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[54] **METHOD FOR PLATING OF PLASTIC**

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[63] Continuation-in-part of Ser. No. 131,428, April 5, 1971, abandoned.

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[51] **Int. Cl.** **B44d 1/092**

[58] **Field of Search** ..... 117/47 A, 119, 106 A, 107, 117/138.8 N, 160 R

[56] **References Cited**

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[57] **ABSTRACT**

The invention relates to a method of plating metal on a polyamide plastic such as nylon in which absorbed moisture in the plastic is at least partially removed under evaporative conditions to provide a surface having an affinity for water. The subsequent treatment of the plastic is carried out with an aqueous solution of palladium chloride at an elevated temperature of 100°–212°F. followed by an aqueous solution of stannous chloride after which the activated surface is metal plated by electroless deposition of metal.

8 Claims, No Drawings

METHOD FOR PLATING OF PLASTIC

RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 131,428 entitled "Method of Plating Plastic" filed Apr. 5, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

As known, plastic articles have been metal plated by an electroless process in which the metal is chemically reduced and deposited on an activated surface of the plastic base. The general process has become of increasing importance for producing articles which have decorative, electrical or other properties. Some of the advantages of the plastic base are its electrical insulating properties, its relatively low cost, its moldability and the like. In many instances, the metal can be applied on the plastic surface in a predetermined pattern which can be further processed by electroplating or other techniques to provide metal surfaces useful for electrical circuits, decorative designs and the like.

In the process, plastics such as ABS, acrylics, polyesters, polyamides, cellulosics and the like are treated to activate the plastic surface to adherently receive the electrolessly deposited metal. Prior to the activation step, the process often includes a roughening of the plastic surface by the use of an acid or an abrasive material to form sites and in some instances, small cavities. In a subsequent processing, the sites are convereted to activated surfaces and through their irregular shapes aid in retaining the deposited metal on the plastic surface.

One of the problems with metal coatings electrolessly deposited on plastic and particularly on polyamides has been associated with low valves of adhesion between the coating and plastic. In some instances with polyamides such as nylon, the coating can be readily removed by use of very little force, thereby often rendering the plated polyamide unsatisfactory for its intended purpose.

SUMMARY

The invention is directed to a method of pretreating a plastic surface to provide sites for activation by a catalytic material and for subsequent metal plating by an electroless process. More particularly, the invention is directed to a method of treating plastic having a hydrophilic surface and absorbed moisture in which at least a portion of the moisture is removed under evaporative conditions to provide a surface having an affinity for water and subsequently the plastic surface is activated through the use of a hot, aqueous medium which serves as a vehicle for seeding the plastic surface with an active material. Advantageously, the activating step is carried out at an elevated temperature to thermally expand the plastic surface. The step of evaporatively removing moisture from the surface of the plastic is particularly important with plastics having significant amounts of moisture such as the conventional polyamides so as to provide sites on the surface for treatment by the aqueous activating medium.

One advantage of the method is that the activated plastic surface can be readily processed by conventional electroless metal deposition techniques to provide the desired plating. Another advantage is the formation of platable surfaces from plastics having a relatively high moisture content which have not always been readily platable with satisfactory results.

Yet another advantage is that polyamides such as nylon can be plated to form coatings having good adhesion to the underlying plastic.

GENERAL DESCRIPTION

The invention is directed to the method of treating plastic to provide activated sites for plating by a metal in an electroless process. The method involves treating of plastic having absorbed moisture under evaporative conditions to remove at least a portion of the moisture to provide a surface having an affinity for water, treating the dry surface with an aqueous activating medium to provide an activated surface, and electrolessly plating metal on the activated surface. Advantageously, the evaporation of absorbed moisture is carried out in the presence of a desiccant which aids in the removal of substantial amounts of the moisture. Also, the plastic surface having an affinity for water is advantageously heated at an elevated temperature in the presence of an aqueous impregnating solution of a catalytic material such as a soluble salt of a noble metal to seed and form sites on the plastic surface with the catalytic material. The impregnated surface is subsequently treated with an aqueous solution of a reducing agent such as stannous chloride to convert the catalytic material to an active form for subsequent treatment in the electroless plating bath.

In the method, a plastic such as polyamide, vinyl chloride polymer, acrylic, cellulosic and the like having significant amounts of absorbed moisture is treated under evaporative conditions to remove at least a portion of the absorbed moisture. Advantageously, with respect to the inventive method, the plastic surface is hydrophilic (inherently or converted thereto by a conditioner as with ABS) with polar groups which aid in the absorption of water. The method is also advantageously carried out with a plastic having a water absorption of at least about 0.3% as measured over a 24-hour period on a ⅛ inch thick sample. Plastics having such characteristics are described in Modern Plastics Encyclopedia, McGraw-Hill, Inc., 1970. Preferably, with the method, the plastic is a polyamide having a water absorption value of at least 1% such as 6 nylon, 6/6 nylon and the like.

Suitably, the plastic is treated under evaporative conditions to remove at least a portion of the absorbed mositure and thereby to provide a surface having an affinity for water with sites capable of attracting and retaining catalytic material from an aqueous medium. Removal of moisture as a vapor can be carried out in a desiccator with a desiccant such as silica gel or other dehydrating medium, by vaccum or the like at a temperature and for a time sufficient to form a surface with an affinity for water. Preferably, the evaporative conditions include the use of a desiccant such as silica gel and are carried out under ambient or slightly elevated temperatures. With a nylon, representative conditions include silica gel as a desiccant, a temperature of 70°–75°F. and a time of about 16 hours. In this step, the moisture content of the plastic is reduced in respect to that at ambient temperatures (70°F).

Prior to the mositure removal, the plastic can be treated by the use of an acid or mechanical roughening agent to form irregular surfaces on the plastic. Suitably, the treatment can be carried out under conditions to

increase the wetability of the plastic surface, which after dehydration is carried out with an aqueous activating medium.

The plastic which has been substantially dehydrated is subsequently treated with an aqueous activating medium such as an aqueous solution of a noble metal salt to provide sites on the plastic surface for subsequent treatment in the electroless metal deposition process. Suitably, the aqueous activating medium is an aqueous impregnating solution of a catalytic material such as a noble metal salt. Various aqueous activating solutions are known in the art and can include those providing a single-stage activation as described in U.S. Pat. No. 3,515,649 or a two-stage activation in which the noble metal salt and reducing agent such as stannous chloride are separately combined to convert the noble metal to its active form with the particular selection of conditions being dependent on the particular plastic and adhesion desired. Preferably with polyamides, the treatment is carried out in a two-stage activation in which an aqueous solution of a noble metal such as palladium chloride is applied on the plastic surface and subsequently treated with an aqueous solution of stannous chloride or other suitable reducing agent. The treatment is advantageously carried out at an elevated temperature with plastics which are heat expandable to aid in the formation of the activated sites. Temperatures of at least about 100°F. are desirable, particularly with a polyamide, although temperatures in the order of about 130°–212°F. and especially about 160°–180°F. are preferable. Times in the order of 3 minutes are common with nylon treated at temperatures in the order of 170°–175°F. The treatment with the reducing agent is under reducing conditions sufficient to convert the impregnated noble metal salt to the active form of the metal. Representative conditions for treatment by the reducing solution of stannous chloride is a time of about 6 minutes and a temperature in the order of about 70°–75°F.

Although the exact mechanism for the invention is not known with certainty, one explanation advanced and not intended to be restrictive is that the removal of absorbed moisture from the plastic such as polyamide provides sites in a form and with an affinity for water such that the active material in the aqueous activating solution is attracted to and retained by the sites on the plastic surface. The impregnated or seeded active material can then be further processed in the electroless metal deposition process. An additional explanation for the usefulness of elevated temperatures is that some expansion occurs in the polyamide plastic which aids in the formation of the activated sites on the plastic surface. With a nylon, temperatures of 160°–180°F. also may cause some crazing of the surface which further aids in the formation of active sites.

The activated plastic surface having sites on which electrolessly deposited metal can adhere, is subsequently treated with a chemical bath containing a soluble salt of the metal selected for deposition. Solutions are commercially available for the deposition of metals such as copper, nickel, silver, gold and the like and usually contain various amounts of other components which aid in the formation of a metal layer on the plastic surface. An illustration of suitable conditions for plating a nylon which has been activated by the application of a solution of palladium chloride at about 170°–175°F. and a solution of stannous chloride at a temperature of about 70°–75°F. is treatment with an electroless copper plating bath ("Copper Mix 328" available from the Shipley Company, Inc., Newton, Mass.) for a time in the order of about 10 minutes.

The plated plastic part is then conveniently water rinsed, alcohol treated, and air dried. If additional metal is to be applied on the metal surface by electroplating, the part is conveniently stored in a desiccator or in a non-oxidizing atmosphere such as nitrogen prior to electroplating. As described in U.S. Pat. No. 3,445,350, electroplating conditions are known for plating of metal on a metallized plastic part.

The following example is provided for illustrative purposes only and is not intended to be restrictive of the invention:

EXAMPLE 1

A sample of nylon having 6 carbons between the amide linkages was chemically copper plated. The sample having a clean surface was initially treated with a neutral cleaning solution for about 10 minutes at approximately 150°F. After a flowing water rinse for about 3 minutes and a distilled water rinse for about 1 minute, the nylon was treated with an alkaline wetting agent for about 2 minutes to remove surface contaminates and again water rinsed. It was then placed in a lab desiccator with a silica gel for about 16 hours.

Activation of the dehydrated nylon was carried out with a solution of a palladium salt (Shipley's Catalyst 6F) at a temperature of about 170°–175°F. for about 3 minutes. This solution of catalytic material was previously treated to about 180°F. for about ½ hour, cooled and filtered to remove precipitated material. During the processing and impregnating of the nylon, the surface became dark brown. A further water rinse was carried out on the nylon after which it was treated with an aqueous solution of stannous chloride for about 6 minutes at room temperature (70°–75°F.).

The activated surface of the nylon was subsequently treated with a commerical copper plating bath (Shipley's Copper Mix 328) at about 70–75°F. for about 10 minutes. It was then rinsed in flowing water for about 2 minutes, treated with alcohol and air dried. A bright, shiny layer of copper was formed on the plastic surface. Resistance of the copper layer to removal during manual handling of the article indicated that the copper was firmly adhering to the plastic surface. Further tests in which a plated nylon sleeve was forced into a restrictive aperture in a metal plate revealed that the metal coating continued to adhere to the nylon during deformation of the sleeve and was very satisfactory.

After being stored in a nitrogen atmosphere overnight (about 16 hours), the plated nylon was subsequently electroplated with tin and exhibited a bright, shiny surface with good adherence properties to the underlying copper and plastic.

Runs were also made in which nylon samples similar to that of Example 1 were electrolessly plated with copper but without first being subjected to evaporative conditions and the subsequent heating step during activation. When a plated sleeve formed in this manner was inserted into a restrictive aperture as described in Example 1, the metal coating readily separated from the nylon. Other runs were made in which other nylon samples similar to that of Example 1 were plated with copper essentially according to the procedure of Example 1, but with the treatment steps with palladium chloride

and stannous chloride being reversed so that stannous chloride was first applied. Tests in which a plated sleeve formed in this manner was inserted into a restrictive aperture as described in Example 1 also revealed that the metal coating readily became separated from the nylon.

As demonstrated by the above example, the invention provides a useful method for plating polyamide plastics with metal and provides advantages over the prior art. As demonstrated with nylon, the same performance is not evident when tests are made without use of the invention.

Since various activating solutions and electroless metal deposition solutions are known in the art, it is understood that the above example is illustrative only and that other compositions may be substituted for activation and metal plating according to the teachings described above. Also, other modifications and ramifications which occur to those skilled in the art are intended to be encompassed within the scope of the invention.

What is claimed is:

1. A method of plating metal on a polyamide plastic surface having absorbed moisture, which comprises removing under evaporative conditions at least a portion of the absorbed moisture to provide a dry surface, heating the plastic in an aqueous impregnating solution of a catalytic material at an elevated temperature of at least 100°F. to impregnate the surface with the catalytic material, treating the impregnated surface with an aqueous solution of a reducing agent to activate said catalytic material, and electrolessly depositing metal on the activated surface.

2. The method of claim **1** wherein the step of removing at least a portion of the absorbed moisture is carried out in the presence of a desiccant, and the step of heating the polyamide plastic is carried out at a temperature of about 160°–180°F.

3. The method of claim **2,** which includes the step of electroplating a second metal on the metallic surface of the electrolessly deposited metal.

4. The method of claim **1** which includes the prior step of conditioning the plastic surface to form irregular sites which are subsequently treated to remove absorbed moisture.

5. The method of claim **1** wherein the heating step is carried out with a solution of a palladium salt and the treating step is carried out with a solution of a stannous salt.

6. The method of claim **5** wherein the treating step is carried out at a temperature of about 70°–75°F.

7. The method of claim **6** wherein the step of removing at least a portion of the absorbed moisture is carried out in the presence of a desiccant and the heating step is carried out at a temperature of about 160°–180°F.

8. A product of the process of claim **1.**

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