inhibit plating on the protective plastics rack coating, and which is versatile and can be used on a variety of conventional platable plastics materials.

According to the present invention an aqueous acidic accelerating solution having a pH of 0 to 7 contains an aqueous soluble compatible substitute alkyl amine, or an alkali metal salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents present on the surface of the activated substrate, and an anion of a mineral acid or an aqueous soluble alkali metal salt thereof or mixtures thereof present in an amount up to 120 g/l, the said substituted alkyl amine corresponding to the following structural formula:



wherein:

R^1 represents organic radical [$R\dot{C}HCOOH$], [$R\dot{C}HCH_2OH$],



, or [$HOOC\dot{C}H\,CH_2(S)_yCH_2$-$CHNH_2COOH$], in which x and y = 1 to 4;

R, R^2 and R^3 represents H or $[CH_2]z\,X$ in which z = 1 to 6 and X is $-OH$, $-SO_3H$, -COOH, $-NH_2$, halide, $-CH_3$ or $-OCH_3$.

The contaminating ions are mainly reducible metal ions, such as cupric and ferric ions. The substituted alkyl amine is further characterised as one which is compatible with the palladium constituent on the plastics surface as well as the polymeric material itself and which is effective to form complexes with ferric and cupric ions present thereby reducing their oxidation potential and helping to prevent oxidation of the palladium constituent on the substrate. The substituted alkyl amine further extends to the alkali metal salts thereof as well as derivatives thereof. The term "alkali metal" is used herein in its broad sense to include ammonium as well as the alkali metals.

The acclerating solution preferably has the substituted alkyl amine present in an amount of from 0.001 to 100 g/l and more preferably from 0.01 to 10 g/l.

Typical of the substituted alkyl amines which are suitable for use in the practice of the present invention are:

Glycine;
$[NH_2CH_2COOH]$

Alanine;
$[CH_3CH(NH_2)COOH]$

Aspartic Acid;
$[COOHCH_2CH(NH_2)COOH]$

Glutamic Acid;
$[COOH(CH_2)_2CH(NH_2)COOH]$

Cystine;
$[HOOCCH(NH_2)CH_2SSCH_2CH(NH_2)COOH]$

Nitrilodiacetic Acid;
$[HN(CH_2COOH)_2]$

Triethanolamine;
$[N(CH_2CH_2OH)_3]$

Nitrilotriacetic Acid;
$[N(CH_2COOH)_3]$

N-Hydroxyethylenethylenediaminetetraacetic Acid, (HEDTA);
$[HOOCCH_2N(CH_2CH_2OH)(CH_2)_2N(CH_2COOH)_2]$

Ethylenediaminetetraacetic Acid, (EDTA);
$[(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2]$

N,N,N',N'-Tetrakis (2-Hydroxypropyl) Ethylene Diamine;
$[(CH_3CHOHCH_2)_2NCH_2CH_2N(CH_2CHOHCH_3)_2]$

Diethylenetriamine Pentaacetic Acid;
$[(HOOCCH_2)_2NCH_2CH_2N(CHCH_2COOH)CH_2CH_2N(CH_2COOH)_2]$

The substituted alkyl amine is preferably ethylenediaminetetraacetic acid or the mono, di, tri or tetra alkali metal salts thereof or mixtures thereof.

The anion in the accelerating solution must be compatible with the other constituents of the accelerating solution as well as with the plastics substrate. The anion of the accelerating solution is preferably a halogen, a sulphate, a bisulphate or a boric acid anion e.g. of hydroboric acid or mixtures thereof. Halogen acids include hydrochloric, hydrobromic, and hydrofluoric, of which hydrochloric acid is the preferred acid. Additionally, acids such as sulphuric acid can also be employed as well as alkali metal bisulphates to introduce suphate and bisulphate ions into the accelerating solution. Nitric acid and the alkali metal salts thereof and phosphoric based acids and the alkali metal salts thereof are also suitable. The presence of such anions further facilitates the extraction and solubilization of the residual tin compounds or constituents on the surfaces of the activated polymeric substrate. Often at least a portion of the halogen and sulphate anions can be introduced by way of salts such as sodium chloride, sodium sulphate and sodium bisulphate. Conventionally, the inclusion of such supplemental acid constituents can be made to provide a pH of the resultant accelerating solution ranging from 0 up to about neutral, and preferably a pH of less than 1. The anions are preferably present in an amount of less than 120 g/l, e.g. from 40 to 90 g/l. When fluoride or nitrate anions or both are employed, their total concentration in the solution should not exceed about 10 g/l because of their relatively high activity toward the plastics substrate.

The accelerating solution also preferably contains an effective amount of an aqueous soluble bath compatible reducing agent to reduce residual hexavalent chromium ions present to the trivalent state. Suitable reducing agents are those compatible with the other constituents of the accelerating solution and include reducing sugars, hydrazine, oxalate, alkali metal hypophosphites and hydroxylamine salts. The reducing agent preferably comprises a hydroxylamine salt. The preferred embodiment of the invention uses hydroxylamine hydrochloride [$NH_2OH.HCl$], hydroxylammonium acid sulphate [$NH_2OH.H_2SO_4$], or hydroxylammonium sulphate [$(NH_2OH)_2.H_2SO_4$], or related compounds or mixtures thereof. Such reducing agents are preferably present in an amount from 0.005 to 10 g/l such as to provide a controlled effective amount to reduce any residual hexavalent chromium to the trivalent state.

In accordance with a further preferred embodiment of the present invention, the aqueous acid solution contains a controlled amount of a surfactant to increase uniformity of reaction with the substrate achieving a more uniform acceleration thereof. Surfactants suitable for use include any of those well known in the art which are compatible with the other bath constituents. Such surfactants, when employed, can be used in amounts up to about 5 g/l.

The invention also extends to a process for treating a polymeric plastics substrate to render it receptive to electroless plating including the steps of etching the substrate with an aqueous acid solution containing hexavalent chromium ions, rinsing one or more times and activating the etched substrate with an acidic tin-palladium complex, rinsing one or more times and accelerating the activated substrate and contacting the activated substrate during the accelerating step with an aqueous acidic accelerating solution according to the invention. The invention also further extends to any plastics surface article when treated by such a process.

The accelerating solution of the present invention can be employed at temperatures ranging from about room temperatures (65°F, 18°C) to temperatures below boiling point of the solution. Ordinarily, the accelerating solution is contained in treating tanks incorporating a protective plastisol lining and for practical consideration, temperatures up to about 160°F (71°C) are employed to avoid any thermal degradation or decomposition of such protective linings. In accordance with a preferred practice, the aqueous accelerating solution is employed at temperatures ranging from about 135°F (57°C) up to about 150°F (65.5°C) which provides for reasonable treating times consistent with the available operating cycle time of the continuous plating system.

The aqueous accelerating solution can be applied to the activated plastics substrate by any one of a variety of techniques of which immersing the plastics parts in the solution constitutes a preferred practice. Generally, immersion times from about 15 seconds up to about 30 minutes can be employed. Time periods ranging from about 30 seconds up to about 5 minutes employing solutions at a temperature of about 135°F (57°C) to about 150°F (65.5°C) are satisfactory for most plastics materials and part configurations. The specific time period will vary somewhat depending upon the nature of the plastics material, the degree of activation of the polymeric substrates and the temperature of the solution. Typically, for ABS type plastics, accelerating treatments of from about 30 seconds to about 90 seconds at temperatures of 135°F (57°C) to about 150°F (65.5°C) are satisfactory. The accelerating solution is operated in the acidic range of pH0 up to about neutral

and preferably less than pH1.

The process of the present invention is applicable for use with any of the various platable plastics or polymeric plastics including acrylonitrile-butadiene-styrene (ABS), polyaryl ethers, polyphenylene oxide and nylon. The polymeric plastics parts are usually subjected to a cleaning treatment to remove any surface contamination which may further include an organic solvent treatment, in some instances, to render the substrate hydrophilic during the subsequent chromic acid etching step. Usually the cleaning step is performed employing an aqueous alkali soak solution followed by contact in an organic solvent medium which may comprise either a single-phase system or an aqueous-organic solvent emulsion. The clean part is thereafter thoroughly water rinsed and is next subjected to an etching treatment in an aqueous acid solution containing hexavalent chromium ions and acid, such as sulphuric acid, to effect an etching of the surface thereof. The specific concentration of the etching solution, the temperature, and the duration of treatment will vary depending upon the specific type of plastics substrate. The parameters of the etching step are, accordingly, dictated by procedures well known and practiced in the art.

Following the etching step, the etched polymeric substrate is subjected to one or more cold water rinses and may additionally include a neutralization step employing an aqueous solution containing a reducing agent to effect a reduction of any residual contaminating hexavalent chromium ions to the trivalent state. A typical neutralization treatment is described in United States Patent No. 3,962,497. Following neutralization, if employed, the substrate is again water rinsed and thereafter is subjected to an activation treatment employing an aqueous acid solution containing a tin-palladium complex of the various types well known in the art. A typical one-step activation treatment is described in United States Patent No. 3,011,920 and United States Patent No. 3,532,518.

Following the activation treatment, the activated polymeric substrate is subjected to one or a series of separate cold water rinse treatments whereafter it is subjected to acceleration in an aqueous solution in accordance with the present invention. Following acceleration, the part is cold water rinsed and thereafter is subjected to an electroless plating to apply a conductive continuous and adherent metallic plating such as copper, nickel, or cobalt over all or selected surface areas thereof. The electroless plating step may be performed in accordance with well known and established practices employing an aqueous solution containing a reducing agent and a reducible salt of the metal to be deposited on the surface. Following the electroless plating step, the part is subjected to one or a plurality of water rinse treatments and is thereafter in condition for conventional electroplating employing normal procedures to apply one or a plurality of overlying plating layers on the polymeric substrate.

In order to achieve selective plating of only certain areas of polymeric plastics articles, it is conventional either prior to or following the cleaning step to apply a stop-off coating to those areas which are not to be plated. Any of the commercially available stop-off compositions can be employed for this purpose. The present invention also provides benefits in this regard by achieving proper acceleration of the plastics substrate to be plated while inhibiting or substantially completely eliminating plating on such stop-off areas.

The invention may be put into practice in various ways and a number of embodiments will be described to illustrate the invention with reference to the accompanying examples.

Examples 1A, 1B and 1C

A series of test panels of a nominal size of 7.62 cms by 10.16 cms by 0.25 cms thick consisting of a platable ABS plastics material were subjected to a pretreatment and electroless plating as described below. Example 1A used one set of such panels consisting of an ABS plastics material commercially available under the designation PG 298 from Monsanto Chemical Example 1B used another set of such panels consisting of ABS plastic commercially available under the designation EP-3510 Marbon Cycolac from Borg-Warner Chemicals. Example 1C used test parts consisting of a modified polyphenylene oxide resin commercially available under the designation Noryl TN-235 from General Electric Company.

Example 1A.

After appropriate cleaning, the plastic panels and parts in Example 1A were etched in an aqueous acid solution containing 356 g/l chromic acid, 412 g/l sulphuric acid and 0.2 g/l of a perfluorinated proprietary wetting agent commercially available under the designation FC-98 from Minnesota Mining and Manufacturing Company. The parts and panels were immersed for a period of five minutes in the aqueous etching solution and the temperature was maintained at 160°F(71°C) while undergoing air agitation. At the conclusion of the etching treatment, the parts and panels were removed and rinsed with cold tap water for a period of 30 seconds. The rinsed parts were thereafter neutralized in an aqueous solution containing 18 g/l hydrochloric acid and 3 g/l hydroxylamine sulphate. The neutralization treatment was carried out for one minute with air agitation at a solution temperature of about 100°F (37.8°C).

After neutralization the panels and parts were cold water rinsed and subjected to an activation treatment in an aqueous acid solution containing 0.77 g/l palladium, 9 g/l tin chloride, 35.2 g/l hydrochloric acid and 192 g/l sodium chloride. An activation treatment of about 3 minutes at a solution temperature of 90°F was employed. Thereafter the parts were cold water rinsed with tap water and subjected to an accelerating solution.

In accordance with the present invention, the aqueous acceleration solution employed was formulated by dissolving 1 gram of the tetra sodium salt of ethylene diamine tetra-acetic acid in one litre of de-ionized

water together with 45 g/l sulphuric acid, 40 g/l sodium chloride and 1 g/l hydroxylammonium sulphate. The plastics parts and test panels were immersed in this accelerating solution for a period of 1.5 minutes at a temperature of 130°F (54.5°C) in the presence of air agitation.

After acceleration the parts were again cold water rinsed and subjected to an electroless plating step to apply a nickel plate thereover employing an aqueous bath containing 12 g/l nickel chloride hexahydrate [$NiCl_2.6H_2O$], 18 g/l of sodium hypophosphite [$NaH_2PO_2.H_2O$], and 9 g/l citric acid. The electroless plating was performed at about 85°F (29.5°C) for a period of about 5 minutes. The electroless plated parts were extracted from the solution, cold water rinsed and thereafter inspected to examine the nature of the electroless plating obtained.

Examples 1B and 1C

The above procedure was repeated using the plastics panels and parts of Examples 1B and 1C.

The resultant nickel electroless plated parts and panels produced were inspected to examine the nature of the electroless plating obtained. They were each observed to contain a lustrous, uniform metal deposit.

Examples 2A, 2B and 2C

In Example 2A ABS test panels and parts consisting of the modified polyphenylene oxide polymer described in Example 1C were accelerated in an aqueous acid accelerating solution containing 30 g/l sulphuric acid, 15 g/l of sodium chloride and g/l N,N,N',N'-Tetrakis (2-hydroxypropyl)-ethylene diamine. The activated and water rinsed plastics panels and parts were immersed in this accelerator solution for 1.5 minutes at 130°F (54.5°C) with air or mechanical agitation. The resultant parts and panels at the completion of the nickel electroless plating step were observed to carry lustrous, uniform metallic nickel deposits.

By employing de-ionized water for preparing the accelerator solution a minimum of contaminating ferric or cupric ions, and preferably none, are present. It was observed that similar good electroless nickel deposits were obtained employing such solution without incorporating the substituted alkyl amine.

In Example 2B, Example 2A was repeated but without any substituted alkyl amine and with 20 mg/l of trivalent iron introduced into the solution in the form of ferric chloride. The nickel electroless plating coverage was found to be reduced by approximately 90%.

In Example 2C, Example 2B was repeated with an equivalent 20 mg/l of trivalent iron introduced in the accelerator solution containing the substituted alkyl amine. The electroless nickel plating coverage was then found to be reduced only by about 10%.

Examples 3A, 3B, 3C and *3D*

In Example 3A plastics panels and parts as described in Example 1A were processed in accordance with the sequence described in Example 1A with the exception that the accelerator solution contained 30 g/l sulphuric acid, 15 g/l sodium chloride and 2 g/l of the tetra-sodium salt of ethylene diamine tetra-acetic acid (EDTA). The plastic test panels and parts were immersed in this accelerator solution for time periods of 30 seconds up to 30 minutes at temperatures varying from 70°F (21°C) up to 150°F (65.5°C). In all cases, lustrous, uniform metallic nickel deposits were rapidly formed during the subsequent electroless plating step.

In Example 3B the aqueous accelerating solution of Example 3A was further modified by the addition of 200 mg/l of cupric ions introduced by way of copper chloride and 10 mg/l of ferric ions introduced by way of ferric chloride. Satisfactory electroless nickel platings were again obtained and it was observed that no rack plating occurred on the plastisol protective rack coating during the electroless plating operations.

In Example 3C the aqueous accelerator solution of Example 3A was prepared but with the omission of the substituted alkyl amine. Processing of the test panels and plastics parts through the sequence as described in Example 1A resulted in a 50% to a 100% rack plating during the subsequent nickel electroless plating step.

In Example 3D a further 200 mg/l of cupric ions and 10 mg/l of ferric ions were added to the accelerator solution devoid of the substituted alkyl amine (Example 3C). This modified accelerator resulted in substantially no nickel deposits on the test panels and parts.

Examples 4A, 4B and *4C*

In Example 4A test panels and plastics parts as described in Example 1A were processed through the sequence as described in Example 1A with the exception that the aqueous accelerator solution employed contained 40 g/l sulphuric acid, 15 g/l sodium chloride and 10 g/l glycine. During the accelerating step, the test panels and plastics parts were immersed for a period of 90 seconds at 130°F (54.5°C). The panels and parts at the completion of the electroless plating step were observed to carry lustrous, uniform metallic nickel deposits.

In Example 4B 20 mg/l of ferric ions was added to the accelerator solution of Example 4A and this did not significantly affect the quality of the electroless nickel deposits obtained.

In Example 4C, the procedure of Example 4A was repeated with the addition of 20 mg/l of ferric ions to the accelerator solution devoid of the glycine additive. This resulted in little or no metallic nickel plating at all on the test panels and parts at the conclusion of the electroless plating step.

Examples 5A, 5B, 5C, 5D, 5E and *5F*

In Example 5A a set of test panels and plastics parts were processed through the sequence as described in Example 1A with the exception that the aqueous accelerator solution employed contained 50 g/l sodium

bisulphate, 58 g/l sodium chloride and 0.016 g/l of the tetra-sodium salt of EDTA.

The acceleration step was performed employing the foregoing accelerating solution for a period of 90 seconds at a temperature of 130°F (54.5°C). Lustrous, uniform nickel metal deposits were obtained during the subsequent electroless nickel plating step.

The foregoing excellent results are obtained in spite of the fact that the commercial grade of sodium bisulphate employed incorporated 0.0276% by weight iron as a normal contaminant. Accordingly, the accelerating solution contained 13.8 mg/l of ferric ions.

In Example 5B the procedure of Example 5A was followed but without the addition of the substituted alkyl amine to the accelerating solution. The resultant test panels and plastics parts at the conclusion of the electroless plating step were observed to incorporate dark deposits of low metal integrity and plate coverage of only about 85% of the plastics surface was obtained.

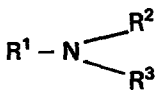
In Example 5C the procedure of Example 5B was repeated with 5 mg/l of cupric ions added to this same solution. The plating coverage was further reduced to only 70%.

In Example 5D, Example 5B was repeated with 10 mg/l of cupric ions added. This caused a further reduction in nickel plating coverage to only 10% of the surface of the panels and parts.

In Example 5E, Example 5B was repeated with 20 mg/l of cupric ions added. This resulted in a nickel plating coverage of substantially zero. In Example 5F, Example 5E was repeated with 1 g/l of the tetra-sodium salt of EDTA added to the solution containing 20 mg/l of cupric ions and the 13.8 mg/l of ferric ions (due to impurities). In accordance with the invention a substituted alkyl amine was then present and this resulted in an immediate restoration of the electroless nickel deposits providing for coverages of at least about 98% to 100% of the plastics surfaces.

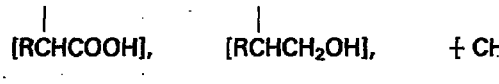
CLAIMS

1. A process for treating a polymeric plastics substrate to render it receptive to electroless plating including the steps of etching the substrate with an aqueous acid solution containing hexavalent chromium ions, rinsing one or more times and activating the etched substrate with an acidic tin-palladium complex, rinsing one or more times and accelerating the activated substrate and contacting the activated substrate during the accelerating step with an aqueous acidic accelerating solution having a pH of 0 to 7 containing an aqueous soluble compatible substituted alkyl amine, or an alkali metal or ammonium salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents present on the surface of the activated substrate, and an anion of mineral acid or aqueous soluble alkali metal or ammonium salt thereof or mixtures thereof present in an amount of up to 120 g/l, the said substitued alkyl amine corresponding to the following structural formula:

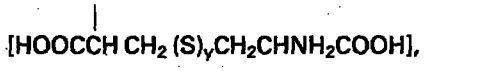


wherein:

R^1 represents an organic radical



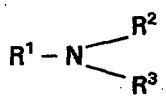
or



in which x and y = 1 to 4;

R, R^2 and R^3 represents H or $-[CH_2]_z X$ in which z = 1 to 6 and X is $-OH$, $-SO_3H$, $-COOH$, $-NH_2$, halide, $-CH_3$, or $-OCH_3$.

2. A process as claimed in Claim 1 in which the accelerating solution contains as ingredient A an aqueous soluble compatible substituted alkyl amine, or an alkali metal or ammonium salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents present on the surface of the activated substrate, and as ingredient B, an anion of a first mineral acid or aqueous soluble alkali metal or ammonium salt thereof, and as ingredient C, an anion of a second mineral acid different to the first mineral acid, B and C being present in an amount in total of up to 120 g/l or as ingredient D, an aqueous soluble bath compatible reducing agent to reduce any residual hexavalent chromium ions present to the trivalent state, or ingredient C and D, the said substituted alkyl amine corresponding to the following structural formula:



bisulphate, 58 g/l sodium chloride and 0.016 g/l of the tetra-sodium salt of EDTA.

The acceleration step was performed employing the foregoing accelerating solution for a period of 90 seconds at a temperature of 130°F (54.5°C). Lustrous, uniform nickel metal deposits were obtained during the subsequent electroless nickel plating step.

The foregoing excellent results are obtained in spite of the fact that the commercial grade of sodium bisulphate employed incorporated 0.0276% by weight iron as a normal contaminant. Accordingly, the accelerating solution contained 13.8 mg/l of ferric ions.

In Example 5B the procedure of Example 5A was followed but without the addition of the substituted alkyl amine to the accelerating solution. The resultant test panels and plastics parts at the conclusion of the electroless plating step were observed to incorporate dark deposits of low metal integrity and plate coverage of only about 85% of the plastics surface was obtained.

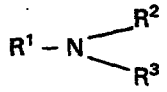
In Example 5C the procedure of Example 5B was repeated with 5 mg/l of cupric ions added to this same solution. The plating coverage was further reduced to only 70%.

In Example 5D, Example 5B was repeated with 10 mg/l of cupric ions added. This caused a further reduction in nickel plating coverage to only 10% of the surface of the panels and parts.

In Example 5E, Example 5B was repeated with 20 mg/l of cupric ions added. This resulted in a nickel plating coverage of substantially zero. In Example 5F, Example 5E was repeated with 1 g/l of the tetra-sodium salt of EDTA added to the solution containing 20 mg/l of cupric ions and the 13.8 mg/l of ferric ions (due to impurities). In accordance with the invention a substituted alkyl amine was then present and this resulted in an immediate restoration of the electroless nickel deposits providing for coverages of at least about 98% to 100% of the plastics surfaces.

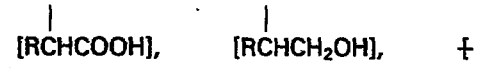
CLAIMS

1. A process for treating a polymeric plastics substrate to render it receptive to electroless plating including the steps of etching the substrate with an aqueous acid solution containing hexavalent chromium ions, rinsing one or more times and activating the etched substrate with an acidic tin-palladium complex, rinsing one or more times and accelerating the activated substrate and contacting the activated substrate during the accelerating step with an aqueous acidic accelerating solution having a pH of 0 to 7 containing an aqueous soluble compatible substituted alkyl amine, or an alkali metal or ammonium salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents present on the surface of the activated substrate, and an anion of mineral acid or aqueous soluble alkali metal or ammonium salt thereof or mixtures thereof present in an amount of up to 120 g/l, the said substitued alkyl amine corresponding to the following structural formula:

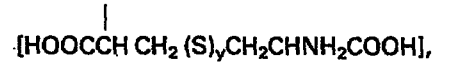


wherein:

R^1 represents an organic radical



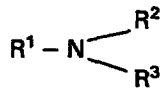
or



in which x and y = 1 to 4;

R, R^2 and R^3 represents H or $-[CH_2]_z X$ in which z = 1 to 6 and X is $-OH$, $-SO_3H$, $-COOH$, $-NH_2$, halide, $-CH_3$, or $-OCH_3$.

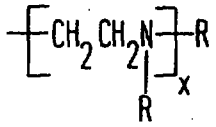
2. A process as claimed in Claim 1 in which the accelerating solution contains as ingredient A an aqueous soluble compatible substituted alkyl amine, or an alkali metal or ammonium salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents present on the surface of the activated substrate, and as ingredient B, an anion of a first mineral acid or aqueous soluble alkali metal or ammonium salt thereof, and as ingredient C, an anion of a second mineral acid different to the first mineral acid, B and C being present in an amount in total of up to 120 g/l or as ingredient D, an aqueous soluble bath compatible reducing agent to reduce any residual hexavalent chromium ions present to the trivalent state, or ingredient C and D, the said substituted alkyl amine corresponding to the following structural formula:



wherein:

R^1 represents an organic radical

$[RCHCOOH]$, $[RCHCH_2OH]$,



or

$[HOOCCH\ CH_2(S)_yCH_2-CHNH_2COOH]$,

in which x and y = 1 to 4;

R, R^2 and R^3 represents H or $-[CH_2]_z X$ in which z = 1 to 6 and X is $-OH$, $-SO_3H$, $-COOH$, $-NH_2$, halide, $-CH_3$ or $-OCH_3$.

3. A process as claimed in claim 1 or claim 2 in which the substituted alkyl amine is present in the accelerating solution in an amount of from 0.001 to 100 g/l.

4. A process as claimed in claim 1 or claim 2 in which the substituted alkyl amine is present in the accelerating solution in an amount of 0.01 to 10 g/l.

5. A process as claimed in claim 1,2,3, or 4 in which the substituted alkyl amine in the accelerating solution is ethylenediaminetetraacetic acid or the mono, di, tri, or tetra alkali metal salts thereof or mixtures thereof.

6. A process as claimed in claim 1,2,3,4 or 5 in which the anion of a mineral acid in the accelerating solution is a halogen, a sulphate, or a bisulphate or mixtures thereof.

7. A process as claimed in any one of the preceding claims in which the anions are present in the accelerating solution in an amount of from 40 to 90 g/l.

8. A process as claimed in any one of the preceding claims in which the accelerating solution contains an aqueous soluble bath compatible reducing agent to reduce any residual hexavalent chromium ions present to the trivalent state.

9. A process as claimed in claim 8 in which the reducing agent in the accelerating solution comprises a hydroxylamine salt.

10. A process as claimed in claim 8 or claim 9 in which the reducing agent is present in the accelerating solution in an amount of from 0.005 to 10 g/l.

11. A process as claimed in claims 9 or 10 in which the hydroxylamine salt in the accelerating solution is hydroxylamine hydrochloride, hydroxylammonium acid sulphate or mixtures thereof.

12. A process as claimed in any one of claims 1 to 11 in which the accelerating solution comprises ingredient A present in an amount of 0.01 to 10 g/l, ingredient B present in an amount of 30 to 50 g/l, and ingredient C present in an amount of 15 to 58 g/l.

13. A process as claimed in any one of claims 1 to 11 in which the accelerating solution comprises ingredient A present in an amount of 0.01 to 10 g/l, ingredient B present in an amount of 30 to 50 g/l, and ingredient D present in an amount of 0.005 to 10 g/l.

14. A process as claimed in any one of claims 1 to 11 in which the accelerating solution comprises tetra sodium ethylene diamine tetra acetic acid, N,N,N',N' - tetrakis (2 - hydroxypropyl) ethylene diamine, or glycine as ingredient A, present in an amount of 0.01 to 10 g/l, sulphuric acid or sodium bisulphate as ingredient B present in an amount of 30 to 50 g/l, and sodium chloride as ingredient C present in an amount of 15 to 58 g/l.

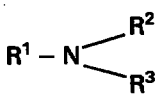
15. A process as claimed in any one of claims 1 to 11 in which the accelerating solution comprises tetra sodium ethylene diamine tetra acetic acid, N,N,N',N'-tetrakis (2 - hydroxypropyl) ethylene diamine, or glycine as ingredient A, present in an amount of 0.01 to 10 g/l, sulphuric acid or sodium bisulphate as ingredient B present in an amount of 30 to 50 g/l and hydroxyl ammonium sulphate as ingredient D present in an amount of 0.005 to 10 g/l.

16. A process as claimed in claim 1 substantially as specifically described herein with reference to any one of Examples 1A to 1C, 2A,2C,3A,3B,4A,4B,5A or 5F.

17. An article whenever treated by a process as claimed in any one of claims 1 to 16.

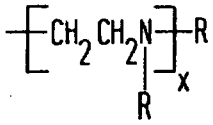
18. An aqueous acidic accelerating solution having a pH of 0 to 7 containing as ingredient A an aqueous soluble compatible substituted alkyl amine, or an alkali metal or ammonium salt thereof, present in an amount effective to complex substantially all of any contaminating cupric and ferric ions present and to extract residual tin constituents, present on the surface of the activated substrate, and as ingredients B, an anion of a first mineral acid or aqueous soluble alkali metal or ammonium salt thereof, and as ingredient C an anion of a second mineral acid different to the first mineral acid, B and C being present in an amount in total of up to 120 g/l or as ingredient D, an aqueous soluble bath compatible reducing agent to reduce any residual hexavalent chromium ions present to the trivalent state, or ingredient C and ingredient D, the said

substituted alkyl amine corresponding to the following structural formula:

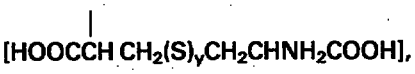


wherein:

R^1 represents an organic radical



or



in which x and y = 1 to 4;

R, R^2 and R^3 represents H or $-[CH_2]_z X$ in which z = 1 to 6 and X is $-OH$, $-SO_3H$, $-COOH$, $-NH_2$, halide, $-CH_3$, or $-OCH_3$.

19. An accelerating solution as claimed in claim 18 in which the substituted alkyl amine is present in an amount of from 0.001 to 100 g/l.

20. An accelerating solution as claimed in claim 18 in which the substituted alkyl amine is present in an amount of 0.01 to 10 g/l.

21. An accelerating solution as claimed in claim 18 19 or 20 in which the substituted alkyl amine is ethylenediaminetetraacetic acid or the mono, di, tri or tetra alkali metal salts thereof or mixtures thereof.

22. An accelerating solution as claimed in claims 18, 19, 20 or 21 in which the anions of the first and second mineral acids are a halogen, a sulphate, or a bisulphate.

23. An accelerating solution as claimed in any one of claims 18 to 22 in which the anions of ingredients B and C are together present in an amount of from 40 to 90 g/l.

24. An accelerating solution as claimed in any one of claims 18 to 23 which contains an aqueous soluble bath compatible reducing agent to reduce any residual hexavalent chromium ions present to the trivalent state as ingredient D.

25. An accelerating solution as claimed in claim 24 in which the reducing agent comprises a hydroxylamine salt.

26. An accelerating solution as claimed in claim 24 or claim 25 in which the reducing agent is present in an amount of from 0.005 to 10 g/l.

27. An accelerating solution as claimed in claim 25 or 26 in which the hydroxylamine salt is hydroxylamine hydrochloride, hydroxylammonium acid sulphate, or hydroxylammonium sulphate or mixtures thereof.

28. An accelerating solution as claimed in any one of claims 18 to 26 which comprises ingredient A present in an amount of 0.01 to 10 g/l, ingredient B present in an amount of 30 to 50 g/l and ingredient C present in an amount of 15 to 58 g/l.

29. An accelerating solution as claimed in any one of claims 1 to 10 which comprises ingredient A present in an amount of 0.01 to 10 g/l, ingredient B present in an amount of 30 to 50 g/l, and ingredient D present in an amount of 0.005 to 10 g/l.

30. An accelerating solution as claimed in any one of claims 1 to 10 which comprises tetra sodium ethylene diamine tetra acetic acid, N,N,N',N' - tetrakis (2 - hydroxypropyl) ethylene diamine, or glycine as ingredient A, present in an amount of 0.01 to 10 g/l, sulphuric acid or sodium bisulphate as ingredient B present in an amount of 30 to 50 g/l, and sodium chloride as ingredient C present in an amount of 15 to 58 g/l.

31. An accelerating solution as claimed in any one of claims 1 to 10 which comprises tetra sodium ethylene diamine tetra acetic acid, N,N,N',N', - tetrakis (2 - hydroxypropyl) ethylene diamine, or glycine as ingredient A, present in an amount of 0.01 to 10 g/l, sulphuric acid or sodium bisulphate as ingredient B present in an amount of 30 to 50 g/l, and hydroxyl ammonium sulphate as ingredient D present in an amount of 0.005 to 10 g/l.

32. An accelerating solution as claimed in claim 18 as specifically described herein with reference to any one of Examples 1A to 1C, 2A,2C,3A,3B,4A,4B,5A or 5F.

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