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(54) **PLATEABLE CONDUCTIVE POLYMERIC PARTS AND METHODS OF FORMING**

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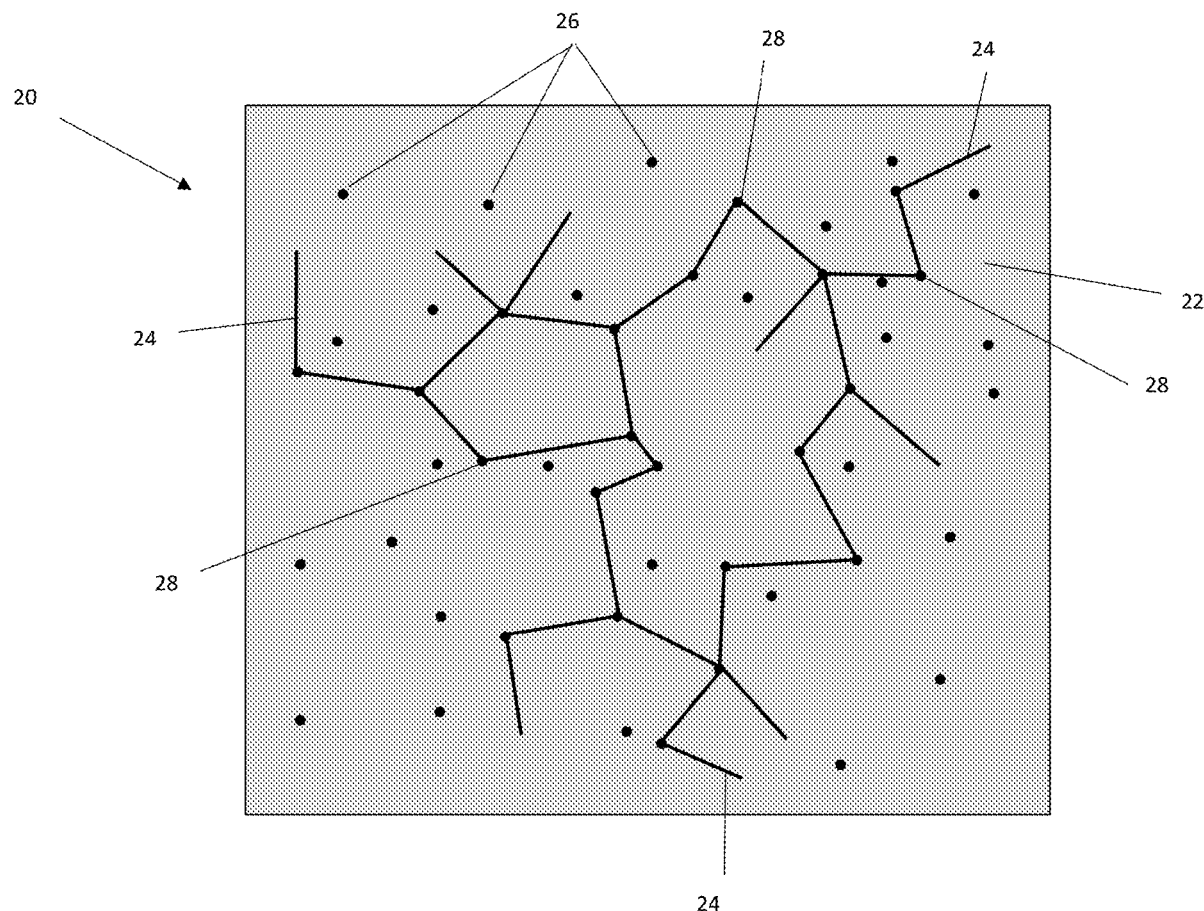
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(57) **ABSTRACT**

A method of plating a substrate includes etching at least a portion of a surface of the substrate to form voids within the surface. The substrate includes a composite material with a network of electrically conductive nanostructures dispersed therein. Electrodes are attached to the substrate, it is placed in a bath of a first electrically conductive metal, and a voltage is applied to the substrate through the electrodes to deposit a first electrically conductive metal layer onto the surface of the substrate, and a second electrically conductive metal layer is electroplated thereon.

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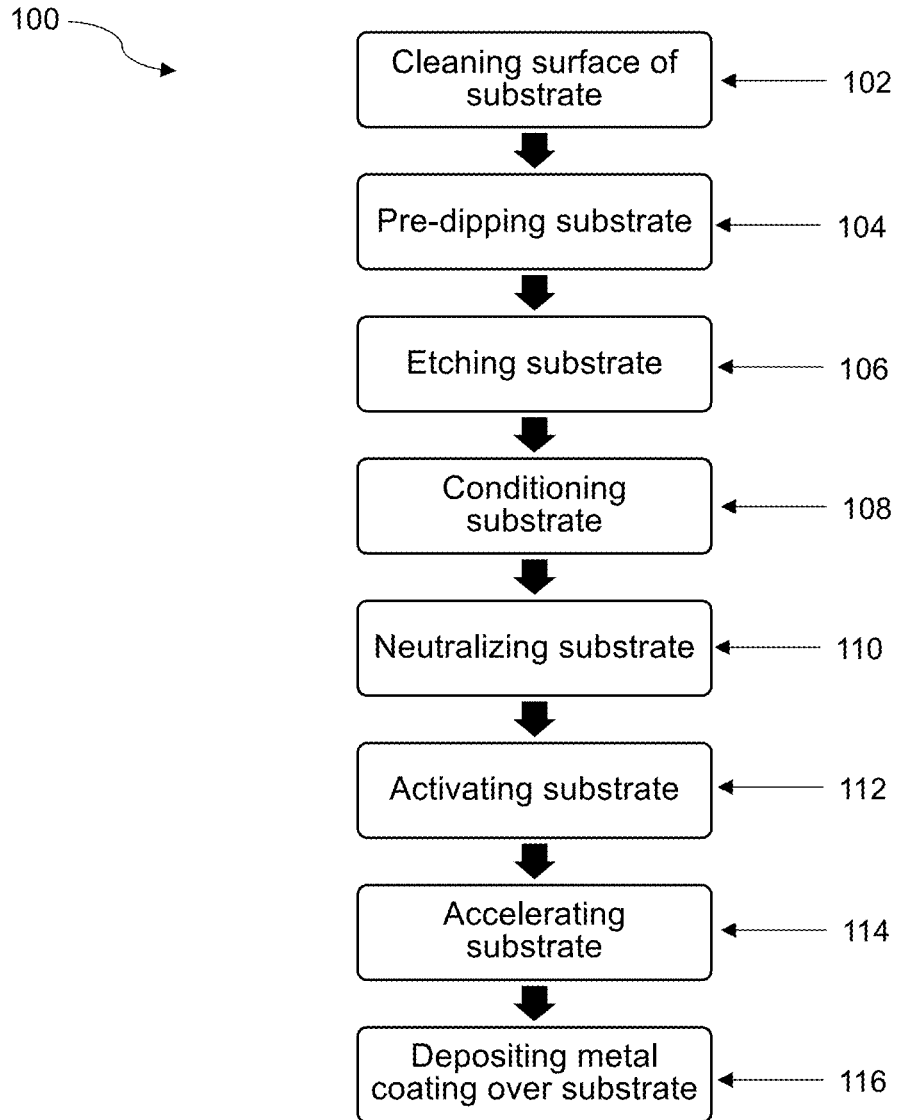


FIG. 1  
*PRIOR ART*

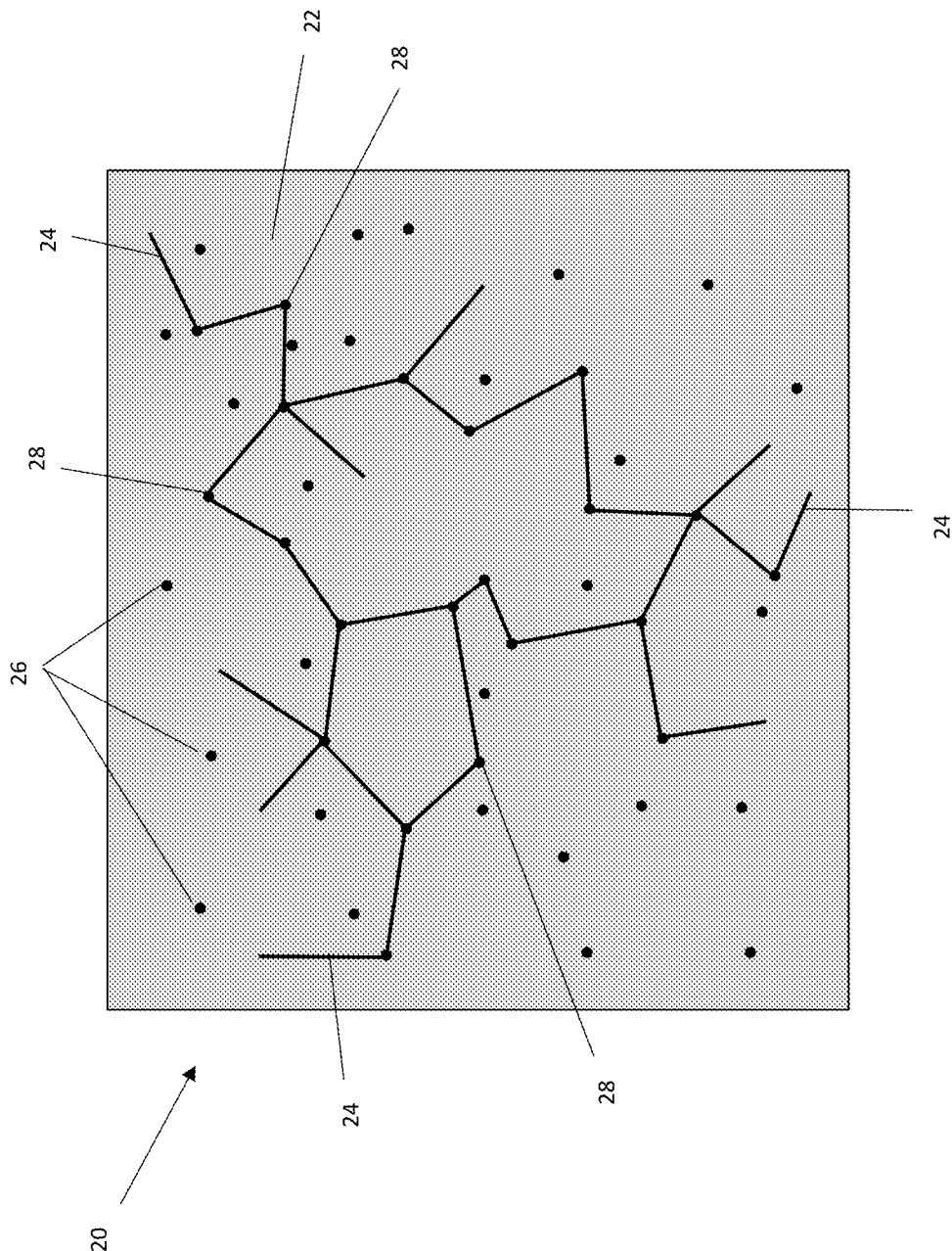


FIG. 2



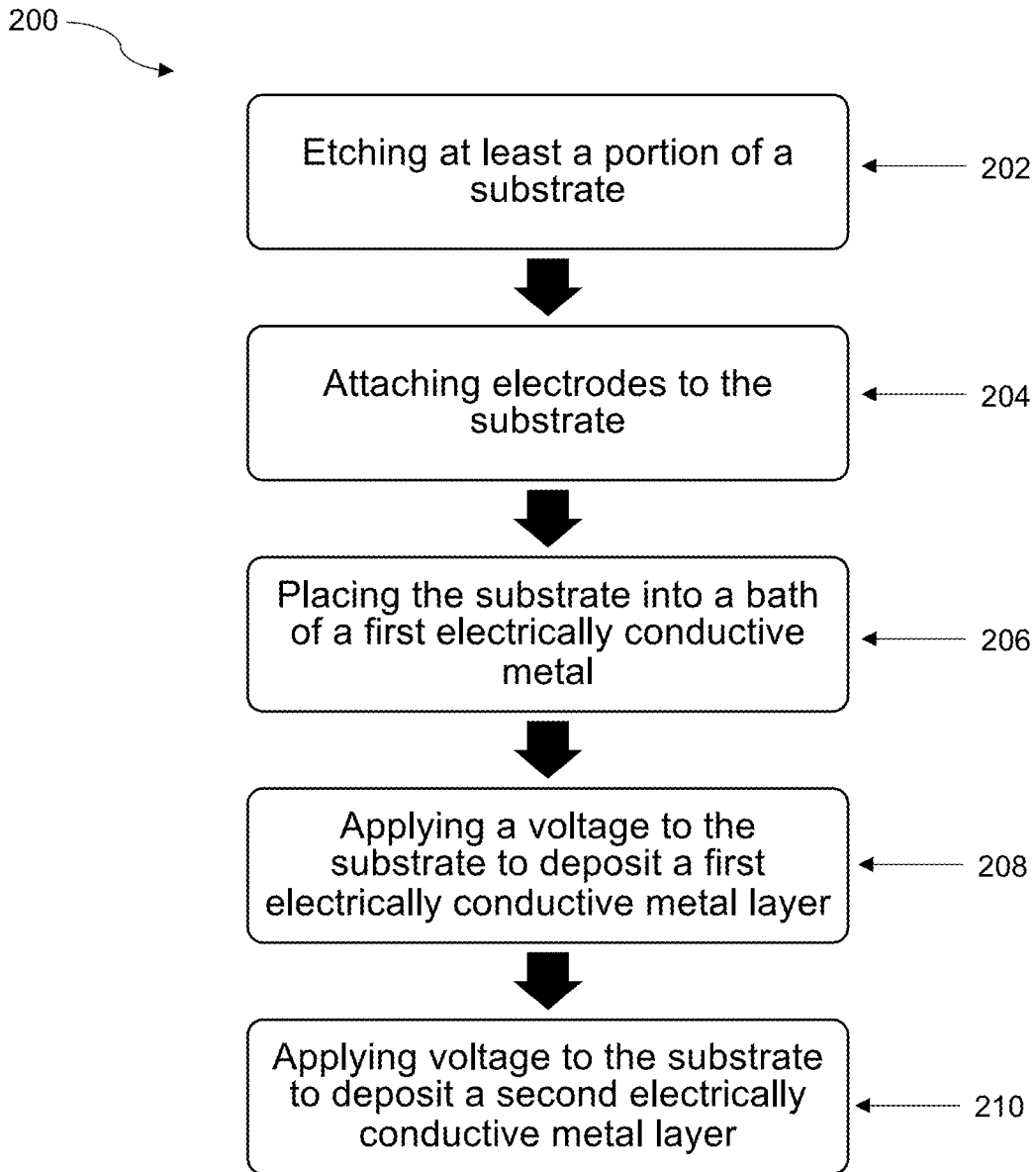


FIG. 4

## PLATEABLE CONDUCTIVE POLYMERIC PARTS AND METHODS OF FORMING

### FIELD

**[0001]** The present disclosure relates to electroplating polymeric parts, and more particularly to electroplating polymeric parts for motor vehicle applications with specific finish requirements.

### BACKGROUND

**[0002]** The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

**[0003]** Plating plastic parts with chromium or other similar materials is generally carried out in order to provide improved aesthetics of exterior components of a motor vehicle, such as by way of example a front grille or other trim components. Conventional processes for coating polymeric, or plastic parts with chromium involves a multi-step process to render the surface of the plastic part electrically conductive.

**[0004]** Referring to FIG. 1, a conventional process **100** for rendering plastic parts conductive includes first cleaning the surface of the substrate at **102**. Cleaning the surface assists in removing debris, dirt, smudges, fingerprints, and the like. A mild alkaline cleaner typically suffices, though thorough wetting with an acid solution (e.g., chromic acid) may be necessary in some applications. After cleaning, the substrate is pre-dipped in a solvent prior to etching at **104**. This can improve the rate at which the etchant reaches and attacks the surface of the substrate. After pre-dipping, the substrate is etched with an etchant at **106**. Etching increases the surface area of the substrate and produces microscopic holes that facilitate bonding with the deposited metal. Suitable etchants include chromic or sulfuric acid. A conditioner is optionally applied over the etched substrate at **108**. The conditioner may promote a more uniform absorption during the activation stage. After optional conditioning or etching if there is no optional conditioning, the etched substrate is neutralized (e.g., rinsed) at **110** to remove excess acid/etchant. Suitable neutralizers include but are not limited to sodium bisulfite or other neutralizers that provide for the removal of etchants. After neutralizing, the etched substrate is activated to serve as a catalyst during plating at **112**. Activation may be facilitated by the introduction of a low-concentration precious metal liquid activator (e.g., palladium, platinum, gold, among others) and serves to significantly reduce drag-out costs. After activation, an accelerator removes excess stannous hydroxide at **114**, which assists the activator to act as a catalyst and inhibit the occurrence of skip plating. The etched substrate may then be rinsed, and a metal coating (e.g., copper, nickel) is deposited over the etched substrate at **116** via an electroless bath, which renders the etched substrate electrically conductive. After the surface of the plastic part is rendered electrically conductive, the process ends and further processing is employed to coat the plastic part with a layer of chromium.

**[0005]** The thickness of a chromium or metal coating on plating parts according to conventional processes can vary across the plastic part as a function of part geometry. For example, an automobile grille plated according to conventional processes may yield thickness variations ranging from about 4 micrometers to 50 micrometers. Such variations can

result from deep surfaces of the part to be coated (e.g., a fog lamp surround). To offset such dimensional variations, the geometry of the substrate itself can be tailored (e.g., to narrow the depth of crevices, pockets, depressions, and the like of the substrate) or by increasing the dwell time the substrate is immersed in the electroless bath. Auxiliary anodes may also be employed to facilitate metal plating over the surfaces of a substrate having deeper crevices, pockets, depressions, or the like. Unfortunately, further finishing is required to provide an even layer of a metallic coating on the substrate when thickness tolerances are exceeded, thus contributing to increased costs and cycle time.

**[0006]** The present disclosure addresses these and other issues related to coating plastic parts with an aesthetically pleasing material such as chromium or nickel.

### SUMMARY

**[0007]** This section provides a general summary of the disclosure and is not a comprehensive disclosure of its full scope or all of its features.

**[0008]** According to one form of the present disclosure, a method of plating a substrate includes etching at least a portion of a surface of the substrate to form voids within the surface. The substrate includes a composite material having a network of electrically conductive nanostructures disposed within a thermoplastic matrix. Electrodes are attached to the substrate, and the substrate is placed into a bath of a first electrically conductive metal. A voltage is applied to the substrate through the electrodes, and the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate. A second electrically conductive metal is electroplated onto the first electrically conductive metal layer to form a second electrically conductive metal layer.

**[0009]** In variations of this form, which may be implemented individually or in any combination: the electrically conductive nanostructures are in an amount of about 0.5 wt. % of the composite material; the first electrically conductive metal is copper, and the second electrically conductive metal is nickel; the first electrically conductive metal includes at least one of copper, copper alloys, nickel, and nickel alloys; the thermoplastic matrix comprises at least one of acrylonitrile-butadiene-styrene (ABS) and polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS); the network of electrically conductive nanostructures comprises carbon nanotubes; the first electrically conductive metal layer has a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ ; the voltage conducted through the auxiliary anodes is disposed along a periphery of the substrate; an electroless plating process is not used to plate the substrate; a third electrically conductive metal is electroplated onto the second electrically conductive metal layer to form a third electrically conductive metal layer; the second electrically conductive metal is nickel, and the third electrically conductive metal is chrome; and a part is plated according to the present method.

**[0010]** According to another form of the present disclosure, a method of plating a substrate includes etching at least a portion of a surface of the substrate to form voids within the surface. The substrate includes a composite material having a network of electrically conductive nanostructures disposed within a thermoplastic matrix. The network of electrically conductive nanostructures is in an amount of about 0.5 wt. % of the composite material. Electrodes are

attached to the substrate, and the substrate is placed into bath of a first electrically conductive metal. A voltage is applied to the substrate through the electrodes, and the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate, and a second electrically conductive metal is electroplated onto the first electrically conductive metal layer to form a second electrically conductive metal layer.

**[0011]** In variations of this form, which may be implemented individually or in any combination: the first electrically conductive metal layer has a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ ; the voltage conducted through the auxiliary anodes is disposed along a periphery of the substrate; and the first electrically conductive metal is copper, and the second electrically conductive metal is nickel.

**[0012]** In yet another form of the present disclosure, a method of plating a substrate includes etching at least a portion of a surface of the substrate to form voids within the surface. The substrate includes a composite material having a network of electrically conductive nanostructures disposed within a thermoplastic matrix, and the network of electrically conductive nanostructures are in an amount of about 0.5 wt. % of the composite material. Electrodes are attached to the substrate, and the substrate is placed into a bath comprising a first electrically conductive metal including one copper and a copper alloy. A voltage is applied to the substrate through the electrodes, and the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate in a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ . A second electrically conductive metal is electroplated onto the first electrically conductive metal layer to form a second electrically conductive metal layer.

**[0013]** In variations of this form, which may be implemented individually or in any combination: the voltage conducted through the auxiliary anodes is disposed along a periphery of the substrate; an electroless plating process is not used to plate the substrate; a third electrically conductive metal is electroplated onto the second electrically conductive metal layer to form a third electrically conductive metal layer.

**[0014]** Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

#### DRAWINGS

**[0015]** In order that the disclosure may be well understood, there will now be described various forms thereof, given by way of example, reference being made to the accompanying drawings, in which:

**[0016]** FIG. 1 is a flowchart illustrating a conventional method for rendering a substrate electrically conductive according to the prior art;

**[0017]** FIG. 2 is a schematic view of a composite material according to the present disclosure;

**[0018]** FIG. 3 is a schematic view of an apparatus for manufacturing a composite material according to FIG. 2; and

**[0019]** FIG. 4 is a flowchart illustrating a method for metal plating a substrate according to the present disclosure.

**[0020]** The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way.

#### DETAILED DESCRIPTION

**[0021]** The following description is merely exemplary in nature and is not intended to limit the present disclosure, application, or uses. It should be understood that throughout the drawings, corresponding reference numerals indicate like or corresponding parts and features.

**[0022]** The present disclosure provides a method of plating substrates (e.g., plastic parts) with a metal layer without the need for an intermediary electroless plating step (set forth above). Generally, substrates having a surface resistivity less than  $1 \times 10^8$  ohm meter ( $\Omega\cdot\text{m}$ ) are suitable to achieve an electrostatic surface for plating a metal layer (e.g., chromium) over the surface of the substrate. In one form, the substrate has a surface resistivity less than  $1 \times 10^4$  ohm meter ( $\Omega\cdot\text{m}$ ).

**[0023]** Referring to FIG. 2, a composite material according to the present disclosure is illustrated and generally indicated by reference numeral 20. The substrates are made of the composite material 20, and the composite material 20 includes a thermoplastic matrix 22 and a network of electrically conductive nanostructures 24 dispersed within the thermoplastic matrix 22. Optionally, the composite material 20 further includes a plurality of additives 26, which are described in greater detail below.

**[0024]** As used herein, the phrase “network of electrically conductive nanostructures” should be construed to mean a crosslinked network of nanostructures connected at a plurality of nodes 28, which together form an electrically conductive pathway throughout the composite material 20. In one form, the nanostructures are carbon nanostructures. The network of electrically conductive nanostructures 24 further reduces the electrical resistivity of the composite material 20, improving the efficiency of the plating process. Therefore, the conductive network of linked nanostructures 24 provides enough conductivity to result in a composite material 20 that is statically dissipative, thus enabling efficient plating, as described in greater detail below. It should be understood that while the network of electrically conductive nanostructures 24 are connected at nodes 28 as shown, not all of the network of electrically conductive nanostructures 24 need be connected while remaining within the scope of the present disclosure. The network of electrically conductive nanostructures 24 are provided in an amount to provide the desired resistivity of the composite material 20 for plating processes.

**[0025]** To form the network of electrically conductive nanostructures 24 that are adequate for the desired conductivity, a high amount of shear is required in processing the nanostructures to untangle the nanostructures, which enables further improvement in conductivity. More specifically, the amount of shear processing during the compounding of the composite material 20 has a significant impact on the final material properties. Accordingly, the conductivity and surface resistivity of the composite material 20 can be tuned as desired, depending on the amount of nanostructures introduced and the amount of shear used in processing the nanostructures.

**[0026]** Referring to FIG. 3, one form of an apparatus 30 is illustrated, which is used to carry out the methods described herein. In this form, the apparatus 30 is a high-speed twin

extruder with co-rotating screws designed to have high shear and low shear sections. The high shear in general will untangle the carbon nanostructures, thus enabling further improvements in conductivity as described above. In one form, the extruder has a length to diameter ratio of at least about 32:1, and more particularly greater than about 40:1, to provide a more homogenized mixture. The thermoplastic matrix **22** and the nanostructures are added at or before a first feeder **32** and mixed at a high shear in a first mixing section **34**. Any additives (e.g., additives **36**) are optionally added following the high shear portion of the extruder in a second feeder **38** and mixed at a lower shear in a second mixing section **40**. From the apparatus **30**, the composite material **20** may be fed into an injection molding apparatus (not shown), or other forming process, and formed into the desired components for the substrates.

**[0027]** The thermoplastic matrix **22** may be any of a variety of thermoplastic materials, including by way of example, an acrylonitrile-butadiene-styrene (ABS) or a polycarbonate/acrylonitrile-butadiene-styrene (In one form, the thermoplastic matrix **22** includes plateable grades of ABS (i.e., ABS having a higher concentration of butadiene than standard grades), which enables effective etching of the surface of the substrate, thereby creating more voids and surface area for copper to fill, as described in greater detail below.

**[0028]** In one form of the present disclosure, the network of electrically conductive nanostructures **24** are added in an amount of about 0.5% by weight to achieve a surface resistivity of about  $1 \times 10^3$  ohm meter ( $\Omega \cdot m$ ). It is contemplated that lower or higher amounts of electrically conductive nanostructures **24** may be implemented depending on the desired resistivity. Substrates prepared according to the present disclosure exhibit improved electrical conductivity, which allows for elimination of electroless plating of the substrate required under conventional processes for metal plating substrates. Moreover, substrates plated according to the present disclosure exhibit more uniform metal plating thicknesses than substrates plated under conventional processes.

**[0029]** In one form of the present disclosure, before electroplating, at least a portion of the surface of the substrate is etched. Etching forms voids within the surface of the substrate, which facilitates bonding with the deposited metal.

**[0030]** Referring now to FIG. 4, a method **200** for plating a substrate comprising the composite material **20** as set forth above includes etching at least a portion of a surface of a substrate at **202**. Etching forms voids within the surface of the substrate as set forth above. Electrodes are attached to the substrate at **204**. At **206**, the substrate is placed into a bath comprising a first electrically conductive material. At **208**, a voltage is applied to the substrate through the electrodes such that the voltage conducts through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate. In one form, the first electrically conductive metal layer has a thickness between about 20  $\mu m$  to about 40  $\mu m$ . At **210**, a second electrically conductive metal is electroplated onto the first electrically conductive metal to form a second electrically conductive metal layer.

**[0031]** In one form, the first electrically conductive metal is copper, and the second electrically conductive metal is nickel, though the present disclosure should be interpreted to

include other metals that allow for further processing/plating according to the teaching of the present disclosure. By way of nonlimiting example, other metals include copper, copper alloys, nickel, and nickel alloys, among others. Optionally, a third electrically conductive metal is electroplated onto the second electrically conductive metal layer to form a third electrically conductive metal layer. In this form, the third electrically conductive metal layer is chrome.

**[0032]** In one form of the present disclosure, voltage is conducted through auxiliary anodes disposed along a periphery of the substrate, which are not shown for purposes of clarity.

**[0033]** The plated parts disclosed herein may be used in various applications where it is desirable to have a more uniform, streamlined process to plate the parts with a metal layer without the need for an intermediary electroless plating step. Such parts may include, by way of example, grilles and trim parts in the automobile and motor vehicle industry but are not limited thereto.

**[0034]** Unless otherwise expressly indicated herein, all numerical values indicating mechanical/thermal properties, compositional percentages, dimensions and/or tolerances, or other characteristics are to be understood as modified by the word “about” or “approximately” in describing the scope of the present disclosure. This modification is desired for various reasons including industrial practice, material, manufacturing, and assembly tolerances, and testing capability.

**[0035]** As used herein, the phrase at least one of A, B, and C should be construed to mean a logical (A OR B OR C), using a non-exclusive logical OR, and should not be construed to mean “at least one of A, at least one of B, and at least one of C.”

**[0036]** The description of the disclosure is merely exemplary in nature and, thus, variations that do not depart from the substance of the disclosure are intended to be within the scope of the disclosure. Such variations are not to be regarded as a departure from the spirit and scope of the disclosure.

What is claimed is:

1. A method of plating a substrate, the method comprising:
  - etching at least a portion of a surface of the substrate to form voids within the surface, the substrate comprising a composite material having a network of electrically conductive nanostructures dispersed within a thermoplastic matrix;
  - attaching electrodes to the substrate;
  - placing the substrate into a bath comprising a first electrically conductive metal;
  - applying a voltage to the substrate through the electrodes, wherein the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate; and
  - electroplating a second electrically conductive metal onto the first electrically conductive metal layer to form a second electrically conductive metal layer.
2. The method according to claim 1, wherein the electrically conductive nanostructures are in an amount of about 0.5 wt. % of the composite material.
3. The method according to claim 1, wherein the first electrically conductive metal is copper, and the second electrically conductive metal is nickel.



4. The method according to claim 1, wherein the first electrically conductive metal comprises at least one of copper, copper alloys, nickel, and nickel alloys.

5. The method according to claim 1, wherein the thermo-plastic matrix comprises at least one of acrylonitrile-butadiene-styrene (ABS) and polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS).

6. The method according to claim 1, wherein the network of electrically conductive nanostructures comprises carbon nanostructures.

7. The method according to claim 1, wherein the first electrically conductive metal layer has a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ .

8. The method according to claim 1, further comprising conducting the voltage through auxiliary anodes disposed along a periphery of the substrate.

9. The method according to claim 1, wherein an electroless plating process is not used to plate the substrate.

10. The method according to claim 1, further comprising electroplating a third electrically conductive metal onto the second electrically conductive metal layer to form a third electrically conductive metal layer.

11. The method according to claim 10, wherein the second electrically conductive metal is nickel, and the third electrically conductive metal is chrome.

12. A part plated according to the method of claim 1.

13. A method of plating a substrate, the method comprising:

etching at least a portion of a surface of the substrate to form voids within the surface, the substrate comprising a composite material having a network of electrically conductive nanostructures dispersed within a thermo-plastic matrix, the network of electrically conductive nanostructures being in an amount of about 0.5 wt. % of the composite material;

attaching electrodes to the substrate;

placing the substrate into a bath comprising a first electrically conductive metal;

applying a voltage to the substrate through the electrodes, wherein the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate; and

electroplating a second electrically conductive metal onto the first electrically conductive metal layer to form a second electrically conductive metal layer.

14. The method according to claim 13, wherein the first electrically conductive metal layer has a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ .

15. The method according to claim 13, further comprising conducting the voltage through auxiliary anodes disposed along a periphery of the substrate.

16. The method according to claim 13, wherein the first electrically conductive metal is copper, and the second electrically conductive metal is nickel.

17. A method of plating a substrate, the method comprising:

etching at least a portion of a surface of the substrate to form voids within the surface, the substrate comprising a composite material having a network of electrically conductive nanostructures dispersed within a thermo-plastic matrix, the network of electrically conductive nanostructures being in an amount of about 0.5 wt. % of the composite material;

attaching electrodes to the substrate;

placing the substrate into a bath comprising a first electrically conductive metal, the first electrically conductive metal comprising one of copper and a copper alloy; applying a voltage to the substrate through the electrodes, wherein the voltage is conducted through the network of electrically conductive nanostructures to deposit a first electrically conductive metal layer onto the surface of the substrate in a thickness between about 20  $\mu\text{m}$  to about 40  $\mu\text{m}$ ; and

electroplating a second electrically conductive metal onto the first electrically conductive metal layer to form a second electrically conductive metal layer.

18. The method according to claim 17, further comprising conducting the voltage through auxiliary anodes disposed along a periphery of the substrate.

19. The method according to claim 17, wherein an electroless plating process is not used to plate the substrate.

20. The method according to claim 17, further comprising electroplating a third electrically conductive metal onto the second electrically conductive metal layer to form a third electrically conductive metal layer.

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