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[54] **COMPOSITIONS FOR AND METHODS OF IMPROVING ADHESION OF PLATED METAL ON PLASTIC SUBSTRATES**

[75] Inventors: **John J. Grunwald,** New Haven; **Eugene D. D'Ottavio,** Thomaston, both of Conn.

[73] Assignee: **MacDermid Incorporated,** Waterbury, Conn.

[*] Notice: The portion of the term of this patent subsequent to May 18, 1988, has been disclaimed.

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Related U.S. Application Data

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[58] **Field of Search**.....106/265, 1; 117/47 R, 47 A, 117/160, 130, 138.8 R, 138.8 E; 252/312; 204/38, 30, 80

[56] **References Cited**

UNITED STATES PATENTS

3,556,955	1/1971	Ancker et al.	117/47 A
3,574,700	4/1971	Sahely	117/47 A
3,501,332	3/1970	Buckman	117/47 A

Primary Examiner—William D. Martin
Assistant Examiner—William R. Trenor
Attorney—Steward & Steward, Roy F. Steward, Merrill F. Steward and Donald T. Steward

[57] **ABSTRACT**

A method of and composition for promoting adhesion between plated metal and a plastic substrate, in which the active agent is provided in finely divided dispersed or colloidal form in an aqueous emulsion. The active agents are any of a group of low molecular weight organic unsaturated compounds of the fatty acid type, and more especially of the group of naturally occurring products such as linseed, tall, tung and castor oils, turpentine and similar wood rosins. These, when dispersed in water to provide stable emulsions, are used as a pretreatment bath for plastic substrates, prior to plating of the substrate, in order to promote the formation of a stronger bond between the metal plate and substrate.

9 Claims, No Drawings

COMPOSITIONS FOR AND METHODS OF IMPROVING ADHESION OF PLATED METAL ON PLASTIC SUBSTRATES

This application is a division of copending application Ser. No. 654,901, filed June 14, 1967, now U.S. Pat. No. 3,579,365.

The present invention relates to the pretreatment of plastic substrates for the chemical plating of a metal thereon. The invention is concerned with novel plating pretreatment bath compositions, and processes of using such compositions, to enhance the adhesive strength of the resultant metal-to-plastic bond in the plated substrates. The invention affords important practical advantages over compositions and processes heretofore known and used for similar purposes.

The successful application of metal plated polymer articles hinges, to a great extent, on the strength of the metal-to-polymer bond. Indeed, properties such as the ability to withstand extreme changes in temperature, impact resistance, tensile strength, and many others, are strongly related to the adhesion of the metal to the polymer substrate.

To achieve adhesion, the prior art teaches subjecting the substrate to a strongly oxidizing chromic-sulfuric acid mixture at elevated temperature, followed by exposure of the surface to stannous chloride and/or palladium chloride solution which prepares the polymer for subsequent catalytic deposition of nickel, copper, cobalt or other suitable conductive metallic coatings that will receive an electroplate when suitably immersed in an electrolytic plating bath. The articles thus obtained consist of plastic-metal composites in which the metallic coating may vary from less than 0.1 mil to as high as 2.0 mils or more in thickness.

Certain limitations are inherent in this prior art teaching which can be summarized as follows:

1. Only specially compounded plastics can be treated to give adequate adhesion. One such plastic is ABS (acrilonitrile-butadiene-styrene), and it accounts for the majority of metal plated plastic articles in use at this time.

2. Even on ABS, the earlier method affords relatively low adhesion values that limit application to functional parts which are not required to undergo extreme temperature variation in use.

3. The earlier method requires carefully molded, stress-free plastic articles, otherwise adhesion failures due to stressed areas are difficult to overcome.

4. ABS, because it requires special and careful formulation, is relatively expensive compared to other available polymers, especially polyolefins.

In order to prepare polymers other than ABS for subsequent metal deposition, methods more recently developed involve subjecting the plastic to certain unsaturated organic solvents, oils, acids, etc., which are retained by the surface of the substrate and facilitate subsequent penetration by the usual chromic-sulfuric etching solution, giving substantial improvement in platability. While the exact nature of this surface impregnation by the organic solvent or adhesion promoter as it is hereinafter referred to is not fully understood, various postulations have been advanced. In U.S. Pat. No. 3,556,955, there are disclosed compositions and processes for conditioning plastic substrates such as polypropylene by the use of some of these organic adhesion promoters. Examples of these

promoters include highly unsaturated fatty acids, e.g., sorbic acid, linoleic acid, linolenic acid, elacostearic acid and liconic acid and their esters, amides and imides; the amides and imides of mono-unsaturated fatty acids such as oleic and ricinoleic acid; also highly unsaturated aliphatic hydrocarbons such as aqualene; highly unsaturated alicyclic compounds such as abietic acid; aliphatic polyethers such as polyethylene glycol, polypropylene glycol, as well as their adducts and esters, as for example, the poly(ethylene oxide) adducts of nonyl phenol; tertiary aliphatic compounds such as isobutyric and isovaleric acid and the esters, amides and imides thereof; and the aliphatic substituted aromatic compounds containing at least one benzylic hydrogen such as cumene, thymol and their derivatives. These compounds may be employed in their more or less natural or crude form, for example by direct use of such products as castor, linseed, tall or tung oil, wood rosin and the like.

The procedures described in the aforesaid prior patent involve both incorporation of the adhesion promoters directly in the resin compositions during compounding, as well as impregnation of the surface of the resin compositions after molding into finished products. Impregnation of the surface of finished molded products in accordance with the method disclosed in said prior patent involves the immersion of those products in a bath of one or more of the aforesaid promoters, for example castor, linseed or tung oil at appropriate temperatures and for suitable times. It is conjectured that the resulting increase in adhesive strength of the metal-to-plastic bond is obtained as the result of providing on or in the surface of the plastic fractions or remnants of the organic promoter materials which after the pretreated substrate has been subjected to an oxidation step, provide carboxyl-containing free radicals attached to the polymer molecule and it is these which serve to link the metal to the plastic.

For practical commercial applications it is considered necessary that the adhesion or minimum "peel" strength of a metal-to-plastic composite be on the order of at least 5 pounds per inch between the plated deposit and the substrate; generally three to five times that value is desired. When organic adhesion promoters such as those described above are used in their more or less natural state, as is disclosed in the aforesaid prior application, it is necessary, in order that effective peel strength in the metal-plastic composite be obtained, that the temperatures of such promoters be maintained at substantially elevated levels, generally on the order of at least 250° to 275° F. While this gives effective results from a bonding standpoint, there are many instances in which the molded plastic product undergoing plating is of complex configuration involving both relatively thick and relatively thin sections of plastic, indentations, pockets or recesses, as well as planar and curvilinear sections. As a result, substantial internal stresses can be and are relieved upon immersing the articles in the hot bath for the substantial periods of time needed. Generally periods of 3 minutes or more are required to be effective. Warping, sinking or other distortion of the parts frequently are encountered as a consequence of relaxing or relieving these internal strains.

There are, in addition, other serious difficulties that limit the applicability of these organic solvents, oils, acids, etc., as adhesion promoters for commercial use as it has heretofore been proposed to use them. Given below are a few of the difficulties encountered.

1. These organic promoters are generally quite flammable and present a definite fire hazard.

2. The prior method of use of these organic adhesion promoters, coupled with the elevated temperatures which they require for adequate surface treatment of the plastic polymer, causes excessive evaporation and requires special ventilation precautions to protect operating personnel.

3. The prior method of use further requires re-racking of the parts because these organic agents under the conditions employed tend to soften and damage the Plastisol coating conventionally used on the article transporting racks, and makes plating of the articles in a single, continuous step-wise sequence difficult or impossible, and in any event seriously increases processing costs.

4. The prior method of use of these organic solvents and especially the highly viscous oils such as castor, linseed or tung oil, causes excessive retention or drag-out by the articles being treated, and necessitates the use of a second organic solvent dip to remove the excess of organic promoter from the surface, blind holes, recesses, etc., of the parts before plating.

5. The parts must be cooled to approximately room temperature prior to removing excess oil in the solvent. This necessitates an increase in production time.

It is one of the principal objectives of the present invention to provide organic adhesion promoter compositions and processes which are effective at substantially lower operating temperatures and which therefore do not give rise to relaxation of internal stress and subsequent warping or deformation of the plastic parts.

Another major objective of the invention is improvement in operating or processing steps whereby re-racking of the plastic articles between the adhesion promoter impregnating step and subsequent pretreatment and plating operations is avoided, thus affording greater simplification of processing operations with resulting economies in the handling of the parts to be plated.

Other objectives include the reduction of evaporation losses, simplification of ventilation requirements, substantial reduction of fire hazard and other advantages flowing from these, as will become apparent hereinafter.

In accordance with the present invention, these objectives are achieved by the use of many of the same adhesion promoting compositions of the organic solvent, oil, acid, etc., type heretofore proposed as well as other similar low molecular weight organic highly unsaturated compounds. However, instead of using those compounds in their normal state, i.e., as a single-phase solution, they are prepared and used in a two-phase system comprising very fine aqueous dispersions of these compounds providing stable emulsions or microemulsions of the oil-in-water type. By using these emulsions in the adhesion promoting bath in place of the single-phase solutions heretofore proposed, the bath temperature may be reduced to a wholly unexpected degree, usually by at least as much as 100° F, so that the operating temperature of the bath is below the boiling point of water and in many cases is as low as 135° to 155° F.

Without intending to be bound by an explanation of the theory or mechanism responsible for this dramatic decrease in practical operating temperatures, it is postulated that this occurs because of the very high surface energy which results from low interfacial surface tension and enormous surface areas of the agent particles in the emulsion system. The heat of wetting is thus increased tremendously, providing increased adhesion of the particles to the substrate and greatly increased rate of diffusion of such agent particles into microscopic or submicroscopic pores of the polymer. In fact, visual evidence of this diffusion is supplied by incorporating a dye into the organic promoter agent of the emulsion system, which dye can then be observed to penetrate substantially into the plastic material itself upon immersing it in the bath.

Numerous other advantages apart from lower temperature operations are also realized by the present invention. Using the organic adhesion promoting agent in the form of a fine disperson or emulsion, the amount of agent needed to effect the desired adhesion properties in the plastic can be reduced to as little as 10 to 15 percent by volume of the total treatment solution in contrast to the 100 percent heretofore used. This in turn substantially reduces fire hazards, ventilation problems to remove fumes that could not be tolerated by operating personnel, evaporation losses, and affords lower costs. Most importantly, by using the emulsion system it no longer is necessary to re-rack articles when transporting them from the adhesion promoting bath to subsequent preconditioning and plating baths, since the adherent solution from the novel adhesion promoting bath can be easily rinsed in plain water and since the bath no longer adversely affects the Plastisol coating on the racks. Thus the invention makes it possible to provide a truly continuous plastic plating process in which the articles are transported by the same rack successively through each of the various preconditioning and plating baths without interruption from start to finish.

The invention is illustrated by the following examples which are given by way of explanation of the concept involved and its application to practical plastic plating applications. The examples are not intended to be all-encompassing of the invention since it will be readily apparent to those skilled in the art that the teaching herein provided may be applied to produce equivalent substitute compositions. The appended claims are accordingly intended to cover not only the specific examples here given but their lawful equivalents.

EXAMPLE I

A compression molded polypropylene automotive instrument bezel having cross sections of various thicknesses, pockets, blind holes and similar recesses, was cleaned in a slightly alkaline aqueous solution and then immersed for a period of about 10 minutes at a temperature of 170° F in an aqueous solution of an adhesion promoting emulsion of the following composition:

a. Linseed oil	3 grams
b. Steam distilled wood turpentine	3 grams
c. Linoleic acid	1.5 grams

d. Surfactant	2% by volume
e. Water	sufficient to make 300 mls. total solution
f. Potassium hydroxide	to bring solution to neutral or slightly alkaline pH e.g., about 7 to 9)

Surfactants such as IGEPAL CO630 and CO730, in substantially equal amounts, are satisfactory. These are non-ionic emulisfying agents produced commercially by General Aniline & Film Corp., Dystuff and Chemicals Division, and comprise alkylphenoxypoly(ethyleneoxy) ethanols produced by reacting an alkylphenol with ethylene oxide. The general formula is

$$RC_6H_4O(CH_2CH_2O)_nCH_2CH_2OH,$$

where R is C_8H_{17} or a higher homolog.

The preparation of the foregoing emulsion is accomplished as follows: 20 grams of linseed oil, 20 grams of turpentine and 10 grams of linoleic acid are mixed with 20 mls. each of IGEPAL CO730 and CO630, heated to about 120° F and 100 mls. of water added with constant stirring. A 10 percent solution of potassium hydroxide is then added until the pH of the solution is about 8.0. Thereafter, additional water is added with constant stirring to give a total volume of 300 mls. This is a concentrated solution and from this the adhesion promoting bath described in the above example is prepared by diluting with additional water so that the concentrate constitutes about 15 percent by volume of the final total solution.

Following the adhesion promoting bath, the treated plastic bezel is run through a cold water rinse and then immersed in a chromic-sulfuric acid oxidizing solution consisting of approximately 30 percent by weight chromic acid, 25 percent by weight sulfuric acid (66°Be), the balance being water. This solution has a specific gravity of approximately 1.48 at a temperature of 170° F and the substrate is held in the solution for a period of about 5 minutes.

The etched substrate is then thoroughly rinsed by a double cold water rinse and is next immersed in a solution of phosphoric acid (40–45 percent by volume) containing 10–20 parts per million of IGEPAL CO630 at a temperature of 80° F. After about 5 minutes soaking in this solution, the bezel is again rinsed in cold water and transferred to an activating solution prepared as follows:

	% by weight
1. Palladium chloride ti (60% palladium)	0.16
2. 37% hydrochloric acid	19.4
3. Deionized water	33.9
4. Stannous chloride (anhydrous)	0.27
5. Stannous chloride (anhydrous)	6.55
6. Sodium stannate ($3H_2O$)	1.13
7. 37% hydrochloric acid	38.6

Components Nos. 1, 2, and 3 in the above composition are mixed at room temperature until all of the palladium chloride is dissolved. The first portion of stannous chloride (component No. 4) is then added and the resulting solution stirred for 10 minutes. Components Nos. 5, 6, and 7 are mixed separately from the foregoing and the first solution is then poured into this second solution with constant stirring. All preparation is done at room temperature. The resulting concentrated activator solution is then heated for about 3 hours at about 150° F and then diluted for use in the activating bath. In general it is satisfactory to use about 10 to 20 percent by volume of the aforesaid concentrate, 20 percent by volume of concentrated hydrochloric acid, the balance being water.

This activating bath is used at 80° F and the bezel is retained in it for about 5 minutes. Thereafter, the bezel is removed and then again rinsed in cold water and subjected to a leaching or accelerating step comprising immersing it in an aqueous solution of fluoboric acid at a concentration of about 2 pounds per gallon at a temperature of 110° F for 1 minute.

Again the bezel is thoroughly rinsed in cold water and immersed in an electroless plating solution. Any number of conventional copper or nickel electroless plating compositions can be used in this step, but for nickel plating a particularly suitable system is described in U.S. Pat. No. 2,532,283, Example V, Table I. Similarly, a highly suitable copper solution is disclosed in U.S. Pat. No. 3,095,309, Example I. Electroless plating is then followed by electroplating in conventional manner.

The resulting plate shows uniform coverage and good adhesion in which the minimum peel strength is about 15 pounds per inch.

EXAMPLE II

Again, a molded polypropylene article was washed and then placed in an adhesion promoting aqueous emulsion of the following composition:

a. linseed oil	22 mls.
b. oleic acid	11 mls.
c. turpentine	22 mls.
d. surfactants	44 mls.
e. water	900 mls.
f. potassium hydroxide to being the solution to neutral or slightly alkaline pH	

The surfactants used here were IGEPAL CO630 and TRITON X–100 in equal amounts. TRITON X–100 is the trade name of Rohm & Haas for surfactants of the alkylarly polyether alcohol water soluble type.

The foregoing emulsion is prepared by heating the water to about 120° F, adding the potassium hydroxide (about 38 grams per liter) and stirring until dissolved, after which the previously mixed linseed oil, oleic acid, turpentine and surfactants are added and stirred in.

The plastic article is retained in the adhesion promoter for about 15 minutes at a solution temperature of 170° F. Thereafter, the article is processed through the balance of the steps outlined in Example I. The adhesion obtained from this procedure varies between 15 and 24 pounds per inch on unaged parts. While useful, the particular adhesion promoting emulsion here described is subject to instability, particularly at bath temperatures of around 175° F., as evidenced by the formation of a separate oil film.

EXAMPLE III

The procedure is the same as in Example I except that the following emulsion is substituted for the adhesion promoter of that example:

a. turpentine	40 mls.
b. surfactants	60 mls.

c. water	900 mls.

In this formulation, a mixture of water soluble surfactants consisting of 50 mls. IGEPAL CO630 and 10 mls. of BENAX 2A1 is especially suitable. BENAX 2A1 is the trade designation of Dow Chemical Co. for sodium dodecyl diphenyl ether disulfonate and is used in the foregoing formulation primarily to prevent clouding of the solution, particularly at the temperature of use. This formulation of adhesion promoter is particularly stable at all temperatures up to and including normal bath operation temperature of from 145° to 155° F. Immersion periods for the parts at this operating temperature range is 10 to 15 minutes. Polypropylene parts treated in this bath, followed by the remainder of the plating cycle steps outlined in Example I, show peel or bond strengths of 25 pounds per inch, or more.

Other promoters such as castor oil, tung oil and tall oil all exhibit similar adhesion improving qualities when used in the form of aqueous oil-in-water emulsions similar to those of the foregoing examples. Accordingly it appears that any of the adhesion promoters of the types disclosed in the aforesaid U.S. Pat. No. 3,556,955 can be successfully used in the form of aqueous emulsions. For economic reasons, as well as ease of handling, the pine derivatives such as turpentine are presently preferred.

As has been pointed out above, the effectiveness of the emulsions in promoting surface modification of the plastic substrates is believed to be due to the tremendous surface energy made available by using the active adhesion promoting agent in finely divided or dispersed condition. The emulsions described in the foregoing examples show a very high order of dispersion. Those of Examples I and II are at least macro-emulsions whose active particle sizes are on the order of one-half to a maximum of about fifty microns. The particle sizes in Example III appear to be more accurately described as micro-emulsions whose size range from 50 to 500 angstroms. The benefits of the invention in respect to lower operating temperatures, lower concentrations, equipment and process simplification, etc., are accordingly believed to be the direct result of employing the active agent in colloidal, highly dispersed form.

What is claimed is:

1. The process of increasing the adhesion of plated metal on polypropylene substrates, which comprises immersing the substrate in aqueous emulsion of an organic latent adhesion promoter consisting essentially of:

a. linseed oil	3 grams
b. turpentine	3 grams
c. linoleic acid	1.5 grams
d. surfactant	2 % by volume
e. deionized water	to make 300 mls. total solution
f. potassium hydroxide	to give a pH of about 8.0

then oxidizing the resulting substrate to develop said adhesion promoter, and thereafter plating the oxidized substrate.

2. The process defined in claim 1, wherein the substrate is immersed in said emulsion for a period of about 10 minutes at a temperature of 170° F.

3. The process defined in claim 1, wherein said adhesion promoter is an aqueous emulsion consisting essentially of:

a. linseed oil	22 mls.
b. turpentine	22 mls.
c. oleic acid	11 mls.
d. surfactant	44 mls.
e. water	900 mls.
f. potassium hydroxide to provide about 38 grams per liter of final emulsion.	

4. The process defined in claim 3, wherein the substrate is immersed in said emulsion for a period of about 10 minutes at a temperature of 175° F.

5. The process defined in claim 1, wherein said adhesion promoter is an aqueous emulsion consisting essentially of:

a. turpentine	44 mls.
b. surfactant	60 mls.
c. water	900 mls.

6. The process defined in claim 5, wherein the substrate is immersed in said emulsion for a period of 10 to 15 minutes at a temperature of 145° to 155° F.

7. The method of plating a polystyrene substrate with a metal film by chemical deposition from an aqueous solution containing a soluble salt of the metal to be deposited, which comprises the steps of

a. cleaning the surface of the resin substrate by immersing it in a hot aqueous alkaline solution;

b. withdrawing the substrate from said cleaning solution and immersing it in the aqueous adhesion promoting emulsion consisting essentially of:

a. linseed oil	3 grams
b. turpentine	3 grams
c. linoleic acid	1.5 grams
d. surfactant	2% by volume
e. water	to make 300 mls. total solution
f. potassium hydroxide	to give a pH of about 8,

for a period of about 10 minutes at a temperature of approximately 170° F;

c. rinsing the substrate and immersing it in a chromic-sulfuric acid oxidizing solution consisting essentially of about 30 percent (weight) chromic acid, 25 percent (weight) sulfuric acid (66° Be), the balance being water, maintaining said substrate in said oxidizing solution while at a temperature of about 170° F for 5 minutes;

d. removing and thoroughly rinsing said substrate in water, then immersing it in an aqueous solution of phosphoric acid containing 10–20 ppm of a surface active agent for about 5 minutes;

e. removing and rinsing the substrate in water and then immersing it in a colloidal activating solution comprising about 20 percent (volume) of concentrated hydrochloric acid, 60–70 percent (volume) water and from 10–20 percent (volume) of the following composition:

	Wt. %
$PdCl_2$	0.16
HCl (37%)	58.0
Water (deionized)	33.9
$SnCl_2$ (anhydrous)	6.82
$Na_2SnO_3 \cdot 3H_2O$	1.13

and maintaining said substrate in said activating solution for about 5 minutes at 80°F;

f. removing said substrate, rinsing in water and then immersing it in an aqueous accelerating solution containing approximately 2 pounds of fluoroboric acid per gallon for 1 minute at 110° F;

g. removing and rinsing the substrate and immersing it in an aqueous electroless copper or nickel plating solution to deposit an adherent film of the metal on said substrate.

8. The method as defined in claim 7, except that in step (b) thereof said substrate is immersed in an aqueous adhesion promoting emulsion consisting essentially of:

a. linseed oil	22 mls.
b. oleic acid	11 mls.
c. turpentine	22 mls.
d. surfactants	44 mls.
e. water	900 mls.
f. potassium hydroxide	38 grams.

9. The method as defined in claim 7, except that in step (b) thereof said substrate is immersed in an aqueous adhesion promoting emulsion consisting essentially of:

a. turpentine	40 mls.
b. surfactant	60 mls.
c. water	900 mls.

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