

[54] **PLATING PRE-TREATMENT IN
ACRYLONITRILE BUTADIENE STYRENE**

[75] Inventors: **William R. Vincent; Ismat A.
Abu-Isa**, both of Birmingham, Mich.

[73] Assignee: **General Motors Corporation**,
Detroit, Mich.

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[58] **Field of Search..... 117/47 A, 160 R, 138.8 R,
117/130 E**

[56] **References Cited**
UNITED STATES PATENTS

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Primary Examiner—Herbert B. Guynn
Assistant Examiner—Bruce H. Hess
Attorney, Agent, or Firm—Lawrence B. Plant

[57] **ABSTRACT**

A process for plating acrylonitrile butadiene styrene (ABS) polymers including treating the ABS in a solution comprising methanol, methyl ethyl ketone, sulfuric acid, and a complex compound of palladium chloride and methyl ethyl ketone.

2 Claims, No Drawings

PLATING PRE-TREATMENT IN ACRYLONITRILE BUTADIENE STYRENE

BACKGROUND OF THE INVENTION

This invention relates to plating acrylonitrile butadiene styrene polymers and more particularly to a process having fewer pre-treatment steps than currently available commercial processes. Acrylonitrile butadiene styrene shall hereinafter be referred to simply as ABS. More specifically, this invention relates to a single pre-treatment solution which eliminates a number of conventionally used pre-treatment solutions and the multiple intermediate rinsing steps accompanying their use. Commercially available plating processes for treating ABS preparatory to plating usually involve immersing the ABS in a strong acidic oxidizing solution to etch the surface and render it hydrophilic. A number of etchants have been proposed for this purpose among which are the sulfuric acid-chromic acid solutions and phosphoric acid-permanganate solutions (see Doty et al U.S. Pat. No. 3,598,630). There are a number of solution variations available in the sulfuric acid-chromic acid group. One such variation includes about 70 percent by volume of sulfuric acid and about 20 - 25 grams per liter of CrO_3 . Another variation includes about 45 percent by volume of sulfuric acid, 22 percent by volume of phosphoric acid and about 30 grams per liter of CrO_3 . Still another variation includes about 20 percent by volume of sulfuric acid and 585 grams per liter of CrO_3 . These solutions are generally used at temperatures of about $50^\circ - 70^\circ \text{C.}$, are highly corrosive and are a waste disposal problem.

Following etching and rinsing the part is immersed in a sensitizing solution and a sensitizer absorbed into the surface. Typical among the known sensitizers are tin and titanium salts, and especially stannous chloride. The part is again rinsed followed by immersion into an activating solution comprising aqueous solution of a salt of a precious metal catalyst, such as gold, silver or the palladium group metals. In the activating solution, the sensitizer reduces the catalyst-bearing salt to the corresponding catalytic metal which in turn provides a plurality of discrete nucleation centers for the subsequent electroless copper or nickel to build on. The parts are rinsed and finally immersed in a reducing electroless copper or nickel bath to provide a uniform coating of metal on the surface to act as a conductor in subsequent electroplating operations. A typical electroless copper bath contains copper salts, copper complexing agents, a pH buffer and a reducing agent. A typical electroless nickel bath includes a nickel salt, a reducing agent (e.g., sodium hypophosphite), acetic acid and sodium hydroxide. These baths are essentially auto-catalytic in that after initiation by the catalytic metal the copper or nickel plate becomes itself a catalyst and plating continues.

The cost of plated ABS automotive exterior trim is not appreciably less than its metal counterpart. Contributing significantly to the cost is the price of the pre-plating solutions, the cost of waste disposal facilities for them, the considerable plant space required to set up for the many steps involved and finally a high reject rate of the parts themselves. As a result, the use of plated ABS, especially for exterior trim purposes, has not had the wide spread acceptance in the automotive industry that early predictions indicated. This situation

is not likely to change unless major cost reductions and improvements in product reliability can be made. If the number or preplating steps can be reduced along with a savings in time, space, maintenance and disposal, then plated plastics will most likely receive greater acceptance as exterior automotive trim material.

It is therefore an object of the present invention to provide a new pre-treatment solution, the use of which eliminates a number of the pre-treatment steps now used in commercially available processes. This and other objects and advantages of the present invention will become apparent from the more detailed discussion which follows.

BRIEF SUMMARY OF THE INVENTION

The present invention comprehends a pre-treatment solution containing about 35 to about 75 cubic centimeters per liter (cc/l) of methyl ethyl ketone, about 5 to about 100 cc/l of concentrated sulfuric acid (1.84 s.g.), up to about 5.6×10^{-4} moles of a complex compound of palladium chloride and methyl ethyl ketone, and the balance methyl alcohol. The aforesaid complex compound of palladium chloride and methyl ethyl ketone is hereinafter referred to as the ketopalladium complex. The pre-treatment solution of this invention is stable for long life use with only makeup additions of ketopalladium complex and acid required. Moreover, the solution is effective for treatment times of less than 10 minutes, and hence does not unduly delay the production line in which it is used. Plated parts destined for mild exposure uses (e.g., interior automobile trim or appliance hardware) are cleaned, immersed in the pre-treatment solution of this invention and, while still wet, electrolessly plated. Plated parts destined for severe exposure (e.g., exterior automobile trim) are cleaned, etched in a conventional ABS etchant, rinsed, immersed in the pre-treatment solution of this invention and, while still wet, electrolessly plated. In both instances, the parts are subsequently electroplated as required.

ABS parts plated using only the pre-treatment solution of this invention and without a pre-etch have produced metal-to-plastic peel strengths of about 5 to about 8 pounds per inch. ABS parts plated using the pre-treatment solution of this invention with a pre-etch have produced metal-to-plastic peel strengths of about 12 to about 16 pounds per inch. Moreover, ABS parts plated according to this invention and using a pre-etch showed no blistering after 48 - 64 hours of CASS testing.

Any conventional ABS etching technique may be used prior to our pre-treatment solution. Hence any one of the aforesaid commercially available chromic acid-sulfuric acid systems mentioned above is acceptable so long as it roughens the surface and provides a plurality of pits for mechanical bonding. An H_3PO_4 - CrO_3 etch is preferred. It has been observed that in some instances, high adhesion values are obtained on ABS parts which have not been etched beforehand but which, after the pre-treatment of this invention, are allowed to soak for a short period in a quiescent water rinse before electroless plating. This soak apparently removes any excess acid without dislodging any catalyst and permits H_2SO_4 concentrations as high as 100 cc/liter to be used without continuing attack of the ABS.

PREFERRED EMBODIMENTS OF THE INVENTION

To prepare the pre-treatment solution of the present invention, a ketopalladium complex concentrate is prepared by dissolving 0.5 grams of palladium chloride (PdCl_2) in 95 cc of methyl ethyl ketone and 5 cc of concentrated hydrochloric acid (1.19 sq.). The HCl is used to aid dissolution of the PdCl_2 . The concentrate described is used as a stock solution to prepare the pre-treatment solution of this invention. No more than about 20 cc of the concentrate is needed per liter of pre-treatment solution. Due to the cost of palladium, no more than is absolutely necessary should be used. Each cubic centimeter of the stock solution contains 2.8×10^{-5} moles of the ketopalladium complex.

A number of Cycloc EP - 3510 test panels (7.5 cm. \times 10 cm.) were cleaned and degreased by rinsing in methyl alcohol. Several of the panels were then immersed for about 10 minutes into a room temperature pre-treatment solution containing about 37 cc of methyl ethyl ketone, 50 cc of sulfuric acid (1.84 sq.), 5 cc of the ketopalladium complex concentrate and the balance methyl alcohol to make one liter of solution. Several other panels were treated for about 5 minutes in a room temperature pre-treatment solution comprising about 68 cc of methyl ethyl ketone, 50 cc of sulfuric acid (1.84 sq.), about 5 cc of the ketopalladium complex concentrate and the balance methyl alcohol to make one liter of solution. These parts were then immersed for about 10 minutes in a 68° C. electroless nickel plating solution comprising about 36 grams per liter of nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), 3.6 grams per liter of sodium hydroxide, 28 grams per liter sodium hyphosphite, 13 cc per liter of acetic acid and 0.5 cc per liter of a lead concentrate comprising 1 gram per liter lead ion, 10 cc per liter of acetic acid and the balance water. A number of each set of samples were then rinsed and electroplated with 0.005 centimeters of conventional acid copper (sulfate type) and aged for at least 48 hours preparatory to peel strength testing according to the Jacquet test described in the article by E. B. Saubestre, J. Durney, G. Hajdowe, E. Bastesbach, Plating, 52, 983, 1965. This test involves scribing a 1 inch strip across and through the copper and nickel layers, lifting a tab at the end of the strip, grasping the tab in an Instron machine, pulling the strip at a rate of 1 inch per minute at an angle of 90° from the face of the panel, and plotting the amount of pull (i.e., pounds/inch) required to peel the strip from the panel. Samples prepared and tested in this manner demonstrated adhesion values of between about 5 to about 8 pounds per inch.

Other tests were conducted in which the H_2SO_4 and methyl ethyl ketone concentration was varied without rinsing after treatment. In this connection, it was observed that peel strength increased with increased concentration of sulfuric acid up to about 55 cc per liter. At concentrations above about 55 cc per liter, the tensile strength of the ABS surface is significantly reduced. It was also observed that the bond strength does not appear to vary significantly with changes in methyl ethyl ketone concentration in the pre-treatment solution, but that a sufficient concentration is important to insure complete coverage of the part with the electroless deposit. Too little methyl ethyl ketone produces spotty plating and too much methyl ethyl ketone tends to re-

sult in blistered substrates. It was noted that for treatment times of about 10 minutes, the methyl ethyl ketone concentration should be no less than about 35 cc per liter and for treatment times of about 5 minutes the methyl ethyl ketone concentration should be at least about 65 cc per liter. This concentration will vary according to treatment time and whether or not a pre etch has been used. In general, the methyl ethyl ketone concentration should be kept as low as possible consistent with complete coverage of the part.

A number of the above electrolessly plated panels were selected for further testing using the CASS test. These parts were subjected to CASS testing to failure of the ABS-metal bond. After the electroless nickel these parts were rinsed and electroplated with 0.8 mils acid copper (UBEC), 0.4 mils semi-bright nickel (Udylite N2E), 0.3 mils bright nickel (Udylite 66) and finally, 0.000003 mils of conventional chromium. The ABS to metal bond on these parts failed after about 48 to about 64 hours of exposure to the CASS solution, at which time the CASS solution had penetrated the deposit and reached the substrate, then, apparently spread out laterally destroying the ABS-to-metal bond at the interface between the two, leaving a blistered product.

The loss of adhesion encountered in the CASS test may be overcome by etching the ABS in the conventional manner to produce a porous surface thereon prior to treatment according to this invention. In this regard, parts were prepared in the same manner as described above except that, prior to the pre-treatment step, they were etched for 5 minutes in an 82° C. solution containing 80 percent by volume concentrated phosphoric acid, 600 grams per liter of CrO_3 and the balance water to make up 1 liter of solution. These samples were subjected to the CASS test. Penetration through the metal deposits occurred in about the same time as for the other samples, but there was no loss of adhesion or apparent lateral spread of the CASS solution after 64 hours of testing.

While we have disclosed our invention solely in terms of specific embodiments thereof, we do not intend to be limited thereto but rather only to the extent set forth in the claims which follow.

We claim:

1. A method of metalizing acrylonitrile-butadiene-styrene surface including the steps of:

contacting said surface with a conditioning and activating solution for preparing the surface to uniformly accept an adherent metal deposit, said solution consisting essentially of in 1 liter thereof about 35 to about 75 cubic centimeters of methyl ethyl ketone to insure uniform coverage of the surface without producing a blistered deposit, about 5 to about 100 cubic centimeters of concentrated sulfuric acid to increase adhesion of the metal deposit to the surface, up to about 5.6×10^{-4} moles of ketopalladium complex formed by the reaction of palladium chloride with methyl ethyl ketone to activate said surface and the balance methyl alcohol; and

contacting said surface with a reducing solution of a reducible compound of a coating metal to electrolessly deposit said coating metal uniformly and adherently onto said surface.

2. A method of metalizing acrylonitrile-butadiene-styrene surface including the steps of:

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contacting said surface with a strong acidic, oxidizing solution to etch said surface;

rinsing said surface to remove said strong, acidic oxidizing solution therefrom;

contacting said surface with a conditioning and activating solution for preparing the surface to uniformly accept an adherent metal deposit, said solution consisting essentially of in one liter thereof about 35 to about 75 cubic centimeters of methyl ethyl ketone to insure uniform coverage of the surface without producing a blistered deposit, about 5 to about 55 cubic centimeters of concentrated sul-

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furic acid to increase adhesion of the metal deposit to the surface, up to about 1.4×10^{-4} moles of ketopalladium complex formed by the reaction of palladium chloride with methyl ethyl ketone to activate said surface and the balance methyl alcohol; and

contacting said surface with a reducing solution of a reducible compound of a coating metal to electrolytically deposit said coating metal uniformly and adherently onto said surface.

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