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3,515,649

PRE-PLATING CONDITIONING PROCESS

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11 Claims

ABSTRACT OF THE DISCLOSURE

A special two stage chemical pre-etch and etch conditioning of plastic parts prior to plating such non-conductive parts, the pre-etch stage being in a special sulfuric acid-chromic acid bath containing a fluorocarbon surfactant, and the etch stage being in a different special sulfuric acid-chromic acid bath.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of copending applications Ser. No. 375,359 filed June 15, 1964 entitled Plating on Non-Conducting Materials, now abandoned, and Ser. No. 499,095 filed Oct. 20, 1965 entitled Plating on Non-Conducting Materials, now U.S. Pat. 3,370,974,

BACKGROUND OF THE INVENTION

This invention relates to a process of preparing plastic objects for plating, and more particularly refers to a special two stage acid bath treatment of plastic objects, followed by plating thereof.

In order for electroplate to have a degree of adhesion on plastic substrates, the surface must be roughened prior to the application of the electrodeposit. One of the first methods used to roughen the surface was to blast the surface by mechanical means, such as sand blasting, etc. In more recent years, the surface has been conditioned, deglazed, or roughened, by immersing the plastic parts in a strong acid solution, i.e., sulfuric and chromic acids. This chemical etching produces a good bond between the electroplate and the plastic substrate. In fact, the advent of this chemical etching procedure prior to plating has made possible large scale production plating of plastic parts. The use of the special acid etching solution of sulfuric and chromic acid is set forth in my copending patent applications, Ser. No. 375,359 and Ser. No. 499,095, noted above. This has found almost instant and tremendous commercial acceptance. Actually, this etching solution is now more commonly called a conditioning solution. A typical procedure used to condition, activate (nucleate), and plate consisted of the basic steps of etching in the special acid etch solution, triple rinsing in cold water, activating or nucleating in a noble metal salt solution, double water rinsing, electroless nickel plating, and applying conventional electrodeposits such as copper, nickel, etc. For many objects, the above procedure works very well to etch the surface for the application of a uniform and adherent plate. There are, however, certain molded plastic configurations which have surfaces containing fine serrations, pebbly surfaces, and other sharply recessed areas which do not always plate completely using this earlier method. As a result, there are "skip" areas in these intricate surfaces where plating does not occur. However, because designers like to use serrated designs and the like in molded parts, attempts were made to modify the etch solution to try to cause better subsequent plating. The addition of surfactant to the etching bath made some im-

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provement, but was not the complete answer since smaller skip areas still occurred in grooves, deep pockets, etc. Lowering the acid concentration of the sulfuric acid also tended to improve the thoroughness of etching and of plating, but this was not the answer either since it resulted in a non-uniform etch, as well as necessitating much longer etching times.

Because of these factors, it was determined that a different pre-plating treatment of the plastic objects must be conceived and developed.

SUMMARY OF THE INVENTION

The primary object of this invention is to provide a novel pre-plating treatment of plastic parts to be plated so that complete and uniform plating will dependably be obtained.

More specifically, it is an object of this invention to provide a novel two stage pre-etch plus etch conditioning of plastic parts prior to plating them, to obtain rapid, complete and uniform conditioning of the object surfaces, even if the configuration and surface character of the object are complex and detailed. The process prevents "skip" plating, yet without sacrificing thoroughness and rapidity of surface conditioning. The first stage employs a special bath which prepares the objects for the second stage. The second stage of the treatment employs this previously taught bath. The use of both stages in succession is important to the novel conditioning.

The pre-etch conditioning bath (first stage) basically is an aqueous sulfuric acid bath at a minimum Baumé of 26° Bé and a maximum Baumé of 37° Bé, containing chromic acid (as measured in weight of CrO₃) of 0-10 ounces per gallon of bath, and containing a fluorocarbon surfactant of 0.01 ounce per gallon of bath, minimum, up to saturation of the particular surfactant for the bath temperature used, and preferably about 0.04-0.12 ounce/gallon of bath.

The etch conditioning bath (second stage) basically is of the type set forth in the copending applications, i.e. sulfuric acid (Conc. 66° Bé H₂SO₄) of 77.0%-92.0% by weight, chromic acid (measured in weight of CrO₃) of 0.10%-4.72% by weight, and water of 21.5%-6.0% by weight, with or without any fluorocarbon surfactant in the amount of 0.01%-0.2% by weight, the Baumé range of such bath being in the range of 57.0°-63.0° Bé.

The novel method enables rapid production processing and plating. The objects are immersed in the first bath, removed, and then immersed directly in the second bath. The two baths complement each other in function to effect results not possible with either bath alone. Further, the solution clinging to the objects removed from the first bath does not cause detrimental action in the second bath, or subsequently, if the composition of the first bath is controlled with the specified limits.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preparation of the non-conductive plastic objects is basic outline form is as follows:

- (1) Pre-etch object surfaces.
- (2) Drain objects but do not rinse.
- (3) Etch objects surfaces.
- (4) Water rinse.
- (5) Activate object surfaces.
- (6) Water rinse.
- (7) Electroless plate object surfaces.
- (8) Electro plate objects.

(A) Pre-etch conditioning

The non-conductive plastic objects are immersed in an aqueous bath containing sufficient sulfuric acid to have a

Baumé reading in the range of 26° Bé. Above this range penetration by the bath into crevices is not dependable, even though the bath contains a surfactant explained below. Below this range, the bath will not dependably clean the object surfaces contacted. The bath preferably also contains chromic acid in the amount, in terms of CrO_3 added, up to a maximum of 10 ounces per gallon of bath. If this amount is exceeded, it becomes insoluble in the subsequent etch bath when small portions of the pre-etch bath cling to the objects transferred. The resulting precipitate is likely to cause roughness and/or skip plating. The presence of chromic acid renders the pre-etch bath much more effective but the bath will be operable through far less effective, if no chromic acid is added.

The bath also contains about 4–12 ounces per 100 gallons of bath of a fluorocarbon surfactant. This has been found to cooperate with the action of the controlled Baumé sulfuric acid to effect complete and uniform first stage conditioning of the surfaces. The particular fluorocarbon surfactant which may be employed is not critical. Satisfactory ones include, for example, those having a general formula of $\text{R}'\text{SO}_3\text{X}$, where R' represents a saturated fluorocarbon chain including straight, branched, and cyclic fluorocarbon chains of 4–18 carbon atoms, and X is a cation which may be hydrogen or may be a metallic ion from the groups including alkali metals, alkaline earth metals, rare earth metals, and heavy metals, such as NH_4 , Mg , Zn , Ca , Cr , Al , Ni , Cu , Ce , etc.

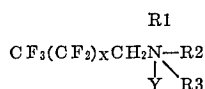
Typical of these are the following:

Perfluoro butyl sulfonic acid
Perfluoro isoamyl sulfonic acid
Perfluoro n-hexyl sulfonic acid
Perfluoro n-heptyl sulfonic acid
Perfluoro n-octyl sulfonic acid
Perfluoro n-decyl sulfonic acid
Perfluoro n-lauryl sulfonic acid
Perfluoro cyclohexane sulfonic acid
Perfluoro (4-methyl cyclohexane) sulfonic acid
Perfluoro (2-methyl cyclohexane) sulfonic acid
Perfluoro cyclohexane methyl alpha-sulfonic acid
Perfluoro dimethyl cyclohexane sulfonic acids
Perfluoro ethyl cyclohexane sulfonic acid
Perfluoro isopropyl cyclohexane sulfonic acid
Perfluoro diethyl cyclohexane sulfonic acids
Perfluoro di(cyclohexane) sulfonic acids
Perfluoro di-(cyclohexane) di-sulfonic acids
Perfluoro naphthalene di-sulfonic acids
Perfluoro naphthalene sulfonic acids

Such a surfactant may also be of the type represented by the general formula $\text{H}(\text{CF}_2\text{CF}_2)_x(\text{CH}_2)_y\text{ZM}$ where X is 2–15, Y is 1–3, M is a cation, and Z is a radical selected from the group consisting of $-\text{SO}_3-$ and $-\text{OSO}_3-$. These compounds may be added in the form of a free acid or a salt which may contain any of a wide variety of ions including Na , K , Li , NH_4 , Ca , St , Mg , ferric ion, trivalent chromium ion, aluminum ion, Zn , Ni , Cu , etc. Typical examples are

$\text{H}(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{SO}_3\text{H}$, $\text{H}(\text{CF}_2\text{CF}_2)_7\text{CH}_2\text{OSO}_3\text{Na}$,
and $\text{H}(\text{CF}_2\text{CF}_2)_5\text{C}_2\text{H}_4\text{SO}_3\text{Na}$.

A third general type of such a fluorocarbon surfactant is represented by the general formula



where $X=2-6$, R1 , R2 , and R3 are hydrogen or carbon atoms carrying hydrogen, the sum of the carbon atoms of R1 plus R2 plus R3 is not more than 6, and Y is an anion, preferably sulfate, methiosulfate, fluoride, or dichromate. Typical examples of such third groups are

$\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{NH}_3$, $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{NH}_3$
 $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{NH}_2$, $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{NH}_2$
 $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{NCH}_2\text{CH}_3$, $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{HC}_2\text{H}_5$

and others. Dozens of additional examples could be given but this would only unduly lengthen the disclosure.

The temperature range of the pre-etch treatment is about 100°–212° F., usually in the range of 100°–150° F., with the time of object immersion being about 1–10 minutes, depending on temperature, the higher the bath temperature the shorter the time required.

After the pre-etch conditioning the parts may be drained, as for a few seconds or so, but not rinsed, and are then placed directly in the etch conditioning bath. The time of draining is not significant, and may only be the time required to physically transfer the objects to the etch bath.

(B) Etch conditioning

The formula range for the etching bath for plastics is:

Sulfuric acid (conc. 66° Bé. H_2SO_4)—77.0%–92.0% by wt.

Chromic acid flakes (CrO_3)—0.10%–4.72% by wt.

Water—21.5%–6.0% by wt.

Surface active agent (generally not required) (fluorocarbon compound)—.01%–.2% by wt.

Temperature—70°–160° F.

Optimum temperature—135° F.

Baumé—57.0–63.0

Optimum Baumé—59.0–61.0

Time of immersion—½–30 minutes

Optimum time—2 minutes

Optimum bath:

Sulfuric acid (conc. 66° Bé. H_2SO_4)—85.56% by wt.

Chromic acid flakes (CrO_3)—1.55% by wt.

Water—12.89% by wt.

Baumé at 135° F.—60.35

Temperature—135° F.

Time of immersion—2 minutes

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 50°–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.

This regular etch solution is more efficiently maintained by the carry-in on objects from the pre-etch bath.

This etchant is quite universal in that it will satisfactorily etch plastics such as ABS (acrylonitrile-butadiene-styrene polymer), nylon, Melamine, Lucite, Bakelite, San, acetal resins, and others, 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.

(C) Post conditioning treatment

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. 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.

(D) 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. 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)—0.25–10.0 grams/gal.

Optimum range—1.0–2.0 grams/gal.

Hydrochloric acid (22° Bé. HCl—36%)—0.5–20.0 ml./gal.

Optimum range—1.0–4.0 ml./gal.

Time of treatment—½–3 minutes

Temperature—70°–212° F.

Optimum temperature—125°–150° F.

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 H_2PdCl_4 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 (chloropalladic 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 does not 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 acetic acid. A typical formulation is as follows:

Palladium chloride ($PdCl_2$)—0.25–10.0 grams/gal.

Optimum range—1.0–2.0 grams/gal.

Hydrochloric acid (HCl sp. gr. 1.191)—0.5–20.0 ml./gal.

Optimum range—1.0–4.0 ml./gal.

Acetic acid—1.5–175 grams/gal.

Optimum range—75 grams/gal.

Time of treatment—½–5 minutes

Optimum range—2–3 minutes

Temperature—70°–212° F.

Optimum temperature—125°–150° F.

pH—1.0–4.8

Optimum pH—1.5–2.5

The acetic acid in addition has been found beneficial to buffer any tendency for pH fluctuation. Acetic 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. Acetic acid tends to buffer the activator solution against a pH drop below a value of about 1.8–2.0. The acetic 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 chloride and gold chloride. A typical formulation is as follows:

Palladium chloride ($PdCl_2$)—0.25–10.0 grams/gal.

Optimum range—1.0–2.0 grams/gal.

Gold chloride ($AuCl_3$)—1–7.5 grams/gal.

Optimum range—0.25–1.0 ml./gal.

Hydrochloric acid (36% HCl)—1.0–20.0 ml./gal.

Optimum range—1.0–4.0 ml./gal.

Time of treatment—½–5 minutes

Temperature—70°–185° F.

Optimum temperature—125°–150° F.

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.

(E) 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 ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)—5–20 grams/liter

Optimum range—22 gram/liter

Sodium hypophosphite (NaH_2PO_2)—5–30 grams/liter

Optimum range—18.75 grams/liter

Buffer (sodium salt of an organic acid)—7.5–37.5 grams/liter

Optimum range—15–30.0 grams/liter

Stabilizer—1–50 p.p.m.

pH adjusted with sulfuric acid to—3.5–5.0

Optimum pH—4.8–5.0

Old baths—4.4–4.6

Temperature—140°–185° F.

Optimum temperature—145°–155° F.

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 satisfactory, 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 salt 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, ammonium perfluorate, 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 methods.

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–.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, .0001–.0006 inch.

Nickel plating examples:

EXAMPLE 1

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

The parts are pre-etch conditioned by immersing the objects for 2 minutes in a bath at 135° F. and of the following composition:

Sulfuric acid (66° Bé.)—30% by vol.

Water—70% by vol.

Baumé—35.5°

Chromic acid—4 ounces CrO_3 /gallon of bath

Perfluoro n-hexyl sulfonic acid—0.08 ounce/gallon of bath

The objects are then directly transferred to the etch conditioner bath with no rinse and with a draining time of about 10 seconds when transferring the objects from one bath to the other.

The etch conditioning bath is as follows:

Sulfuric acid (66° Bé. H_2SO_4)—85.56% by wt.

Chromic acid (CrO_3)—1.55% by wt.

Water—12.89% by wt.

Temperature—135° F.

Time of immersion—2 minutes

Baumé—60.35° Bé

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—1.0 grams/gallon

HCl (conc.—36%)—2.0 ml./gallon

pH—2.0

Temperature—150° F.

Time of immersion—1–3 minutes

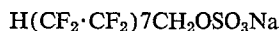
Parts cold water rinsed

Parts electroless nickel plated in bath:

Nickel sulfate—22 grams/liter
Sodium hypophosphite—18.75 grams/liter
Sodium salt of an organic acid—22 grams/liter
Stabilizer (sodium thiosulfate)—25 p.p.m.
Temperature—150° F.
Time of immersion—3–9 minutes
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

Objects are pre-etch conditioned by immersion for 8 minutes at 110° F. in an aqueous bath of sulfuric acid of 30° Bé, containing 8 ounces of CrO₃ per gallon of bath to form chromic acid, and 0.04 ounces of



surfactant per gallon of bath.

Objects directly transferred, with 3 seconds drainage time during transfer, and deglazed by chemical etching in a bath comprising:

Sulfuric acid—86.90% by wt.
Chromic acid—3.20% by wt.
Water—9.90% by wt.
Temperature—100° F.
Time of immersion—10 minutes
Baumé—61° Bé.
Parts rinsed in water

Objects immersed in a hot noble metal salt solution:

Gold chloride—0.1 gram/gallon
Palladium chloride—0.9 gram/gallon
HCl—2.0 ml./gallon
Temperature—150° F.
Time of immersion—1–3 minutes

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

Objects transferred to electroless nickel plating bath:

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

To electroless copper plate objects or parts, the process is basically of the following nature:

- (1) Pre-etch condition the objects;
- (2) Momentarily draining but not rinsing;
- (3) Etch condition the objects without rinsing after the pre-etch;
- (4) Water rinse;
- (5) Maintain the articles free of sensitizing reducing type agents;
- (6) Activate article surfaces by immersion in a noble metal salt solution;
- (7) Water rinse;
- (8) Treat article surfaces by rinsing in a cold dilute solution of sodium hypophosphite bath;
- (9) Optional water rinse;
- (10) 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.

- 5 After the activation and subsequent rinse steps, the parts are treated by immersing them in an aqueous solution of the following:

Sodium hypophosphite (NaH_2PO_2)—0.01%–10% by wt.
Optimum concentration (NaH_2PO_2)—0.5%–2% by wt.
10 Temperature—Ambient (i.e. 70°–90° F.)
Time—10–180 seconds

- 15 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. The copper plating bath is as follows:

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)—15–40 grams/liter
Rochelle salts ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)—40–140 grams/liter
20 Sodium hydroxide (NaOH)—8–39 grams/liter
Soda ash (Na_2CO_3)—10–35 grams/liter
Tetra sodium-ethylene diamine tetra acetate—2–15 grams/liter
Formaldehyde (37%)—10–150 cc./liter
25 Stabilizer (of those mentioned previously)—1–100 p.p.m.
Time of immersion—1–20 minutes
Temperature—(room i.e. 70°–90° F.)

A specific preferred composition is:

30 Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)—22 grams/liter
Rochelle salts ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)—44 grams/liter
Sodium hydroxide (NaOH)—9 grams/liter
Soda ash (Na_2CO_3)—15 grams/liter
35 Tetra sodium-ethylene diamine tetra acetate—5 grams/liter
Formaldehyde (37%)—12.24 cc./liter
Stabilizer (of those mentioned previously)—50 p.p.m.
Time of immersion—10 minutes
40 Temperature—80° F.

Copper plating example:

EXAMPLE 3

The surfaces of the plastic objects are pre-etch conditioned by immersion in an aqueous sulfuric acid bath of 30° Bé, and 125° F., for 5 minutes, such bath containing 2 ounces of CrO₃ per gallon of bath and 0.09 ounce of $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{NH}_3$ per gallon of bath.

The objects are removed from this bath, drained for 5 seconds, not rinsed, and then etch conditioned in a bath comprising:

50 Sulfuric acid (66° Bé. H_2SO_4)—86.2% by wt.
Chromic acid (CrO_3)—1.9% by wt.
Water—11.9% by wt.
55 Temperature—135° F.
Time—2 minutes
Baumé—60° Bé.

The objects are then rinsed in water. They are then immersed in hot noble metal salt solution comprising:

60 Palladium chloride—0.75 gram/gallon
Gold chloride—0.25 gram/gallon
Hydrochloric acid (22° Bé.)—1–2 ml./gallon
Time—2 minutes
65 Temperature—150° F.

They are then rinsed in water, and then treated by immersion in an aqueous solution comprising:

70 Sodium hypophosphite—1% by wt.
Temperature—75° F.
Time—30 seconds

The objects are next transferred directly to an electroless copper plating bath comprising:

75 Copper sulfate ($\text{CuS}_4 \cdot 5\text{H}_2\text{O}$)—22 grams/liter

Rochelle salts ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)—44 grams/liter
 Sodium hydroxide (NaOH)—9 grams/liter
 Soda ash (Na_2CO_3)—15 grams/liter
 Tetra sodium-ethylene diamine tetra
 acetate—5 grams/liter
 Formaldehyde (37%) (HCHO)—12.24 cc./liter
 Stabilizer (of those mentioned previously)—50 p.p.m.
 Time of immersion—15 minutes
 Temperature—80° F.

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.

Some advantages of the two stage conditioning are as follows:

Processing time is not critical;

Solution ingredients of the pre-etch bath are the same as the regular etching solution, thus carry-over of solution does not matter. In fact, it helps to maintain the etch solution;

Being of low viscosity, the pre-etch bath cleans and wets all surfaces regardless of configuration of parts;

No water rinsing is required after this pre-etch solution prior to immersion in the regular etch solution;

The pre-etch bath removes oils, molding release compounds, and other extraneous soils without substantially affecting the plastic surface;

The solubility of chromic acid is much greater in the lower concentration of sulfuric acid and does not offer dissolution problems in the original make-up;

The pre-etch bath treatment causes perfect and uniform etching in the subsequent etching solution;

There is no problem of absorption of water from the atmosphere;

There are less acid fumes involved due to lower acid content and to presence of the fluorocarbon wetting agent;

The pre-etch solution has excellent long life;

Maintenance and additions are low;

Due to the low surface tension, gas bubbles formed in crevices and on all surfaces are released so no gas pockets remain on surfaces to cause "skip" plating;

Solution is easier to agitate than the regular etch solution because of lower density;

The pre-etch solution is less corrosive to equipment, etc;

There is less drag-out in usage due to lower concentration of acids.

After this special conditioning and electroless plating, the articles are electroplated, according to known and conventional techniques, i.e. normally in a bath containing the metal to be plated in a dissolved (ionized) form, and using one or more anodes of the metal to be plated for constant metal ion supply. However, according to this novel concept, the articles are electroplated while still on the same racks, which are coated with polyvinyl chloride, or a polymerized fluorocarbon such as tetra fluoro ethylene or mono chloro, tri fluoro ethylene, or polypropylene.

As an example, any of the articles treated according to the previous examples and electroless plated as explained can be electroplated, as with copper as follows:

Immersion of the articles, on the same racks, in a bath at about 140° F. and at about 3 volts until the articles are covered, the bath containing 8.2 ounces/gallon of bath of copper pyrophosphate, 30.0 ounces/gallon of potassium pyrophosphate, 0.6 fluid ounce/gallon of ammonium hydroxide, 3.0 ounces/gallon of copper metal, using copper anodes and the articles as the cathodes.

The process is applicable to most of the common plastics on the market today. 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.

In addition to these advantages, added advantages exist for the total process, with these being recited in the above identified parent applications. One of the most important of these added advantages is the ability to employ the same racks throughout the entire process, from pre-etch through electroplating.

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.

I claim:

1. A process of preparing non-conductive plastic articles for electroless plating, comprising the steps of:

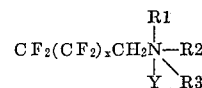
(a) pre-etch conditioning the articles by immersion in an aqueous, pre-etch bath containing sufficient sulfuric acid to cause said bath to have a Baumé in the range of 26°–37° Bé, containing chromic acid in the amount of 0–10 ounces of CrO_3 per gallon of bath, and containing a fluorocarbon surfactant of 0.01 ounce per gallon of bath up to saturation of the surfactant in the bath;

said fluorocarbon surfactant being from the group consisting of compounds having the general formulae:

(A) $\text{R}'\text{SO}_3\text{X}$, where R' represents a saturated fluorocarbon chain including straight branched, and cyclic fluorocarbon chains of 4–18 carbon atoms, and X is a cation;

(B) $\text{H}(\text{CF}_2\text{CF}_2)_x(\text{CH}_2)_y\text{ZM}$ where X is 2–15, Y is 1–3, M is a cation, and Z is a radical selected from the group consisting of $-\text{SO}_3-$ and $-\text{OSO}_3-$; and

(C)



where $\text{X}=2-6$, R1 , R2 , and R3 are hydrogen or carbon atoms carrying hydrogen, the sum of the carbon atoms of R1 plus R2 plus R3 is not more than 6, and Y is an anion;

(b) removing the objects from this pre-etch bath and transferring them without rinse and with a momentary draining to an etch conditioning bath; and

(c) etch conditioning the articles by immersion in an aqueous bath of 77.0%–92.0% by weight sulfuric acid, 0.10%–4.72% by weight CrO_3 in the form of chromic acid, and about 21.5%–6.0% by weight water.

2. The process in claim 1 wherein the articles are immersed in said pre-etch bath for about 1–10 minutes, and are subsequently immersed in said etch bath for about 1/2–30 minutes.

3. The process in claim 2 wherein said pre-etch bath has a temperature of about 100°–212° F., and said etch bath has a temperature of about 70°–160° F.

4. The process in claim 1 wherein said surfactant is at a concentration of about 0.04–0.12 ounce per gallon of bath.

5. The process in claim 1 wherein said pre-etch bath has a temperature of about 100°–150° F.

6. The process in claim 3 including the subsequent steps of:

(d) Water rinsing the articles;

(e) maintaining the articles free of sensitizing reducing agents; and

(f) immersing the articles in an activating solution at a temperature between 70°–212° F. and a pH between 1.0 and 4.8 and containing a noble metal salt in the range of 0.25–2.0 grams/gallon of solution and hydrochloric acid in a concentration of 0.05–10 ml. of 36% acid per gallon of solution.

7. The process in claim 3 including the steps of:
 (d) water rinsing the articles; and activating the articles by maintaining said articles free of a sensitizing reducing agent bath and immersing them in a solution containing a noble metal salt with a concentration equivalent to 0.25–10.0 grams of PdCl_2 /gallon of solution, and 0.5–20. ml of HCl of 36% concentration/gallon of solution, at an elevated temperature between 70°–212° F. and a bath pH of 1.0–4.8.
8. The process in claim 3 including the steps of:
 (d) water rinsing the articles;
 (e) immersing the plastic articles directly in an aqueous, actuating bath solution at a temperature between 70°–212° F. while maintaining the articles free of sensitizing reducing agent, said bath containing a soluble noble metal salt equivalent to 0.25–10.0 grams of palladium chloride per gallon of solution, and 0.5–20 milliliters of hydrochloric acid of a concentration of 36% HCl per gallon of solution;
 (f) rinsing the activated parts in water; and
 (g) electroless nickel plating the articles in a bath containing a soluble nickel salt equivalent in concentration to 5–40 grams/liter of nickel sulfate, 5–30 grams/liter of sodium hypophosphite, 1–50 p.p.m. of a plating bath stabilizer, and at a plating bath temperature between 140°–185° F.
9. The process in claim 8 wherein 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.

10. The process in claim 8 including the step of:
 (h) electroplating a metal on the electroless plated articles.
11. The process in claim 10 wherein the articles are kept on the same plating racks throughout the process.

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U.S. Cl. X.R.

106—1; 117—47, 138.8, 160, 212, 227; 156—2, 3, 14; 204—30, 20; 252—79.3

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,515,649 Dated June 2, 1970

Inventor(s) Ivan C. Hepfer

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

Column 3, line 1;

After "be'" and before the "period (.)" insert
--- to 37⁰ Be' ---.

Column 3, line 74;

"CF₃(CF)₃CH₃NH₂, CF₃(CF₂)₄CH₂NH₃" should read
--- CF₃(CF₂)₃CH₃NH₂; CF₃(CF₂)₄CH₂NH₃, ---.

Column 12, line 37;

"CF₂" should be --- CF₃ ---.

SIGNED AND
SEALED

OCT 27 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

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Commissioner of Patents