A process for direct metal-plating of a plastic substrate (14). The process comprises the steps of: (i) activating a surface of modified polyolefin substrate to produce an active surface (16), the active surface (16) having at least about 7% of carbon atoms in the form of carbonyl; (ii) electrochemically depositing metal layer (18) on the active surface (16).
PROCESS FOR THE DIRECT METAL-PLATING OF A PLASTIC SUBSTRATE

FIELD OF THE INVENTION

[0001] The present invention relates to a process for direct metal-plating of a plastic substrate.

DESCRIPTION OF THE PRIOR ART

[0002] Metal-plating of substrate materials is known. For example, chrome-plating of automobile trim components is periodically popular.

[0003] Many years ago such chrome-plating was achieved by plating a metal substrate (e.g., a bumper).

[0004] Over the years, chrome-plating of metal substrates for use in automobile trim parts has been reduced for a variety of reasons, including: the need to reduce the weight of the vehicle; corrosion problems with the metal substrate; the advance of other systems for energy absorption if the substrate was being used as a bumper and the like. Thus, the state of the art has advanced over the years in the general subject matter area of metal-plating of substrates (both metal and non-metal).

[0005] U.S. Pat. No. 5,468,518 [Lein et al. (Lein)] teaches a combined primer/basecoat island coating system for manufacturing a metallized part. Generally, the process relates to metallizing a substrate material selected from the group comprising thermoplastic urethane (TPU), TPU alloys, polyester alloys, nylon, thermoplastic olefins (TPO) and aluminum. In the process, a protective layer (primer/basecoat) is sprayed deposited, flushed and cured over the substrate. The protective layer comprises clear urethane resin, black pigment paste, a solvent blend and a catalyst solution. Thereafter, a layer of corrosion prone metal is vacumin deposited to form a discontinuous film covering the combined primer/basecoat layer. Finally, a layer of clear resinous protective dielectric topcoat is sprayed deposited and cured to completely cover the layer of corrosion prone metal material. Apparently, the process provides metallized parts which have a metallic rather than satin appearance and which may be produced relatively rapidly and cost-effectively. Thus, Lein teaches a general plating technique for metal and non-metal substrates.

[0006] U.S. Pat. No. 5,591,488 [Schäfer et al. (Schäfer)] teaches a process for treatment of polymer-containing workpiece surfaces and to an aqueous non-aging solution. The focus of Schäfer is in a preconditioning process and materials for use therein to prepare a substrate material for application of a metal plating layer. In Schäfer, the substrate is a polymeric material—e.g., polycarbonate, optionally admixture with acrylonitrile-butadiene-styrene copolymer. Schäfer is not particularly concerned with direct coating of a specific type of polymer substrate with a metal-plating layer.

[0007] U.S. Pat. No. 5,693,209 [Bressel et al. (Bressel)] teaches a process for direct metallization of a circuit board having nonconductive surfaces. The process comprises reacting the nonconductive surface with an alkylamine permanganate solution to form manganese dioxide chemically absorbed on the nonconductive surface. Thereafter, an aqueous solution of a weak acid and of a pyrrole or a pyrrole derivative and soluble oligomeric metal is formed and contacted with the nonconductive surface to deposit an adherent, electrically conducting, insoluble polymer product on the nonconductive surface. Thereafter, a metal is directly electrodeposited onto the nonconductive surface. The process is principally directed to the process useful in the production of circuit boards.

[0008] U.S. Pat. No. 5,882,736 [Stein et al. (Stein)] teaches a process for deposition of a palladium layer on a metal surface. Specifically, the process is for the deposition of highly adhesive, permanently glossy palladium layers having very few pores on the metal surface. This is achieved by immersing the metal surface in a formaldehyde-free chemical bath, with or without pretreatment.

[0009] U.S. Pat. No. 5,985,418 [Lein et al. (Lein)] teaches a process for manufacturing a metallized substrate using a so-called island coating method. Particularly adapted for application of a metal layer to a substrate used in the apparel industry. The process comprises depositing a first coating layer containing a radiation curable non-volatile film former. The coated substrate is then vacuum metallized to form the metal islands of the invention and thereafter, a layer of clear resinous protective dielectric top coat containing a radiation curable non-volatile film former is deposited to completely cover the layer of "metal islands". The substrate can be polymeric or metallic.

[0010] Thermoplastic Olefin (TPO) is commonly molded into exterior trim components for automobiles. In particular, vehicles are commonly fitted with a front and rear fascia which cover or conceal a front and rear bumper beam assembly. Molded TPO rocker panels and fenders are also commonly utilized on vehicles. The trim panels are molded and then painted to match the color of the remaining portion of the vehicle.

[0011] Prior to the use of molded fascia, vehicles were fitted with steel bumpers that had a chromed outer surface. Slowly, the design of vehicles shifted to the use of color matched molded fascia concealing the bumper beam minimizing the use of chrome. However, there has been a "retro" trend in automotive design and designers are again requiring chromed exteriors.

[0012] However heretofore, conventional TPO does not accept metal plating despite the advances in the art. There is a need for a relatively simple process which would allow for direct metal-plating on a polymer surface, particularly a thermoplastic olefin (TPO) surface of an article adapted to be used in an automotive trim application.

SUMMARY OF THE INVENTION

[0013] The disadvantages of the prior art may be overcome by providing a novel process for direct metal-plating of a plastic substrate.

[0014] Accordingly, in one of its aspects, the present invention provides a process for direct metal-plating of a plastic substrate comprising the steps of:

[0015] (i) activating a surface of a TPO substrate to produce an active surface thereof, the active surface having at least about 7% of carbon atoms being in the form of carboxyl;

[0016] (ii) electrochemically depositing metal layer on the activated surface.
The functionality of carbon atoms at the surface of an activate thermoplastic olefin (TPO) substrate (i.e., the active surface of the substrate) to be metal-plated plays an important role in facilitating direct metal-plating. Specifically, it is important that the active surface of the substrate comprise carbon atoms of which at least about 7% are in the form of carbonyl in order to produce a durable, good quality metal plate coating on the substrate. If the active surface of the substrate comprises carbon atoms of which is less than about 7% in the form of carbonyl, the metal-plating coating will be inferior and subject to detachment from the thermoplastic olefin substrate. As used throughout this specification, the term “active surface” is intended to denote a surface layer of the TPO substrate having a thickness of from about 3 to about 5 nm.

As used throughout this specification, the term “modified TPO” is intended to mean polypropylene-based materials such as polyolefin modified with a first elastomeric material such ethylene propylene diene monomer (EPDM) and further modified with a second elastomer including a diene and triene type polymer.

DESCRIPTION OF THE DRAWINGS

In drawings which illustrate embodiments of the present invention,

FIG. 1 is a perspective view of an automotive trim piece of the present invention; and

FIG. 2 is a cross sectional view of the automotive trim piece of FIG. 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the present invention is useful to directly metallize a TPO substrate. In the first preferred embodiment, the TPO substrate is a modified TPO comprising a polyolefin material modified with a first elastomer, such as EPDM and then modified with a second elastomer, including diene and triene type polymers, such as acrylonitrile and butadiene. The elastomers are added in effective amounts providing a basis for an active surface as discussed below.

The TPO is molded in a conventional manner into a substrate. Preferably, the substrate is in the form of an automotive component such as a grill. However, other components such as fascia, trim panels, rocker panels, fenders, trim strips are also contemplated in the present invention. A surface of the TPO substrate is activated by one of the methods described below to provide an active surface. Preferably, the active surface is a presentation or exterior-facing surface of the molded part on which a metal layer is deposited.

Active surface of the TPO substrate comprises carbon atoms of which at least about 7% are in the form of carbonyl. Preferably from about 7% to about 25% of carbon atoms at the active surface are in the form of carbonyl. More preferably, from about 7% to about 20% of carbon atoms at the active surface are in the form of carbonyl. Most preferably, about 7% to about 15% of carbon atoms at the active surface are in the form of carbonyl.

The presence of the carbonyl groups at the active surface may be confirmed by conventional techniques—e.g., FTIR (Fourier Transform Infrared spectroscopy). The concentration of carbonyl groups at the active surface may be confirmed by conventional techniques—e.g., XPS (X-ray photoelectron spectroscopy).

In the first preferred method, a modified TPO is utilized and the desired amount of carbonyl content can be conferred to the surface of a modified TPO substrate by controlling preferred pretreatment steps in the process.

It is preferred to pretreat the modified TPO substrate using an etching technique—i.e., this is a preferred embodiment of Step (i) of the present process. Preferably, the etching technique comprises contacting the modified TPO substrate with an etching solution comprising chromic acid or a mixture of chromic acid and sulfuric acid. During this etching step the active surface is formed. It is believed that chromic acid is reduced on the surface of the modified TPO substrate to provide oxygen containing moieties (e.g., hydroxyl, ether and the like), including the desired carbonyl groups. The amount of desired carbonyl groups may be controlled by the time period during which the substrate is immersed in the etching solution. The chemicals used in the above-mentioned etching step may be obtained commercially from Atotech Canada Ltd. under the tradename Futuron™.

Next, it is preferred to subject the active surface of the modified TPO substrate to chromic acid reduction to reduce any residual chromic acid left in the pores of the substrate from Cr⁶⁺ to Cr⁢⁴⁺ (the reason for this is that Cr⁶⁺ is detrimental if present during later steps in the process).

Next, it is preferred to subject the active surface of the modified TPO substrate to a pre-dipping step in which the active surface of the modified TPO substrate is contacted with an acid. A non-limiting useful such acid is hydrochloric acid.

The chemicals used in the above-mentioned chromic acid reduction and pre-dipping steps are commercially available under the tradename Futuron™ from Atotech Canada Ltd.

The active surface of the modified TPO substrate is then ready for further activation wherein a surface thereof is fully activated for electrolytic metallization. This involves contacting the active surface with an aqueous solution comprising a palladium salt and a tin salt in hydrochloric acid. Preferably, the solution comprises palladium chloride and stannous chloride.

Practically, it is preferred to immerse the substrate in a bath containing stannic palladium in a concentration of from about 5 to about 20,000 ppm (0.005 to 20 g/L), preferably from about 20 to about 300 ppm (0.02 to 0.3 g/L), more preferably from about 20 to about 250 ppm (0.02 to 0.25 g/L) for a period of at least about one minute, preferably from about one minute to about ten minutes, more preferably from about two minutes to about four minutes.

This activation step serves to anchor the palladium/tin complex to the surface of the TPO substrate. By controlling the oxygen content in the substrate, a desirable level of palladium/tin complex is dispersed over the surface of the substrate.

Preferably, the next step in the process is to exchange the tin in the palladium/tin complex with copper. This is done in a conventional manner.
The chemical(s) used in the above-mentioned electrolytic metallization steps may be obtained commercially from Atotech Canada Ltd. under the tradename Futuron™.

Optionally, a layer of nickel or copper can be deposited on the active surface in a conventional manner, including electroless deposition whereby nickel or copper salt is reduced onto the active surface of the TPO substrate. Advantages of the nickel or copper layer include increased conductivity, reduced bath time and lower palladium concentrations (<100 ppm or 0.1 g/L) in the palladium bath discussed above.

Step (ii) of the present process comprises electrochemically depositing a metal layer on the active surface of the TPO substrate. This can be done in a conventional manner.

Embodiments of the present invention will be described with reference to the following examples which are provided for illustrative purposes only and should not be used to construe or limit the scope of the invention.

EXAMPLES

In the Examples, a modified TPO obtained from Solvay Engineered Polymers was activated, treated and electrolytically metallized in the following manner.

All samples were TPO panels which were treated using chemicals commercially available from Atotech Canada Ltd. in the Futuron™ pre-plating process. As is known in the art, the Futuron™ pre-plating process comprises the following general steps: (i) cleaner (optional); (ii) etching (typically with chromic sulfuric acid); (iii) reduction (typically with Cr (VI), (iv) pre-dip solution; (v) Pd/Sn activation and (vi) Cu-link. In the Examples, the modified TPO substrate was treated according to the particulars set out in Tables 1 and 2.

Etch time was varied as set out in Table 3 below.

Four panels per Example were processed through to copper plating.

Pre-plate tank conditions (dwell times, concentrations, temperatures) are reported below. All panels were plated using a conventional acid copper-electroplating bath, followed by conventional electroplating nickel and chrome baths. Panels were plated for 60 minutes at 30 amps/ft² to achieve 40+/-5 microns of copper thickness for peel testing as defined in ASTM B533.

The test panels were stripped of palladium and copper using a solution of Aqua Regia (1:1). Solutions were analysed for metal content using Atomic Adsorption spectrophotometry. Samples were tested for peel strength using the 90° tensile test, on an Instron™ instrument in accordance with ASTM B533. Each sample panel was cut into three strips and each strip tested. The overall average of the strips for each Example is reported as the peel strength of the panel.

The peel tests results illustrate that significantly improved adhesion of the metal plating layer is achieved in Examples 2 and 3 (carbonyl content of at least 7%) compared with that achieved in Example 1 (carbonyl content less than 7%).

While the present invention has been described with reference to preferred and specifically illustrated embodiments, it will of course be understood by those skilled in the art that various modifications to these preferred embodiments and illustrated embodiments may be made without departing from the scope of the invention as defined in the appended claims.

While the carbonyl content described in the Examples was achieved with chemical etching of a modified TPO, it is of course possible to confer the carbonyl functionality to the surface of TPO using other conventional techniques such as flaming, vacuum plasma and electrical discharge (e.g., Corona surface treatment).

In the case of vacuum plasma and Corona surface treatment, it is possible to achieve the requisite active surface of a conventional TPO substrate without the need for modifying the TPO with the second elastomer.

Still further, while the carbonyl content described in the Examples was varied by varying the period chemical etching, it is of course possible to control the amount of carbonyl functionality on the substrate surface using other means such as temperature of the etching bath and/or the concentration the chemicals used in the etching bath. Other modifications which do not depart from the scope of the present invention will be apparent to those of skill in the art.

All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

**TABLE 1**

<table>
<thead>
<tr>
<th>Tank</th>
<th>Immersion Time (minutes)</th>
<th>Temperature (° C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromo/Sulphuric Etch</td>
<td>Varied (2-20)</td>
<td>(60-70)</td>
</tr>
<tr>
<td>Chrome Reducer</td>
<td>0.5</td>
<td>25</td>
</tr>
<tr>
<td>Pre-Dip</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>Pd/Sn Activator</td>
<td>4</td>
<td>44</td>
</tr>
<tr>
<td>Cu-Link</td>
<td>3</td>
<td>55</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Etch</th>
<th>Reducer</th>
<th>Pre-Dip</th>
<th>Activator</th>
<th>Cu-Link</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI) (g/L)</td>
<td>H₂SO₄ (g/L)</td>
<td>Cr(III) (g/L)</td>
<td>HCl (%)</td>
<td>Pd (ppm)</td>
</tr>
<tr>
<td>390</td>
<td>400</td>
<td>25</td>
<td>11</td>
<td>30</td>
</tr>
</tbody>
</table>
What is claimed is:

1. A process for direct metal-plating of a plastic substrate comprising the steps of:

(i) activating a surface of a TPO substrate to produce an active surface, the active surface having at least about 7% of carbon atoms at the active surface being in the form of carbonyl;

(ii) electrochemically depositing a metal layer on the activated surface.

2. The process defined in claim 1, wherein from about 7% to about 25% of carbon atoms at the active surface are in the form of carbonyl.

3. The process defined in claim 1, wherein from about 7% to about 20% of carbon atoms at the active surface are in the form of carbonyl.

4. The process defined in claim 1, wherein from about 7% to about 15% of carbon atoms at the active surface are in the form of carbonyl.

5. The process defined in claim 1, comprising, prior to Step (ii), the further step of depositing a layer of palladium on the active surface.

6. The process defined in claim 1, wherein, prior to Step (ii), the further step of reduction of a palladium salt on the active surface.

7. The process defined in claim 6, wherein the palladium salt is selected from the group comprising palladium sulfate, palladium nitrate, palladium perchlorate and mixtures thereof.

8. The process defined in claim 6, comprising immersing the active surface in a bath comprising the palladium salt.

9. The process defined in claim 8, wherein the palladium salt is present in the bath in a concentration of from about 0.005 to about 20 g/L.

10. The process defined in claim 8, wherein the palladium salt is present in the bath in a concentration of from about 0.02 to about 2.0 g/L.

11. The process defined in claim 8, wherein the palladium salt is present in the bath in a concentration of from about 0.02 to about 0.3 g/L.

12. The process defined in claim 8, wherein the palladium salt is present in the bath in a concentration of from about 0.02 to about 0.25 g/L.

13. The process as claimed in claims 5 to 12, wherein immediately prior to Step (ii) said process includes a step of depositing a layer of a metal onto said active surface, said metal selected from a group comprising nickel and copper.

14. The process as claimed in claim 13 wherein said depositing step comprises reducing a respective metal salt onto the active surface by electroless deposition.

15. The process as claimed in any preceding claim wherein prior to Step (i) said process includes a first pre-step of modifying a TPO by adding an effective amount of an elastomer selected from a monomer group comprising diene and triene type polymers to a thermoplastic olefin.

16. The process as claimed in claim 15 wherein said diene and triene type polymers include acrylonitrile and butadiene.

17. The process as claimed in claims 15 or 16 wherein prior to said Step (i) said process includes a second pre-step of modifying said modified TPO into said substrate.

18. The process as claimed in any preceding claim wherein said Step (i) of activating includes chemically etching said surface with an etching solution selected from a group comprising chromic acid and a mixture of chromic acid and sulfuric acid.

19. The process as claimed in claim 18 wherein said percentage of carbon atoms at said active surface in the form of carbonyl is controlled by an amount of time said active surface is etched by said etching solution.

20. The process as claimed in claim 19 wherein said percentage of carbon atoms at said active surface in the form of carbonyl is controlled by varying a temperature of the etching solution.

21. The process as claimed in claim 19 wherein said percentage of carbon atoms at said active surface in the form of carbonyl is controlled by varying a concentration of chemicals used in the etching solution.

22. The process as claimed in claims 18 to 21 wherein said Step (i) of activating includes subjecting said surface to a chromic acid reduction to reduce any residual chromic acid on said surface from Cr⁶⁺ to Cr³⁺.

23. The process as claimed in claim 22 wherein said Step (i) of activating includes pre-dipping the substrate with a pre-dipping acid.

24. The process as claimed in claim 23 wherein said pre-dipping acid includes hydrochloric acid.

25. The process as claimed in claims 1 to 15 wherein said Step (i) of activating includes flaming, vacuum plasma and electrical discharge.

26. The process as claimed in any preceding claim wherein said active surface has a thickness of from about 3 to 5 μm.

27. A plastic substrate plated with metal according to the process of any one of the preceding claims.

* * * * *