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(54) **Method of providing a metal mirror.**

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Description

The invention relates to a method of providing a metal mirror on an article of which at least the surface on which the metal mirror is to be provided is manufactured from a synthetic resin, whereby the said surface is treated with tannic acid and provided with a metal mirror by means of an electroless metallization process.

A suitable method of providing a metal mirror on a substrate of a synthetic resin is known from Technical Proceedings of the 51st Annual Convention of the American Electroplaters' Society, June 14—18, St. Louis, 1964, *pp.* 139—149. According to this known process, an aqueous metal salt solution and a solution of a reducing agent are simultaneously atomised (sprayed) onto the surface to be metal plated. In metal-plating synthetic resins, the comparatively low polar of a polar surface must first be pretreated chemically or mechanically and then be sensitized with a reducing agent, for example $SnCl_2$. In Table 2 on page 140 of the above-mentioned literature reference, various chemical pretreatment agents for synthetic resins are recorded.

United States Patent Specification 3,094,430 states that upon silver-plating acrylic plastics, the surface is pretreated with a solution of tannic acid. A sensitizing treatment with $SnCl_2$ is not used. Experiments have demonstrated that a silver mirror provided in this manner on an acrylate synthetic resin or a methacrylate synthetic resin shows an insufficient adhesion.

It is known from Netherlands Patent Application No. 81.03.375 and the corresponding European Patent Application No. 0.070.595 in the name of Applicants to polymerize a polymerisable monomer composition which comprises monomeric acrylates and an N-substituted pyrolidone compound, to treat the resulting synthetic resin surface with, for example, tannic acid, and then to provide a metal mirror by means of a metal-plating process.

The treatment of an acrylic plastic with tannic acid known from the above-mentioned United States Patent Specification has the disadvantage that an adherent silver mirror cannot be obtained. The treatment with tannic acid known from the above-mentioned Netherlands Patent Application has the disadvantage that it can be applied only to a special synthetic resin, namely an acrylate synthetic resin which comprises an N-substituted pyrolidone compound. In the preparation of this special synthetic resin the pyrolidone compound is not completely copolymerized. The remaining pyrolidone molecules are volatile and in the course of time can adversely influence the quality of the provided metal mirror.

It is the object of the invention to provide a method which does not exhibit the above-mentioned disadvantages.

According to the invention this object is achieved by means of a method of the type mentioned in the opening paragraph which is characterized in that prior to the said treatment with tannic acid, the said surface which is manufactured from a polyester or a polyolefine possibly substituted with halogen atom(s) or aromatic group(s), is subjected to an oxidizing corona discharge treatment or a chromic acid treatment.

The invention is based on the recognition gained by Applicants that a pretreatment with tannic acid in combination with an oxidising pretreatment step, has a more universal character and can be applied to the above-mentioned types of synthetic resin, in which after metallisation, a very adherent metal mirror is obtained. The metal mirror also remains bonded to the synthetic resin surface after ageing tests, for example a cyclic moisture test.

In a favourable embodiment a surface of polyethylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, polyacrylate or polymethylmethacrylate is subjected to a corona discharge, is treated with tannic acid, and is provided with a metal mirror by means of an electroless metallization process.

A corona discharge is a known process in which a high voltage is applied between the synthetic resin surface and an electrode. As a result of electric discharge, high-energy particles will be formed, for example atomic oxygen, electrons, ions and the like which impact against the synthetic resin surface, the composition of the synthetic resin at the surface varying and in particular oxygen being bound to the surface of the synthetic resin. The synthetic resin surface is oxidized and obtains a hydrophilic character.

The use of a Corona discharge alone, as a pretreatment prior to metallization of a synthetic resin is known from French Patent Application No. 2.381.081. More particularly this reference teaches a Corona discharge pretreatment applied to polyethylene or polyimides, polyhydantoïnes, ionomeric resins and epoxy resins and a subsequent metallisation with copper.

In another favourable embodiment of the method in accordance with the invention a surface of polyvinyl chloride or polycarbonate is treated with chromic acid, then with tannic acid, and is provided with a metal mirror by means of an electroless metallization process.

The invention will be described in greater detail with reference to the following example.

Example

The surface of a synthetic resin as recorded in column 1 of the Table below is subjected for a few seconds to a corona discharge by means of a HF generator having a sinusoidal alternating voltage of 12018 kV and a frequency of 20—40 kHz which is connected to an electrode placed above the surface of the synthetic resin. The surface of the synthetic resin is then treated with an aqueous solution of tannic acid for at most one minute at a temperature of 25°C. The concentration of tannic acid in the solution is not restricted to narrow limits and may be chosen, by way of example, between 0.1 and 10 g of tannic acid per

litre. If desired the solution may also comprise water-miscible organic solvents, for example, an organic acid, alcohol, ketone, ether or ester. The synthetic resin surface may be dipped in the solution of tannic acid. A solution of tannic acid may also be sprayed or poured onto the surface to be treated.

The synthetic resins recorded in column 1 of the Table have been pretreated only with tannic acid in a second series of tests, no preceding oxidising treatment being used.

After the treatment with tannic acid, a metal mirror, for example an Ag mirror, is provided by electroless metal-plating. For this purpose, the synthetic resin surface is treated with a sensitising solution. In the case of providing an Ag layer, the surface is treated for 1—60 seconds with a sensitizing solution which comprises an aqueous, acid $SnCl_2$ solution. The concentration of $SnCl_2$ is not restricted to narrow limits and is preferably from 0.01 to 1 g of $SnCl_2$ per litre, such as 0.1 g per litre. The treatment may be carried out by means of, for example, a dipping process, a pouring process or a spraying process. The synthetic resin surface is then treated with the actual metal-plating solutions, hence with the aqueous metal salt solution, for example, an ammoniacal silver nitrate solution and an aqueous reducing agent solution. An example of a suitable reducing agent is formaldehyde in combination with a sugar, for example, sodium gluconate. The metal-plating solutions are preferably provided according to the aerosol metal-plating process in which the solutions are simultaneously sprayed onto the synthetic resin surface. This process, as well as the metal salt solutions and reduction agent solutions used therein are described, for example, in the above-mentioned literature reference "Technical Proceedings etc.". Various metal-plating chemicals are commercially available from, for example, Messrs. Ermax, London Laboratories Ltd. or Merck.

The bonding of the silver layer thus plated on the underlying synthetic resin surface is tested according to the so-called diamond scratching test (DIN 53151). According to this standard test, twelve scratches are provided in the surface of the metal layer so as to extend over the whole width of the metal layer. The pattern of scratches comprises 6 parallel scratches having a mutual distance of 1 mm which are crossed at right angles by likewise 6 parallel scratches having a mutual distance of 1 mm so that the pattern of scratches comprises 25 areas of 1 mm^2. An adhesive tape is pressed on the pattern of scratches and is then pulled off from the surface. The extent of bonding is expressed in numbers 0—5, in which:

0 = optimum bonding; O areas work loose.
1 = good bonding; 1—5 areas work loose.
2 = reasonable bonding; 6—10 areas work loose.
3 = insufficient bonding; 11—15 areas work loose.
4 = poor bonding; 16—20 areas work loose.
5 = no bonding; 21—25 areas work loose.

The results of the diamond scratch test are recorded in columns 2 and 3 of the Table.

TABLE

Synthetic resin	results bonding test: Pre-treatment: tannic acid	Pre-treatment: corona discharge and tannic acid
polyethylene	5	0
polyvinyl chloride	5	0
polystyrene	5	0
polyethylene terephthalate	5	0
polyacrylate	5	0
polymethyl methacrylate	5	0
		Pre-treatment: chromic acid & tannic acid
polyvinyl chloride	5	0
polycarbonate	5	0

It will be seen from the Table that a combined pretreatment is necessary in which an oxidising treatment, for example a corona discharge or a treatment with chromic acid, is succeeded by a treatment

with tannic acid. The synthetic resins of the polyester type recorded in the Table are polyethylene terephthalate, polyacrylate, polymethyl methacrylate and polycarbonate. The polyolefine synthetic resins recorded in the Table which may be substituted with halogen atoms or with aromatic groups are polyethylene, polyvinyl chloride and polystyrene. Other representatives of the said types of synthetic resin, for example polypropylene, may also be used successfully in the method in accordance with the invention.

The combined pretreatment of a corona discharge and tannic acid presents the advantage that the metal mirror can be provided very accurately on certain parts of the synthetic resin surface. This is because a corona discharge can be carried out very accurately in which there exists a sharp boundary between parts of the surface which have been subjected to a corona discharge and parts which have not been subjected to a corona discharge.

The method according to the invention may be used in the metallization of all kinds of products of synthetic resin, in particular optical components, for example mirrors. The method according to the invention is suitable in particular for providing a metal mirror on a synthetic resin surface which has a finely detailed structure which may not or only slightly be attacked during the metallization. This applies in particular to the provision of a metal mirror on an optically readable information disc which has an optically readable information track of information areas situated alternately at a higher level and at a lower level on one or both sides. The areas have very small dimensions in which the difference in height is 0.1—0.2 μm and the length of the areas is between 0.3 and 3 μm. The disc is known by the tradenames Laser Vision and Compact Disc. The disc is usually manufactured from an acrylate synthetic resin, methacrylate synthetic resin or polycarbonate. On the side of the information track, the disc is coated with a metal layer, for example a silver layer. The silver layer must follow the contours of the information track very accurately and be firmly bonded to the synthetic resin substrate. The difference in level between the information areas must be maintained during and after providing the metal layer because this difference is decisive of the quality of the reproduction (reading) of the stored information. Moreover, the provision of the metal layer must not cause cloudiness of the synthetic resin of the synthetic resin-metal interface. These requirements are satisfied if the metal layer is provided according to the method of the invention.

In addition to the silver layer mentioned hereinbefore, other metal layers may also be provided on a synthetic resin surface by means of the method according to the invention while using an electroless metallization process. A copper layer, for example, can also be provided very readily by the electroless metallization process according to the present invention. After the required pretreatment, as disclosed hereinbefore, the synthetic resin surface to be copper-plated, is sensitized with an acid $SnCl_2$ solution. The sensitized surface is treated with an aqueous ammoniacal silver salt solution in which a redox reaction takes place at the surface according to the equation $Sn^{2+} + 2Ag^{+} \rightarrow 2Ag + Sn^{4+}$. The resulting surface which comprises one or a few monolayers of Ag is then provided with a copper layer by using an ammoniacal cuprous salt solution and an acid. This type of copper plating is known per se, as the disproportioning process and is described *inter alia* in Technical Proceedings 51st Annular Convention of the American Electroplaters' Society, *p.* 147, right-hand column and in German Offenlegungsschrift 2,527,096.

Claims

1. A method of providing a metal mirror on an article of which at least the surface on which the metal mirror is to be provided is manufactured from a synthetic resin, whereby the said surface is treated with tannic acid and provided with a metal mirror by means of an electroless metallization process, characterized in that prior to the said treatment with tannic acid, the said surface which is manufactured from a polyester or a polyolefine possibly substituted with halogen atom(s) or aromatic group(s), is subjected to an oxidising corona discharge treatment or a chromic acid treatment.

2. A method as claimed in Claim 1, characterized in that a surface of polyethylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, polyacrylate or polymethyl methacrylate is subjected to an oxidizing corona discharge pre-treatment.

3. A method as claimed in Claim 1, characterized in that a surface of polyvinyl chloride or polycarbonate is pre-treated with chromic acid.

Patentansprüche

1. Verfahren zum Herstellen eines Metallspiegels auf einem Gegenstand, von dem wenigstens die Oberfläche, auf welcher der Metallspiegel vorgesehen werden soll, aus einem Kunststoff hergestellt ist, wobei diese Oberfläche mit Tannin behandelt und unter Anwendung eines stromlosen Metallisierungsverfahrens mit einem Metallspiegel versehen wird, dadurch gekennzeichnet, dass die Oberfläche, die aus einem Polyester oder einem Polyolefin hergestellt ist, das ggf. durch ein Halogenatom bzw. Halogenatome oder eine aromatische Gruppe bzw. aromatische Gruppen ersetzt sein kann, einer oxidierenden Koronaentladungsbehandlung oder einer Behandlung mit Chromsäure ausgesetzt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass eine Oberfläche aus Polyäthylen, Polyvinylchlorid, Polystyrol, Polyäthylenterephthalat, Polyacrylat oder Polymethylmethacrylat einer oxidierenden Koronaentladungsvorbehandlung ausgesetzt wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass eine Oberfläche aus Polyvinylchlorid oder Polykarbonat mit Chromsäure vorbehandelt wird.

Revendications

1. Procédé pour la réalisation d'un miroir métallique sur un objet dont au moins la surface sur laquelle doit être appliqué le miroir métallique est réalisée en une matière synthétique, ladite surface est traitée avec de l'acide tannique et munie d'un miroir métallique à l'aide d'un processus de métallisation sans courant, caractérisé en ce qu'avant ledit traitement avec de l'acide tannique, ladite surface, qui est réalisée en polyester ou un polyoléfine éventuellement substituée avec un ou plusieurs atome(s) d'halogène ou groupe(s) aromatique(s), est soumise à un traitement d'oxydation par décharge de couronne ou un traitement à l'aide d'acide chromique

2. Procédé selon la revendication 1, caractérisé en ce qu'une surface de polyéthylène, chlorure polyvinylique, polystyrène, térèphtalate de polyéthylène, polyacrylate ou polyméthylméthacrylate est soumise à un traitement préalable d'oxydation par décharge de couronne.

3. Procédé selon la revendication 1, caractérisé en ce qu'une surface de chlorure polyvinylique ou de polycarbonate est préalablement traitée avec de l'acide chromique.