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(54) **Title**: SURFACE METALLIZING METHOD, METHOD FOR PREPARING PLASTIC ARTICLE AND PLASTIC ARTICLE MADE THEREFROM

(57) **Abstract**: Disclosed is a method for metallizing a plastic surface. The method may comprise the steps: 1) gasifying the plastic surface to expose the electroless plating promoter; and 2) electroless plating a layer of copper or nickel on the plastic surface, followed by electroplating or a second electroless plating to form a metallized layer on the plastic surface. Further, disclosed are a method for preparing a plastic article and a plastic article as manufactured by the method as described.

SURFACE METALLIZING METHOD, METHOD FOR PREPARING PLASTIC ARTICLE AND PLASTIC ARTICLE MADE THEREFROM

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priorities to the following applications:

1) Chinese Patent Application No. 200910261216.2, filed to the State Intellectual Property Office, P. R. China on December 17, 2009; and
2) Chinese Patent Application No. 200910238957.9, filed to the State Intellectual Property Office, P. R. China on December 30, 2009,

The above enumerated patent applications are incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

The present invention relates to surface treatment, more particularly to surface metallization on non-metal material such as plastic.

BACKGROUND OF THE INVENTION

Plastics having metallized layer on their surface as pathways of electromagnetic signal conduction are widely used in automotive, industrial, computer, telecommunications and other fields. Selectively forming a metallized layer is one of important processes for preparing such plastic products. The method for forming a metallized layer in prior art is usually normally practiced by forming a metal core as a catalytic center on the plastic support surface so that electroless plating may be performed. However, processes related thereto are complex where strict demand on equipment is needed whereas the energy consumption is high. Further, there is a low adhesive force between the coating and the plastic support.

SUMMARY OF THE INVENTION

In view of the foregoing, there remains an opportunity to provide a method for metallizing a plastic surface, in which the plastic metallization is easily performed with lower energy consumption. Further, there remains an opportunity to provide a method for preparing a plastic article and a plastic article made therefrom, in which the adhesive force between the coating layer and the plastic or non-metal support is enhanced.

According to an embodiment of the invention, a method for metallizing a plastic surface may be provided. The plastic may comprise a supporting material and an electroless plating promoter, the method comprising the steps of: 1) gasifying the plastic surface to expose the electroless plating promoter; and 2) electroless plating a layer of copper or nickel on the plastic surface, followed by electroplating or a second electroless plating to form a metallized layer on the plastic surface.

According to an embodiment of the invention, the electroless plating promoter includes one or more members selected from a group consisting of: (a) oxides of the metal elements selected from Co, Ni, Ag; (b) silicate, borate or oxalate of metal elements selected from Co, Ni, Cu; (c) hydrogenation catalysts having one or more metal elements selected from Co, Ni, Cu, Ag; or (d) ABO_2 type composite oxides having a delafossite structure, in which A is one of metal elements selected from Co, Ni, Cu, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe where A, B are different; and (e) multicomponent oxides selected from a group consisting of Cu/Fe/Mn, Cu/Fe/Al and/or Cu/Fe/Al/Mn multicomponent oxides.

According to another embodiment of the invention, a method for preparing a plastic article may be provided. The method may comprise the steps of: 1) forming at least a part of the plastic article with a support comprising a supporting material and an electroless plating promoter; 2) gasifying a surface of the support to expose the electroless plating promoter; and 3) electroless plating a layer of copper or nickel on the surface followed by electroplating or electroless plating at least one time, to form a metallized layer on the surface.

According to still another embodiment of the invention, a plastic article made by the method as described above may be provided.

As found by the inventors, the surface containing the electroless plating promoter may be directly performed with electroless plating, and the plastic will not be degradated. According to an embodiment of the invention, the electroless plating promoter may be at least one selected from a grouping consisting of Ni_2O_3, Co_2O_3, CoO, Co_3O_4, $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CoC_2O_4, CuC_2O_4, $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$, $MFeO_2$, $CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$ and $CuFe_aAl_bMn_cO_d$, in which M is selected from Cu, Ni or Co; $0.01\leq x\leq 2$, $0.01\leq y\leq 2$, $2\leq z\leq 4$; $0.01\leq e\leq 2$, $0.01\leq f\leq 2$, $2\leq g\leq 4$; and $0.01\leq a\leq 2$, $0.01\leq b\leq 2$, $0.01\leq c\leq 2$, $2\leq d\leq 4$.

In the method for preparing a plastic article, the electroless plating promoter may be distributed evenly in the plastic support, a predetermined area on the surface of the plastic support may be gasified by, for example, laser to expose the electroless plating promoter so that the electroless plating promoter may be reduced into pure metal without high energy consumption. And further electroplating or electroless plating may be performed to form the desired metallized layer, thus achieving the selective surface metallization with simple process, lower energy consumption and reduced cost.

In addition, the electroless plating promoter may be evenly distributed in the plastic support, so that the adhesive force between the coating layer and the plastic support after electroless plating is high, thus improving the quality of the plastic article manufactured.

Other variations, embodiments and features of the presently disclosed permanent magnetic materials will become evident from the following detailed description, drawings and claims.

DETAILED DESCRIPTION OF THE EMBODIMENTS OF THE INVENTION

It will be appreciated by those of ordinary skill in the art that the present disclosure can be embodied in other specific forms without departing from the spirit or essential character thereof. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive.

In the following, a method for metallizing a plastic surface may be provided. The plastic may comprise a supporting material and an electroless plating promoter. According to an embodiment of the invention, the method may comprise steps of: 1) gasifying the plastic surface to expose the electroless plating promoter; and 2) electroless plating a layer of copper or nickel on the plastic surface, followed by electroplating or a second electroless plating to form a metallized layer on the plastic surface. According to an embodiment of the present invention, the plastic surface may be gasified by laser to expose the electroless plating promoter. And the laser may have a wavelength ranging from about 157 nm to about 10.6 um with a scanning speed from about 500 to about 8000 mm/s, a scanning step size from about 3 to about 9um, a scan time delay from about 30 to 100us, a laser power from about 3 to 4 W, a frequency from about 30 to 40 KHz and a filled distance from about 10 to 50um.

The electroless plating promoter may be a particle with an average diameter of not greater than 100 microns. According to an embodiment of the present invention, the

average diameter of the electroless plating promoter may range from about 20 nanometers to about 100 microns.

According to an embodiment of the invention, the electroless plating promoter may include one or more members selected from a group consisting of: (a) oxides of the metal elements selected from Co, Ni, Ag; (b) silicate, borate or oxalate of metal elements selected from Co, Ni, Cu; (c) hydrogenation catalysts having one or more metal elements selected from Co, Ni, Cu, Ag; or (d) ABO_2 type composite oxides having a delafossite structure, in which A is one of metal elements selected from Co, Ni, Cu, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe where A, B are different; and (e) multicomponent oxides selected from a group consisting of Cu/Fe/Mn, Cu/Fe/Al and/or Cu/Fe/Al/Mn multicomponent oxides.

Preferably, the electroless plating promoter may include one or more members selected from a group consisting of (a) Ni_2O_3, Co_2O_3, Co_3O_4; (b) $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CoC_2O_4, CoC_2O_4; (c) hydrogenation catalysts of Cu-Zn, Cu-Zn-Ni, Cu-Zn-Co, Cu-Zn-Ga, Co-La, Cu-Cd and Cu-Zn-Si; and (d) $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$, $MFeO_2$ in which M is Cu, Ni or Co. And the multicomponent oxides has the following formulas respectively: $CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$ and $CuFe_aAl_bMn_cO_d$, in which x, y, z, e, f, g, a, b, c, and d satisfy: $0.01\leq x\leq 2$, $0.01\leq y\leq 2$, $2\leq z\leq 4$; $0.01\leq e\leq 2$, $0.01\leq f\leq 2$, $2\leq g\leq 4$; and $0.01\leq a\leq 2$, $0.01\leq b\leq 2$, $0.01\leq c\leq 2$, $2\leq d\leq 4$.

The supporting material may be a thermoplastic or thermosetting resin, and the thermoplastic may include one or more members selected from a group consisting of polyolefin, polycarbonate, polyester, polyamide, polyaromatic ether, polyester-imide, polycarbonate/acrylonitrile-butadiene-styrene composite, polyphenylene oxide, polyphenylene sulfide, polyimide, polysulfone, poly (ether ether ketone), polybenzimidazole and liquid crystalline polymer; the thermosetting resin may include one or more members selected from a group consisting of phenolic resin, urea-formaldehyde resin, melamine-formaldehyde resin, epoxy resin, alkyd resin and polyurethane.

In the surface metallizing method as described above, because the surface of the plastic support may be gasified by, for example, laser to expose the electroless plating promoter, the electroless plating promoter may be reduced into pure metal without high energy consumption. And the adhesive force between the coating layer and the plastic support after electroless plating is very high, thus improving the process of selective surface metallization.

However, it should be noted, the method for metallizing a plastic surface may be used for manufacturing plastic article, such as a shell of an electrical device, for example, a mobile phone, a laptop computer, a shell of an refrigerator, a lamp stand, a plastic container etc., where selective surface metallizing may be desired. And in the following, a method for preparing a plastic article will be described in detail.

According to an embodiment of the invention, the method for preparing a plastic article may comprise the steps of: 1) forming at least a part of the plastic article with a support comprising a supporting material and an electroless plating promoter; 2) gasifying a surface of the support to expose the electroless plating promoter; and 3) electroless plating a layer of copper or nickel on the surface followed by electroplating or electroless plating at least one time, to form a metallized layer on the surface.

According to an embodiment of the invention, the electroless plating promoter may include one or more members selected from a group consisting of: oxide of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements except Cu, such as Co, Ni, Ag; silicate, borate or oxalate of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements, such as Co, Ni, Cu; hydrogenation catalysts having one or more metal elements selected from ninth, tenth, eleventh columns of the Periodic Table of Elements, which hydrogenate aldehyde, ketone, fatty acid or fatty acid ester containing carboxyl into alcohol; composite oxide having a delafossite structure of ABO_2; and Cu/Fe/Mn, Cu/Fe/Al or Cu/Fe/Al/Mn co-fired oxides. A, B may be different elements, and A may be one of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements, such as Co, Ni, Cu. And B may be an element selected from a group consisting of Ni, Mn, Cr, Al and Fe.

According to an embodiment of the invention, the oxide of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements except Cu may include those of Co, Rh, Ir, Ni, Pd, Pt, Ag and Au. According to an embodiment of the present invention, the oxides may be those of the metal elements selected from Co, Ni, Ag based on catalyzing. And preferably, those oxides of Ni or Co may be used, such as Ni_2O_3, Co_2O_3 and Co_3O_4.

According to an embodiment of the invention, the silicate, borate or oxalate of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements may include those of Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au. According to an embodiment of the present invention, the silicate, borate or oxalate may be those of the metal elements

selected from Co, Ni and Cu. In some instances, it may include $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CuC_2O_4 and CoC_2O_4.

According to an embodiment of the invention, the hydrogenation catalysts may promote the reduction of hydrogenation of carbonyl compounds including aldehyde, ketone, fatty acid, or fatty acid ester to alcohols. In some instances, it may include at least one member selected from a group consisting of Cu-Zn hydrogenation catalysts, Cu-Zn-Ni hydrogenation catalysts, Cu-Zn-Co hydrogenation catalysts, Cu-Zn-Ga hydrogenation catalysts, Co-La hydrogenation catalysts, Cu-Cd hydrogenation catalysts and Cu-Zn-Si hydrogenation catalysts.

According to an embodiment of the invention, element A of the composite oxide ABO_2 may be selected from Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au. Ni, Pd, Pt, Cu, Ag or Au is preferable in view of catalyzing, and Ni, Cu or Co is more preferable. Element B may be Ni, Mn, Cr, Al or Fe where A and B are different. According to an embodiment of the invention, the composite oxide ABO_2 without Cr is preferable in view of pollution to the environment. More specifically, the composite oxide ABO_2 may include $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$ or $MFeO_2$, where M may be selected from Cu, Ni or Co.

According to an embodiment of the invention, the Cu/Fe/Mn multicomponent or co-fired oxide may have general formulas of $CuFe_xMn_yO_z$, where $0.01\leq x\leq 2$, $0.01\leq y\leq 2$, $2\leq z\leq 4$; the Cu/Fe/Al co-fired oxide may have general formulas of $CuFe_eAl_fO_g$, where $0.01\leq e\leq 2$, $0.01\leq f\leq 2$, $2\leq g\leq 4$; and the Cu/Fe/Al/Mn co-fired oxide may have general formulas of $CuFe_aAl_bMn_cO_d$ in which $0.01\leq a\leq 2$, $0.01\leq b\leq 2$, $0.01\leq c\leq 2$, $2\leq d\leq 4$.

Research shows that, in addition to pure Cu and Pd as nucleus or grain for electroless plating, nano-CuO can promote the speed of chemical deposition of electroless plating on plastic surface. However, nano-CuO may also cause the degradation of the plastic. Through many experiments, the inventors have found that one or more electroless plating promoters selected from Ni_2O_3, Co_2O_3, CoO, $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CoC_2O_4, CuC_2O_4, $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$, $MFeO_2$, $CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$, $CuFe_aAl_bMn_cO_d$ may be used for surface treatment, and these material may be remained in the plastic without causing plastic degradation.

According to an embodiment of the invention, the electroless plating promoter in step 1) may include one or more members selected from a group consisting of Ni_2O_3, Co_2O_3, CoO, $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CoC_2O_4, CuC_2O_4, $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$, $MFeO_2$, $CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$ and $CuFe_aAl_bMn_cO_d$, M

may be selected from Cu, Ni or Co; $0.01 \leq x \leq 2$, $0.01 \leq y \leq 2$, $2 \leq z \leq 4$; $0.01 \leq e \leq 2$, $0.01 \leq f \leq 2$, $2 \leq g \leq 4$; and $0.01 \leq a \leq 2$, $0.01 \leq b \leq 2$, $0.01 \leq c \leq 2$, $2 \leq d \leq 4$. Such electroless plating promoters can promote the chemical deposition of electroless plating on their surface without causing the degradation of the plastic while remained in the support for a long time.

According to the method for preparing a plastic article of the present invention, a support may be firstly provided, comprising a supporting material and an electroless plating promoter. The electroless plating promoter may be evenly distributed in the supporting material.

According to an embodiment of the invention, the average particle diameter of the electroless plating promoter may be not greater than 100 microns. In other embodiments, the average particle diameter of the electroless plating promoter may range from about 20 nanometers to about 10 microns. Most of the electroless plating promoters can be commercially obtained. And the composite oxide ABO_2 and co-fired oxides may be prepared by following steps: providing corresponding oxides as mentioned above; After ball milling and mixing, sintering a mixture thereof in a vacuum furnace under a temperature ranging from about 700 to 1500 ℃; and ball-milling the mixture to the desired particles.

According to an embodiment of the invention, the supporting material may be thermoplastic or thermosetting resin. The thermoplastic may include one or more members selected from a group consisting of polyolefin, polycarbonate (PC), polyester, polyamide, polyaromatic ether, polyester-imide, polycarbonate/acrylonitrile-butadiene-styrene composite (PC/ABS), polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyimide (PI), polysulfone (PSU), poly (ether ether ketone) (PEEK), polybenzimidazole (PBI) and liquid crystalline polymer (LCP); wherein the polyolefin may be polystyrene (PS), polypropylene (PP), polymethyl methacrylate(PMMA) or acrylonitrile-butadiene-styrene (ABS); the polyester may be polycyclohexylene dimethylene terephthalate (PCT), poly(diallyl isophthalate) (PDAIP), poly(diallyl terephthalate) (PDAP), polybutylene naphthalate (PBN), Poly(ethylene terephthalate) (PET), or polybutylene terephthalate (PBT); the polyamide may be polyhexamethylene adipamide (PA-66), Nylon 69 (PA-69), Nylon 64 (PA-64), Nylon 612 (PA-612), polyhexamephylene sebacamide (PA-610), Nylon 1010 (PA-1010), Nylon 11 (PA-11), Nylon 12 (PA-12), Nylon 8 (PA-8), Nylon 9 (PA-9), polycaprolactam (PA-6), poly(p-phenytene terephthalamide) (PPTA), poly-meta-xylylene adipamide (MXD6), polyhexamethylene terephthalamide (PA6T), and Nylon 9T (PA9T); the thermosetting resin may include one or more members selected from a group consisting of

phenolic resin, urea-formaldehyde resin, melamine-formaldehyde resin, epoxy resin, alkyd resin and polyurethane.

According to an embodiment of the invention, the support may be formed by any method known in the art:

Firstly, the supporting material and the electroless plating promoter may be mixed by , for example, internal mixer, single screw extruder, twin screw extruder, or mixer; and

Then the mixture may be processed by injection molding, blow molding, pressing or hot-pressing to form a support with a desired shape.

As known in the art, CuC_2O_4 may be unstable under high temperature and may cause the degradation of the support, and the forming temperature of the support may be not greater than 300 ℃ generally. The temperature may ensure the CuC_2O_4 not decomposed when the support comprises the electroless plating promoter of CuC_2O_4.

According to an embodiment of the invention, the amount of electroless plating promoter may be ranged from about 1 % to about 40 % of the support by weight. In other embodiments, the amount of electroless plating promoter may be ranged from about 2 % to about 30 % of the support by weight.

According to an embodiment of the invention, the support may further comprise at least one member selected from antioxidant, light stabilizer, lubricant and inorganic filler. The antioxidant, light stabilizer, lubricant and inorganic filler may be bought in market, and may be mixed with the supporting material and the electroless plating promoter to form the support.

According to an embodiment of the invention, the antioxidant may be about 0.01 % to about 2 % of the support by weight; the light stabilizer may be about 0.01 % to about 2 % of the support by weight; the lubricant may be about 0.01 % to about 2 % of the support by weight; and the inorganic filler may be about 1 % to about 70 % of the support by weight.

The antioxidant may enhance the oxidation resistance of the support and the light stabilizer may enhance the light stability of the support.

The lubricant may enhance fluidity of the plastic so that the plastic support may be evenly mixed. It may include one or more members selected from a group consisting of methylpolysiloxane, ethylene/vinyl acetate wax (EVA wax), polyethylene wax and stearate.

The inorganic filler may be talcum powder, calcium carbonate, glass fiber, calcium silicate fiber, tin oxide or carbon black. The glass fiber may increase the etched depth of the support while gasifying by laser which is favorable for the adhesion of the Cu during

electroless plating of Cu. And the tin oxide or carbon black may enhance the energy efficiency of the laser. In some instance, the inorganic filler may further be glass bead, calcium sulfate, barium sulfate, titanium dioxide, pearl powder, wollastonite, diatomite, kaolin, coal powder, argil, mica, oil shale ash, aluminum silicate, alumina, carbon fiber, silicon dioxide or zinc oxide. The inorganic filler may preferably that not containing Cr, which is amicable to environment and human body.

According to an embodiment of the invention, the electroless plating promoter may be evenly distributed in the supporting material, the adhesive force between the electroless plating promoter and the supporting material is very high so that the following electroless plating may be achieved on the surface of the electroless plating promoter directly. As a result, the adhesive force between the formed coating and the support is increased tremendously.

The laser-gasifying may be achieved on the surface of the plastic article where the part is made of plastic to expose the electroless plating promoter. According to an embodiment of the invention, the desired pattern may be formed on the surface of the support by the method of the present invention. The laser equipment may be infrared laser, CO_2 laser marking system for example, the conditions of laser-gasifying may include that the wavelength of the laser may be about 157nm to about 10.6um, scanning speed may be from about 500 to about 8000 mm/s, scanning step size may be about 3 to about 9um, scan time delay may be about 30 to 100us, laser power may be about 3 to 4 W, the frequency may be from about 30 to 40 KHz, and the filled distance may be about 10 to 50um. The energy demand of the present disclosure may be low, it just need to gasify the surface of the support to expose the electroless plating promoter, without reducing the support to the metal core.

According to an embodiment of the invention, the thickness of the support may be greater than about 500um, and the etched depth of the support may be about 1 to about 20um, the electroless plating promoter may be exposed to form a microscopic and coarse surface on which the followed electroless plating may be performed.

The gasifying of plastic support may cause plastic smoke, which may drop down and cover the exposed electroless plating promoter. According to an embodiment of the invention, a ventilating unit may be used during laser-gasifying for exhausting the smoke. Additionally, the support may be performed with ultrasonic cleaning after laser-gasifying.

According to an embodiment of the invention, electroless plating a copper or nickel layer may be performed on the exposed electroless plating promoter, and then electroplating or electroless plating again to form a metallized layer area on the support. The electroless plating method may be those normally practiced in the art. For example, the support may be immersed into an electroless plating bath.

After contacting with the chemical-copper solution or chemical-nickel solution in the electroless plating bath, the exposed electroless plating promoter may promote the Cu ion and Ni ion to undertake reduction to form pure Cu or Ni particles which envelop the surface of the electroless plating promoter so that a compact or dense first plating layer may be formed on the laser-gasified area.

To increase the surface decoration, applicability and corrosion resistance, one or more plating layers may be formed on the first plating layer to obtain the final metallizating layer.

In one embodiment, the first plating layer may be nickel layer, a second electroless plating may be performed on the nickel layer to form a second copper layer, and then a third electroless plating may be performed on the second layer to form a third nickel layer, as the result, the metallized layer may be Ni-Cu-Ni from inside the plastic article to outside thereof. In another embodiment, an Au layer may be strike plated on the Ni-Cu-Ni layer to obtain a metallized layer of Ni-Cu-Ni-Au.

In another embodiment, the first plating layer may be copper layer, a second electroplating may be performed on the copper layer to form a second nickel layer, as the result, the metallized layer may be Cu-Ni from inside the plastic article to outside thereof. In yet another embodiment, an Au layer may be strike plated on the Cu-Ni layer to obtain a metallized layer of Cu-Ni-Au.

In the Ni-Cu-Ni, Ni-Cu-Ni-Au, Cu-Ni or Cu-Ni-Au layers, the thickness of the Ni layer may be about 0.1 to about 10um; the thickness of the Cu layer may be about 0.1 to about 100um; and the thickness of the Au layer may be about 0.01 to about 10um.

The electroless plating solution and the electroplating solution may be that known in the art or may be commercially obtained. According to an embodiment of the invention, the electroless plating copper solution having a pH value of about from 12 to 13 may comprise a copper salt and a reducing agent which may reduce the copper salt to copper metal, the reducing agent may be one or more selected from glyoxylic acid, hydrazine and sodium hypophosphite. In one instance, the electroless plating copper solution having a pH value of about 12.5 to 13 may be proposed as follows: $CuSO_4 \cdot 5H_2O$ of about 0.12mol/L, $Na_2EDTA \cdot$

$2H_2O$ of about 0.14mol/L, potassium ferrocyanide of about 10mg/L, 2, 2'-bipyridine of about 10mg/L, HCOCOOH of about 0.10mol/L, NaOH and H_2SO_4. According to an embodiment of the invention, the electroless plating nickel solution having a pH value of about 5.2 may be proposed as follows: nickel sulfate of about 23g/l, sodium hypophosphite of about 18g/l, lactic acid of about 20g/l, malic acid of about 15g/l adjusted by NaOH under a temperature of 85-90℃.

According to an embodiment of the invention, the electroless plating copper time may be about 10 to 240 minutes, the electroless plating nickel time may be about 8 to 15 minutes.

According to an embodiment of the invention, there is substantially no electroless plating promoter or electroless plating deposit on the surface of the support where no electroless plating promoter is existed. Thus, the electroplating speed is very low with weak adhesive force. Even there is little chemical deposition, it may be erased easily. Thus, direct selective surface metallizing may be achieved easily according to the present invention.

Further, the present invention discloses a plastic article as manufactured by the method as mentioned above. The plastic article may comprise a support and a metallized layer area on a surface of the support. The metallized layer may be Ni-Cu-Ni, Ni-Cu-Ni-Au, Cu-Ni or Cu-Ni-Au from the inner portion of the plastic article to the outer portion thereof.

The following provides additional details on some embodiments of the present disclosure.

Embodiment 1

Step (1) $CuC_2O_4 \cdot 2H_2O$ is dehydrated with crystal water under vacuum, and then the CuC_2O_4 is ball milled so that D50 is not greater than 1um, and dried; PP resin, CuC_2O_4, talcum powder, and antioxidant 1010 are mixed with a mass ratio of 100: 15: 10: 0.2 by a mixer, and then the mixture is operated by a single screw extruder to form a pipe article.

Step (2) An outer surface of the pipe article is irradiated by a infrared laser (DPF-M12); the conditions thereof include the following: the wavelength of the laser is about 1064 nm, the scanning speed is about 1000 mm/s, the scanning step size is about 9um, the scan time delay is about 30us, the laser power is about 3 W, the frequency is about 40 KHz, and the filled distance is about 50um. And then the pipe article is ultrasonically cleaned.

Step (3) The pipe article is placed in an electroless plating copper solution for 3 hours to form a copper layer of about 10um, and then placed in an electroless plating nickel solution for 10 minutes to form a nickel layer with a thickness of about 3um. The electroless

plating copper solution having a pH value of about 12.5 to 13 is proposed as follows: $CuSO_4 \cdot 5H_2O$ of about 0.12mol/L, $Na_2EDTA \cdot 2H_2O$ of about 0.14mol/L, potassium ferrocyanide of about 10mg/L, 2, 2'-bipyridine of about 10mg/L, HCOCOOH of about 0.10mol/L, NaOH and H_2SO_4. The electroless plating nickel solution having a pH value of about 5.2 is proposed as follows: nickel sulfate of about 23g/l, sodium hypophosphite of about 18g/l, lactic acid of about 20g/l, malic acid of about 15g/l adjusted by NaOH and H_2SO_4.

Thus, a pipe article is manufactured by the above steps.

Embodiment 2

The embodiment 2 is substantially similar in all respects to that of Embodiment 1, excepting that:

Step (1) $CuSiO_3$ is ball milled so that D50 is not greater than 2um; PC resin, $CuSiO_3$, antioxidant 168, and EVA wax are mixed by a mass ratio of 100: 20: 0.2: 0.1, and then the mixture is performed with injection molding to form a shell of an electric device.

Step (2) A circuit pattern is printed on the surface of the shell by the infrared laser (DPF-M12); and then the shell is ultrasonically cleaned.

Step (3) The shell is placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um, then placed in an electroless plating copper solution for 3 hours to form a copper layer of about 11um, and lastly, the shell is placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um.

Thus, a plastic shell of an electric device is formed by above steps.

Embodiment 3

The embodiment 2 is substantially similar in all respect to that of Embodiment 2 with the exception that:

Step (1) Co_2O_3 is ball milled so that D50 is not greater than 5um; PBT resin, Co_2O_3, glass fiber, and light stabilizer 944 are mixed by a mass ratio of 100: 15: 35: 0.2 with a twin screw extruder, and then the mixture is performed with injection molding to form a shell of auto connecter.

Step (3) The shell is placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um, then placed in an electroless plating copper solution for 2 hours to form a copper layer of about 6um, then placed in an electroless plating nickel

solution for 10 minutes to form a nickel layer of about 3um, and lastly, the shell is formed with a Au layer of about 0.03um by strike plating.

Thus, the shell of an auto connecter is formed by the above steps.

Embodiment 4

The embodiment 4 is substantially similar in all respects to that of Embodiment 2 with the exception that:

Step (1) Ni_2O_3 is ball milled so that D50 is not greater than 10um; PC resin, Ni_2O_3, antioxidant 1076, and polyethylene wax are mixed by a mass ratio of 100: 10: 0.2: 0.1; and then the mixture is performed with a blow molding to form a shell of an electric device for an auto.

Step (3) The shell is placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um, then placed in an electroless plating copper solution for 2 hours to form a copper layer of about 6um, and lastly, the shell is placed in an electroless plating nickel solution for 12 minutes to form a nickel layer of about 4um.

Thus, the shell of an electric device for an auto is formed by the above steps.

Embodiment 5

Step (1) 54.1g of CuO (0.68mol), 27.13g of Fe_2O_3 (0.17mol) and 26.87g of Mn_2O_3 (0.17mol) are mixed and stirred in a vacuum furnace under a temperature of about 1000 ℃ for 2 hours; and then the mixture is ball milled to an average particle diameter of about 0.8um, and then the mixture is analyzed as $CuFe_{0.5}Mn_{0.5}O_{2.5}$ by XPS.

Step (2) PPO resin, $CuFe_{0.5}Mn_{0.5}O_{2.5}$, calcium silicate fiber, and antioxidant 1076 are mixed by a mass ratio of 100: 10: 0.2: 0.1, and then the mixture is performed with injection molding to form a connector shell of a solar panel.

Step (3) A circuit pattern is printed on the surface of the shell by an infrared laser (DPF-M12); and then the shell is ultrasonically cleaned.

Step (4) The shell is placed in an electroless plating nickel solution for 8 minutes to form a nickel layer of about 2um, then placed in an electroless plating copper solution for 4 hours to form a copper layer of about 15um, and lastly placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um.

Thus, the connector shell of the solar panel is formed by the above steps.

Embodiment 6

The Embodiment 6 is substantially similar in all respects to those of Embodiment 5 with the exception that:

Step (1) 54.1g of CuO (0.68mol), 27.13g of Fe_2O_3 (0.17mol) and 17.33g of Al_2O_3 (0.17mol) are mixed and stirred in a vacuum furnace under a temperature of about 1000 ℃ for 2 hours; and then the mixture is ball milled to an average particle diameter of about 0.5um, and then the mixture is analyzed as $CuFe_{0.5}Al_{0.5}O_{2.5}$ by XPS.

Step (2) PA6T resin, $CuFe_{0.5}Al_{0.5}O_{2.5}$, antioxidant 1076, and polyethylene wax are mixed by a mass ratio of 100: 10: 0.2: 0.1, and then the mixture is performed with injection molding to form a connector shell of an electric device for an auto.

Step (4) The shell is placed in an electroless plating nickel solution for 8 minutes to form a nickel layer of about 2um, then placed in an electroless plating copper solution for 4 hours to form a copper layer of about 15um, and placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um, and lastly, the shell is formed with a Au layer of about 0.03um by strike plating.

Thus, the shell of the electric device for an auto is produced by the above steps.

Embodiment 7

The Embodiment 7 is substantially similar in all respects to those of Embodiment 5 with the exception that:

Step (1) 54.1g of CuO (0.68mol), 13.56g of Fe_2O_3 (0.085mol), 8.67g of Al_2O_3 (0.085mol) and 26.87g of Mn_2O_3 (0.17mol) are mixed and stirred in a vacuum furnace under a temperature of about 1000 ℃ for 2 hours; and then the mixture is ball milled to an average particle diameter of about 1.0um, and then the mixture is analyzed as $CuFe_{0.25}Al_{0.25}Mn_{0.5}O_{2.5}$ by XPS.

Step (2) PPS resin, $CuFe_{0.25}Al_{0.25}Mn_{0.5}O_{2.5}$, antioxidant 1076, and polyethylene wax are mixed with a mass ratio of 100: 10: 0.2: 0.1, and then the mixture is performed injection molding to form a shell of an electric connector.

Step (4) The shell is placed in an electroless plating copper solution for 3 hours to form a copper layer of about 12um, and then placed in an electroless plating nickel solution for 10 minutes to form a nickel layer of about 3um.

Thus, the shell of the electric connector is formed by the above steps.

Embodiment 8

Step (1): Ni_2O_3 with an average particle diameter 50nm of 100g and talcum powder of 10g are added into polycarbonate of 1000g; The mixture is mixed with high speed and transferred into an extruder to form particles, then the mixture is performed with injection molding to form a plastic sample with a thickness of 2 mm;

Step (2): A surface of the plastic sample is irradiated by laser with substantially the same steps as those in step (2) of Embodiment 1;

Step (3): The treated plastic sample is immersed in the electroless plating copper solution as adopted in step (3) of Embodiment 1 for electroless copper plating with a measured copper plating speed of 4um/h.

Embodiment 9

The steps in Embodiment 9 are the same as those in Embodiment 8 for preparing the plastic article as defined in the present invention, with the exceptions that:

Step (1): Co_2O_3 with an average particle diameter 100nm of 100g and glass fiber of 30g are added into PC of 5000g; the mixture is rotated and mixed with high speed, and then the mixture is transferred into an extruder to form particles; And the particles are performed with injection molding to form a plastic sample with a thickness of 2mm;

Step (2): the laser has the following parameters: wavelength 300nm; scanning speed 5000mm/s; scanning step 3um; time delay 60us; frequency 40kHz; power 3W; and a filling distance 30um;

Step (3): The treated plastic sample is immersed in the electroless plating copper solution as adopted in step (3) of Embodiment 1 for electroless copper plating with a measured copper plating speed of 2um/h.

Embodiment 10

The steps in Embodiment 10 are the same as those in Embodiment 8 for preparing the plastic article as defined in the present invention, with the exceptions that:

Step (1): $CuSiO_3$ with an average particle diameter 500nm of 100g and kaolin of 70g are added into PET of 10000g; the mixture is rotated and mixed with high speed, and then the mixture is transferred into an extruder to form particles; and the particles are performed with injection molding to form a plastic sample with a thickness of 2mm;

Step (2): the laser has the following parameters: wavelength 10600nm; scanning speed 8000mm/s; scanning step 6um; time delay 100us; frequency 30kHz; power 4W; and a filling distance 40um;

Step (3): The treated plastic sample is immersed in the electroless plating copper solution as adopted in step (3) of Embodiment 1 for electroless copper plating with a measured copper plating speed of 5um/h.

Embodiments 11-26

The embodiments 11-26 use the same surface metallizing processes as those in Embodiment 8 with the difference lie in that the components in Table 1 are adopted for the electroless plating promoter with the measured copper plating speed of the embodiments 11-26 being shown in Table 1.

The hydrogenation catalysts in embodiments 20-22 are prepared by the methods disclosed in *Acta Physico-Chimica Sinica*, 2004, 20(5): 524-528 and *Angew. Chem. Int. Ed. 2003, 42, 3815-3817*.

For example, the Cn-Zn hydrogenation catalyst may be prepared as follows: a mixed nitrate solution of Cu and Zn is prepared with a Cu : Zn mole ratio of 8:1 so that the total concentration of metal ions in the mixed solution is 0.5mol/L. With Na_2CO_3 of a concentration of 0.5 mol/L as precipitant and under a temperature of 85℃ with rapid stirring, the Na_2CO_3 solution and the Na_2CO_3 solution are added into a reactor to obtain a solution with a pH of 6.8-7.0. At the end of the reaction, the solution has a pH value of 7.0. The solution is aged for 1 hour under this temperature. After cooling, the solution is filtered and cleaned with deionized water, and dried under a temperature of 110℃. After that, it is baked under a temperature of 350℃ for 4 hours, thus obtaining the desired Cu-Zn hydrogenation catalyst. Based on the oxides, the Cu-Zn hydrogenation catalyst is detected to have a Cu : Zn mass ratio of 8.1 : 1.

Reference 1

Reference 1 uses the same method as used in Embodiment 8 for selective plastic surface metallization. The difference therebetween lies in that the electroless plating promoter in step (1) uses the components as shown in Table 1 with the measured copper plating speed also indicated in Table 1.

Table 1

	Type of electroless plating promoter	Example	Electroless copper plating speed （μm/h）
Embodiment8	Oxides of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements except Cu	Ni_2O_3	4
Embodiment9		Co_2O_3	2
Embodiment10	Silicate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	$CuSiO_3$	5
Embodiment11		$NiSiO_3$	3
Embodiment12		$CoSiO_3$	2
Embodiment13	Borate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	CuB_2O_4	5
Embodiment14		$Cu_3B_2O_6$	9
Embodiment15		$Ni_3B_2O_6$	6
Embodiment16		CoB_2O_4	4
Embodiment17	Oxalate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	CuC_2O_4	5
Embodiment18		NiC_2O_4	4
Embodiment19		CoC_2O_4	3
Embodiment20	Hydrogenation catalyst having one or more elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	Cu-Zn	8
Embodiment21		Cu-Zn-Ni	6
Embodiment22		Cu-Zn-Co	7
Embodiment23	ABO_2 type composite oxides having a delafossite structure (A is one of metal elements selected from ninth, tenth, eleventh columns of the Periodic Table of Elements, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe and A, B are different from each other)	$CuNiO_2$	5
Embodiment24		$CuMnO_2$	4
Embodiment25		$CuFeO_2$	3
Embodiment26		$CoAlO_2$	2
Reference 1	——	ZnO	0.05

From Embodiment 8 and Reference 1, it can seen that the electroless copper plating speed is only 0.05um/h for the existing catalyst ZnO whereas the electroless copper plating speed may reach up to 4um/h for Ni_2O_3 as the catalyst under the same conditions.

Embodiments 27-45

Embodiments 27-45 adopt the same processes used in Embodiments 8-26 for performing selective metallizing on plastic surface. The differences therebetween lie in that it is performed with electroless nickel plating in an electroless nickel plating solution before electroless copper plating in step (3), the plating solution has a temperature of 90 ℃, and the measured nickel plating speed is also shown in Table 2.

The electroless nickel plating solution having a pH value of 5.2: nickel sulfate of about 23g/l, sodium hypophosphite of about 18g/l, lactic acid of about 20g/l, malic acid of about 15g/l adjusted by NaOH.

Reference 2

Reference 2 uses the same method as used in Embodiment 27 for selective plastic surface metallization. The difference therebetween lies in that the electroless plating promoter in step (1) uses the components as shown in Table 2 with the measured nickel plating speed also indicated in Table 2.

Table 2

	Type of electroless plating promoter	Example	Electroless nickel plating speed (μm/h)
Embodiment 27	Oxides of the metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements except Cu	Ni_2O_3	3
Embodiment 28		Co_2O_3	1
Embodiment 29	Silicate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	$CuSiO_3$	5
Embodiment 30		$NiSiO_3$	3
Embodiment 31		$CoSiO_3$	2
Embodiment 32	Borate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	CuB_2O_4	5
Embodiment 33		$Cu_3B_2O_6$	6
Embodiment 34		$Ni_3B_2O_6$	5
Embodiment 35		CoB_2O_4	4
Embodiment 36	Oxalate of metal elements selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	CuC_2O_4	5
Embodiment 37		NiC_2O_4	4
Embodiment 38		CoC_2O_4	3
Embodiment 39	Hydrogenation catalyst having one or more elements	Cu-Zn	6

Embodiment 40	selected from the ninth, tenth, eleventh columns of the Periodic Table of Elements	Cu-Zn-Ni	8
Embodiment 41		Cu-Zn-Co	7
Embodiment 42	ABO_2 type composite oxides having a delafossite structure (A is one of metal elements selected from ninth, tenth, eleventh columns of the Periodic Table of Elements, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe and A, B are different from each other)	$CuNiO_2$	5
Embodiment 43		$CuMnO_2$	4
Embodiment 44		$CuFeO_2$	3
Embodiment 45		$CoAlO_2$	2
Reference 2	——	ZnO	0.05

From Embodiment 27 and Reference 2, it can seen that the electroless nickel plating speed is only 0.05um/h for the existing catalyst ZnO whereas the electroless nickel plating speed may reach up to 3um/h for Ni_2O_3 as the catalyst under the same conditions.

Although explanatory embodiments have been shown and described, it would be appreciated by those skilled in the art that changes, alternatives, and modifications can be made in the embodiments without departing from spirit and principles of the invention. Such changes, alternatives, and modifications all fall into the scope of the claims and their equivalents.

WHAT IS CLAIMED IS:

1. A method for metallizing a plastic surface, the plastic comprising a supporting material and an electroless plating promoter, the method comprising the steps of:

1) gasifying the plastic surface to expose the electroless plating promoter; and

2) electroless plating a layer of copper or nickel on the plastic surface, followed by electroplating or a second electroless plating to form a metallized layer on the plastic surface.

2. The method according to claim 1, wherein the electroless plating promoter includes one or more members selected from a group consisting of:

(a) oxides of the metal elements selected from Co, Ni, Ag;

(b) silicate, borate or oxalate of metal elements selected from Co, Ni, Cu;

(c) hydrogenation catalysts having one or more metal elements selected from Co, Ni, Cu, Ag;

(d) ABO_2 type composite oxides having a delafossite structure, in which A is one of metal elements selected from Co, Ni, Cu, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe where A, B are different; and

(e) multicomponent oxides selected from a group consisting of Cu/Fe/Mn, Cu/Fe/Al and/or Cu/Fe/Al/Mn multicomponent oxides.

3. The method according to claim 1, wherein the plastic surface is gasified by laser to expose the electroless plating promoter.

4. The method according to claim 3, wherein the laser has a wavelength ranging from about 157 nm to about 10.6 um with a scanning speed from about 500 to about 8000 mm/s, a scanning step size from about 3 to about 9um, a scan time delay from about 30 to 100us, a laser power from about 3 to 4 W, a frequency from about 30 to 40 KHz and a filled distance from about 10 to 50um.

5. The method according to claim 3, wherein the electroless plating promoter is a particle with an average diameter of not greater than 100 microns.

6. The method according to claim 2, wherein the electroless plating promoter includes one or more members selected from a group consisting of

(a) Ni_2O_3, Co_2O_3, Co_3O_4;

(b) $CuSiO_3$, $NiSiO_3$, $CoSiO_3$, CuB_2O_4, $Cu_3B_2O_6$, NiB_2O_4, $Ni_3B_2O_6$, NiC_2O_4, CoC_2O_4, CoC_2O_4;

(c) hydrogenation catalysts of Cu-Zn, Cu-Zn-Ni, Cu-Zn-Co, Cu-Zn-Ga, Co-La, Cu-Cd and Cu-Zn-Si; and

(d) $MNiO_2$, $MMnO_2$, $MCrO_2$, $MAlO_2$, $MFeO_2$ where M is Cu, Ni or Co.

7. The method according to claim 2, wherein the multicomponent oxides has the following formulas respectively:

$CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$ and $CuFe_aAl_bMn_cO_d$, in which x, y, z, e, f, g, a, b, c, and d satisfy:

$0.01\leq x\leq 2$, $0.01\leq y\leq 2$, $2\leq z\leq 4$; $0.01\leq e\leq 2$, $0.01\leq f\leq 2$, $2\leq g\leq 4$; and $0.01\leq a\leq 2$, $0.01\leq b\leq 2$, $0.01\leq c\leq 2$, $2\leq d\leq 4$.

8. The method according to claim 1, wherein the supporting material is a thermoplastic material or thermosetting resin material.

9. The method according to claim 1, wherein the electroless plating promoter amounts to about 1 % to about 40% of the supporting material by weight.

10. The method according to claim 8, wherein the support material further comprises at least one member selected from inorganic filler, antioxidant, light stabilizer and lubricant.

11. A method for preparing a plastic article, comprising the steps of:

1) forming at least a part of the plastic article with a support comprising a supporting material and an electroless plating promoter;

2) gasifying a surface of the support to expose the electroless plating promoter; and

3) electroless plating a layer of copper or nickel on the surface followed by electroplating or electroless plating at least one time, to form a metallized layer on the surface.

12. The method according to claim 11, wherein the electroless plating promoter in step 1) includes one or more members selected from a group consisting of:

(a) oxides of the metal elements selected from Co, Ni, Ag;

(b) silicate, borate or oxalate of metal elements selected from Co, Ni, Cu;

(c) hydrogenation catalysts having one or more metal elements selected from Cu, Zn, Ni, Co, Ga, La, Cd, Si;

(d) ABO_2 type composite oxides having a delafossite structure in which A is one of metal elements selected from Co, Ni and Cu, B is an element selected from a group consisting of Ni, Mn, Cr, Al and Fe where A, B are different from each other; and

(e) multicomponent oxides selected from a group consisting of Cu/Fe/Mn, Cu/Fe/Al and/or Cu/Fe/Al/Mn multicomponent oxides.

13. The method according to claim 12, wherein the plastic article is formed by injection molding, blow molding, extruding or hot pressing.

14. The method according to claim 13, wherein the surface is gasified by laser to expose the electroless plating promoter.

15. The method according to claim 14, wherein the laser has a wavelength ranging from about 157 nm to about 10.6 um with a scanning speed from about 500 to about 8000 mm/s, a scanning step size from about 3 to about 9um, a scan time delay from about 30 to 100us, a laser power from about 3 to 4 W, a frequency from about 30 to 40 KHz and a filled distance from about 10 to 50um.

16. The method according to claim 11, wherein the step 3) further comprises

performing additional electroplating or/and electroless plating to form a Ni-Cu-Ni, Ni-Cu-Ni-Au, Cu-Ni, or Cu-Ni-Au layer on the support respectively.

17. The method according to claim 16, wherein the Ni layer has a thickness of about 0.1-50um, the Cu layer has a thickness of about 0.1-100um and the Au layer has a thickness of about 0.01-10um respectively in the layers of Ni-Cu-Ni, Ni-Cu-Ni-Au, Cu-Ni and Cu-Ni-Au.

18. The method according to claim 11, wherein the electroless plating promoter is a particle with an average diameter of not greater than 100 microns.

19. The method according to claim 12, wherein the multicomponent oxides has the following formulas respectively:

$CuFe_xMn_yO_z$, $CuFe_eAl_fO_g$ and $CuFe_aAl_bMn_cO_d$, in which x, y, z, e, f, g, a, b, c, and d satisfy:

$0.01 \le x \le 2$, $0.01 \le y \le 2$, $2 \le z \le 4$; $0.01 \le e \le 2$, $0.01 \le f \le 2$, $2 \le g \le 4$; and $0.01 \le a \le 2$, $0.01 \le b \le 2$, $0.01 \le c \le 2$, $2 \le d \le 4$.

20. The method according to claim 11, wherein the electroless plating promoter amounts to about 1 % to about 40 % of the support by weight.

21. The method according to claim 20, wherein the support material further comprises at least one member selected from inorganic filler, antioxidant, light stabilizer and lubricant.

22. The method according to claim 12, wherein the hydrogenation catalyst is at least one selected from a group consisting of Cu-Zn hydrogenation catalysts, Cu-Zn-Ni hydrogenation catalysts, Cu-Zn-Co hydrogenation catalysts, Cu-Zn-Ga hydrogenation catalysts, Co-La hydrogenation catalysts, Cu-Cd hydrogenation catalysts and Cu-Zn-Si hydrogenation catalysts.

23. The method according to claim 12, wherein the electroless plating promoter is evenly distributed in the supporting material.

24. A plastic article as manufactured by the method according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/072055

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C23C; C25D; C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, CNKI, WPI, EPODOC: METALLIZ+; METAL LAYER; PLASTIC; RESIN; POLYMER; EXPOS+; IRRADIAT+; LASER; LIGHT; COPPER; NICKEL; CU; NI; MODIF+; PLAT+; AUTOCATALYTIC; ELECTROLESS+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X / A	US5599592 A (LAUDE L D) 04 Feb. 1997 (04.02.1997) claims 1, 7-9, 11, column 2, line 33 to column 3, line 39, examples 1, 3, 5	1, 3-5, 8-11, 16-18, 20, 21, 24 / 2, 6, 7, 12-15, 19, 22, 23
Y	DE19852776 A1 (FRAUNHOFER GES FOERDERUNG ANGEWANDTEN) 18 May 2000 (18.05.2000) abstract	1, 3-5, 8-11, 16-18, 20, 21, 24
Y	US5702584 A (FORD MOTOR CO) 30 Dec.1997 (30.12.1997) claim 1	1, 3-5, 8-11, 16-18, 20, 21, 24
Y	US5198096 A (GENERAL ELECTRIC CO) 30 Mar. 1993 (30.03.1993) claims 1-3, figure 1	1, 3-5, 8-11, 16-18, 20, 21, 24
Y / A	US2004241422 A1 (LPKF LASER & ELECTRONICS AG) 02 Dec.2004 (02.12.2004) claim 1, paragraph [0014]	1, 3-5, 8-11, 16-18, 20, 21, 24/ 2, 6, 7, 12-15, 19, 22, 23

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 Sep. 2010 (06.09.2010)	**23 Sep. 2010 (23.09.2010)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer LI, Jiagang Telephone No. (86-10)62084094

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A. CLASSIFICATION OF SUBJECT MATTER

C23C 18/54 (2006.01)i

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