

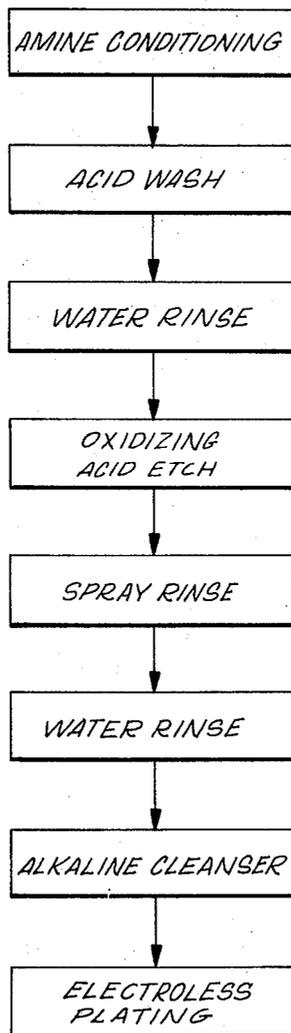
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CONDITIONING OF PROPYLENE POLYMERS FOR ELECTROLESS PLATING

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3,686,016  
**CONDITIONING OF PROPYLENE POLYMERS  
FOR ELECTROLESS PLATING**  
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U.S. Cl. 117-47 A **13 Claims**

## ABSTRACT OF THE DISCLOSURE

Amines having the structure



wherein  $R_1$  and  $R_2$  are alkyl groups containing up to four carbon atoms, and  $R_3$  is hydrogen or a hydrocarbon radical, are used as pre-etch conditioners to improve the adhesion of electrolessly deposited metals to the surface of propylene polymers.

## BACKGROUND OF THE INVENTION

The present invention relates to electroless plating of propylene polymers, such as polypropylene, and more particularly to improving the bond strength between an electroless deposited metal coating and the polymer substrate.

Recently, considerable demand has developed for metal plating on non-conductive articles, particularly plastic articles. In the finished product the desirable characteristics of the plastic and metal are combined to offer thereby the technical and aesthetic advantages of each. The properties of propylene polymers, for instance, could be aesthetically and mechanically enhanced by metal coatings.

Propylene polymers, like most plastics, are electrically non-conductive. It has, however, been sought to achieve a good metal bond to the surface of propylene polymers by an initial plating operation, known as "electroless plating." This procedure generally consists of conditioning the surface of the plastic article for plating by etching with a strong oxidizing acid, seeding the surface by contact with a noble metal salt solution, e.g., a palladium chloride solution, then immersing the seeded surface in an auto-catalytic electroless solution where an initial coating of a conductive metal, e.g., copper and nickel, is established by chemical deposition. The metal coating formed acts as a bus which allows a thicker metal coating to be built up electrolytically.

It has been, however, most difficult to achieve a plate on propylene polymers. Even the so-called "platable grades" of propylene polymers are difficult to plate well and the bond strength of the metal deposited electrolessly has been generally poor.

## SUMMARY OF THE INVENTION

It has now been found that the adhesion of electroless deposited metals to the surface of propylene polymers can be substantially improved without a detrimental effect on the appearance of the polymeric substrate by preceding etching with a strong oxidizing acid with an organic etch in which the surface of the propylene polymer is brought in contact with an amine having structure



wherein  $R_1$  and  $R_2$  are alkyl groups containing from one to about four carbon atoms and  $R_1$  and  $R_2$  provide a

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total of no more than 8 carbon atoms and wherein  $R_3$  is hydrogen or a hydrocarbon radical. Adhesion is further enhanced by terminating the etching or conditioning effect of the amine by contacting the conditioned polymer substrate with an acidic wash immediately after conditioning and before contact with the oxidizing acid.

Conditioning with the amines of this invention has been found to increase adhesion of electrolessly deposited metals to propylene polymers to an excess of 20 lbs. per inch. Adhesion is further optimized by employing as the strong oxidizing acid the solution containing chromic acid and trivalent chromium ions and by immersing the electrolessly plated substrate in a dilute aqueous anionic or non ionic surfactant solution prior to normal aging to prevent the drying out of absorbed salts and oxidation of the electrolessly deposited layer.

## DRAWING

Attached drawing contains schematic representation of the preferred procedure followed in preparing a propylene polymer for electroless plating.

## DESCRIPTION

According to the present invention, the bond strength of metals electrolessly deposited on propylene polymer substrates is remarkably improved by preceding etching with a strong oxidizing acid with contact with certain secondary and/or tertiary amines.

The propylene polymers treated in accordance with the practice of this invention include homopolymers of propylene and interpolymers of propylene with one or more ethylenically unsaturated monomers such as ethylene and butene, and including among others, the so-called platable grades of polypropylene.

The amine pre-etch conditioners of this invention are compounds having the general structure



wherein  $R_1$  and  $R_2$  are alkyl groups containing from one to about four carbon atoms and the total number of carbon atoms provided by  $R_1$  and  $R_2$  is between two and eight, preferably about four to about six, and wherein  $R_3$  is hydrogen or a hydrocarbyl group.

While the nature of the two alkyl groups of the amines used to condition the surfaces of propylene polymers for electroless plating appears important, the nature of the third group attached to the amine does not appear to be critical. It may, as indicated, be hydrogen or a hydrocarbon radical such as straight chain, branched chain, saturated or unsaturated aliphatic, cycloaliphatic, aromatic and the like. What appears to be important, however, is that a certain balance be reached between the two functional alkyl groups of the amine such that good wetting contact exists between the amine conditioner and the surface of the propylene polymer.

Illustrative, but no wise limiting, of the amines which may be used as conditioners for the surface propylene polymers there may be mentioned diethyl amine, dipropyl amine, diisopropyl, dibutyl amine, diisobutyl amine, trimethyl amines, tripropyl amine, triisopropyl amine, tributyl amine, triisobutyl amine, N-methylbutyl amine, N-ethylbutyl amine, N,N-diethyl ethylenediamine, N,N-dimethylaniline, N,N-diethylaniline, diethylamino phenol, diethylamino benzaldehyde, N,N-diethyl cyclohexylamine, and the like, as well as mixtures thereof. The preferred amine conditioner is N,N-diethylaniline.

While the secondary and tertiary amines of this invention may be used as such they also may be diluted with organic solvents, which play no part as conditioners in conditioning the surface of the propylene polymers for

electroless plating. Preferably, however, the conditioners are used full strength.

The temperature at which the propylene polymers are conditioned using secondary and tertiary amines of this invention is not narrowly critical. They may range from about 90° F. up to the softening point of the propylene polymer or the boiling point of the conditioner, whichever is lower. We have generally found, however, that conditioning is favored by higher temperatures and it is preferred to use amines which are relatively nonvolatile in the temperature range of from about 90° to about 170° F.

The amount of contact between the propylene polymer and the amine conditioners of this invention will vary somewhat depending on the nature of the polymer as well as the temperature at which it is conditioned. Conditioning times will generally range up to about 15 minutes, with shorter times being employed for the so-called platable grades of polypropylene and the longer conditioning times employed for the propylene polymers which will not, under normal conditions accept an electrolessly deposited plate even after conditioning with a strong acid.

The action which the amine conditioners of this invention have on the surface of the propylene polymer is not well understood. Articles removed from the amine conditioner show no softening or other modification which would indicate that a change has occurred. However, once it has passed through a strong oxidizing acid such as sulfuric acid, chromic acid or a mixture of such acids, there is a general deglazing and dulling of the surface of the propylene polymer which permits catalysis and electroless deposition of either copper or nickel.

While propylene polymers conditioned with the amines of this invention are adapted for an electroless plating operation, to obtain optimum results it is preferred to follow the procedure schematically shown in the drawing.

With reference thereto, the article is first conditioned by contact with the amine for a desired period of time, then rinsed with water, preferably de-ionized water, and passed directly to the strong oxidizing acid etchant. It is preferred to wash the article for a short period of time, generally from about 30 to about 120 seconds, with an acid, such as 80% sulfuric acid, to quench the etch and initiate deglazing of the polymer surface.

After quenching, the article is rinsed in water again, preferably de-ionized water, and passed on to a strong oxidizing acid etch. While any of the known oxidizing acid solutions may be employed, it is preferred to use a pure chromic acid etch. The chromic acid etch used contains from about 8.5 to about 10.5 lbs. of chromic acid per gallon of solution, which is above the normal solubility of chromic acid in water. Higher solubility, however, is achieved by the presence of trivalent chromium, which is formed in the reduction of the hexavalent chromium during oxidation of the polymer surface.

An initial solution of high chromic acid content may be conveniently obtained by the addition of oxalic acid to a chromic acid solution to form trivalent chromium ions followed by the addition of chromium trioxide to the resultant solution to form an oxidizing acid of the desired hexavalent chromium assay. The etch with the strong oxidizing acid is generally at a temperature from about 110° F. to distortion temperature of the propylene polymer, preferably from about 110° to about 200° F., and more preferably from about 150° to about 185° F. Residence times ranging from about 5 to about 10 minutes, depending upon the nature of the propylene polymer treated, are generally employed.

After etching with the strong oxidizing acid, the article is then passed on to a spray rinse where any of the remaining acid is forcibly washed from its surface.

Following this there may be one or more rinses in water and then a final cleansing with an alkaline cleanser, which is free of silicates. This cleanser is preferably mild and free of caustics. The cleanser is generally maintained at

temperatures from about 110° to about 130° F. and the residence time of the article is from about 3 to about 5 minutes.

After final alkaline cleansing, the article may now be passed on to any of the electroless plating operations, employing either copper or nickel. Conveniently, the conditioned article may be immersed in a solution of stannous chloride-hydrochloric acid to sensitize the plastic surface by absorption of stannous ions. This is generally followed by immersion in a solution of a noble metal salt, e.g., palladium chloride, to activate the surface of the article by a reaction resulting in the reduction of the noble metal ions to the metal. The noble metal film on the article surface then acts as a catalyst in the electroless metal bath into which the activated article is passed.

A variety of electroless copper and nickel formulations may be used. For example, electroless copper formulations essentially consist of a soluble cupric salt, such as copper sulfate; a complexing agent for the cupric ion, such as Rochelle salt; and alkali hydroxide for adjustment of pH; a carbonate radical as a buffer; and a reducing agent for the cupric ion, such as formaldehyde. The mechanism by which objects having catalyzed surfaces, as previously discussed, is plated autocatalytically in such solutions, has been explained in the literature, for example, U.S. Pat. No. 2,874,072, issued Feb. 17, 1959.

Following electroless plating the article may be electrolytically plated by conventional means with copper, nickel, gold, silver, chromium and the like to provide the desired finish on the article.

Although many of the steps may be conveniently eliminated and the amine conditioned article may be passed after a water rinse directly to the oxidizing acid and thereafter directly to the electroless plating step, it has been observed that exercising care in thoroughly cleansing the article after each conditioning step has a cumulative beneficial effect on improving overall adhesion.

The deposited metal coating will be uniform and the bond strength of both electrolessly deposited copper and nickel to the surface will be unusually high independent of the electroless deposition technique employed. Moreover, high bond strengths, often above 25 lbs./inch, are achieved without undermining or adversely affecting the resin integrity. During standard destruct peel tests it has been determined that failure is mainly at the resin-metal interface and there is little or no removal of plastic from the substrate with the metal.

While no wise limiting, the following are illustrative examples of the practice of this invention in which peel strengths were determined by pulling a one-inch strip of the deposited metal at an angle of 90° to the propylene polymer surface using a Dillon pull tester.

#### Example 1

Using the procedure set forth above and as illustrated by the drawing, a plaque fabricated from a propylene polymer was conditioned for electroless copper plating by first immersing the plaque in a dipropyl amine bath maintained at a temperature of 140° F. for 15 minutes. Following immersion the plaque was acid rinsed by immersion in 80% sulfuric acid bath for 90 seconds and then etched in a chromic acid bath maintained at 190° F. for 6 minutes. After electroless plating, a copper plate was built up electrolytically to a thickness of about 4 mils. It was found that the plate had an average bond strength of 27 lbs. per inch when adjusted to a plate thickness of 4 mils.

#### Example 2

The procedure of Example 1 was repeated except that the dipropyl amine bath was maintained at a temperature between 100°-118° F. The resultant plate had an average bond strength of 15 lbs. per inch.

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## Example 3

The procedure of Example 1 was repeated except a mixture of sulfuric and chromic acids were used instead of a chromic acid as the etch. The resultant copper plate had a bond strength of 12 lbs. per inch.

## Example 4

Following the procedure set forth in Example 1, a propylene polymer was etched in an amine mixture containing about 86.5 percent by weight dipropyl amine and 13.5 percent by weight N,N'-diethyl aniline. The mixture of amines was maintained at 150° F. and conditioning time was 15 minutes. After a 90 second acid dip, the plaque was etched for 7 minutes in an etch comprising a major amount of chromic acid and a minor amount of sulfuric acid. The resultant plate had a bond strength of 20 lbs. per inch.

## Example 5

The procedure of Example 1 was repeated except that N,N-diethyl aniline was used as the conditioner and conditioning was carried out at a temperature of 170° F. Average bond strength of the copper to the plaque was 22.25 lbs. per inch.

## Example 6

The procedure of Example 1 was repeated except dibutyl amine was used as the conditioner and conditioning temperature was between 105° and 110° F. A good bond of copper to the conditioned and etched propylene polymer was obtained.

## CONTROLS

When hexylamine and diallylamine were used as conditioner in a procedure set forth in Example 1, no copper deposition on the propylene was obtained.

What is claimed is:

1. In a process for electrolessly plating propylene polymers, which includes the step of contacting the propylene polymer surface with a strong oxidizing acid to promote adhesion of the metal to the propylene polymer, the improvement which comprises conditioning the polymer surface prior to contact with the oxidizing acid by contact with at least one amine having the structure



wherein R<sub>1</sub> and R<sub>2</sub> are alkyl groups containing from 1 to about 4 carbon atoms and provide a total of from 2 to 8 carbon atoms and R<sub>3</sub> is hydrogen or a hydrocarbon radical.

2. A process as claimed in claim 1 in which the amine is at a temperature of from about 90° to about 170° F.

3. In process for electrolessly plating propylene polymers, which includes the step of contacting the propylene polymer surface with a strong oxidizing acid to promote adhesion of the metal to the propylene polymer, the improvement which comprises conditioning the polymer surface prior to contact with the oxidizing acid by contact with at least one amine selected from the group consisting of dipropyl amine, dibutyl amine and N,N-diethyl-aniline.

4. A process as claimed in claim 3 in which the propylene polymer is contacted with the amine for a period of time from about 1 to about 15 minutes.

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5. A process as claimed in claim 3 in which the amine is at a temperature of from about 90° to about 170° F.

6. In a process for electrolessly plating propylene polymers which includes the step of contacting the propylene polymer surface with a strong oxidizing acid to promote adhesion of the electrolessly deposited metal to the propylene polymer, the improvement which comprises:

(a) contacting the polymer surface with at least one amine having the structure



wherein R<sub>1</sub> and R<sub>2</sub> are alkyl groups containing from 1 to about 4 carbon atoms and provide a total of from 2 to 8 carbon atoms and R<sub>3</sub> is hydrogen or a hydrocarbon radical; and

(b) washing the amine conditioned propylene polymer surface with an acid prior to contact with a strong oxidizing acid.

7. A process as claimed in claim 6 in which the amine conditioned propylene polymer is washed with an acid for a period of time from 30 to 120 seconds.

8. A process as claimed in claim 6 in which the propylene polymer is contacted with the amine for a period of time from about 1 to about 15 minutes.

9. A process as claimed in claim 6 in which the amine is at a temperature of from about 90° to about 170° F.

10. In a process for electrolessly plating propylene polymers which includes the step of contacting the propylene polymer surface with strong oxidizing acid to promote adhesion of an electrolessly deposited metal to the propylene polymer, the improvement which comprises:

(a) conditioning the polymer surface with at least one amine selected from the group consisting of dipropyl amine, dibutyl amine and N,N-diethylaniline; and  
(b) washing the conditioned propylene polymer surface with an acid prior to contact with the strong oxidizing acid.

11. A process as claimed in claim 10 in which the amine conditioned propylene polymer is washed with an acid for a period of time from 30 to 120 seconds.

12. A process as claimed in claim 10 in which the propylene polymer is contacted with the amine for a period of time from about 1 to about 15 minutes.

13. A process as claimed in claim 10 in which the amine is at a temperature of from about 90° to about 170° F.

## References Cited

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U.S. Cl. X.R.

117-118, 160 R; 156-2, 3; 204-30

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,686,016 Dated August 22, 1972

Inventor(s) Eileen Magurie, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Patent, Col. 2, line 61, the word "diisobutyl" should read --disobutyl--. Col. 3, line 25, the word "will" should read --well--. Col. 5, line 35, after the word "propylene" insert --polymer--; Col. 5, line 54, claim 3, after the word "In" insert --a--.

Signed and sealed this 6th day of March 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents