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(54) Title: PROCESS FOR COPPER PLATING OF POLYAMIDE ARTICLES

(57) Abstract: This invention relates to a process for metal-coating a polyamide surface, to achieve metal-polyamide adhesion, and such metal-coated polyamide articles.



WO 2012/129190 A2

TITLE

PROCESS FOR COPPER PLATING OF POLYAMIDE ARTICLES

FIELD OF THE INVENTION

5 This invention relates to processes to achieve improved adhesion of a metal to a polyamide article surface and to the preparation of metal coated polyamide articles prepared from such processes.

BACKGROUND OF THE INVENTION

10 Plastic or polymeric articles can be coated with a layer of metal for aesthetic, conduction, and static reduction purposes. Coating polymeric articles with metal can be difficult because traditional metal coating methods rely on high temperatures or electrical conductivity, neither of which is ideal for untreated polymeric articles. Some methods for applying a metal coating on polymeric articles use some of the same principles as those used to coat metal parts, but with some differences to take
15 into account the material properties of the polymeric articles.

 Methods used for coating plastic or polymeric parts with metal include electroless plating, vapor deposition, and conductive paints. One method uses a combination of electroless plating and electrolytic plating to coat the polymeric article as disclosed in Novigath PA Process by Atotech, in combination with Aldolyte Bright Acid Plating Process by Aldoa. When a metal is coated as a layer
20 onto a polymeric or plastic surface, the ability to obtain a tenacious or strong bond of the metal layer to the polymeric article surface can be difficult.

 US20090143520 teaches the use of a copper sulfate solution to plate copper or other metals onto a polyamide article.

 US20090038947 discloses an electroplating aqueous solution comprising at least two acids,
25 copper, at least one accelerator agent, and at least two suppressor agents.

 US20060065536 teaches a copper electroplating bath composition and a method of copper electroplating to improve gap fill. The method of electroplating includes providing an aqueous electroplating composition comprising copper, at least one acid, at least one halogen ion, an additive including an accelerating agent, a suppressing agent, and a suppressing-accelerating agent, and the

solution and mixture products thereof; contacting a substrate with the plating composition; and impressing a multi-step waveform potential upon the substrate, wherein the multi-step waveform potential includes an entry step, wherein the entry step includes a first sub-step applying a first current and a second sub-step applying second current, the second current being greater than the first current.

WO2001083854 teaches an electroplating composition comprising copper, at least one acid, at least one halogen, at least one accelerating agent or a suppressing agent, and an accelerating-suppressing agent.

Great Britain 2,167,445 discloses a mineral or metal filled polyamide composition which is electroplated with a copper sulfate, sulfuric acid, hydrochloric acid, and additional additives mixture to provide a metal coated polyamide composition.

U.S. 5,326,811 teaches a polyamide composition which is chemically plated with nickel, acid activated with sulfuric acid, and electroplated with a copper sulfate solution.

A common metal coating process used to coat a chemically treated polymeric surface is the Aldolyte bright acid copper plating process supplied by the Aldoa Company.

However, there is still a need for an improved metal electroplating process for achieving a metal coating on the surface of a polyamide article resulting in a strong bond of the metal with the polyamide article.

SUMMARY OF THE INVENTION

Described herein is a process for applying a copper-coating to a polyamide article surface, the process comprising the steps of: (i) chemically treating a surface of a polyamide article to provide an electrically conductive polyamide article; (ii) immersing the electrically conductive polyamide article into an electroplating solution comprising:

- (a) 188 – 250 ml/L copper sulfate
- (b) 47 – 78 ml/ L sulfuric acid
- (c) 20 – 200 mg/L chloride ion
- (d) greater than 1.0 – 2.4 % of Aldolyte AC-12E
- (e) greater than 0.78 – 1.88 ml/L of Aldolyte AC-14L

- (f) greater than 3 - 6% Aldolyte AC-W-22
- (iii) applying a cathode current density of 359.5-601 A/m² to the electroplating solution cathode using phosphorized copper anodes to obtain a copper coated polyamide article; wherein the copper coated polyamide article has a peel strength between the copper and polyamide article surface of greater than 12 N cm⁻¹; and wherein electroplating solution concentrations are based on the total volume of the electroplating solution.

Also described herein are polyamide articles prepared from the processes of the invention.

DETAILED DESCRIPTION

Many articles are made from polymer compositions which have a metal coating. It is desirable for the metal coating to be strongly bonded to the surface of the polymer so that the coating cannot be easily removed or compromised in normal use.

One method for coating a metal onto the surface of a polymeric article uses a combination of polymeric surface treatment, typically with a strong acid solution, followed by an electroless plating operation and concluding with an electrolytic operation to obtain a metal-coated polymeric article.

The type and concentration of acid, base, or other polymer surface treatment agent(s) used in polymer surface preparation is determined by the specific class of polymer to be metal coated. In the present disclosure, polyamide polymers are the class of polymers disclosed herein for preparing metal-coated polymeric articles in which the metal coating has improved adhesion (meaning, it is strongly bonded) to the surface of the polymer.

Definitions

As used herein, the terms “about” and “at or about” mean that the amount or value in question may be the value designated or some other value approximately or about the same. The term is intended to convey that similar values promote equivalent results or effects recited in the claims.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation of these, refer to a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not limited to only the listed elements but may include other elements not expressly listed or inherent. Further, unless expressly

stated to the contrary, “or” refers to an inclusive, not an exclusive, or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

As used herein, the term “metal-coating” means a thin, typically 0.1 microns to several
5 hundred microns thickness, coating of metal on a polymer surface which is applied to the surface of a polyamide polymer by processes such as electroless plating, electroplating, spraying, vapor deposition, powder coating, immersion processes, and solution dipping processes. Metals used can be any metal such as copper, nickel, iron, cobalt, silver, zinc, titanium, platinum, palladium, aluminum, tin, lead, and other metals or any combination of metals to make a metal alloy. This
10 definition also includes multiple layers of different metals.

As used herein, the term “chemically treating” means to treat or modify a polyamide surface using chemical means such that the polyamide surface is altered in some way compared to the same polyamide surface which is not mechanically or chemically treated.

As used herein, the term “activating” means to alter the surface of a polymeric material by
15 reaction with chemicals that introduce a catalyst onto the surface of the polymeric material.

As used herein, the term “electrolessly applying” means to coat or place on the surface of an article or polymer a layer of material by a method which does not involve the use of electricity.

As used herein, the term “immersing” means to place a material or polymer into a solution such that the surface or portion of the surface of the article or polymer which is to be treated is in
20 physical contact with the solution.

Polyamide Polymers

Suitable polyamides described herein which can be used to prepare polyamide articles disclosed herein can be condensation products of one or more dicarboxylic acids and one or more
25 diamines, and/or one or more aminocarboxylic acids, and/or ring-opening polymerization products of one or more cyclic lactams. Polyamides may include aliphatic, aromatic, and/or semi-aromatic or partially aromatic polyamides and can be homopolymer, copolymer, terpolymer or higher order polymers. Blends of two or more polyamides may also be used.

Suitable dicarboxylic acids include, but are not limited to, adipic acid, azelaic acid, terephthalic acid, isophthalic acid, sebacic acid, and dodecanedioic acid. Preferred dicarboxylic acids are adipic, isophthalic and terephthalic acid. A suitable aminocarboxylic acid is 11-aminododecanoic acid. Suitable cyclic lactams include caprolactam and laurolactam.

5 Suitable aliphatic diamines include, but are not limited to, tetramethylenediamine; hexamethylenediamine; octamethylenediamine; nonamethylenediamine; 2-methylpentamethylenediamine; 2-methyloctamethylenediamine; trimethylhexamethylenediamine; bis(*p*-aminocyclohexyl)methane; *m*-xylylenediamine; *p*-xylylenediamine, decamethylenediamine; undecamethylenediamine; dodecamethylenediamine; tridecamethylenediamine;
10 tetramethylenediamine; pentamethylenediamine; hexamethylenediamine; and the like.

 Suitable aromatic and/or heterocyclic diamines can be represented by the structure: H₂N-R₁₀-NH₂, wherein R₁₀ is an aromatic group containing up to 16 carbon atoms and, optionally, containing up to one hetero atom in the ring, the hetero atom comprising -N-, -O-, or -S-. Also included herein are those R₁₀ groups wherein R₁₀ is a diphenylene group or a diphenylmethane
15 group. Representative of such diamines are 2,6-diaminopyridine, 3,5-diaminopyridine, meta-phenylene diamine, para-phenylene diamine, *p,p'*-methylene dianiline, 2,6-diamino toluene, and 2,4-diamino toluene.

 Other examples of the aromatic diamine components, which are merely illustrative, include benzene diamines such as 1,4-diaminobenzene, 1,3-diaminobenzene, and 1,2-diaminobenzene;
20 diphenyl(thio)ether diamines such as 4,4'-diaminodiphenylether, 3,4'-diaminodiphenylether, 3,3'-diaminodiphenylether, and 4,4'-diaminodiphenylthioether; benzophenone diamines such as 3,3'-diaminobenzophenone and 4,4'-diaminobenzophenone; diphenylphosphine diamines such as 3,3'-diaminodiphenylphosphine and 4,4'-diaminodiphenylphosphine; diphenylalkylene diamines such as 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylpropane, and
25 4,4'-diaminodiphenylpropane; diphenylsulfide diamines such as 3,3'-diaminodiphenylsulfide and 4,4'-diaminodiphenylsulfide; diphenylsulfone diamines such as 3,3'-diaminodiphenylsulfone and 4,4'-diaminodiphenylsulfone; and benzidines such as benzidine and 3,3'-dimethylbenzidine.

 Preferred diamines include hexamethylenediamine, 2-methylpentamethylenediamine, decamethylenediamine, and dodecamethylenediamine.

Preferred polyamides include aliphatic polyamides such as polyamide 6; polyamide 6,6; polyamide 4,6; polyamide 6,9; polyamide 6,10; polyamide 6,12; polyamide 11; polyamide 12; polyamide 9,10; polyamide 9,12; polyamide 9,13; polyamide 9,14; polyamide 9,15; polyamide 6,16; polyamide 9,36; polyamide 10,10; polyamide 10,12; polyamide 10,13; polyamide 10,14; polyamide 12,10; polyamide 12,12; polyamide 12,13; polyamide 12,14; polyamide 6,14; polyamide 6,13; polyamide 6,15; polyamide 6,16; polyamide 6,13; and semi-aromatic polyamides such as poly(*m*-xylene adipamide) (polyamide MXD,6) and polyterethalamides such as poly(dodecamethylene terephthalamide) (polyamide 12,T), poly(decamethylene terephthalamide) (polyamide 10,T), poly(nonamethylene terephthalamide) (polyamide 9,T), hexamethylene adipamide/hexamethylene terephthalamide copolyamide (polyamide 6,T/6,6), hexamethylene terephthalamide/2-methylpentamethylene terephthalamide copolyamide (polyamide 6,T/D,T); hexamethylene isophthalamide and hexamethylene adipamide (polyamide 6I/66); hexamethylene adipamide/hexamethylene terephthalamide/hexamethylene isophthalamide copolyamide (polyamide 6,6/6,T/6,I); poly(caprolactam- hexamethylene terephthalamide) (polyamide 6/6,T); and copolymers and mixtures of these polymers.

Examples of suitable aliphatic polyamide copolymers and terpolymers include polyamide 66/6 copolymer; polyamide 66/68 copolymer; polyamide 66/610 copolymer; polyamide 66/612 copolymer; polyamide 66/10 copolymer; polyamide 66/12 copolymer; polyamide 6/68 copolymer; polyamide 6/610 copolymer; polyamide 6/612 copolymer; polyamide 6/10 copolymer; polyamide 6/12 copolymer; polyamide 6/66/610 terpolymer; polyamide 6/66/69 terpolymer; polyamide 6/66/11 terpolymer; polyamide 6/66/12 terpolymer; polyamide 6/610/11 terpolymer; polyamide 6/610/12 terpolymer; and polyamide 6/66/PACM (bis-*p*-{aminocyclohexyl} methane) terpolymer.

The numerical suffix of the polyamide specifies the numbers of carbons donated by the diamine and the diacid. The diamine first and the diacid second. For example, polyamide 6,6 is a polyamide prepared from hexamethylenediamine and hexane-1,6-dicarboxylic acid repeat units and polyamide 66/612 copolymer is a blend of polyamide 6,6 and polyamide 6,12.

Exemplary polyamides include hexamethylene adipamide (polyamide PA66), hexamethylene terephthalamide (polyamide PA6T), hexamethylene isophthalamide (polyamide PA6I), 2-methyl

pentamethylene terephthalamide (polyamide PADT), p-phenylene terephthalamide, m-phenylene adipamide, and similar polyamides or combinations of them.

Preferred polyamides are aliphatic or aromatic polyamides or blends of two or more polyamides. Preferred polyamides have a glass transition temperature (T_g) greater than 40°C, preferably greater than 80°C, and most preferably greater than 110°C. Preferred polyamides have a melting point greater than 200°C, preferably greater than 260°C, and most preferably greater than 290°C.

The polyamide polymers can contain one or more additives such as fiber(s), particle(s), filler(s), stabilizer(s), and similar additives commonly added to polymers where a surface of the polymer is coated by at least one metal in elemental form ("metal" unless otherwise specified).

Physical blends of aliphatic polyamides and semiaromatic polyamides are useful in articles to obtain properties intermediate between or synergistic of the properties of each polyamide. However, it has been noted that semiaromatic polyamides in comparison to aliphatic polyamides are more difficult to coat with a metal or metals that remains tenaciously bonded to the surface and physical blends containing semiaromatic polyamide and aliphatic polyamide can be more difficult to coat than the same aliphatic polyamide. Blends may be expressed by known abbreviations, such as PA6T/DT for a blend of two polyamides, PA6T and PADT. Some amount of copolymers may also be present.

A preferred blend of polyamides has at least one aliphatic and a semiaromatic polyamide. One such preferred blend is a blend having an aliphatic polyamide with mostly (>50%) or almost all (> 90%) hexamethylene adipamide, or poly(hexamethylene adipamide) itself, optionally in combination with a semiaromatic polyamide having mostly (>50%) or almost all (> 90%) hexamethylene terephthalamide monomer instances and/or hexamethylene isophthalamide monomer instances, with the ratio of aliphatic to semiaromatic polyamides by weight being greater than or equal to one or more of 0.2, 0.5, or 0.8 (e.g. copoly(hexamethylene isophthalamide (0.666 parts)-hexamethylene terephthalamide (0.334))). The preferred ratio of aliphatic to semi-aromatic polyamide is greater than 0.4 and most preferred is greater than 0.5.

The polyamide polymer(s) that is suitable herein may comprise one or more mixtures of fiber(s). Each fiber can be chopped into lengths or "continuous" and have various diameters, cross

sections, lengths, and aspect ratios. The fiber may comprise ingredients such as glass, carbon, graphite, and polymer. A preferred fiber is short chopped glass fiber with a flattened cross section, in a ratio by weight to the polyamide blend of about 0.2, 0.5, 1, 2, or 5. The weight percentage of fiber used in a polymer composition can be from about 10 to about 60 weight percent, based on the total weight percent composition of the polyamide polymer and fiber.

Mineral Fillers

An optional ingredient of the polyamide polymer composition is one or more mineral fillers, such as calcium carbonate particles, clay particles, and similar materials. Any filler can have various average diameters, cross sections, lengths, and aspect ratios; the filler can include ingredients such as glass, carbon, graphite, polymer, and similar fillers. A preferred filler is calcium carbonate particles. The weight percentage of filler used in a polymer composition can be from about 1 weight percent to about 50 weight percent based on the total weight percent of the total composition.

Certain types of fillers are extractable by the surface preparation process for metallization, thereby creating surface roughness which can improve adhesion of the polyamide article to the metal coating. These fillers can be any filler which can be removed by the surface preparation process. The fillers can be used alone or in combination with other fillers. One preferred filler is calcium carbonate. The total weight percentage of fillers used in the polyamide article of this invention can be from about 1 weight percent to about 30 weight percent based on the total weight percent of the polyamide article.

Additional components which may be added to the polyamide compositions of the invention include tougheners (rubber-like), small polymeric molecules, and the like.

Reinforcing Agents

The polyamide article or the invention may optionally contain a reinforcing agent. The reinforcing agent can be in any suitable form such as a mat, fabric, or web form known to those skilled in the art. Suitable examples of such reinforcing agents include woven or nonwoven fabrics or mats, unidirectional strands of fiber, and similar materials or mixtures of them. The polyamide article may contain multiple layers of fibrous materials. Additionally, any given fibrous layer may be formed from two or more kinds of fibers (e.g., carbon and glass fibers). The fibers may be

unidirectional, bi directional, or multidirectional. Pre-impregnated unidirectional fibers and fiber bundles may be formed into woven or nonwoven mats or other structures suitable for forming the fibrous material. The fibrous material may be in the form of a unidirectional pre-impregnated material or a multi-axial laminate of a pre-impregnated material.

5 The fibrous material is preferably selected from woven or non-woven structures (e.g., mats, felts, fabrics and webs) textiles, fibrous battings, a mixture of two or more materials, and combinations thereof. Non-woven structures can be selected from random fiber orientation or aligned fibrous structures. Examples of random fiber orientation include without limitation material which can be in the form of a mat, a needled mat or a felt. Examples of aligned fibrous structures
10 include without limitation unidirectional fiber strands, bidirectional strands, multidirectional strands, multi-axial textiles. Textiles can be selected from woven forms, knits, braids and combinations thereof.

 The polyamide article may also contain fibrous materials which are encapsulated by the polyamide polymer so as to form an interpenetrating network of fibrous material substantially
15 surrounded by the polyamide polymer. For purposes herein, the term "fiber" is defined as a macroscopically homogeneous body having a high ratio of length to width across its cross-sectional area perpendicular to its length. The fiber cross section can be any shape, but is typically round or oval shaped. Depending on the end-use application of the polyamide article and the required mechanical properties, more than one fibrous material can be used, either by using several of the
20 same fibrous materials or a combination of different fibrous materials. An example of a combination of different fibrous materials is a combination comprising a non-woven structure such as for example a planar random mat which is placed as a central layer and one or more woven continuous fibrous materials that are placed as outside layers or layers above or below or both above and below the central layer. Such a combination allows an improvement of the processing and thereof of the
25 homogeneity of the polyamide article interior, thus leading to improved mechanical properties of the composite structure. The polyamide article interior is not subjected to the processes of the invention.

 Preferably, the fibrous material comprises glass fibers, carbon fibers, aramid fibers, graphite fibers, metal fibers, ceramic fibers, natural fibers or mixtures thereof; more preferably, the fibrous material comprises glass fibers, carbon fibers, aramid fibers, natural fibers or mixtures thereof; and

still more preferably, the fibrous material comprises glass fibers, carbon fibers and aramid fibers or mixture mixtures thereof. By natural fiber, it is meant any material of plant origin or of animal origin. When used, the natural fibers are preferably derived from vegetable sources such as for example from seed hair (e.g. cotton), stem plants (e.g. hemp, flax, bamboo; both bast and core
5 fibers), leaf plants (e.g. sisal and abaca), agricultural fibers (e.g., cereal straw, corn cobs, rice hulls and coconut hair) or lignocellulosic fiber (e.g. wood, wood fibers, wood flour, paper and wood-related materials). As mentioned above, more than one fibrous materials can be used. A combination of fibrous materials made of different fibers can be used such as for example a first component comprising one or more central layers made of glass fibers or natural fibers and one or
10 more outer layers (relative to central layer) made of carbon fibers or glass fibers. Preferably, the fibrous material is selected from woven structures, non-woven structures or combinations thereof, wherein said structures are made of glass fibers and wherein the glass fibers are E-glass filaments with a diameter between 8 and 30 mm, and preferably with a diameter between 10 to 24 mm. The fibrous material can also be chopped fibers or particles.

15 The fibrous material may further comprise a thermoplastic material, for example the fibrous material may be in the form of commingled or co-woven yarns or a fibrous material impregnated with a powder made of a thermoplastic material that is suited to subsequent processing into woven or non-woven forms, or a mixture for use as a uni-directional material.

Preferably, the ratio between the fibrous material and the polyamide polymer is at least 30%
20 fibrous material and more preferably between 40 and 60% fibrous material, the percentage being a volume-percentage based on the total volume of the polyamide article.

The polymer composition can optionally include other ingredients, such as catalyst, polymers other than polyamide, adhesion promoters, ions, compounds, preservatives such as heat stabilizers and antioxidants, lubricants, flow enhancers, or other ingredients as known in the art.

25 In general, the process for coating a polyamide article with metal consists of several operations. First, the surface of a polyamide polymer undergoes chemical treatment such as with a concentrated acid solution. Polyamide surface treatment may include multiple steps. The surface treated polyamide is then activated with metal ions followed by electroless plating with a metal. The final step is electrolytically plating a metal onto the polyamide-surface. Such operations are

typically conducted sequentially, in which case it can be advantageous to carry out pretreatments or post treatments such as washing, cleaning, drying, heating, and partial or full neutralization of pH extremes while optionally the treating solutions are agitated or undergo ultrasonification during these operations.

5 **Polyamide Surface Treatment**

Etching: The first step or operation of the process described herein is exposure of at least part of a polyamide article surface to an aqueous acidic liquid mixture which chemically treats the polyamide article surface. The acidic liquid mixture can have dissolved, dispersed, or undissolved components, and can include one or more solvents such as water, ethylene glycol, and similar
10 solvents. The dissolved and undissolved components can include ions, ionic and covalent compounds including organic compounds or elements. Examples include hydronium ion; hydroxide ion; chloride ion; sulfate ion, bisulfate ion, fluoride ion, bifluoride ion, ammonium ion; sodium ion, ionic and elemental metals such as iron, nickel, cobalt, chromium, and the like in charge states such as 0, +1, +2, +3, +6 or compounds such as hydrogen chloride. The amount of any component of a
15 treating liquid mixture can be greater than, equal to, or less than one or more of 0.1, 1, 5, 10, 30, 50, 90, or 95 weight %.

The pH of the aqueous acidic liquid mixture used to chemically treat the polymeric article surface can be an important aspect of treatment, as can treating temperature, agitation and time. The aqueous acidic liquid mixture typically has a pH of about 3 or less. Acidity can be established by the
20 use of acids such as inorganic and organic acids. Non-limiting examples of inorganic acids include hydrochloric acid, sulfuric acid, nitric acid, and hydrofluoric acid. Non-limiting examples of organic acids include oxalic acid, acetic acid, and benzoic acid. Buffers can also be used, established by the presence of one or more of bicarbonate, bifluoride, bisulphate, or similar compounds, with one or more of carbonic acid, carbonate, hydrofluoric acid, fluoride, sulfuric acid, sulfate, or similar
25 compounds.

Acid treatments are typically carried out at from ambient temperatures to about 85° C in air or optionally under nitrogen, argon, or other inert gases for about 10 to 15 minutes resulting in an acid treated polyamide article. One example of an acid etching solution is Noviganth PA Conditioner supplied by Atotech USA, Rock Hill, SC. The process comprises immersion in the

Noviganth PA Sweller Plus for 4 – 7 min at 35 C, followed by 1 – 3 rinses at RT, followed by immersion in the acidic solution Noviganth PA Conditioner for 5 – 7 min at 35 C.

The above described surface preparation process is not meant to be limiting. Other surface preparation processes can be used for this invention as long as the process creates a polyamide surface which is capable of undergoing the metal plating process. Mechanical abrading of the polyamide surface is one alternative method of treating the polyamide surface.

Metal Plating Process

After undergoing chemical surface treatment, the polyamide article undergoes a metal plating process. Typically, during the metal plating process, the chemically treated polyamide article surface undergoes a series of chemical reactions to render conductive the portion of its surface that is to be metal plated: first, a catalyst is applied on the polyamide article surface (e.g., Noviganth PA Activator) followed by chemical (electroless) deposition of a thin layer of metal (e.g., Noviganth PA Reducer), enough to render at least part of the surface of the polyamide article conductive. The metal used in the electroless deposition solution is typically copper or nickel (e.g., Noviganth Ni PA), but other metals may be used. After this step, electrolytic deposition of additional metal is possible to the desired thickness.

The metal coatings can comprise at least one metal in elemental form, alloys of such, or metal matrix composites. The coatings can have a thickness of from less than 1 micron to more than 50 microns, preferably from less than 5 micron to more than 20 microns, and more preferably from 10 microns to 20 microns. It is often useful to coat more than one layer of different metals in a combination that may offer a desired advantage. For example, a more ductile metal such as copper may be used for the first layer, and a stronger metal, such as nickel, iron, cobalt, tin, or other metals or their alloys, or alloys with phosphorus, may be used for an intermediate or the outermost metal layer for their strength and hardness.

Drip drying and rinse step(s) in the above process described herein can be from a few seconds to several minutes. The purpose of the drip drying and rinse operation is to remove and collect residual treatment chemicals so they do not interfere with subsequent or future processing steps as well being collected for recycling. Deionized water is preferably used in the rinse step but other rinse solutions can also be used. The number of drip drying and water wash operations as well

as the length of time that each operation is performed is within the skill level of one knowledgeable in the art.

An example of the above process steps is listed in Table 1 as steps 1 to 14 which are prior art, and conducted according to the process taught by Atochem using the Novigarth® process as
5 described in the Novigarth® PA data sheet (IMDS-No.:926754). Step 15 represents the inventive step of the overall process described herein.

Table 1
Surface Preparation and Metallization Processes

Step #	Process Step	Time [min.]	Optimum Temperature [°C]
1	Noviganth PA Sweller Plus	6	35
2	Drip Dry	1	RT
3	Rinse	1	RT
4	Noviganth PA Conditioner	6	35
5	Drip Dry	1	RT
6	Rinse	1	RT
7	Noviganth PA Activator	6	35
8	Drip Dry	1	RT
9	Rinse	1	RT
10	Noviganth PA Reducer	3	45
11	Drip Dry	1	RT
12	Rinse	1	RT
13	Noviganth Ni PA	10	55
14	Rinse	1	RT
15	Metal electroplating	see examples	See examples
16	Rinse	1	RT
RT – room temperature which is 20-25°C			

- 5 The metal electroplating process (step 15 in Table 1) used to electroplate a metal onto the nickel plated polyamide from step 14 in table 1 is the Aldolyte bright acid copper plating process taught by the Aldoa Company. The process is described in detail in Aldoa's technical bulletin titled "Aldolyte Bright Acid Copper Plating Process" revised September 11, 2003. This process involves the use of a copper solution composition comprising copper sulfate, sulfuric acid, chloride ion, and
- 10 three materials as shown in Table 2.

Table 2				
Constituents	Aldolyte Copper Solution (prior art)	Aldolyte Optimum (prior art)	Inventive Copper Solution	Inventive Optimum
Copper Sulfate	188 – 250 ml/L	30 oz/gal	188 – 250 ml/L	234 ml/ L
Sulfuric Acid	47 – 78 ml/ L	8 oz/gal	47 – 78 ml/ L	63 ml/L
Chloride Ion	20 – 200 mg/L	50 mg/L	20-200 mg/L	50 mg/L
Aldolyte AC-12E	0.6 – 1.0%*	0.8%*	>1.0 – 2.4%*	1.6%*
Aldolyte AC14L	3 – 10 ^a	8 ^a	>0.78 – 1.88 ml/L	1.25 ml/L
Aldolyte AC-W-22	1.5 – 3.0%*	2%*	>3 – 6 %*	4.0%*
*By volume where volume is total volume of the solution				

- 5 The recommended Aldolyte operating conditions for electroplating the metal onto the surface-prepared polyamide are listed in Table 3.

Table 3		
Operation Conditions	Aldolyte Conditions	Inventive Conditions
Cathode Current Density (Average)	323 – 646 amp/sq. meter	360 – 601 amp/ sq. meter
Anode Current Density	161 – 323 amp/ sq. meter	180 – 300 amp/ sq. meter
Temperature	70-80°F	70-80°F
Agitation	Air	Air

- 10 When step 15 is carried out using the prior art Aldolyte copper solution for applying copper on polyamides which have undergone steps 1-14 in Table 1, bonding of the metal to the polyamide was poor. The use of Aldolyte copper solution in step 15 as disclosed herein results in a copper-

coated polyamide article having improved adhesion of the ~~coated~~ metal to the polyamide article surface.

Aldolyte bright acid copper solution was modified as described herein by substantially increasing the concentration of the Aldolyte AC-12E, Aldolyte AC14L, and Aldolyte AC-W-22 in the copper solution (Table 2) and modifying the conditions for applying the copper to the polyamide as shown in table 3.

By using the inventive copper solution disclosed in Table 2 and modified conditions disclosed in Table 3 for applying the copper metal-coating the resulting copper plated or coated polyamide article has excellent adhesion of copper to the polyamide article.

The strength of the bond between the metal ~~coating~~ and the polyamide article surface is determined by measuring the peel strength of the metal-polymer interface. Peel strengths/adhesion between polyamide resins and metal-coatings have traditionally only been used for decorative/aesthetic applications due to their poor adhesion performance. Increasing the peel strengths/adhesion between the substrate and deposited metals from 5-7 N cm⁻¹ to greater than 12 N cm⁻¹ allows use of the metal coated polyamide article in more demanding higher performance applications. Peel strength of copper coated polyamide articles prepared by the process described herein has a minimum peel strength between the copper surface and polyamide polymer surface of greater than 12 N cm⁻¹.

Peel strength of the metal from the plated articles was measured by a Z005 tensile tester (Zwick USA LP, Atlanta, GA) with a load cell of 2.5 kN using ISO test Method 34-1. An electroplated plaque was fixed on a sliding table which was attached to one end of the tensile tester. Two parallel cuts 1 cm apart was made into the metal surface so that a band of metal on the surface 1 cm wide was created. The table slid in a direction parallel to the cuts. The 1 cm wide copper strip was attached to the other end of the machine, and the metal strip was peeled (at a right angle) at a test speed of 50 mm/min (temperature 23°C , 50% relative humidity).

The processes described herein to achieve improved adhesion of a metal to a polyamide article surface can be used to apply metals such as copper, nickel, iron, cobalt, silver, zinc, titanium, platinum, palladium, aluminum, tin, lead, and other metals or any combination of metals to make a metal alloy. The processes described herein can also be used to apply multiple metal layers onto the

polyamide article surface in which each metal layer comprises a different metal or the same metal or metal alloy.

Additionally, polyamide articles can be prepared using the process described herein in which different metals are coated or plated onto different sections or portions of the polyamide article surface.

Applications where favorable or improved peel strength or adhesion of metal coatings onto polyamide article surfaces is desirable include electrical and electronic components, PDAs, cell phone components, computer notebook components, and the like, automotive components, aerospace parts, defense parts, consumer products, medical components and sporting goods. Suitable parts include tubes or shafts used in sporting goods such as ski and hiking poles, fishing rods, golf club shafts, hockey sticks, lacrosse sticks, baseball/softball bats, bicycle frames, skate blades, snow boards. Other applications include plates such as golf club head face plates and complex shapes such as sports racquets (tennis, racquetball, squash and the like), golf club heads, automotive grill-guards, pedals such as brake and gas pedals, fuel rails, running boards, spoilers, muffler tips, wheels, vehicle frames, structural brackets, and similar articles.

The article, whose surface is to be coated with metal, can be formed by processes such as by injection molding a polymer composition and subsequently removing the molded article from the mold and cooling.

Examples

The present invention is further defined by the following example. A comparative example is included. It should be understood that these examples, while indicating preferred embodiments of the invention, are given by way of illustration only.

All percentages are by weight unless otherwise specified.

Peel Strength

Peel strength of the metal from the plated articles was measured by a Z005 tensile tester (Zwick USA LP, Atlanta, GA) with a load cell of 2.5 kN using ISO test Method 34-1. An electroplated plaque was fixed on a sliding table which was attached to one end of the tensile tester. Two parallel cuts 1 cm apart was made into the metal surface so that a band of metal on the surface 1 cm wide was created. The table slid in a direction parallel to the cuts. The 1 cm wide copper strip

was attached to the other end of the machine, and the metal strip was peeled (at a right angle) at a test speed of 50 mm/min (temperature 23°C , 50% relative humidity). The peel strengths of each example are shown in Table 4.

Compositions

5 Polyamide PA-1 – Minlon® 73M40 is a 38 wt % mineral reinforced, heat stabilized polyamide 6 resin (61.8 wt %). Minlon® 73M40 has a density of 1450 kg/m³, a mp of 221°C and a Tg of 40°C, and a tensile modulus of 6000 MPa. The mineral filler is silanated clay (polarite 102A) and the heat stabilizer (0.2 wt %) is a KBr based heat stabilizer. Minlon® 73M40 is available E. I. du Pont de Nemours and Company, Wilmington, DE.

10 Plaque Preparation

Polyamide plaques were prepared to chemically treat the surface of a polyamide article and applying a metal-coating as described herein. Pellets of PA-1 were dried at 100°C for 6-8 hours in a dehumidified dryer and then molded with a Nissei Corp., Model FN4000, 1752 KN, 148cc (6 oz.) molding machine into a standard ISO 294 type D2 plaque of 6 cm x 6 cm x 2 mm, at a melt
15 temperature of 260°C to 300°C and mold temperature of 85-105°C.

Comparative Example 1

The surface of the polyamide plaque was prepared by treating the polyamide plaque for about 6 minutes at about 35°C in a solution bath of Noviganth PA Sweller Plus. The plaque was removed from the bath, drip drying for 1 minute, followed by a water rinse for 1 minute at room temperatures.
20 The plaque was then treated for about 6 minutes at about 35°C using a solution of Noviganth PA Conditioner followed by drip drying for 1 minute and a water rinse for 1 minute. The plaque was then treated with a solution of palladium ions using Noviganth PA Activator (a solution of 150 ppm palladium ions) for about 6 minutes at about 35°C followed by a drip dry for about one minute, then a rinse in water for about 1 minute. The plaque was treated with Noviganth PA Reducer for about 3
25 minutes at about 45 °C followed by a drip dry for about one minute, then a rinse in water for about 1 minute at room temperature. Electroless nickel deposition was applied using Noviganth Ni PA for about 10 minutes at about 55°C, followed by a water rinse for about 1 minute at room temperature. All of the proprietary Noviganth solutions used above were obtained from Atotech USA, Rock Hill, SC.

The plaque was then treated using the proprietary Aldolyte bright acid copper plating process taught by the Aldoa Company at the optimum concentrations of constituents listed in Table 2 and Aldolyte operating conditions in Table 3 (33.4 A/sq. ft. was passed for 28.2 minutes). The efficiency of the copper electroplating process was 99%. Peel strength was determined to be 6 N/cm.

Example 1

The surface of the polyamide plaque was prepared by treating the polyamide plaque for about 6 minutes at about 35°C using a solution of Noviganth PA Sweller Plus. The plaque was removed from the bath, drip drying for 1 minute, followed by a water rinse for 1 minute at room temperatures.

The plaque was then treated for about 6 minutes at about 35°C using a solution of Noviganth PA Conditioner followed by drip drying for 1 minute and a water rinse for 1 minute. The plaque was then treated with a solution of palladium ions using Noviganth PA Activator (a solution of 150 ppm palladium ions) for about 6 minutes at about 35°C followed by a drip dry for about one minute, then a rinse in water for about 1 minute. The plaque was treated with Noviganth PA Reducer for about 3 minutes at about 45 °C followed by a drip dry for about one minute, then a rinse in water for about 1 minute at room temperature. Electroless nickel deposition was applied using Noviganth Ni PA for about 10 minutes at about 55°C, followed by a water rinse for about 1 minute at room temperature. All of the proprietary Noviganth solutions used above were obtained from Atotech USA, Rock Hill, SC.

The plaque was then treated using the Aldolyte bright acid copper plating process taught by the Aldoa Company at the optimum inventive concentrations of constituents listed in Table 2 and inventive operating conditions in Table 3 (55.8 A/sq. ft. was passed for 21.2 minutes). The efficiency of the copper electroplating process was 97%. Peel strength was determined to be > 13 N/cm.

Table 4		
	Resin	Peel (N/cm)
Comparative Example 1	PA-1	6
Example 1	PA-1	13

Table 4 reveals the peel strength of the example of the invention using the inventive concentrations of Aldolyte AC-12E, Aldolyte AC14L, and Aldolyte AC-W-22, which were twice the recommended concentrations, had a peel strength value, which was more than two times the peel strength of the comparative example which used Atotech's recommended concentrations of Aldolyte additives.

CLAIMS

What is claimed is:

1. A process for applying a copper-coating to a polyamide article, the process comprising the steps of:
 - 5 i) chemically treating a surface of a polyamide article to provide an electrically conductive polyamide article;
 - ii) immersing the electrically conductive polyamide article into an electroplating solution comprising:
 - (a) 188 – 250 ml/L copper sulfate
 - 10 (b) 47 – 78 ml/ L sulfuric acid
 - (c) 20 – 200 mg/L chloride ion
 - (d) greater than 1.0 – 2.4 % of Aldolyte AC-12E
 - (e) greater than 1.25 ml/L of Aldolyte AC-14L
 - (f) greater than 3 - 6% Aldolyte AC-W-22
 - 15 iii) applying a cathode current density of 360 – 601 amp/ sq. meter to an electroplating solution cathode using phosphorized copper anodes to obtain a copper coated polyamide article;
- wherein the copper coated polyamide article has a peel strength between the copper and polyamide article surface of greater than 12 N cm⁻¹; and
- 20 wherein electroplating solution concentrations are based on the total volume of the electroplating solution.

2. The process of claim 1 wherein said polyamide article further comprises at least one reinforcing agent.

3. A metal coated polyamide article obtained by the process of claim 1.

4. A metal coated polyamide article of claim 3 in the form of electronic components, PDAs, cell phone components, computer notebook components, automotive components, aerospace parts, defense parts, consumer products, medical components, ski and hiking poles, fishing rods, golf club shafts, hockey sticks, lacrosse sticks, baseball bats, softball bats, bicycle frames, skate blades, snow boards, golf club head face plates, racquets for tennis, racquetball, squash, golf club heads, automotive grill-guards, pedals, fuel rails, running boards, spoilers, muffler tips, wheels, vehicle frames, and structural brackets.

5. The polyamide article of claim 1 wherein the polyamide is selected from poly(hexamethylene adipamide), polycaprolactam, poly(hexamethylene dodecanoamide), poly(decamethylene decanamide), poly(hexamethylene terephthalamide), poly(hexamethylene isophthalamide), and blends thereof.