



(86) **Date de dépôt PCT/PCT Filing Date:** 2013/06/05
(87) **Date publication PCT/PCT Publication Date:** 2013/12/12
(45) **Date de délivrance/Issue Date:** 2020/08/25
(85) **Entrée phase nationale/National Entry:** 2014/12/01
(86) **N° demande PCT/PCT Application No.:** EP 2013/061568
(87) **N° publication PCT/PCT Publication No.:** 2013/182590
(30) **Priorité/Priority:** 2012/06/05 (LT2012042)

(51) **Cl.Int./Int.Cl. C23C 18/20** (2006.01),
C23C 18/24 (2006.01), **C23C 18/30** (2006.01)
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(54) **Titre : PROCÉDE POUR LA METALLISATION DE SURFACES DE MATIÈRES PLASTIQUES NON CONDUCTRICES**
(54) **Title: PROCESS FOR METALLIZING NONCONDUCTIVE PLASTIC SURFACES**

(57) **Abrégé/Abstract:**

The present invention relates to a process for metallizing nonconductive plastics using an etching solution free of hexavalent chromium. The etching solution is based on an sulphuric acidic solution containing a source of chlorate ions. After the treatment of the plastics with the etching solution, the plastics are metallized by means of known processes.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2013/182590 A1

(43) International Publication Date
12 December 2013 (12.12.2013)

(51) International Patent Classification:

C23C 18/20 (2006.01) *C23C 18/30* (2006.01)
C23C 18/24 (2006.01)

(21) International Application Number:

PCT/EP2013/061568

(22) International Filing Date:

5 June 2013 (05.06.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2012042 5 June 2012 (05.06.2012) LT

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR METALLIZING NONCONDUCTIVE PLASTIC SURFACES

(57) Abstract: The present invention relates to a process for metallizing nonconductive plastics using an etching solution free of hexavalent chromium. The etching solution is based on an sulphuric acidic solution containing a source of chlorate ions. After the treatment of the plastics with the etching solution, the plastics are metallized by means of known processes.



WO 2013/182590 A1

Process for metallizing nonconductive plastic surfaces

Field of the invention

The invention regards the pretreatment of nonconductive plastic surfaces prior to their metallization and may be applied in various industries where decorative or functional metal coating of plastic parts is required. The pretreatment is performed in a solution of free of hexavalent chromium.

Background of the invention

A conventional method of pretreatment of nonconductive plastic surfaces prior to their electroless metallization, mostly electroless nickel-plating or copper-plating, consists of etching the surface in hexavalent chromium containing solution, followed by the activation in a ionic or colloidal solution of palladium compounds and either the reduction in the sodium hypophosphite solution (in most cases) or the acceleration in an acid solution (usually hydrochloric acid) of the palladium ions or colloidal palladium particles, respectively, adsorbed on the plastic surface.

Etching during of the pretreatment step of the nonconductive substrate surface is required for hydrophylisation purposes so that the surface becomes hydrophilic in other phases of the process in water solutions, with sufficient quantities of palladium salts adsorbed, and for ensuring proper binding of the metal coating to the nonconductive plastic surface . The activation with the subsequent reduction or acceleration is performed in order to initiate the electroless deposition of the metal on the plastic. Thereafter, electroless plating with metal in the metallization solution takes place through auto-catalytic reaction where the metal deposited on the surface acts as a catalyst for further depositing. The metals nickel and copper are mostly used for this electroless plating.

Thereafter, electrolytic or galvanic plating can be performed on the first metal layer. Various metals can be applied, for example chromium, nickel, copper and brass or other alloys of the foregoing metals.

The main shortcomings of the conventional method are related to the cancerogenicity of the chromic acid in the etching solution. Furthermore the metal deposited during the electroless deposition step, for example a nickel, also covers parts of rack insulated with plastisol, which results in the metal losses in the solutions of subsequent metal plating electrochemically and therefore is undesired.

Various methods to overcome this problem have been suggested in the prior art.

US Patent Application No. 2005/0199587 A1 discloses a method of etching of nonconductive plastic surfaces in an acidic solution containing 20-70 g/l of potassium permanganate. Optimal KMnO_4 concentration in above mentioned solution is close to 50 g/l. When the concentration is below 20 g/l, the solution is ineffective, with the upper concentration limit determined by the solubility of potassium permanganate. The etching is followed by the activation in a palladium salt solution containing amine and by further reducing treatment, e.g. in a borohydride, hypophosphite or hydrazine solution.

This method, however, has substantial shortcomings. At high permanganate concentrations in the etching solution (recommended approx. 50 g/l, with phosphoric acid approx. 48% v/v), it decomposes very quickly, in particular at high temperatures. The recommended temperature is 100°F, i.e. 37°C. Tests have shown that at this temperature the solution becomes ineffective after 4 to 6 hours, i.e. the plastic surface is not hydrophylated and remains uncoated at some places during metallization; in the coated areas, adhesion with the plastic is very weak. Often adjustments of the solution with new portions of permanganate, which is not cheap, are required. Furthermore, insoluble permanganate decomposition products are formed, contaminating the surface being metallized;

Furthermore, etching in the permanganate solutions activates the surface of the rack's plastisol insulation as it is coated with the product of the etching reaction, i.e. manganese dioxide. The latter stimulates adsorption of palladium compounds on plastisol, which tends to metallize in the solutions of electroless metal deposition. Formation of manganese dioxide on surfaces is characteristic of the permanganate etching solutions of any composition. Therefore, a very important objective of the present invention is to avoid rack metallization and resulting metal losses in the subsequent metallisation stage.

Lithuanian patent application number LT 2008-082 also concerns the pretreatment of nonconductive plastic surfaces prior to metallisation. Disclosed is a pretreatment composition for etching e.g. polyimide for 1 - 2 minutes with a temperature of 10 – 80 °C, 0,005 - 0,2M oxidizing solution in sulfuric acid in a concentration of between 13 mol/L (about 75 vol.%) and 17 mol/L (about 90 vol.%), wherein the oxidizers can be KMnO_4 , HClO_4 , V_2O_5 , KClO_3 . In case of a chlorate (ClO_3^- , $M = 83.5 \text{ g/mol}$), this corresponds to a concentration of between 0.4 – 16.7 g/l.

An example is provided in this application in the Table 2 which contains 7 mol/L (about 50 vol.%) sulfuric acid and 0.2 mol/L (16.7 g/L) chlorate. it has been shown, however, that

such high chlorate at concentrations result in rapid decomposition of the pretreatment solution which is undesired.

Description of the invention

5 The present invention is therefore based on the problem that it has not been possible to date to achieve metallization of articles made from electrically nonconductive plastic in an environmentally safe manner with sufficient process reliability and adhesion strength of the metal layers applied subsequently.

10 It is therefore an object of the present invention to find etching solutions for pretreatment of electrically nonconductive plastic surfaces of articles, these being non-toxic but providing sufficient adhesion strength of the metal layers applied on the plastic surface.

This purpose is achieved by using an etching solution comprising 0.2 to 15.0 g/l of soluble chlorate (based on KClO_3 , $M = 122.55$, i.e. 0.0016 mol/l to 0.12 mol/l) in 50-80% v/v
15 sulfuric acid. for the etching of the plastic surface in the application as the method of treatment of the plastic surface prior to its electroless metallization consisting of the etching of the plastic by means of an inorganic acid solution with an oxidizer, activation by the palladium salt solution, and treatment by either reducing or accelerating solution. The etching preferably is performed at room temperature (15 – 28°C, preferred 20 – 25°C), but
20 can also be at higher temperatures of up to 40°C or 50°C provided the stability of the solution is controlled. The pretreatment solution can optionally contain up to 20 g/l of another oxidizer, with the standard oxidising potential exceeding that of the chlorate.

The etching time varies with the substrate material and its shape and can be determined by routine experiments. Generally, it varies between 1 and 20 minutes, preferred not
25 longer than 10 minutes.

The source of chlorate ions can be any any water soluble salt. Most commonly used are sodium and potassium chlorate.

The concentration of the chlorate ions in the etching solution ranges between 0.0016 mol/l and up to 0.12 mol/l, or preferably up to 0.03 mol/l or even more preferred up to 0.04
30 mol/l. Preferred ranges vary between 0.003 mol/l and 0.08 mol/l or between 0.01 mol/l and 0.06 mol/l or 0.004 mol/l and 0.04 mol/l.

The concentration of the sulfuric acid ranges between 50 and 80 vol.%, preferably between 55 and 70 vol.% and even more preferred between 60 and 65 vol.%.

Optionally phosphoric acid as an additional acid can be comprised in the etching solution. The concentration of the phosphoric acid typically ranges from 10 to 40 vol.%, preferably between 15 and 25 or 30 vol.%. When phosphoric acid is additionally be used, the adhesion of the plated metal layer can surprisingly additionally be increased.

- 5 A mixture of between 60 and 65 vol.% sulphuric acid and 20 and 30 vol.% phosphoric acid is particularly preferred.

The method of pretreatment of the plastics surface prior to their electroless metallization, comprising of the etching of the plastic in an inorganic acid solution with an added oxidizer, the activation in the palladium salt solution, and the treatment in either reducing
10 or accelerating solution, characterised in the etching of the plastic surface by the solution of 0.02 – 15.0 g/l soluble chlorate (e.g. 0.5 – 5 g/l soluble chlorate) in 50-80% v/v sulphuric acid at room temperature and in additional treatment, prior to the activation by means of the palladium compound solution and the treatment with a reducing/accelerating solution, in the alkali metal hydroxide solution.

- 15 The etching solution can optionally contain 2 to 20 g/l of additional oxidizer, with the standard oxidising potential exceeding that of the chlorate ions.

The alkali metal chlorate and sulfuric acid form a yellow compound, the normal oxidising potential of which in the H_2SO_4 solution medium is sufficient for the reaction with the plastic surface at room temperature. Due to this reaction, the plastic surface becomes
20 hydrophilic and adsorbs the palladium compounds with sufficient strength. The yellow colour product of the reaction between chlorate and the sulfuric acid is a poison for palladium catalyst. During etching, it penetrates the surface layers of the rack's plastisol insulation and prevents electroless metal deposition on plastisol in the electroless metallisation solutions; the metallization process taking place on thenonconductive plastic
25 surface is not affected.

Upon dissolution of 1 to 2 g/l of sodium or potassium chlorate plus 5 to 10 g/l of a second strong oxidizer, e. g., NaBiO_3 the etching properties are retained, at room temperature, for several days and the solution may be used without adjustments. In case if only sodium/potassium chlorate is contained in the solution, the etching properties remain for a
30 much shorter period (up to 24 hours).

An important distinctive feature of the proposed method that makes it different from the permanganate etching is that very high values of adhesion between the coating and the plastics are obtained, often exceeding 1.2 to 1.3 kg/cm). These values depend, in addition to the composition of the etching solution and the etching time (there is an optimal etching

time for each composition), on the composition of the activation solution. Normally, when the real activation solutions are used, the resulting adhesion values are higher than those obtained with the colloidal activation solutions.

The etching solution can be prepared as follows:

- 5 700 ml of concentrated sulfuric acid is mixed with 300 ml of deionised water. The solution is left to cool down. Then 2 g of potassium chlorate plus 10 g of sodium perchlorate are dissolved in the solution. The solution is ready for use. The second oxidising agent sodium perchlorate, which is stronger than potassium chloride, is optional. It enhances the life time of the composition, but is not required to obtain a good adhesion of the
- 10 subsequently plated metal layer.

When the quantity of water used for the preparation of the solution exceeds 50% by volume compared with the sulfuric acid, no yellow plastic-oxidising compound is formed between the chlorate ions and the sulfuric acid molecules, therefore, the water content of the solution preferably should not exceed 50% by volume.

- 15 When the quantity of water used for the preparation of the solution is less than 20% by volume compared with the sulfuric acid, the surface of plastics is decomposed during etching due to too high concentration of sulfuric acid, therefore, no adhesion between the chemical nickel coating and the plastic is obtained.

- If the quantity of potassium chlorate dissolved in the solution is smaller than 0.5 g/l, the
- 20 etching process takes longer than 15 min., therefore, such concentration is not acceptable.

- If the quantity of potassium chlorate dissolved in the solution exceeds 5.0 g/l, over-etching may be observed after the minimum etching period, i. e. 2 to 3 min., which results in a much weaker adhesion strength, due to which such high concentration of chlorate is not
- 25 acceptable either. However, depending on the substrate material, higher concentrations of up to 15 g/l may be acceptable resulting in sufficient adhesion.

The objective of the present invention is further achieved by the following process according to the invention:

- 30 Process for metallizing electrically nonconductive plastic surfaces of articles, comprising the process steps of:

- A) etching the plastic surface with an etching solution as described above
comprising a source of chlorate ions resulting in a concentration of 0.0016 to 0.12

mol/l of chlorate ions in 50-80% v/v sulfuric acid;

- B) treating the plastic surface with a solution of a metal colloid or of a compound of a metal, the metal being selected from the metals of transition group I of the Periodic Table of the Elements and transition group VIII of the Periodic Table of the Elements, and
- 5 C) metallizing the plastic surface with a metallizing solution;

Articles in the context of this invention are understood to mean articles which have been manufactured from at least one electrically nonconductive plastic or which have been covered with at least one layer of at least one electrically nonconductive plastic. The articles thus have surfaces of at least one electrically nonconductive plastic. Plastic surfaces are understood in the context of this invention to mean these said surfaces of the articles.

15 The process steps of the present invention are performed in the sequence specified, but not necessarily in immediate succession. It is possible for further process steps and additionally rinse steps in each case, preferably with water, to be performed between the steps.

20 The plastic surfaces have been manufactured from at least one electrically nonconductive plastic. In one embodiment of the present invention, the at least one electrically nonconductive plastic is selected from the group comprising an acrylonitrile-butadiene-styrene copolymer (ABS copolymer), a polyamide (PA), a polycarbonate (PC) and a mixture of an ABS copolymer with at least one further polymer.

25 In a preferred embodiment of the invention, the electrically nonconductive plastic is an ABS copolymer or a mixture of an ABS copolymer with at least one further polymer. The at least one further polymer is more preferably polycarbonate (PC), which means that particular preference is given to ABS/PC mixtures.

30 The inventive etching solution preferably does not contain any chromium or chromium compounds; the etching solution contains neither chromium(III) ions nor chromium(VI) ions. The inventive etching solution is thus free of chromium or chromium compounds; the etching solution is free of chromium(III) ions and chromium(VI) ions.

35 In a further preferred embodiment of the invention, the following further process step is performed between process steps A) and B):

A i) treating the plastic surface in a solution comprising an alkaline solution.

The further process step A i) is also referred to as neutralizing treatment. Any source of alkalinity can be used, an aqueous solution of sodium hydroxide is a preferred.

- 5 In a further alternative embodiment of the invention, the following further process step is performed between process steps A) and B):

A i) treating the plastic surface in a solution comprising a reducing agent for chlorate ions and optionally a second oxidizing agent.

- 10 The further process step A i) is also referred to as reduction treatment. This reduction treatment reduces chlorate ions and optionally a second oxidizing agent adhering to the plastic surfaces and facilitates removal of such ions. The reducing agent is for example selected from the group comprising hydroxylammonium sulphate, hydroxylammonium chloride and hydrogen peroxide.

15

The process of the present invention further comprises process step B), in which a plastic surface is treated with a solution of a metal colloid or of a compound of a metal.

The metal of the metal colloid or of the metal compound is selected from the group comprising the metals of transition group I of the Periodic Table of the Elements (PTE)

- 20 and transition group VIII of the PTE.

The metal of transition group VIII of the PTE is selected from the group comprising palladium, platinum, iridium, rhodium and a mixture of two or more of these metals. The metal of transition group I of the PTE is selected from the group comprising gold, silver

- 25 and a mixture of these metals.

A preferred metal in the metal colloid is palladium. The metal colloid is stabilized with the protective colloid. The protective colloid is selected from the group comprising metallic protective colloids, organic protective colloids and other protective colloids. As a metallic protective colloid, preference is given to tin ions. The organic protective colloid is selected from the group comprising polyvinyl alcohol, polyvinylpyrrolidone and gelatine, preferably polyvinyl alcohol.

- 30

In a preferred embodiment of the invention, the solution of the metal colloid in process step B) is an activator solution with a palladium/tin colloid. This colloid solution is obtained from a palladium salt, a tin(II) salt and an inorganic acid. A preferred palladium salt is

- 35

palladium chloride. A preferred tin(II) salt is tin(II) chloride. The inorganic acid may consist in hydrochloric acid or sulfuric acid, preferably hydrochloric acid. The colloid solution forms through reduction of the palladium chloride to palladium with the aid of the tin(II) chloride. The conversion of the palladium chloride to the colloid is complete; therefore, the colloid solution no longer contains any palladium chloride. The concentration of palladium is 5 mg/l – 100 mg/l, preferably 20 mg/l – 50 mg/l and more preferably 30 mg/l – 45 mg/l, based on Pd^{2+} . The concentration of tin(II) chloride is 0.5 g/l – 10 g/l, preferably 1 g/l – 5 g/l and more preferably 2 g/l – 4 g/l, based on Sn^{2+} . The concentration of hydrochloric acid is 100 ml/l – 300 ml/l (37% by weight of HCl). In addition, a palladium/tin colloid solution additionally comprises tin(IV) ions which form through oxidation of the tin(II) ions. The temperature of the colloid solution during process step B) is 20°C – 50°C and preferably 35°C – 45°C. The treatment time with the activator solution is 0.5 min – 10 min, preferably 2 min – 5 min and more preferably 3 min – 5 min.

In a further embodiment of the invention, in process step B), the solution of a compound of a metal is used in place of the metal colloid. The solution of a metal compound used is a solution comprising an acid and a metal salt. The metal in the metal salt consists in one or more of the above-listed metals of transition groups I and VIII of the PTE. The metal salt may be a palladium salt, preferably palladium chloride, palladium sulphate or palladium acetate, or a silver salt, preferably silver acetate. The acid is preferably hydrochloric acid. Alternatively, it is also possible to use a metal complex, for example a palladium complex salt, such as a salt of a palladium-aminopyridine complex. The metal compound in process step B) is present in a concentration of 40 mg/l to 80 mg/l, based on the metal. The solution of the metal compound can be employed at a temperature of 25°C to 70°C, preferably at 25°C. The treatment time with the solution of a metal compound is 0.5 min – 10 min, preferably 2 min – 6 min and more preferably 3 min – 5 min.

Between process steps A) and B), the following further process step can be performed:

A ii) treating the plastic surface in an aqueous acidic solution.

Preference is given to performing process step A ii) between process steps A i) and B). If, in the process according to the invention, process step A i) was followed by the protection of the racks, process step A ii) is more preferably performed between the protection of the racks and process step B).

The treatment of the plastic surfaces in process step A ii) is also referred to as preceding

dipping, and the aqueous acidic solution used as a preceding dipping solution. The preceding dipping solution has the same composition as the colloid solution in process step B), without the presence of the metal in the colloid and the protective colloid thereof. The preceding dipping solution, in the case of use of a palladium/tin colloid solution in process step B), comprises exclusively hydrochloric acid if the colloid solution likewise comprises hydrochloric acid. For preceding dipping, brief immersion into the preceding dipping solution at ambient temperature is sufficient. Without rinsing the plastic surfaces, they are treated further directly with the colloid solution of process step B) after the treatment in the preceding dipping solution.

10

Process step A ii) is preferably performed when process step B) involves the treatment of a plastic surface with a solution of a metal colloid. Process step A ii) can also be performed when process step B) involves the treatment of a plastic surface with a solution of a compound of a metal.

15

After the treatment of the plastic surfaces with the metal colloid or the metal compound in process step B), these can be rinsed.

In a further embodiment of the invention, the following further process steps are performed between process steps B) and C):

20

- B i) treating the plastic surface in an aqueous acidic solution and
- B ii) electrolessly metallizing the plastic surface in a metallizing solution.

The embodiment is shown schematically in Table 1.

Process step	Constituents	Time	Temperature
A) Etching	Table 2	4-6 min	22°C
A i) Neutralize	10 g/l NaOH	4 min	20°C
A ii) Preceding dipping	Hydrochloric acid, about 10% by wt.	1 min	20°C
B) Activation	Palladium/tin colloid in hydrochloric acid solution	3-6 min	20-45°C
B i) Acceleration	Sulfuric acid (5%)	2-6 min	40-50°C
B ii) Electroless metal deposition	Chemically reductive nickel-plating or copper-plating	6-20 min	30-50°C
C) Metal deposition	For example, electrochemical copper-plating or nickel-plating	15-70 min	20-35°C

Table 1: Embodiment of plastic metallization

25

These further process steps B i) and B ii) are employed when the articles are to be

metallized by an electroless metallization process, i.e. a first metal layer is to be applied to the plastic surfaces by an electroless process.

If the activation in process step B) has been performed with a metal colloid, the plastic surfaces are treated in process step B i) with an accelerator solution in order to remove constituents of the colloid in the colloid solution, for example a protective colloid, from the plastic surfaces. If the colloid in the colloid solution in process step B) is a palladium/tin colloid, the accelerator solution used is preferably an aqueous solution of an acid. The acid is selected, for example, from the group comprising sulfuric acid, hydrochloric acid, citric acid and tetrafluoroboric acid. In the case of a palladium/tin colloid, the accelerator solution helps to remove the tin compounds which served as the protective colloid.

Alternatively, in process step B i), a reductor treatment is performed when, in process step B), a solution of a metal compound has been used in place of a metal colloid for the activation. The reductor solution used for this purpose then comprises, if the solution of the metal compound was a hydrochloric acid solution of palladium chloride or an acidic solution of a silver salt, hydrochloric acid and tin(II) chloride. The reductor solution may also comprise another reducing agent, such as NaH_2PO_2 or else a borane or borohydride, such as an alkali metal borane or alkaline earth metal borane or dimethylaminoborane. Preference is given to using NaH_2PO_2 in the reductor solution.

After the acceleration or treatment with the reductor solution in process step B i), the plastic surfaces can first be rinsed.

Process step B i) and optionally one or more rinse steps are followed by process step B ii) in which the plastic surfaces are metallized electrolessly. Electroless nickel-plating is accomplished, for example, using a conventional nickel bath which comprises, inter alia, nickel sulphate, a hypophosphite, for example sodium hypophosphite, as a reducing agent, and also organic complexing agents and pH adjusters (for example a buffer). The reducing agent used may likewise be dimethylaminoborane or a mixture of hypophosphite and dimethylaminoborane.

Alternatively, it is possible to use an electroless copper bath for electroless copper-plating, the electroless copper bath typically comprising a copper salt, for example copper sulphate or copper hypophosphite, and also a reducing agent, such as formaldehyde or a hypophosphite salt, for example an alkali metal or ammonium salt, or hypophosphorous

acid, and additionally one or more complexing agents such as tartaric acid, and also a pH adjuster such as sodium hydroxide.

The surface thus rendered conductive can subsequently be electrolytically further metallized in order to obtain a functional or decorative surface.

Step C) of the process according to the invention is the metallization of the plastic surface with a metallization solution. The metallization in process step C) can be effected electrolytically. For electrolytic metallization, it is possible to use any desired metal deposition baths, for example for deposition of nickel, copper, silver, gold, tin, zinc, iron, lead or alloys thereof. Such deposition baths are familiar to those skilled in the art. A Watts nickel bath is typically used as a bright nickel bath, this comprising nickel sulphate, nickel chloride and boric acid, and also saccharine as an additive. An example of a composition used as a bright copper bath is one comprising copper sulphate, sulfuric acid, sodium chloride and organic sulphur compounds in which the sulphur is in a low oxidation state, for example organic sulphides or disulphides, as additives.

The effect of the metallization of the plastic surface in process step C) is that the plastic surface is coated with metal, the metal being selected from the above-listed metals for the deposition baths.

In a further embodiment of the invention, after process step C), the following further process step is performed:

C i) storage of the metallized plastic surface at elevated temperature.

As in all electroplating processes in which a nonconductor is coated by wet-chemical means with metal, the adhesion strength between metal and plastic substrate increases in the first period after the application of the metal layer. At room temperature, this process is complete after about three days. This can be accelerated considerably by storage at elevated temperature. The process is complete after about one hour at 80°C. It is assumed that the initially low adhesion strength is caused by a thin water layer which lies at the boundary between metal and nonconductive substrate and hinders the formation of electrostatic forces.

The process according to the invention thus enables, with good process reliability and excellent adhesion strength of the subsequently applied metal layers, achievement of

metallization of electrically nonconductive plastic surfaces of articles. The adhesion strength of the metal layers applied to plastic surfaces reaches values of up to 2.7 N/mm (corresponding approximately to 2.7 kg/cm, 1 kg/cm = 0.98 N/mm) or higher. Thus, the adhesion strengths achieved are also well above those obtainable according to the prior art after etching of plastic surfaces with chromosulfuric acid (see Examples 2 and 3).

In general, adhesion values of more than 0.8 N/mm are required for industrial applications and non-complex shaped objects are to be plated. In general, the higher the adhesion of the better the stability of the deposit is.

In addition, not just planar plastic surfaces are metallized with high adhesion strength by the process according to the invention; instead, inhomogeneously shaped plastic surfaces, for example shower heads, are also provided with a homogeneous and strongly adhered metal coating.

The treatment of the plastic surfaces by the process according to the invention is preferably performed in a conventional dipping process, by dipping the articles successively into solutions in vessels, in which the respective treatment takes place. In this case, the articles may be dipped into the solutions either fastened to racks or accommodated in drums. Fastening to racks is preferred. Alternatively, the articles can also be treated in what are called conveyor plants, by lying, for example, on trays and being conveyed continuously through the plants in horizontal direction.

Working examples

The working examples described hereinafter are intended to illustrate the invention in detail.

Example 1

- 5 ABS (acrylonitrile-butadiene-styrene copolymer) and PC/ABS (a mixture of 45% of polycarbonate and 55% of acrylonitrile butadiene styrene copolymer) are etched, according to the US Patent Application No. 2005/0199587 A1: in a 45% v/v phosphoric acid solution containing 50 g/l KMnO_4 at 37°C during 5 min. (for ABS) or 15 min. (for PC/ABS), or in a 50 to 80% v/v sulphuric acid solution with a 0.5 to 5.0 g/l KClO_3 and
- 10 added oxidizer at 20°C during 1 to 12 min. Upon etching, the plastics are immersed for 1 to 2 min. in a neutralizing solution of room temperature containing 10 g/l NaOH, followed by the activation in the real (5 min. at 20°C) or colloidal (2 min. at 35°C) solution of palladium compounds (colloidal solution is proprietary solution of The DOW Chemical Company ("DOW")). The PdCl_2 concentration in the real solution is 0.1 g/l, the solution pH
- 15 is 2.7. Upon activation in the real Pd solution the plastics are held during 5 min. in a solution containing 20 g/l of sodium hypophosphite, pH 9, at 60°C. Upon activation in the proprietary colloidal solution, the plastics are treated, during 2 min. at 40°C, with DOW'S proprietary accelerating solution. Thereafter the plastics are nickel-plated using DOW's Niposit-PM nickel-plating process. The coating quality is evaluated based on factors such
- 20 as the plastic surface plated completely/non-completely, the plastisol insulated rack plated or not plated and the adhesion strength of electroless nickel with plastic. To evaluate the adhesion, the Ni plating is thickened in a galvanic copper bath and the strength necessary to peel a 1 cm wide strip off the plastic is measured (kg/cm). For ABS test pieces, the etching time in the permanganate solution was 5 min., for the PC/ABS test pieces 15 min.
- 25 The time of etching in the chlorate solution was 5 min. for all the pieces. The conditions of the plastics pretreatment for the metallization and the results of the metallization (electroless nickel-plating) are presented in the Table 2 below.

30 Table 2

Test piece	Plastic	Acid and its concentration in etching	Main oxidizer in the etcher and its	Complete (+) / incomplete	Partial coating (+) / or no	Adhesion values obtained,
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No		solution, % v/v	concentration, g/l	(-) coating on plastic	coating (-) of rack's plastisol insulation	kg/cm
1	ABS	H ₃ PO ₄ 45	KMnO ₄ 50	+	+	0.5 – 0.7
2	ABS	H ₂ SO ₄ 70	KClO ₃ 2	+	-	1.0 – 1.3
3*	ABS	H ₃ PO ₄ 45	KMnO ₄ 50	+	+	0.2 – 0.3
4*	ABS	H ₂ SO ₄ 70	KClO ₃ 2	+	-	0.8 – 1.0
5	PC/ABS	H ₃ PO ₄ 45	KMnO ₄ 50	-	+	-
6	PC/ABS	H ₂ SO ₄ 70	KClO ₃ 2	+	-	0.7 – 0.9
7*	PC/ABS	H ₃ PO ₄ 45	KMnO ₄ 50	+	+	0.1 – 0.3
8*	PC/ABS	H ₂ SO ₄ 70	KClO ₃ 2	+	-	0.5 – 0.7
9	ABS	H ₂ SO ₄ 70	KClO ₃ 0.2	-	-	-
10	ABS	H ₂ SO ₄ 70	KClO ₃ 8	+	-	0.1- 0.3
11	PC/ABS	H ₂ SO ₄ 70	KClO ₃ 0.3	-	-	-
12	PC/ABS	H ₂ SO ₄ 70	KClO ₃ 10	+	-	0-0.2
13	ABS	H ₂ SO ₄ 45	KClO ₃ 2	-	-	-
14	ABS	H ₂ SO ₄ 85	KClO ₃ 2	+	-	0-0.2

* Activation in the proprietary DOW's colloidal solution (the remaining ones activated in the ionic activating solution).

Test Pieces 1 to 4 show that, in the case of permanganate-based etching, the rack's
5 plastisol insulation is partially coated with electroless nickel, whereas in the case of
chlorate-based etching the insulation remains clean. Furthermore, the values of adhesion

between the Ni coating and ABS are considerably higher in the case of the chlorate etching for both ionic and colloidal activating solutions.

Same results are observed in the case of the electroless nickel-plating of PC/ABS (Test Pieces 5 to 8): in the chlorate etching process, the plastisol insulation is not coated at all and the adhesion values are considerably higher, in particular when the ionic activating solution is used.

When the KClO_3 concentration in the etching solution is under 0.5 g/l, ABS is either not coated with electroless nickel or is coated incompletely (Test Piece 9). When the KClO_3 concentration is over 5 g/l (Test Piece 10), over-etching occurs after 5 min. of etching, therefore, the coating adhesion value is considerably lower (insufficient for practical applications). When the recommended KClO_3 concentration values are exceeded, analogous results are obtained for PC/ABS metallization as well (Test Pieces 11 and 12).

In the case when the H_2SO_4 concentration in the etching solution is lower than 50% v/v, the etching agent is not effective enough, therefore, the plastic is either not coated by electroless nickel at all or is coated incompletely (Test Piece 13). When the H_2SO_4 concentration is higher than 80% v/v (Test Piece 14), over-etching of the plastic occurs and the adhesion between the chemical nickel coating and the plastic is insufficient.

20 Example 2

A disc of ABS plastic (Novodur P2MC, from Ineos) round shape substrate having a diameter of 7 cm was fastened to a stainless steel wire. The substrate was then dipped in various pretreatment etching solutions according to the invention as specified in the Table 4 for 4 minutes at a temperature of 22°C (process sequence is shown in Table 3). Subsequently, the substrate was rinsed under running water for about one minute. After subsequent rinsing, neutralization (process step A i)) and brief dipping into a solution of 300 ml/l 36% hydrochloric acid (process step A ii)), the substrate was activated in a colloidal activator based on a palladium colloid (Adhemax Aktivator NA from Atotech, 100 ppm of palladium) at 40°C for three minutes (process step B)). After subsequent rinsing, the protective shells of the palladium particles were removed at 40°C for three minutes (Adhemax ACC1 accelerator from Atotech, process step B i)). The substrate was subsequently nickel-plated at 45°C without external current for ten minutes (Adhemax LFS, from Atotech, process step B ii)), rinsed and copper-plated at 3.5 A/dm² at room temperature for 70 minutes (Cupracid HT, from Atotech, process step C)). After

rinsing, the panel was stored at 70°C for 60 minutes (process step C i)). Subsequently, a knife was used to cut out a strip of the metallized plastic substrate of width about 1 cm, and a tensile tester (from Instron) was used to pull the metal layer away from the plastic (ASTM B 533 1985 Reapproved 2009). Adhesion strengths as shown in Table 4 were

5 obtained.

Table 3: Sequence of process steps in Example 2

Process step	Chemistry	Time	Temperature
A) Etching	Table 4	4 min	22°C
A i) Neutralization	10 g/l NaOH	4 min	20°C
A ii) Preceding dipping	hydrochloric acid, 10% by weight	1 min	20°C
B) Activation	palladium colloid, 100 ppm of palladium Adhemax Activator PL, from Atotech	3 min	40°C
B i) Acceleration	sulfuric acid 5%	3 min	40°C
B ii) Electroless metal deposition	Chemically reductive nickel-plating, Adhemax LFS, from Atotech	10 min	45°C
C) Electrolytic metal deposition	Electrochemical copper-plating, Cupracid HT, from Atotech, 3.5 A/dm ²	70 min	21°C
C i) Storage	---	60 min	70°C

Table 4: Adhesion strengths of a copper/nickel layer on various ABS mixtures of a

10 according to Example 2

Test piece No	Plastic	Acid and its concentration in etching solution, % v/v	Main oxidizer in the etcher and its concentration, g/l	Some of you Adhesion values obtained, N/mm
1	ABS	H ₂ SO ₄ 70	KClO ₃ 0,2	0,85
2	ABS	H ₂ SO ₄ 70	KClO ₃ 0,5	1,50
3	ABS	H ₂ SO ₄ 70	KClO ₃ 1,0	1,66

4	ABS	H ₂ SO ₄ 70	KClO ₃ 1,5	1,84
5	ABS	H ₂ SO ₄ 70	KClO ₃ 2,0	1,28
6	ABS	H ₂ SO ₄ 70	KClO ₃ 3,0	1,43
7	ABS	H ₂ SO ₄ 70	KClO ₃ 5,0	1,25
8	ABS	H ₂ SO ₄ 70	KClO ₃ 7,0	0,89
9	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 0,2	1,0
10	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 0,5	1,8
11	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 1,0	1,8
12	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 1,5	2,7
13	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 2,0	1,9
14	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 3,0	1,7
15	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 5,0	1,6
16	ABS	H ₂ SO ₄ 60 H ₃ PO ₄ 25	KClO ₃ 7,0	1,5

From Table 4 it becomes apparent that by the careful selection of the concentration of chlorate in combination with sulfuric acid very high adhesion values they can be obtained.

Test piece number one shows that as lower concentrations as 0.2 g/l of the potassium chlorate (corresponding to a ClO_3^- concentration of 0.0016 mol/l) are sufficient to obtain a good adhesion. Maximum values are obtained in a range of about 1.5 g/l of potassium chlorate. Thereafter, a decline in adhesion strength can be observed. It is noted that

5 compositions comprising a mixture of sulfuric acid and phosphoric acid (Table 4, the pieces of Nos. 9 to 16 generally show higher adhesion values in at the same chlorate ion concentration when compared to etching in solutions containing sulfuric acid only and are thus particularly preferred.

Claims

1. Process for metallizing electrically nonconductive plastic surfaces of articles, comprising the process steps of:
 - A) etching the plastic surface with an aqueous etching solution;
 - B) treating the plastic surface with a solution of a metal colloid or of a compound of a metal, the metal being selected from the group consisting of the metals of transition group I of the Periodic Table of the Elements and transition group VIII of the Periodic Table of the Elements, and
 - C) metallizing the plastic surface with a metallizing solution;characterized in that the etching solution comprises a source of chlorate ions resulting in a concentration of 0.0016 to 0.12 mol/l of chlorate ions and 50-80% v/v sulfuric acid and wherein the etching solution is free of chromium III ions and chromium VI ions.
2. Process according to claim 1, characterized in that the source for chlorate ions in the etching solution in process step A) is selected from the group consisting of sodium and potassium chlorate.
3. Process according to claim 1 or 2, characterized in that the chlorate ion concentration ranges between 0.003 and 0.08 mol/l.
4. Process according to claim 1 or 2, characterized in that the chlorate ion concentration ranges between 0.01 and 0.06 mol/l.
5. Process according to claim 1 or 2, characterized in that the chlorate ion concentration ranges between 0.004 and 0.04 mol/l.
6. Process according to any one of claims 1-5, characterized in that the sulfuric acid ion concentration ranges between 60 and 70 vol.%.
7. Process according to any one of claims 1-6, characterized in that the etching solution further comprises an oxidizing agent in an amount of 2 to 20 g/l with the standard oxidising potential exceeding that of chlorate ions.
8. Process according to any one of claims 1-7, characterized in that the etching solution further comprises phosphoric acid.

9. Process according to claim 8, characterized in that the phosphoric acid concentration ranges between 10 and 30 vol.%.
10. Process according to any one of claims 1-9, characterized in that metal in process step B) is palladium.
11. Process according to any one of claims 1-10, characterized in that the plastic surface has been manufactured from at least one electrically nonconductive plastic and the at least one electrically nonconductive plastic is selected from the group consisting of an acrylonitrile-butadiene-styrene copolymer, a polyamide, a polycarbonate and a mixture of an acrylonitrile-butadiene-styrene copolymer with at least one further polymer.
12. Process according to any one of claims 1-11, characterized in that the following further process step is performed between process steps A) and B):
 - A i) treating the plastic surface in a solution comprising a reducing agent for chlorate ions.
13. Process according to claim 12, characterized in that the reducing agent is selected from the group consisting of hydroxylammonium sulphate, hydroxylammonium chloride and hydrogen peroxide.
14. Process according to any one of claims 1-13, characterized in that the following further process step is performed between process steps A) and B):
 - A i) treating the plastic surface in a solution comprising a neutralizing agent comprising a source of hydroxide ions.
15. Process according to any one of claims 1-14, characterized in that the following further process steps are performed between process steps B) and C):
 - B i) treating the plastic surface in an aqueous acidic solution and
 - B ii) electrolessly metallizing the plastic surface in a metallizing solution.