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SURFACE TREATMENT FOR POLYSTYRENE WHICH IS TO BE ELECTROLESS PLATED AND COMPOSITIONS THEREFOR

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ABSTRACT OF THE DISCLOSURE

Treatment of polystyrene with a mixture of SO_3 complexed with trimethyl phosphate and a halogenated aromatic hydrocarbon prior to dipping in concentrated acid and electroless plating metal on the surface of polystyrene, and treatment bath compositions comprising SO_3 complexed with trimethyl phosphate, and a halogenated aromatic hydrocarbon.

The present invention is directed to a treatment of the surface of polystyrene which is to be electroless plated and compositions therefor.

In recent years there has been a rapid growth of the plating of plastics with metals. Thus, plated plastics offer a number of advantages over metals including lightweight, corrosion resistance, greater design latitude, simplified assembly, controlled conductivity and economy.

It has long proven to be desirable to plate polystyrene and, in particular, high impact polystyrene. By "high impact" polystyrene is meant rubber modified polystyrene, a wide variety of which are commercially available. Barrel plating of polystyrene, and high impact polystyrene, has been done for many years. In this method, a complete envelope of electroplated metal surrounds the molded object. The electroplating baths used in barrel plating do not produce a smooth, bright deposit, but this plated metal can readily be polished by barrel polishing. There is no need for a strong bond between the plated metal and the polystyrene substrate. Recently, however, electroplating baths have been developed for the bright plating of plastics. These baths make possible plating of large, irregular shaped moldings which cannot be successfully barrel polished, and which cannot be economically polished by buffing. In this case, a strong bond between the plated metal and the plastic substrate is essential. Methods of pre-treating the surface of plastics such as ABS (acrylonitrile-butadiene-styrene copolymers) have been developed. The treating bath consists of a concentrated aqueous solution of chromic acid. This oxidizes the surface of the ABS plastic, so that a strong bond is developed between the surface and the plated metal. However, the plating of polystyrene or high impact polystyrene by this method has not proved to be commercially successful. The chemical inertness of the polystyrene and high impact polystyrene is probably the cause of the lack of chemical attack. Thus, prior attempts to bright plate polystyrene or high impact polystyrene, has resulted in a low bond strength between the surface and the plated metal.

In the past, silver has been the most successful electroless metal deposit on the surface of plastics in order to make them conductive and receptive to thicker deposits of electroplated metal. The high cost and scarcity of silver has resulted in the development of electroless copper and electroless nickel plating baths which have been successfully used for making the surface of treated ABS moldings receptive to electroplated copper or nickel deposits. Treatment of polystyrene and high impact polystyrene surfaces by similar methods has not resulted in producing a receptive surface for electroplating.

This invention has as an object the provision of a surface treatment for polystyrene, and in particular high impact polystyrene, whereby the surface may be conditioned to receive a satisfactory copper coating by electroless plating.

This invention has as another object the provision of a surface treatment bath for conditioning polystyrene and in particular, high impact polystyrene, for electroless plating of copper or nickel in preparation for subsequent electroplating.

Other objects will appear hereinafter.

The present invention is directed to the electroless plating of polystyrene, and in particular high impact polystyrene. The present invention is broadly applicable to a wide variety of polystyrene which are available. The properties of both the general purpose polystyrenes and the impact polystyrenes comprehended within the subject invention are generally set forth in the Table I at pages 308 and 309 of the Modern Plastics Encyclopedia, 1967, published by McGraw-Hill, Inc. We have found that the surface treatment and the treating bath of the present invention may be used with all types of polystyrene. We have determined that there is an improvement in the adhesion between the polystyrene and the plated metal with increasing molding temperature, and hence it is normally desirable that as high a molding temperature as is feasible (temperature degradation is to be avoided), should be used, prior to the preplating treatment. As with all plastic plating methods, the polystyrene to be plated in accordance with the present invention should be as clean as is feasible. To this end, mold release agents should be avoided, and rigorous care taken to achieve clean and careful handling of the polystyrene which is to be plated.

The surface treating baths of the present invention comprise a complex of from 20 to 65 parts by weight of sulfur trioxide and 80 to 35 parts by weight of trimethyl phosphate, and 2 to 20 parts by weight of a halogenated aromatic hydrocarbon solvent, which is substantially stable to the aforesaid complex.

We have found that when the complex contains more than about 65 parts by weight of sulfur trioxide to 35 parts by weight of the trimethyl phosphate the shelf life of the preplating bath decreases drastically. While the preferred concentration ratio of sulfur trioxide to trimethyl phosphate will vary depending upon the type of polystyrene which is used, we have found that in most cases, and in particular with high impact polystyrene, a concentration ratio of from 40 to 55 parts by weight of sulfur trioxide to 60 to 45 parts by weight of trimethyl phosphate is to be preferred.

The presence of the halogenated aromatic hydrocarbon solvent, which is stable in the aforesaid complex, in a concentration of above about 2 weight percent based on the total mixture enhances the efficacy of the preplating bath. In particular, we have achieved excellent results with o-dichlorobenzene.

The optimum concentration of the halogenated aromatic hydrocarbon solvent is dependent upon three factors which are within the control of the user of the process of the present invention, namely the type of polystyrene to which the invention is applied, the time duration of the surface treatment, and the temperature of the bath.

The concentration of the holegenated aromatic hydrocarbon solvent should be sufficiently low so that no undue solvent attack of the plastic, or undue roughening of the plastic's surface will result from the preplating treatment.

Examples of halogenated aromatic hydrocarbons which may be used in the present invention include orthodichlorobenzene, metadichlorobenzene, metadibromobenzene,

fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene.

In the process of the present invention the polystyene, which has been thoroughly cleaned, is treated in the bath at a temperature between 25° C. and below a temperature which will result in heat distortion for the particular polystyrene and molded shape which is being treated. As a general rule, the maximum temperature which can be used without adverse heat distortion should be used so as to reduce the treatment time, and to minimize the roughening of the surface. With most polystyrenes this will range from about 60° to 80° C. There is a treatment temperature-time interrelationship, with the higher the temperature the shorter the treatment time. The optimum conditions will vary depending up the nature of the plastic, and the chemical composition of the bath. However, these conditions can be determined by one having ordinary skill in the art by routine testing of a non-inventive nature. Generally, the longer the treatment, the stronger the bond strength of the plated copper to the polystyrene. However, this is offset by the increased roughness of the treated surface, so that in many cases there is a balance between duration of treatment, desired bond strength, and appearance of the plated surface.

After the surface treatment in the treatment bath it is necessary to remove the residues left on the plastic surface. This is accomplished by thorough water rinsing, followed by soaking at 25° C. or higher, in a concentrated aqueous acid solution. The acids that work well for this final treatment are concentrated hydrochloric acid, phosphoric acid, or nitric acid. The preferred acid is hydrochloric acid, and soaking times range from 10 minutes to 60 minutes, the time varying inversely with the temperature. Hydrochloric acid is the preferred acid, because it is most easily rinsed off after the soaking, and small traces of it do not contaminate the subsequent sensitizing and activating baths.

The electroless plating of plastics is usually preceded by sensitizing and activation steps, well known in the art. In the sensitizing step the plastic is immersed in an acidified solution of stannous chloride, and in the activation step the surface is treated with a solution of acidified palladium chloride. This is immediately followed by electroless plating which may be a well known formula or a proprietary bath containing copper, nickel, silver, or gold.

While copper is most generally used as the metal which is electroless plated, the process of the present invention is equally applicable to the electroless plating of other metals, such as nickel, silver, or gold. The conditions for electroless plating and the apparatus and means used form no part of the present invention, and come within the skill of one having ordinary skill in the electroless plating art. A large literature has developed in connection with the plating of plastics, see the article on Electroplating Plastics at pages 1019 through 1024 of Modern Plastics Encyclopedia, 1967, and the references cited therein.

The thickness of the electroless deposited copper (or other metal) will vary depending upon the requirements of the user, and the means for regulating such thickness can be accomplished by techniques available to one having ordinary skill in the art. With copper the thickness of the initial electroless plating may be on the order of from ten millionths of an inch thickness up to as much as several mils. The ultimate thickness of the plating depends upon the end use of the finished product, and the electroless plating may be followed by conventional electroplating on the original electroless plating to any desired thickness. The plating subsequent to the electroless plating may be accomplished by conventional means, including the use of the new "bright" plating baths.

In order to illustrate the present invention, Lustrex HT-88, a high impact polystyrene containing 88% by weight of styrene, and 12% of butadiene, and manufactured by the Monsanto Chemical Company, was used as the polystyrene being treated. The bond strength test in which the plated metal was pulled at 90° to the treated plastic surface, and the force in pounds per inch measured, is "peel strength."

In each of the following examples the treatment bath contained 46.2% sulfur trioxide in trimethyl phosphate, and the final acid conditioner was concentrated hydrochloric acid.

All test samples were then sensitized with a solution containing 10 grams of stannous chloride and 40 ml. of concentrated hydrochloric acid per 1000 ml. of water. The sensitization was accomplished by treatment of the samples with this solution for 2 minutes at room temperature. The samples were then activated by dipping them for two minutes at room temperature into a solution containing 1 gram of palladium chloride and 10 ml. of concentrated hydrochloric acid per gallon of water. All of the test samples were then plated with an electroless copper plating bath which plated at the rate of .1 of a mil per hour, and they were plated for 10 minutes in this bath, thus producing an electroless copper plate 0.0166 mils thick. This was followed by electroplating bright copper to a thickness of 3 mils in order to provide sufficient thickness for the peel test.

EXAMPLE 1

The sample was treated in the sulfur dioxide bath containing 10% orthodichlorobenzene at a temperature of 25° C. for 30 minutes, and was soaked in concentrated hydrochloric acid at 25° C. for 60 minutes. The peel strength obtained was 2 pounds per inch. The bright plated surface reflected some roughness from the etched surface.

EXAMPLE 2

The sample was treated in the sulfur trioxide bath containing 3½% orthodichlorobenzene at 60° C. for 60 minutes, followed by 60 minutes soak at 25° C. in the concentrated hydrochloric acid bath. The resulting peel strength was 3 pounds per inch, and the plated surface was bright and smooth.

EXAMPLE 3

The sample was treated in the sulfur trioxide bath containing 7% orthodichlorobenzene at 60° C. for 7 minutes, followed by a soak for 60 minutes in concentrated hydrochloric acid. The resulting peel strenght was 3½ pounds per inch, and the plated surface was smooth and bright.

EXAMPLE 4

The same procedure was used as in Example 3, except the time of treatment in the sulfur trioxide bath was increased to 10 minutes. The peel strength increased to 7 pounds per inch, and the plated surface was moderately roughened by the treatment.

EXAMPLE 5

The same procedure was used as in Example 3, except the time in the sulfur trioxide bath was increased to 13 minutes. The resulting peel strength increased to 9 pounds per inch, and the plated surface was roughened by the treatment.

EXAMPLE 6

The same procedure was used as in Example 3, but the time in the sulfur trioxide bath was increased to 30 minutes. The result was a peel strength of 14 pounds per inch, but the surface was very rough.

EXAMPLE 7

The sample was treated in the sulfur trioxide bath containing 7% orthodichlorobenzene at 60° C. for 10 minutes, and was followed by a 20-minute soak in the concentrated HCl. The resulting peel strength was 6½ pounds per inch, and the plated surface was moderately rough.

EXAMPLE 8

A sample of general purpose polystyrene was treated in the sulfur trioxide bath containing 7% orthodichlorobenzene for 12 minutes at 60° C., and followed by a soak

in concentrated hydrochloric acid for 12 minutes at 25° C. The resulting peel strength was 5 pounds per inch, and the plated surface was moderately rough.

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification as indicating the scope of the invention.

In the following claims "polystyrene" includes both high impact polystyrenes which are copolymers of polystyrene and a synthetic rubber, as well as general purpose polystyrene.

It is claimed:

1. A treating bath for the surface conditioning of polystyrene which is to be electroless plated consisting essentially of a solution of a complex of from 20 to 65 parts by weight of sulfur trioxide and from 80 to 35 parts by weight of a trimethyl phosphate, and a halogenated aromatic hydrocarbon solvent which is stable in the presence of said complex, the concentration of said halogenated aromatic hydrocarbon solvent being sufficient to enhance the preplating efficacy of the bath for polystyrene and below the concentration which adversely roughens the surface of the polystyrene or adversely swells the polystyrene.

2. A treating bath in accordance with claim **1** in which the halogenated aromatic hydrocarbon solvent is orthodichlorobenzene.

3. A treating bath in accordance with claim **1** in which the halogenated hydrocarbon solvent is present to the extent of 2 weight percent and below a concentration of 20 weight percent.

4. A process for preconditioning and plating polystyrene which comprises contacting the polystyrene with a preplating bath of the type set forth in claim **1** at a temperature of between 30° C. and below a temperature which will result in adverse heat distortion of said polystyrene for a time sufficient to condition the surface of the polystyrene for electroless plating, rinsing the polystyrene with water to remove the preplating bath, treating the surface of the polystyrene with a strong acid selected from the group consisting of hydrochloric acid, phosphoric acid, and nitric acid, and the electrolessly metal plating the treated polystyrene.

5. A process in accordance with claim **4** in which the acid is hydrochloric acid.

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