METHOD OF AND SOLUTION FOR ACCELERATING ACTIVATION OF PLASTIC SUBSTRATES IN ELECTROLESS METAL PLATING SYSTEM

ABSTRACT: A method is disclosed for accelerating the activation of a polymeric plastic substrate in a chemical plating process incorporating a preliminary chromic acid etch involving immersing the substrate in an acidic dilute palladium chloride solution following activation, and rejuvenating that accelerating solution with periodic additions of stannous ions sufficient to reduce hexavalent chromium contamination carried over from the preliminary chromic acid etch to a prescribed maximum level without incurring substantial precipitation of palladium in the accelerating solution.
3,622,370

1. METHOD OF AND SOLUTION FOR ACCELERATING ACTIVATION OF PLASTIC SUBSTRATES IN ELECTROLESS METAL PLATING SYSTEM

This invention is concerned with metal plating of polymeric resin substrates, and is more particularly directed to improvements in that portion of the metalizing process involving the laying down of an initial deposit or film of a desired metal, which deposit is continuous in its coverage of the substrate and is firmly bonded thereto.

The art of metalizing plastics both for decorative and functional applications is undergoing rapid development. The general method employed consists of first chemically depositing on a polymeric plastic substrate a preliminary conductive metallic coating after which the substrate can then be electroplated by standard electrochemical techniques. The successful application of the initial conductive metallic layer is of crucial importance to the subsequent successful electroplating of one or more layers of the same or different metal in building up a structure of treatment desired thickness and finish characteristics. Copper, nickel, chromium and sometimes cobalt are the metals most commonly applied to commercial articles, and the process is used extensively in the automotive, appliance, plumbing and related industries today.

There are various methods in regular use for metalizing plastics. Most comprise a first or chemical, i.e., electrola, plating cycle of steps which consists of immersing the object to be plated in a number of aqueous or nonaqueous solutions, with each of such solutions contributing to a specific alteration of the polymer surface of the substrate to cause it to accept a thin and adherent initial metal layer. Thereafter a second processing phase or sequence of steps is involved during which thicker metal deposits are applied electrochemically, that is, by the application of an external source of electrical energy. In the course of these operations, the substrates or articles to be plated are sequentially subjected to various treatment solutions, as by spraying them with or immersing them in such solutions. In a commercial installation where mass production techniques are employed, the articles are generally supported from racks carried by endless conveyor means, by which the articles are progressed through the sequence of treatment steps, including the chemical or electrola plating cycle as well as the final electroplating operations.

This invention is concerned primarily with improvements in the chemical or electrola plating cycle of operations, and it will be appropriate therefore, as background for the invention here disclosed, to consider first of all the sequence of operations involved in a typical, current procedure. In general, the steps in chemical plating of a polymeric plastic substrate comprise the following:

1. Clean the plastic part of surface grime, etc., in an aqueous alkali soak solution.
2. Contact the cleaned part with an organic solvent medium which may be either a single-phase system or an admixed water-organic solvent emulsion. An example of such material and treatment is disclosed in a copending application, Ser. No. 654,901, filed June 14, 1967.
3. Thorough water rinse of the part.
4. Contact of the part with an aqueous acid solution containing hexavalent chromium ions to etch the surface of the plastic. An example of such treatment is disclosed in U.S. Pat. No. 3,370,974; a different example is disclosed in a copending application, Ser. No. 474,198, filed June 25, 1965.
5. One or more rinses in water and/or solutions containing chromium-reducing or chromium-extracting agents. An example of this is disclosed in a copending application Ser. No. 758,589, filed Sept. 9, 1968.
6. Contact the surface of the substrate with an acid tin-lead hydroxyl using a "one-step" activator. An example is found in U.S. Pat. No. 3,011,920; also a further modification is disclosed in U.S. Pat. No. 3,532,518.
7. Again carefully rinse the surface.
8. Accelerate the activated surface of the plastic, using a dilute solution of an acid or alkali. Examples of suitable solutions are shown in U.S. Pat. Nos. 3,011,920 and 3,532,518.
9. Rinse in water.
10. Immerse or otherwise contact the substrate surface with a chemical plating solution containing a reducible salt of the metal to be deposited on the surface. Examples are found in the patent and application listed in Step 6 above; also in U.S. Pat. Nos. 3,212,918 and 3,370,974 for nickel and cobalt; also 3,095,309 for copper.
11. Rinse the metalized surface in water, which is now ready for conventional electroplating.

While the foregoing general sequence of steps is employed commercially, there are certain deficiencies in the process which have manifested themselves. Small changes in operating procedures or ambient conditions tend to give rise to difficulties, the cause or reason for which is often unknown or hard to recognize since the art of plating on plastics is still largely empirical. This is particularly true in commercial operation where conditions are far less accurately controllable than in laboratory tests.

One of the most important problems is plating "skip" or lack of continuity in the coverage of the substrate by the deposited metal. This is commonly noted on areas of the plastic which are highly stressed due to the method of molding the particular part. Plating skips often occur in other nonstressed areas also. Poor adhesion is another important problem, and often this does not show up until a later stage in the process, usually not until after completion of the metalizing procedure. All of this adds to the expense because the part must then be scrapped. Quite frequently these deficiencies arise from completely unrecognized conditions which further complicate the process.

It is known, of course, that any surface contamination of the substrate at the time it is introduced into the chemical plating solution plays an important role in the success of the plating operation and gives rise to the type of difficulties mentioned above. It is also known that hexavalent chromium, which is present in the usual etching step preceding activation, is a potent deterrent or poison to good deposition of the desired metal coating on the substrate. It is common practice, accordingly, to incorporate after the etching step and before the chemical plating operation one or more thorough water rinses or other treatment solutions containing chrome-reducing agents to kill residual hexavalent chromium ions that may be present on the substrate. Obviously such preactivation chrome-kill treatments must not also act to impede the activation of the substrate surface. There is always too a problem of simple mechanical trapping of trace amounts of hexavalent chromium in crevices or other inaccessible areas where the substrate article has a complex shape or configuration.

It has now been discovered and it is a central concept of the present invention that many of the difficulties previously encountered with regard to skipping and poor adhesion of chemically deposited metal plates on polymeric substrates can be reduced or eliminated by the use of a special "accelerating" solution composition and procedure following activation of the plastic surface. Before discussing the present invention in detail, a brief discussion of accelerating procedures will be helpful to a better understanding of the invention.

Accelerating a substrate surface after its activation is of course a generally well-known procedure. The use of this step is postulated on the assumption that during activation of the substrate not only is palladium (or other catalytic metal) laid down to provide the desired initiating foci for the reduction of metal ions in the plating solution, but excess stannous ions and/or other impurities which are also present in all of the commercial activating solutions, are also deposited on or at least adhere to the surface of the substrate. These stannous ions and other impurities are deterrents to subsequent deposition of metal, just as are the residual adherent hexavalent chromium ions mentioned above, and must be removed. This
removal of impurities is the primary function of the usual accelerating solution. Ordinary water rinses have some beneficial effect but commonly the practice has been to incorporate an acid, such as hydrochloric or sulfuric, or to use perchloro or perchloro compounds, to speed up the process. The problem is one of promoting removal of these poisons preferentially to palladium particles or foci, since the latter are necessary as catalyzing sites. The known accelerating solutions are quite effective in removing stannous ions but their use is critical in that they must be accurately controlled to avoid also removing excess amounts of the palladium and thus impeding successful or adequate plating on that account. The presence at this stage of hexavalent chromium ions at extremely low levels has not been recognized heretofore as a source of trouble, and the usual accelerating treatments are largely ineffective in respect to this problem.

To overcome these deficiencies, it has now been found that effective and more readily controllable acceleration can be accomplished with the use of an acidic dilute palladium chloride solution following activation. It has also been found, however, that the effectiveness of this accelerating solution is seriously impeded by the very low-level or trace amounts of hexavalent chromium ion carried in by the substrate from the prior etching operation. The level of hexavalent chromic ion contamination found to be critical in this accelerator is unusually low, being on the order of one part per million, otherwise it will interfere and cause plate skipping and/or poor adhesion. It is therefore an important part of this invention to control the hexavalent chromium ion contamination of the accelerating solution by the periodic addition of a soluble solution of stannous ions and thereby to effect reduction of the hexavalent chromium to trivalent condition before such critical point is reached. Since the addition of stannous ions to the palladium chloride accelerating solution gives rise to a competing reaction, namely the undesirable reduction of palladinous ions to colloidal or particulate metal, the addition is preferably effected in dilute solution and in such total amount as to avoid substantial formation of particulate palladium in the accelerating solution, certainly always insufficient to effect stoichiometric reduction of the palladium chloride. The use of a dilute stannous solution avoids high local ion concentration at the point of addition, which could cause palladium deposition even though the total amount of stannous ions present in the accelerating solution would not produce significant amounts of particulate palladium. Within these limits there is a preferential reaction of the stannous ions with hexavalent chromium, which affords reasonable leeway in effecting the selective reduction of that contaminant.

The invention is illustrated by the following example.

EXAMPLE I

A molded polypropylene (Shell 5520) substrate, previously cleaned of surface grime and grease in a mild aqueous alkali proprietary cleaner solution was plated with a continuous, firmly adherent nickel deposit in the following manner:

a. Immerse substrate in an aqueous emulsion of an organic preconditioning agent comprising approximately, per liter of solution, 40 mls of steam-distilled turpentine emulsified in water with surfactants. This emulsion and its preparation is more fully disclosed in copending application Ser. No. 654,901, filed June 14, 1967. Immersion of the part in this solution is maintained for approximately 5 minutes at a temperature of 150°-160° F.

b. Cold water rinse.

c. Etch five minutes in a chromic sulfuric acid aqueous bath at a temperature of 75°-180° F.

d. Double-cold water rinses in separate rinsing tanks.

e. Immerse substrate in an aqueous solution containing controlled amounts of surfactants. Compositions useful in this step are shown more particularly in copending application Ser. No. 758,589, filed Sept. 9, 1968.

f. Cold water rinse.

g. Immerse substrate in an acid tin-palladium hydrosol activator solution containing the palladium in particulate or colloidal condition. Immersion is maintained for about 3 minutes in such solution at room temperature.

h. Cold water rinse.

i. Immerse the activated substrate for 1 to 3 minutes in an aqueous accelerating solution at about 120° F, containing approximately 0.087 g/l palladium chloride and sufficient hydrochloric acid to lower the pH of the solution to about 0.5.

j. Cold water rinse.

k. Immerse substrate in any of the standard commercial electroless nickel plating baths for 5 minutes at a bath temperature of 85°-90° F.

l. Cold water rinse.

m. Electroplate using conventional procedures.

The resulting nickel deposit is smooth, bright and completely continuous in coverage of the substrate, including such difficult platable areas as locations corresponding to gaging points in the mold, or where the surface configuration of the substrate produces deep crevices or relatively inaccessible pockets.

Copper plating of the substrate in place of nickel can similarly be effected with equally good result simply by substituting a commercial electroless copper plating solution for the nickel in Step (k) of the foregoing cycle, all other steps being unchanged. A typical copper plating solution is disclosed in U.S. Pat. No. 3,095,309. The system is also effective for electroless plating of cobalt, using any of the commercially available electroless cobalt plating solutions.

The adverse effect upon complete metal coverage of the substrate article due to the presence of minute or trace amounts of hexavalent chromium ion carried into the palladium chloride accelerating solution by the articles themselves is demonstrated by the following.

EXAMPLE II

An accelerating solution identical with that used in Step (i) of example I is purposely contaminated with incremental additions of hexavalent chromium ion in controlled amounts, and identical polypropylene samples are plated in accordance with the previously described procedure at each of the different hexavalent chromium ion concentration levels in the accelerating solution. It is found that the addition of up to a total of 0.5 parts per million p.p.m. to the accelerating solution produces no noticeable effect upon the resulting nickel or copper plate, the deposit still being complete and showing no evidence of skipping. However, upon further addition, at approximately a level of 0.6 p.p.m. (total) hexavalent chromium ion in the accelerating solution, skipping or misplating of the part results.

EXAMPLE III

A test similar to that described in example II was run but in this instance the concentration of the palladium chloride accelerating solution was increased to a level of approximately 0.0261 percent (wt.) palladium chloride. The incremental addition to this accelerating solution of hexavalent chromium ion in 0.5 p.p.m. amounts produced no evidence of skipping after a total of 1.0 p.p.m. of contaminant had been added, but severe skipping did occur when the level reached 1.5 p.p.m. hexavalent chromium ion.

Further increase in concentration of the palladium chloride appears to result in proportional increase in tolerance of the accelerating solution to hexavalent chromium ion, but for practical purposes it becomes uneconomical to operate the accelerating solution at palladium concentrations higher than 0.03 percent (wt.). In the other direction, effective results generally require a minimum palladium chloride concentration of the order of 0.002 percent. Although lower concentrations will work, solution temperature must be increased in such case and the tolerance to hexavalent chromium becomes critically low.
Before the contaminant level of the accelerating solution reaches the maximum tolerable state, the solution can be readily rejuvenated by the addition of a soluble source of stannous ions to reduce the hexavalent chromium to trivalent condition. This latter ion does not interfere or cause plating skip. This is illustrated by the following.

**EXAMPLE IV**

Again the same cycle of plating operation is followed as given in example I, and the palladium chloride accelerating solution deliberately contaminated in this case with 2 p.p.m. of hexavalent chromium ions. At this level of contaminant, almost no plated deposit is obtained on the substrate. With incremental additions of stannous ions, as dilute stannous chloride in hydrochloric acid solution, severe skipping in the plated deposit of the substrate continues to appear until a total of 35 p.p.m. of stannous ion has been added to the accelerating solution. At this point, all skipping disappears and complete coverage of the surface of the substrate by the plated metal is obtained. The reaction involved in the addition of the stannous ion appears to be reduction of the hexavalent chromium ion to trivalent condition, with simultaneous oxidation of the stannous to the stannic condition. The chromium ion poisons the plating operation only when present in the hexavalent form, as it has been found that the presence of trivalent chromium up to at least 650 p.p.m. in the accelerating solution produces no adverse effects on the coverage or adhesion of the plate. However, the manner of adding the stannous ions to the accelerating solution is important in order to avoid simultaneous reduction of palladium ions to particulate palladium and deterioration of the accelerating solution for that reason. For example, the addition of 0.1 ml of a rejuvenating solution containing 0.84 pounds of stannous chloride, 3.96 pounds of concentrated hydrochloric, balance water, per gallon of total solution, results in immediate formation of substantial particulate palladium in the accelerating solution. Still, 0.1 ml of that solution is effective in countering the adverse effect of 2 p.p.m. of hexavalent chromium ion in 1 liter of accelerating solution, in that complete plating coverage of the substrate article is obtained. A 1 ml portion of a substantially more dilute stannous chloride solution (5 percent by volume of the rejuvenating solution just mentioned, balance water) when added to one liter of palladium chloride accelerating solution containing 2 p.p.m. of hexavalent chromium ion is also effective to suppress the contaminating effect and to get complete plating coverage of substrate articles. Even at this diluted level of stannous ion, formation of some particulate palladium will occur. Further dilution of the stannous rejuvenating solution to 3 percent (volume) is effective to suppress the contaminating effect of 2 p.p.m. of hexavalent chromium ion in the accelerating solution when about 3 ml of this diluted solution is added to the accelerating solution; but even here slight amounts of particulate palladium form. This undesirable side reaction can, however, be completely avoided by utilizing a 1 percent (volume) solution of the rejuvenating stannous chloride first mentioned. The hydrochloric acid level in such solution is 0.05N. In a palladium chloride accelerating solution containing 2 p.p.m. hexavalent chromium ion as contaminant, the plating skip occasioned by the contaminant will disappear upon the addition of 7 ml per liter of the 1 percent rejuvenating solution, and no particulate palladium formation is observed in this case. The operative range of solutions comprised from about 0.05 to 0.3 percent by weight (0.5 to 3.0 g/l) stannous chloride and 0.05N to 0.15N hydrochloric acid.

The rejuvenating effect of the stannous ion upon the accelerating solution appears to be unique in that other common reducing agents do not overcome the poisoning effect of hexavalent chromium ion. For example, in an accelerating solution containing 2 p.p.m. of hexavalent chromium as contaminant, the addition of as much as 24 ml per liter of hydrogen peroxide (30 percent) still is not effective to overcome the complete inhibition by the contaminant of any metal deposit upon the substrate.

Hexavalent chromium ion is not the only trace contaminant or impurity in the accelerating solution which will inhibit the satisfactory deposit of a metal plate on the substrate, although it is the principal one usually encountered by reason of the preceding chromic-sulfuric acid etch step in the plating cycle. For example, ferric ions in the accelerating solution will also produce serious skipping in the plated deposit. In this case it is generally found that the level at which skipping begins to occur is on the order of 5–6 p.p.m. of ferric ion. The inhibiting action of this contaminant can likewise be countered by the addition of stannous ions to the accelerating solution to maintain the ferric ion concentration below the aforesaid level of 5–6 p.p.m.

Thus it appears that, in relation to the palladium ion concentration in the accelerating solution, maintaining the hexavalent chromium ion concentration at a ratio not greater than about 1 p.p.m. to 145 p.p.m. of palladium ion, by the addition of the stannous rejuvenating solution, is effective in maintaining the operability of the accelerating solution.

The improvement afforded by the present invention is applicable to substrates other than polypropylene mentioned in the foregoing examples. The plating of phenolic, epoxy and polysulfone polymers, as well as copolymers, such as acrylonitrile-buta diene-styrene is similarly improved, and it appears that the invention is applicable to any of the usual chemical-platable plastics.

We claim:

1. In a chemical plating process for depositing a continuous, adherent metal film on the surface of a polymeric plastic substrate, including the steps of etching the substrate surface in a chromic acid containing bath, activating the substrate surface by immersion in an acid tin-palladium hydrosol, subjecting the activated surface to contact with an accelerating solution to reduce excess stannous ions codeposited with palladium during the activating step and thereafter immersing the surface in a chemical plating solution of the metal to be deposited, the improvement which comprises: employing in said accelerating step an acidic dilute palladium chloride solution, periodically adding to said accelerating solution an aqueous rejuvenating solution consisting essentially of a dilute source of stannous ions in soluble form sufficient to reduce the hexavalent chromium ion contamination carried into said accelerating solution from the etching step to a level not in excess of about 0.1 p.p.m. hexavalent chromium per 145 p.p.m. palladium ion present in said solution.

2. A chemical plating process as defined in claim 1, wherein the polymeric plastic substrate is selected from the group consisting of acrylonitrile-buta diene-styrene, polypropylene, phenolic, epoxy and polysulfone plastics.

3. A chemical plating process as defined in claim 1, wherein said accelerating solution contains about 0.002 to 0.03 percent by weight of palladium chloride and hydrochloric acid to give a pH of not over about 1.0; said substrate being maintained in said accelerating solution at about 120°F. for 1 to 3 minutes.

4. A chemical plating process as defined in claim 1, wherein said rejuvenating solution consists essentially of about 0.05 to 0.03 percent by weight stannous chloride in 0.05 to 0.15N hydrochloric acid.

5. A chemical plating process as defined in claim 4, wherein the rejuvenating solution contains from 0.1 to 0.2 percent by weight of stannous chloride.

6. An aqueous accelerating solution for a chemical plating process which consists essentially of from about 0.002 to 0.03 percent by weight palladium chloride, hydrochloric acid to provide a solution pH not over about 1.0, and from about 0.05 to 0.3 percent by weight stannous chloride but always insufficient in amount to effect stochiometric reduction of the palladium chloride, wherein any hexavalent chromium ion is not in excess of about p.p.m.

7. In a chemical plating process for depositing a continuous, adherent metal film on the surface of a polymeric plastic substrate, including the steps of etching the substrate surface in a chemical etchant solution, activating the substrate surface by
immersion in an acid tin-palladium hydrosol, accelerating the activated surface and thereafter immersing the surface in a chemical plating solution of the metal to be deposited, the improvement which comprises conducting the accelerating step by immersing the plastic substrate in an acidic dilute palladium chloride solution.

8. The process of claim 7 wherein the polymeric plastic substrate is selected from the group consisting of acrylonitrile-butadiene-styrene, polypropylene, phenolic, epoxy and polysulfone plastics.

9. The process of claim 7 wherein the plastic substrate surface is etched in a chromic acid containing bath.

10. The process of claim 7 wherein the said accelerating solution contains about 0.002 to 0.03 percent by weight of palladium chloride and hydrochloric acid to give a pH of not over about 1.0.

11. The process of claim 7 wherein the said plastic substrate is polypropylene.

12. The process of claim 7 wherein the accelerating solution is maintained at a temperature of about 120°F. and the time of immersion of the plastic substrate therein is from 1 to 3 minutes.