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ELECTROLESS PLATING ON NON-CONDUCTIVE MATERIALS

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5 Claims. (Cl. 117—47)

ABSTRACT OF THE DISCLOSURE

A process for pre-treating and electroless plating plastic articles on vinyl coated racks without re-racking the articles during the entire process, with the steps of racking on vinyl coated racks, etching the racked articles under special conditions, activating the articles, while still on the same racks, under special conditions in an activating bath while maintaining the articles free from sensitizing reducing agents, and immersing the articles, while still on the same rack, in a designated electroless plating bath.

This is a continuation-in-part application of my co-pending application entitled Plating on Non-Conductive Materials, filed June 15, 1964, Serial No. 375,359, now abandoned.

This invention relates to plating of metal on non-conductive articles, especially plastic articles, and more particularly relates to a novel process for pre-treating and electroplating non-conductive plastic elements.

The increasingly common usage of small, lightweight plastic articles for decorative and/or functional purposes, e.g., as knobs in automobiles, makes metallic plating of such objects desirable to provide them with a particular decorative finish. Extensive efforts have been applied in this regard heretofore, since the plastic is non-conductive, and it presents substantial problems of coverage when it is to be electroplated, especially under mass production conditions. In order to electroplate on plastic, the article surface must be made conductive. This is commonly done by applying an initial very thin metallic coating by vacuum metallizing, cathode sputtering, silver reduction, metal spraying, metal cladding, or chemical reduction. The chemical reduction method, more commonly known as electroless plating, is preferred. Currently, known methods of electroless plating such objects employ a series of specific steps which include "sensitizing" the plastic surface with a reducing agent in the form of a stannous salt bath, rinsing off the stannous solution, "activating" the surface in a noble metal salt solution, sometimes treating with a second reducing agent, and then electroless plating. The stannous salt sensitizer must be thoroughly rinsed from the surface before the activating dip in a noble metal salt bath since otherwise the activating bath will "go wild" due to the action of the stannous salt. This is especially troublesome with articles having deep dead end holes.

Throughout this disclosure, the terms "sensitizing," "activating," and "going wild" will be used. These terms are common in the art and have developed through extensive usage. "Sensitizing" refers to the treating of the plastic article surface in a reducing agent bath containing a stannous salt to cause adsorption of stannous ions on the surface. "Activating" normally refers to the treatment of the conditioned (deglaed) plastic surface in a noble metal salt bath. "Going wild" refers to the random, generally uncontrolled plating out of metal particles throughout the entire electroless plating bath used subsequent to activation, rather than the regular controlled plating of

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the metal only on the activated plastic surface, due to spontaneous decomposition.

These teachings of the prior art have been employed extensively by the applicant in his plating business, especially on articles supplied to the appliance and automotive industry. Repeated difficulties have been experienced, however, with these known methods because of inconsistent results during production, especially in regard to incomplete coverage of the metal over the article surface. This results in a high percentage of rejected parts and/or repeated expensive activation and plating treatment until the parts become covered with sufficient plate. Further, plating according to these methods is slow, and the total treating process requires an extended time.

Because prior art used a sensitizing solution prior to activation, the insulating vinyl plastisol coating on the plating racks also became metallized. This necessitated re-racking the parts on clean racks prior to electroplating in order to conserve plated metals and to produce proper plate distribution on the articles. The other alternative was to process the articles in baskets prior to racking before plating. If the articles were plated throughout on the totally metallized plating rack much metal was wasted, poor plate distribution resulted, and stripping of the racks after each plating cycle was necessary. All these extra operations were costly, time consuming, and damaging to the plating racks and the amount of rejected articles was also high.

Consequently, by extensive analysis and experimentation, the inventor herein has devised a new method of electroless plating that eliminates problems of prior methods and provides a dependable process.

It is therefore an object of this invention to provide novel methods of electroless plating by chemical reduction methods which enables assured complete coverage even under production conditions.

It is another object of this invention to provide novel methods of electroless plating of non-conductive articles, especially of plastic, which allows complete coverage of the articles, rapid treatment in a relatively short time, and effective plating of plastic articles, even those with deep dead end holes.

Still another object of this invention is to provide a method of applying metallic plating to a non-conductive article while utilizing substantially less of the noble metal solution.

Still another object of this invention is to provide a method of plating articles with sequential electroless plating and electroplating steps that achieve a more rapid and uniform coating, a plate with more stability against scuffing off, and more stability to adverse temperature conditions due to a hard, scuff-resistant coating.

It is still a further object of this invention to provide a novel quicker method of electroless plating of metal on non-conductive articles by eliminating steps previously thought essential, but actually found to be troublesome, while employing other characteristics found to improve the plating and to remove the necessity of the eliminated steps. This invention contains fewer steps with shorter processing times in the deglazing and electroless plating solutions.

Still the main object of this invention is to provide a simple, fast method of plating on plastics or non-conductors by three simple preplate steps, namely:

- (1) Chemical etch
- (2) Activate
- (3) Electroless (nickel) plate

This invention sets forth the composition and control of the above processing solutions whereby it is possible to plate plastic parts on conventional vinyl coated racks or fixtures throughout the entire above three preplate steps

and subsequent electroplating cycles using the same racking and handling procedures as used to electroplate the common commercial metals.

This invention has eliminated the following which were required or which occurred in the practice of the previous art:

(1) It has eliminated the plating out of the electroless deposit on the rack insulating coating with the further elimination of the following:

- (a) Elimination of wasteful deposition of electroless deposits on rack coating thus prolonging the life of the electroless plating bath;
- (b) It has eliminated the necessity of stripping the plating racks after each plating cycle;
- (c) It has eliminated wasteful deposition of electroless deposits on the rack coating where it is not desired;
- (d) It has eliminated the necessity of transferring articles from a preprocessing rack to a "clean" rack for electroplating;
- (e) It has eliminated "robbing" or "shielding" effects caused by plate build up on the insulating rack coating (by previous methods);
- (f) It has eliminated the need to preprocess the parts in bulk in baskets so as to prevent plating on the rack insulating coating.

(2) Because better electrical contact is made between the coated article and the rack contact, it has eliminated the need to turn the articles on the plating rack in order to make better contact.

(3) It has eliminated "misplating" in the electroplating baths because of better electrical contact to the article.

(4) It has eliminated the necessity of lowering the current in the starting electroplating bath without destroying the electrical contact. This is particularly true with the electroless copper plating processes.

Orthodox conventional methods employ as essential steps the pre-plating treatment of the plastic parts in two particular types of aqueous salt solution baths, the first being a reducing stannous salt bath, and the second being a relatively high concentration noble metal salt bath.

The stannous salt sensitizing bath prior to the novel metal salt solution dip usually causes rapid chemical reduction of the noble metal salt and soon renders this latter dip unusable due to carry over of the stannous salt. Prior art teaches the use of a rinse step between the two baths to lessen this. However, carry over always occurs, and is particularly great when processing parts with deep dead end holes.

NOVEL PROCESSES BRIEFLY STATED

Two novel electroless plating processes were developed to solve these problems with the use of a single one stage activating step with only one special salt bath and no so-called sensitizing, reducing, stannous salt bath. Briefly these electroless plating processes entail the following main steps:

(A) *Electroless nickel process*

- (1) Deglaze surface, chemical etch (1-5 minutes)
- (2) Activate (1/2-5 minutes)
- (3) Electroless nickel plate (4-7 minutes)

(B) *Electroless copper process*

- (1) Deglaze surface, chemical etch (1-5 minutes)
- (2) Activate (1/2-5 minutes)
- (3) Condition
- (4) Electroless copper plate (10-20 minutes).

Process A is preferred for the application of commercial electroplates finishes because of a shorter processing time and better electrical contact to the articles in the subsequent electroplating baths.

A.—THE ELECTROLESS NICKEL PROCESS

To employ the process the parts must of course be clean. The plastic parts are cleaned to remove mold release compounds, machining oils, or other soils. Cleaning may be performed by alkaline soak cleaning, solvent

cleaning with a compatible solvent, or cleaning in a sulfuric acid-chromic acid type cleaner which is formulated to clean rather than etch. After alkaline cleaning, it is necessary to water rinse and dip in a weak acid solution, then water rinse, and drain or dry parts prior to immersing in the chemical etching bath.

NOTE: In many cases, it is not necessary to clean the plastic parts prior to chemical etching.

The clean parts then are treated in general as follows:

(1) Deglaze surface of plastics by one of the following methods:

- (a) Tumble in a barrel with a fine abrasive.
- (b) Blast with fine abrasives (either wet or dry method). After the above mechanical methods of deglazing, the parts are cleaned and given a mild acid dip prior to immersion in the activating solution.
- (c) Chemical etch and thoroughly water rinse, (preferred).
- (2) Cold water rinse (with air agitation preferred).
- (3) Cold water rinse again.
- (4) "Activate" in a hot, specially formulated low concentration solution of a noble metal salt, 1/2-5 minutes.

NOTE: Do not conduct usual "sensitizing" step prior to this "activating" step.

(5) Cold rinse, preferably twice.

(6) Immediately apply an electroless coating of nickel to the rinsed parts in a specially formulated electroless nickel bath, until the parts are completely covered, 4-7 minutes.

(7) Cold or hot water rinse.

After step 7, if desired, the parts may subsequently be further plated at any time in a conventional copper or nickel electroplating bath (either barrel or rack plating), and then plated with the desired final plates such as nickel, brass, gold, chromium, etc.

EXPLANATION IN DETAIL

(Electroless nickel process)

Cleaning.

For the most part, cleaning is not required prior to deglazing of the plastic surface as the deglazing process is a good cleaning method in itself. However, in case oil, molding lubricants, or other heavy soils are present on the plastic parts it is necessary to clean according to conventional methods prior to deglazing. It is usually more important to have a clean surface before chemical deglazing than it is before mechanical methods of deglazing the surface. Most mild alkaline cleaners can be used for cleaning plastic parts, providing the alkaline content is not too strong and the temperature not over 180° F. Most mild alkaline cleaners used for metals are satisfactory.

If a solvent cleaner is used, it must be carefully selected so it does not soften or attack the plastic surface.

A modified sulfuric-chromic acid solution may be used to clean light soils from plastic parts. This type cleaner is advantageous to use prior to our chemical etching solution.

Other methods of cleaning may be used to remove soils. The type of cleaner used is related to the type of soil to be removed as well as to the type of plastic material.

Deglazing.

The deglazing operation is essential in order to obtain wetting in processing solutions, as well as adherent plates. In mechanical deglazing methods, very fine abrasives are used so that bright electrodeposits may be obtained. It is essential that surface gloss be removed, or otherwise, non-adherent plates will result. The chemical etching method is preferred because it reaches all areas, produces a more uniform deglazed surface, and produces smoother and more adherent subsequent plated coatings.

The formula range for the etching bath for plastics is:

Sulfuric acid (conc. 66° Bé. H ₂ SO ₄)	-----pct. by wt.	77.0-92.0
Chromic acid flakes (CrO ₃)	-----pct. by wt.	0.10-4.72
Water	-----pct. by wt.	21.5-6.0
Surface active agent (generally not required) (fluorocarbon compd)	-----pct. by wt.	0.01-0.2
Temperature	-----° F.	70-160
Optimum temperature	-----° F.	135
Baumé (deg.)	-----	57.0-63.0
Optimum Baumé (deg.)	-----	59.0-61.0
Time of immersion	-----min.	½-30
Optimum time	-----min.	2

Optimum bath for processing ABS plastics:

Sulfuric acid (conc. 66° Bé. H ₂ SO ₄)	-----pct. by wt.	85.56
Chromic acid flakes (CrO ₃)	-----pct. by wt.	1.55
Water	-----pct. by wt.	12.89
Baumé at 135° F.	-----	60.35
Temperature	-----° F.	135
Time of immersion	-----min.	2

The bath temperature is 135° F. optimum with a range of from room temperature to 160° F. The optimum concentration of the solution is maintained at 59°-61° Baumé (Sp. Gr. 1.69-1.74). The proper concentration is maintained with additions of sulfuric and chromic acids. Below the noted minimum value of specific gravity (too much water) the etch attacks plastics too slowly. Too high a temperature may form undesirable dark brown (carbonization) or chalky films, or unduly soften or etch the surface. The chromium must also be in the hexavalent state. The etch is inoperative when trivalent chromium builds up in the bath beyond about two ounces per gallon. Thus, the water content of the etch solution and the trivalent chromium content must also be controlled closely.

This etchant is quite universal in that it will satisfactorily etch plastics such as ABS (acrylonitrile-butadiene-styrene polymer), Nylon, Melamine, Lucite, Bakelite, San, and acetal resins, with slight appropriate adjustments. For acetal resins, much lower concentrations of the etch solution are used. The time in the etching bath varies from ½-15 minutes at 135° F. Beyond about fifteen minutes, the surface of the plastic may become powdery, darkened in color (light carbonization) or be otherwise damaged. These conditions lower the adhesive bond of subsequent plates. Below a minimum time in the etch solution, etching or roughening of the surface is insufficient and causes poor adhesion.

A chemically etched surface gives much better adhesion than a mechanically deglazed surface. Probably this is due to a greater area created by "micro-pits" in the surface, and due to better wetting and activation in the noble metal activating solution. The increased wetting of the surface is believed to be due to the oxidizing property of the chemical etch solution. The hydrogen atoms of some of the hydrocarbon molecules in the plastic are believed to be replaced by —OH groups. The attachment of the —OH groups to the molecules makes the plastic surface hydrophilic. It is the intimate wettability of the surface that provides the increased adhesion of plated coatings to the plastic. The rate of etch is affected by the degree of polymerization of the plastic, molding temperature, type of plastic, and type of pigments or other fillers which have been added to the plastic. In some instances the addition of a surface active agent such as a fluorocarbon compound is added to increase the wetting properties of the etch.

The parts are thoroughly water rinsed after the chemical etching step. In most cases, thorough water rinsing is all that is required, prior to "activation" in the novel, low concentration, noble metal salt solution. However, parts with deep dead end holes may require an alkaline rinsing operation in order to help in the removal of chromium compounds from the dead end holes. Parts which have

been mechanically deglazed by blasting or tumbling operations also need cleaning to remove loose abrasive materials or other soil. If alkaline cleaned, the bath used is a mild conventional alkaline cleaner which is subsequently rinsed off.

After the alkaline rinsing or cleaning treatment, the parts are rinsed and dipped in a mild acid dip to neutralize any alkali on the surface and to remove fine abrasives embedded in the surface. For this purpose, it is preferable to use a 10% by volume solution of 70% hydrofluoric acid. However, other acids can be used, such as sulfuric acid or hydrochloric acid, in similar concentrations. The immersion time in both the alkaline cleaner and acid dip is usually short, e.g. 10-30 seconds.

15 Activating in salt bath:

The parts are subsequently "activated" by immersing them directly in a special, low concentration, noble metal salt solution. The term noble metal salt includes mixtures of several salts of the noble metals especially palladium and gold, as well as the salt of a single preferred noble metal, palladium.

It is to be noted that no sensitizing step whatever is employed in this novel method, even though it was previously considered essential in the art. In so doing, applicant has found that he can successfully do this, and achieve even better results, if the activating bath is kept in a specific critical range in composition, pH, and temperature. In fact, far lower concentrations are possible than before. Since palladium salts are preferred, especially the chloride, the critical formulation is given in terms by weight of the very soluble palladium chloride. It will be obvious to any chemist that changing the noble metal cation or the salt anion will necessitate an appropriate change in parts by weight (obtained by the molecular weight ratios) to have an equivalent bath. Also, although the weight is given in the units of grams per gallon of solution, other units can be used.

The critical range of the aqueous activating solution is as follows:

Noble metal salt (palladium chloride)	-----grams/gal.	0.25-10.0
Optimum range	-----grams/gal.	1.0-2.0
Hydrochloric acid (22° Bé. HCl—36%)	-----ml./gal.	0.5-20.0
Optimum range	-----ml./gal.	1.0-4.0
Time of treatment	-----min.	½-5
Optimum time	-----min.	2-3
Temperature	-----° F.	70-212
Optimum temperature	-----° F.	125-150
pH	-----	1.0-4.8
Optimum pH	-----	1.5-2.5

The elevated temperature of the bath has been found to be important if the sensitizing bath is to be successfully eliminated. It should not drop below about 70° F., and preferably is increased up to a point near the maximum of about 212° F. Higher temperatures are generally not used because of distortion of plastic parts.

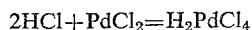
The single stage, one bath activation step is followed by an immediate thorough water rinse. This rinsing is done with cold water, preferably by two cascading cold rinses.

Activation in a hot noble metal salt solution effects proper "activation" by increasing the amount of noble metal salt adsorbed by the roughened (conditioned) surface of the plastic, thus complete subsequent electroless plating is assured.

The correct acidity of the noble metal salt activation solution is very important. If the hydrochloric acid concentration is too low, the noble metal salt is not completely soluble. When the acidity of the palladium salt dip is too high, the speed of the chemical reduction of the palladium is decreased. That is, the palladium is held more securely in the complexed form of H₂PdCl₄ and has

less tendency to revert to free Pd atoms. Also, poorer initiation and slower coverage will result in the electroless plating bath, since high acidity (on the plastic surface) suppresses plating in an electroless nickel bath. It has been found by experimentation that just enough acid to "complex" the palladium chloride to form H_2PdCl_4 (chloro-palladic acid) gives optimum activation results. However, it has been found to be advisable to add a slight amount of hydrochloric acid in excess of what is required to form the "complex" in order to keep the palladium more completely in solution. At too low a concentration of HCl, the palladium chloride can hydrolyze to $Pd(OH)_2$ and precipitate out.

The amount of ingredients to form the H_2PdCl_4 (complex) is 1 milliliter of concentrated hydrochloric acid (36%) for each 1 gram of palladium chloride as derived from the following equation:



As noted above, the optimum range of the palladium chloride concentration is kept at 1.0–2.0 grams per gallon and the hydrochloric acid (22° Bé.) (36%) in slight excess at 1.0–4.0 milliliters per gallon. The higher range of hydrochloric acid is preferred to keep the palladium salt well solubilized but maintaining pH no lower than 1.5. If the pH drops below 1.5 it is cautiously raised to a pH of 2.0 with potassium or sodium hydroxide (KOH or NaOH) in solution form. Care must be used that the pH doesn't go above 2.5 as beyond this range palladium hydroxide may precipitate out. If the pH becomes too high, above 2.5, it is lowered with the addition of sulfuric acid. Hydrochloric acid is not normally used to lower the pH because the chloride ions form a more tightly bound complex with the palladium ions which in turn results in poorer activation of the treated plastic surface. The above concentrations are not absolute fixed limits of concentration. Higher total concentrations can be used as long as the ratio of $PdCl_2$ and HCl exists to form the H_2PdCl_4 complex. However, the higher concentrations do not appreciably improve the activation and are more costly.

This ratio of noble metal salt to acid is markedly different from the 1–10 ratio necessary for the prior double salt bath sensitizing and activating processes.

Another single stage activation solution found to work very satisfactorily is a combination of palladium chloride and boric acid. A typical formulation is as follows:

Palladium chloride ($PdCl_2$)	grams/gal.	0.25–10.0
Optimum range	grams/gal.	1.0–2.0
Hydrochloric acid (HCl sp. gr. 1.191)	ml./gal.	0.5–20.0
Optimum range	ml./gal.	1.0–4.0
Boric acid (H_3BO_3)	grams/gal.	1.5–175
Optimum range	grams/gal.	
Time of treatment	min.	½–5
Optimum time	min.	2–3
Temperature	° F.	70–212
Optimum temperature	° F.	125–150
pH		1.0–4.8
Optimum pH		1.5–2.5

The boric acid in addition has been found beneficial to buffer any tendency for pH fluctuation. Boric acid buffers the solution mainly at a pH of 2.0 at which pH the bath functions best.

Because of drag-in of acid from the chemical etching solution, the pH of the activator solution tends to drop with usage. If the pH drops much below a pH of 1.5 the coverage in the subsequent electroless nickel bath is impaired. Boric acid tends to buffer the activator solution against a pH drop below a value of about 1.8–2.0. The boric acid also in no way affects the activation properties of the bath.

Another single stage activating solution found to work very satisfactorily is a combination of palladium chlo-

ride and gold chloride. A typical formulation is as follows:

Palladium chloride ($PdCl_2$)	grams/gal.	0.25–10.0
Optimum range	do.	1.0–2.0
Gold chloride ($AuCl_3$)	do.	1–7.5
Optimum range	ml./gal.	0.25–1.0
Hydrochloric acid (36% HCl)	ml./gal.	1.0–20.0
Optimum range	ml./gal.	1.0–4.0
Time of treatment	min.	½–5
Temperature	° F.	70–185
Optimum temperature	° F.	125–150
pH*		1.0–4.8
Optimum pH		1.5–2.5

*The pH is controlled by KOH or NaOH or sulfuric acid additions.

The amount of HCl must again be at least 1 milliliter per each gram of noble metal salt. Small amounts of other noble metal salts can be added also, providing they are water soluble. Palladium chloride is preferred due to its high water solubility. The palladium-gold salt mixture can be varied in ratio from that given in the specific example above, provided the gold salt does not become insoluble due to over-concentration, and the combined weight does not substantially exceed the combined maximum in the above example.

Rinsing after the activation treatment:

Thorough rinsing is advisable as by cascading water to prevent carry over of the activating solutions into the electroless plating bath.

Electroless nickel plating:

After activation and rinsing, the parts are electroless plated with nickel. The specially formulated, electroless nickel bath set forth below is important to electroless plate plastics for several reasons cited hereinafter.

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	grams/liter.	5–20
Optimum range	do.	22
Sodium hypophosphite (NaH_2PO_2)	do.	5–30
Optimum range	do.	18.75
Buffer (sodium salt of an organic acid)	do.	7.5–37.5
Optimum range	do.	15–30.0
Stabilizer	p.p.m.	1–50
pH adjusted with sulfuric acid to		3.5–5.0
Optimum pH		4.8–5.0
Old baths*		4.4–4.6
Temperature	° F.	140–185
Optimum temperature	° F.	145–155

*The pH is allowed to drop in older baths which have an increased sodium phosphite concentration. The lower pH tends to dissolve the insoluble sodium phosphite and thus tends to make an older bath more stable and decreases the tendency for roughness in the nickel deposit.

In place of nickel sulfate, other salts have been successfully used, such as nickel chloride, nickel formate, nickel citrate, nickel acetate, nickel sulfamate, and others. All of the above nickel salts were successfully used in concentrations similar to the nickel sulfate concentrations shown, but of course adjusted for molecular weight variations. (The sodium hypophosphite was always kept at the same range of concentration.) Baths with these different nickel salts worked satisfactorily, although the sulfate bath is preferred because in almost every case the nickel sulfate bath covered the activated plastic surface faster than baths using other nickel salts, and the nickel sulfate bath is also the least costly of the salts cited.

Instead of sulfuric acid to adjust the pH of the electroless plating bath, other acids such as acetic, formic, citric, hydrochloric, boric, glycolic, gluconic, and others have been used with equal success. The pH is usually raised with ammonium hydroxide.

It is important that the plating bath contain a stabilizing ingredient. Stabilizers which may be used to control the rate of plating include sodium thiosulfate, thiourea, diethyl thiourea, molybdic acid, and other molybdenum compounds, tungstic acid, hydrogen peroxide, am-

monium persulfate, cadmium salts, tin salts, and lead sulfide. These materials are used only at very low concentrations between 1-50 p.p.m. The concentration is very critical. Too much of the stabilizer material can stop all plating. The addition of a stabilizer is very beneficial and necessary for maintaining the useful life of the electroless bath when employing the novel method.

It is a natural tendency for most electroless plating baths to "go wild" and/or to plate rough. In the novel electroless nickel plating bath for plastics, these tendencies are greatly reduced by:

(1) The added stabilizer, which gives the bath long life,

(2) The purposeful use of a proper buffer in the bath with which to control pH. As the bath ages the pH is permitted to drop from the original pH of 5.0 to 4.4. A pH of 4.4-4.6 is then maintained until the bath is spent (use ammonium hydroxide to maintain pH at this point),

(3) At also the lower pH iron or nickel hydrates are not precipitated out,

(4) The absence of any exultants such as fluorides in the bath and normally added to increase the speed of plating, and

(5) The relatively low temperature of the bath (150° F. compared to the usual 180-212° F.).

All of the above factors in combination have been found to help prevent the natural tendency of the electroless nickel bath to "go wild," and if it does, to do so gradually. A very smooth initial plate is thus maintained. The bath also has a greater ability to withstand the drag-in of noble metals without "going wild." Another distinct advantage is the fact that the bath "goes wild" slowly so that, at any signs of "greyness" in the bath, the parts can be removed without any danger of roughness developing on the parts. No wetting agent is used in the bath either.

If articles are processed in baskets it is sometimes advantageous to use two (2) electroless plating baths, especially with articles containing deep dead end holes with resulting carry over of the activator solution. The first bath is usually small in volume and expendable (goes wild). Here a thin initial coating is applied before transferring to the second bath where the final total plate is applied without danger of roughness developing.

The parts remain in the first electroless nickel plating solution until the surfaces are completely covered. This need be only a flash coating 0.000001-0.000010 inch thick. This usually requires 20 seconds-1 minute. After a quick rinse, they are then transferred to a second electroless nickel plating bath for further build-up of the nickel coating, 0.00001-0.00006 inch.

Nickel plating examples:

EXAMPLE #1

The plastic articles are racked on conventional plastisol coated plating racks or processed in bulk in baskets.

Surfaces of the plastic articles pre-cleaned in a mild conventional alkaline cleaning solution to remove molding compounds, oils, and other soils according to conventional teachings.

Cleaned parts deglazed by chemical etching in a bath comprising:

Sulfuric acid (66° B _é . H ₂ SO ₄)	-----pct. by wt.	85.56
Chromic acid (CrO ₃)	-----pct. by wt.	1.55
Water	-----pct. by wt.	12.89
Temperature	-----° F.	135
Time of immersion	-----min.	2
Baumé (deg.)	-----	60.35

Parts rinsed in water very thoroughly. (If the parts contain deep dead end holes, they may be alkaline rinsed to remove entrapped acids, as explained in detail hereinabove.)

Parts immersed in hot noble metal salt solution:

Palladium chloride	-----grams/gal.	1.0
HCl (conc.-36%)	-----ml./gal.	2.0
pH	-----	2.0
Temperature	-----° F.	150
Time of immersion	-----min.	1-3

Parts cold water rinsed.

Parts electroless nickel plated in bath:

Nickel sulfate	-----grams/liter	22
Sodium hypophosphite	-----grams/liter	18.75
Sodium salt of an organic acid	-----grams/liter	22
Stabilizer (sodium thiosulfate)	-----p.p.m.	25
Temperature	-----° F.	150
Time of immersion	-----min.	3-9
pH adjusted with acetic or sulfuric acid to	-----	4.8-5.0

(Subsequent steps are optional as indicated below.)

Parts are cold water rinsed.

Parts are acid dipped 10-20 seconds in 10% by volume of concentrated sulfuric acid with 1-2% by volume of conc. HCl added, temperature 100-120° F.

Parts are water rinsed.

Parts are copper plated in a pyrophosphate copper bath at 140° F. for 1-2 minutes at 4-6 volts.

Parts are rinsed.

Parts are acid copper or nickel plated with subsequent final plates.

EXAMPLE #2

Parts pre-cleaned as above.

Parts deglazed by chemical etching in a bath comprising:

Sulfuric acid	-----pct. by wt.	86.90
Chromic acid	-----pct. by wt.	3.20
Water	-----pct. by wt.	9.90
Temperature	-----° F.	100
Time of immersion	-----min.	10
Baumé (deg.)	-----	61

Parts rinsed in water.

Parts immersed in a hot noble metal salt solution:

Gold chloride	-----grams/gal.	0.1
Palladium chloride	-----grams/gal.	0.9
HCl	-----ml./gal.	2.0
Temperature	-----° F.	150
Time of immersion	-----min.	1-3

Parts cold water or hot water rinsed (preferably 150° F.).

Parts transferred to electroless nickel plating bath:

Nickel sulfate	-----grams/liter	22
Sodium hypophosphite	-----grams/liter	22
Sodium salt of an organic acid (buffer)	-----grams/liter	18.75
Stabilizer (diethyl thiourea)	-----p.p.m.	15
Temperature	-----° F.	145
Time of immersion	-----min.	3-10
pH adjusted with sulfuric acid to	-----	4.8-5.0

EXAMPLE #3

The same as Example #1, except that the parts cold water rinsed after activation, stabilizer of ammonium persulfate, and pH adjusted with formic acid.

EXAMPLE #4

The same as Example #1, except that the parts deglazed by barrel tumbling or vapor blasting with a fine abrasive, stabilizer of mixture of molybdic acid, thiourea and sodium thiosulfate.

EXAMPLE #5

The same as Example #1, except that the activator solution contains boric acid as a buffer, as for example:

Palladium chloride (PdCl)	grams/gal.	1.0
Hydrochloric acid (HCl sp. gr. 1.191)	ml./gal.	2.0
Boric acid (H ₃ BO ₄)	grams/gal.	75.0
HCl	ml./gal.	2.0
Temperature	° F.	140-150
Time of immersion	min.	1-3

Electroless copper plating:

In some instances, it is desirable to electroless plate copper on the pretreated plastic parts instead of nickel. In my above identified co-pending application, I disclosed a copper electroless plating bath useful with this new process. Subsequent experimentation and operations have shown the importance of an added novel process step, after the activation treatment in the noble metal salt bath, and prior to plating in the electroless copper bath. This novel step in the process is a "conditioning" action, which, unlike orthodox methods, is conducted after noble metal activation, not prior to it. This conditioning has been found to accelerate reduction of the previously applied noble metal salt, resulting in an over-all process which, compared to conventional methods, has savings of 30% in operation time, far fewer process steps, lower labor costs, less costly processing solutions. It further extends the life of the electroless bath because of little or no carry-over of unreduced noble metal salt solutions, and has no adverse effect on the expensive noble metal salt solution (in contrast to prior methods).

Briefly, the steps of the novel process, when electroless copper plating are as follows:

- (1) Rack on conventional plastisol coated racks or process in bulk in baskets and preclean if necessary;
- (2) Deglaze the surface of the articles, preferably by chemical etching;
- (3) Water rinse;
- (4) Maintain the articles free of sensitizing reducing type agents;
- (5) Activate article surfaces by immersion in a noble metal salt solution;
- (6) Water rinse;
- (7) Condition article surfaces by rinsing in a cold dilute solution of sodium hypophosphite bath;
- (8) Optional water rinse;
- (9) Immerse articles in a special electroless copper plating bath.

In detail, the complete copper plating process is conducted according to the novel teachings set forth hereinabove, up to and including the thorough water rinse after the noble metal bath activation step.

After, and only after, the activation and subsequent rinse steps, the parts are conditioned by immersing them in an aqueous solution of the following:

Sodium hypophosphite (NaH ₂ PO ₃)	pct. by wt.	0.01-10
Optimum concentration (NaH ₂ PO ₃)	pct. by wt.	0.5-2
Temperature, ambient (i.e. 70-90° F.)		
Time (sec. as necessary)		10-180

The parts may then be water rinsed and passed to the special electroless copper plating bath, or may be passed directly to the latter bath. A special copper plating bath has been developed for use with the novel process to obtain a bath with a commercially useful long life and reasonably low initial cost. Such a bath is as follows:

Copper sulfate (CuSO ₄ ·5H ₂ O)	grams/liter	15-40
Rochelle salts (NaKC ₄ H ₄ O ₆ ·4H ₂ O)	grams/liter	40-140
Sodium hydroxide (NaOH)	grams/liter	8-39
Soda ash (Na ₂ CO ₃)	grams/liter	10-35
Tetra sodium-ethylene diamine tetra acetate	grams/liter	2-15
Formaldehyde (37%)	cc./liter	10-150
Stabilizer (of those mentioned previously)		
Time of immersion	p.p.m.	1-100
Temperature (Room i.e.)	° F.	70-90

A specific preferred composition is:

Copper sulfate (CuSO ₄ ·5H ₂ O)	grams/liter	22
Rochelle salts (NaKC ₄ H ₄ O ₆ ·4H ₂ O)	grams/liter	44
Sodium hydroxide (NaOH)	grams/liter	9
Soda ash (Na ₂ CO ₃)	grams/liter	15
Tetra sodium-ethylene diamine tetra acetate	grams/liter	5
Formaldehyde (37%)	cc./liter	12.24
Stabilizer (of those mentioned previously)		
Time of immersion	p.p.m.	50
Temperature	° F.	80

Copper plating example:

EXAMPLE #6

The surfaces of the plastic articles are precleaned in a mild sulfuric chromic acid solution according to conventional teachings.

Cleaned parts are deglazed by chemical etching in a bath comprising:

Sulfuric acid (66° Bé. H ₂ SO ₄)	pct. by wt.	86.2
Chromic acid (CrO ₃)	pct. by wt.	1.9
Water	pct. by wt.	11.9
Temperature	° F.	135
Time	min.	2
Baumé (deg.)		60

Parts rinsed in water.

Parts immersed in hot noble metal salt solution comprising:

Palladium chloride	grams/gal.	0.75
Gold chloride	grams/gal.	0.25
Hydrochloric acid (22° Bé.)	ml./gal.	1-2
Time	min.	2
Temperature	° F.	150

Parts rinsed in water.

Parts conditioned by immersion in an aqueous solution comprising:

Sodium hypophosphite	pct. by wt.	1
Temperature	° F.	75
Time	sec.	30

Parts transferred directly to electroless copper plating bath comprising:

Copper sulfate (CuSO ₄ ·5H ₂ O)	grams/liter	22
Rochelle salts (NaKC ₄ H ₄ O ₆ ·4H ₂ O)	grams/liter	44
Sodium hydroxide (NaOH)	grams/liter	9
Soda ash (Na ₂ CO ₃)	grams/liter	15
Tetra sodium-ethylene diamine tetra acetate	grams/liter	5
Formaldehyde (37%) (HCHO)	cc./liter	12.24
Stabilizer (of those mentioned previously)		
Time of immersion	p.p.m.	50
Temperature	° F.	80

EXAMPLE #7

The same as Example #6, except plastic articles are immersed in a hot noble metal salt solution comprising:

Palladium chloride -----	grams/gal.	0.75
Gold chloride -----	grams/gal.	.25
Boric acid -----	grams/gal.	75.0
pH -----		2.0
Time of immersion -----	min.	1/2-5
Temperature -----	° F.	80

By the combination of the special process steps employing the uniquely composed hot low concentration, single stage activating bath and the uniquely composed low temperature nickel electroless plating bath, or copper electroless plating bath, the sensitizing bath previously taught to be essential, and the problems found to be generated thereby, can be completely eliminated. This reduces the number and duration of processing steps, with a resulting savings in costs. The elimination of a sensitizing treatment also has been found to greatly extend the life of the noble metal activation solution, and even allows it to be operated at an elevated temperature. The elevated temperature condition helps to activate the plastic surface much more thoroughly, so that faster and more complete coverage results in the electroless plating baths. Further, because of the elimination of the sensitizing step and by the use of the single activating step only, there is no deposit formed on the insulating rack coating in either the electroless nickel or copper plating baths; thus all the inherent problems connected with this plating on the rack coating has been eliminated as described previously.

It has been found that the novel electroless nickel process plates a very smooth and adherent plate. In comparison to the electroless copper process, the time of immersion required in the electroless nickel bath is also shorter. The deposit is much harder, thus it is much more scuff resistant and it gives better electrical contact between rack clips and the coated part, thus electroless nickel deposits are more commonly used.

The process is applicable to most of the common plastics on the market today, although it works best on ABS articles. The chemical costs for all processing solutions are relatively low. Also, fewer solutions are required as compared to solutions presently used to plate on plastics. Other advantages are set forth in the introduction.

Extensive experimentation has been conducted on this novel method with its particular baths used in the special relationship stated. It has been found that the range of composition set forth are necessary for a proper process. The total ranges have been tried and proven.

The resulting process has many advantages as noted above and including the following:

- (1) Adherent deposits
- (2) Much shorter processing times as compared to previous methods
- (3) No reracking after electroless plating to make better electrical contact between metallized articles and rack contact
- (4) No plating on the plastisol coating on plating racks; the racks remained free and clear of any deposited metal(s)
- (5) A process which is very suited to automated plating equipment
- (6) A process with no highly corrodable copper layer (electroless nickel and electrodeposited nickel)
- (7) An improved process that shortens the etch (or conditioner) times from about 15-30 minutes to 1-4 minutes.
- (8) A metallizing process (electroless nickel) that allows conventional plating methods to be used in plating over the initial electroless coating without special electroplating techniques

(9) An improved process for plating ABS and other plastics that gives improved solution life and improved economics

(10) A process with no sensitizing solution prior to the activation step which shortens processing time and greatly increases the life of the activation solution as well as eliminating plating on the plastisol rack coating with all the attendant problems.

(11) A process and controls for process that makes it possible to plate ABS and other plastics with conventional equipment and with about the same number of steps as the plating of common commercial metals.

The number of examples could be added into the hundreds but would only be superfluous since all test runs were found to necessarily be according to the criteria set forth above. Minor deviations could conceivably be made in consistency with the criteria discussed. Thus, this invention is only to be limited by the attached claims.

It is realized that the disclosure herein actually concerns unique processes with respect to pre-plating treatment for either subsequent nickel or copper electroless plating, to the complete specific nickel plating process, to the complete specific copper plating process, and to particular copper plating bath and preconditioning. Conceivably these could be separated in more than one application, but since these are so interwoven, it is deemed best to incorporate them all in this same application.

I claim:

1. A process for pre-treating and electroless plating plastic articles on vinyl coated racks without re-racking the articles during the entire process, comprising the steps of:

(1) racking deglazed articles on vinyl coated plating racks;

(2) etching the racked articles in a sulfuric acid-chromic acid bath at the following conditions:

Chromic acid -----	0.10-4.72% by wt.
Sulfuric acid -----	77.0-92.0% by wt.
Water -----	6.0-21.5% by wt.
Temperature -----	70°-160° F.
Baumé -----	57°-63°
Time -----	1/2-30 minutes
Concentration of tri - valent chromium -----	less than 2 oz./gal.

(3) water rinsing the racked articles;

(4) maintaining the racked articles free of sensitizing reducing agent;

(5) immersing the etched articles while still on the same racks in an aqueous activating bath at the following conditions:

Soluble noble metal salt equivalent to 0.25-10.0 grams of palladium chloride per gallon of solution

Hydrochloric acid of 0.5-20 milliliters of such of a concentration of 36% HCl per gallon of solution

pH ----- 1.5-2.5

Temperature ----- 70°-212° F.

Time of immersion ----- 1/2-5 minutes

(6) water rinsing the racked articles;

(7) then immersing the activated articles, while still on the same racks, in one of the baths from a group consisting of (a) a chemical reduction electroless nickel plating bath, and (b) a chemical reduction electroless copper plating bath.

2. The process in claim 1 wherein, in step 5, the temperature is 125°-150° F., and the time is 2-3 minutes.

3. The process in claim 1 wherein said soluble noble metal salt in step 5 comprises:

Palladium chloride (PdCl₂) --- 0.25-10.0 grams/gal.

Gold chloride (AuCl₃) ----- 0.1-7.0 grams/gal.

4. A process for pre-treating and electroless plating plastic articles on vinyl coated racks without re-racking

the articles during the entire process, comprising the steps of:

- (1) racking deglazed articles on vinyl coated plating racks;
- (2) etching the racked articles in a sulfuric acid-chromic acid bath at the following conditions:

Chromic acid	0.10-4.72% by wt.	
Sulfuric acid	77.0-92.0% by wt.	
Water	6.0-21.5% by wt.	
Temperature	70°-160° F.	10
Baumé	57°-63°	
Time	½-30 minutes	
Concentration of tri - valent chromium	less than 2 oz./gal.	15
- (3) water rinsing the racked articles;
- (4) maintaining the racked articles free of sensitizing reducing agent;
- (5) immersing the etched articles while still on the same racks in an aqueous activating bath at the following conditions:

Soluble noble metal salt equivalent to 0.25-10.0 grams of palladium chloride per gallon of solution		20
Hydrochloric acid of 0.5-20 milliliters of such of a concentration of 36% HCl per gallon of solution		25
pH	1.5-2.5	
Temperature	70°-212° F.	30
Time of immersion	½-5 minutes	
- (6) water rinsing the racked articles;
- (7) then immersing the activated articles, while still on the same racks, in one of the baths from a group consisting of:
 - (a) an electroless nickel plating bath comprising:

NiSO ₄ ·6H ₂ O	5-40 grams/liter
NaH ₂ PO ₂	5-20 grams/liter
Buffer (organic salt of an organic acid)	7.5-30 grams/liter
Stabilizer	1-50 p.p.m.
pH	5.0-3.5
Time of treatment	4-7 minutes
At a temperature of between	140°-185° F.

where said stabilizer is one or more of the group consisting of sodium thiosulfate, thiourea, diethyl thiourea, molybdic acid, and other molybdenum compounds, tungstic acid, hydrogen peroxides ammonium persulfate, cadmium salts, and lead sulfide, and

(b) an electroless copper plating bath comprising:

- | | |
|---|-----------------------|
| Copper sulfate (CuSO ₄ ·5H ₂ O) | 15-40 grams/liter |
| Rochelle salts (NaKC ₄ H ₄ O ₆ ·4H ₂ O) | 40-140 grams liter |
| Sodium hydroxide (NaOH) | 8-39 grams/liter |
| Soda ash (Na ₂ CO ₃) | 10-35 grams/liter |
| Tetra sodium-ethylene diamine tetra acetate | 2-15 grams /liter |
| Formaldehyde (37%) (HCHO) | 10-150 cc./liter |
| Stabilizer | 1-100 p.p.m. |
| Time of immersion | 1-20 minutes |
| Temperature | Room, i.e. 70°-90° F. |

where said stabilizer is one or more of the group consisting of sodium thiosulfate, thiourea, diethyl thiourea, molybdic acid and other molybdenum compounds, tungstic acid, hydrogen peroxide, ammonium persulfate, cadmium salts, and lead sulfide.

5. The process in claim 4 wherein said soluble noble metal salt in step 5 comprises:

- | | |
|---|----------------------|
| Palladium chloride (PdCl ₂) | 0.25-10.0 grams/gal. |
| Gold chloride (AuCl ₃) | 0.1-7.5 grams/gal. |

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