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3,632,704

METHOD FOR MODIFYING ELECTRICALLY NON-CONDUCTIVE SURFACES FOR ELECTROLESS PLATING

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U.S. Cl. 264—49 7 Claims

ABSTRACT OF THE DISCLOSURE

Electrically non-conductive organopolymeric surfaces are prepared for electroless plating by including in the organopolymeric surface an extractable filler and extracting the filler from the surface prior to plating. Improved adherency between the electrolessly deposited metal plate and the surface is effected.

The present invention relates to methods for preparing electrically non-conductive surfaces for electroless deposition of metallic films which films exhibit improved adhesion to the surfaces so prepared.

Electrically non-conductive materials such as plastics, hard rubber, wood, ceramics, glass and the like are not adaptable to be plated electrolytically. However, in the past few years extensive efforts have been put forth to find commercially acceptable methods for electrolytically plating objects formed from these materials. These efforts have been undertaken in order to utilize inexpensive materials, such as plastics, in the place of metal. Also, materials such as plastic are more easily worked and can be formed easily into extremely diverse shapes. Metallized articles of the above nature are finding particular use in the automobile industry where parts of the interior and exterior trim can be easily and inexpensively formed in extremely intricate designs and then coated with a metallic coating so as to simulate the appearance of metal articles.

One of the presently known processes for metallizing articles formed from electrically non-conductive materials is the electroless plating process. This process involves the catalytically induced reduction of a metal salt in a plating bath to form a metal plate. The basic steps of the process include the activation of the surface to be plated by depositing on or including in the surface thereof catalytic metal particles, such as palladium, followed by immersing the activated surface in a plating bath containing the metal to be plated in a reducible ionic form and a reducing agent. The metal plate so formed may be utilized as is, increased in thickness by further electroless plating or used as an electroconductive metallic film in standard electrolytic deposition techniques to effect further metallic coating with the same or different metals. While electroless plating is a well known process, the use of this process has been hampered by the difficulty in obtaining good adhesion of the plate to the plated surface. Specifically, it has been extremely difficult to sufficiently adhere electrolessly deposited metal plates to electrically non-conductive surfaces, such as plastic, so as to allow the use of these items under a thermal cycle ranging from —20° F. to about 200° F. Due to the vast differences in the thermal expansion ratios of the metal and the base material, the deposited metal film tends to delaminate when subjected to an extended thermal cycle if not sufficiently adhered to the base. The problem of adhesion is compounded by the various types of base materials which can be used, and by the size and intricacy of design into which these materials can be formed.

The prior art has suggested abrading the surface of the base in order to provide mechanical adhesion sites for the metal film as a means for improving adhesion of the film through an extended thermal cycle. However, the use of mechanical treatments, such as abrading, on intricately designed complex objects are essentially non-effective due to the nature of the item itself in that the intricate designs do not allow for easy, uniform and complete abrasion treatment. Chemical etching has also been utilized. However, this procedure is not sufficiently controllable so as to provide a plating surface having the uniform distribution of adhesion sites necessary to effect good overall adhesion of the electrolessly deposited metal plate. In the field of plastics, the foregoing methods are generally ineffective on most types of plastics. The problem of adhesion of the electrolessly deposited film to plastic has dictated the use of certain plastics, such as ABS (acrylonitrile-butadiene-styrene). These materials are chemically corroded to apparently form a porous surface therein so as to improve the adhesion of the metal plate to the surface. Other plastics, which might be more desirable for a specific use because of inherent physical and chemical properties, or cost, cannot be treated in the same manner to obtain the same results and, therefore, these plastics are not considered as base materials for electroless plating. Also, it is extremely difficult to treat bases formed from materials such as wood and ceramics to provide sufficient adhesion sites for the electrolessly deposited metal film.

The method of the present invention provides means of preparing electrically non-conductive surfaces for electroless plating so as to improve the adhesion of the electrolessly deposited plate to the surface and which method is adaptable for use on plastics generally and on intricately shaped articles.

In accordance with the present invention, electrically non-conductive surfaces are prepared for electroless plating by including, at least at the surface thereof, an extractable filler and extracting the filler from the surface prior to plating. By using controlled amounts of filler and controlled filler particle size, the surface to be plated can be provided with numerous microporous openings therein of controlled size and distribution. The microporous openings act as adhesive sites for the electroless plate in that, theoretically, the metal fills the pores as the plate is formed and thus the plate becomes mechanically anchored to the surface being plated. Due to the large number of mechanical adhesion points made available by the method of the present invention, electroless plates characterized by improved surface adherency can be formed even on intricately shaped objects.

In one form of the invention, moldable base materials such as plastics, hard rubber and the like, e.g., an organopolymeric material, are compounded to include an extractable filler material which is immiscible in the base material. Following the formation of the base material into a shaped article, the surface of the article is treated so as to effect the removal of filler material from the surface of the base. A metallic film is then deposited over the so treated base which film is characterized by improved adhesion to the base due to the increased number of mechanical adhesion points available on the surface of the base.

In another form of the present invention, the surface of a previously shaped article is coated with a plastic, hard rubber, or like material (organopolymeric material) which material has been compounded to include an extractable filler. Following solidification of the coating, the filler is extracted and a metallic film is electrolessly deposited on the coated surface which film is similarly characterized by improved adhesion to the plated surface.

Plastics having some elasticity are advantageously used to form the coatings as the elasticity can provide a buffer for the stresses encountered during expansion of the plate during the thermal cycle. Also, plastics having the same thermal expansion ratio as the metal plate can be advantageously used. The foregoing method is adaptable to provide bases for electroless plating prepared from plastics in general and also from other materials such as wood, glass, and ceramics which bases have sufficient mechanical adhesion sites to provide for good adhesion of the electrolessly deposited plate to the base.

In a further form of the present invention, the surface of a shaped article prepared from materials such as plastics, wood, glass and ceramics is coated with a film-forming polymer dissolved in a solvent/non-solvent mixture which polymer is at the point of incipient precipitation, and a porous film of polymer is formed on the base by causing substantially complete precipitation of the polymer within the solution by modifying the solvent/non-solvent ratio.

Each of the foregoing methods of accomplishing the present invention are particularly adapted to be used in effecting the electroless plating of intricately shaped articles, and in particular, articles formed of organopolymeric materials.

The extractable filler is preferably included within an organopolymeric material, e.g., a plastic or rubber material. The organopolymeric material can be utilized to form shaped articles for plating or it can be used as a coating on a preformed base. In either case, the finally prepared article for electroless plating has an organopolymeric surface including an extractable filler.

The organopolymeric material can be any one of the many known natural or synthetic, plastic and rubber materials. These materials may be of either the thermoplastic or thermosetting type. The natural organopolymeric materials can be illustrated by natural rubber, hard waxes and resinous gums, such as gum arabic and gutta-percha. The synthetic organopolymeric materials can be illustrated by the many known moldable and extrudable thermoplastic hydrocarbon and substituted hydrocarbon polymers illustrated by polyethylene, polypropylene, polybutene, polyvinyl chloride, polystyrene, polyisoprene, polychloroprene, polybutadiene, styrene/butadiene copolymers thereof with other ethylenically unsaturated monomers. Other forms of synthetic organopolymeric materials can be illustrated by polyester polymers such as the reaction product of ethylene glycol and maleic anhydride, and phthalic anhydride and propylene glycol; acrylates such as polymers and copolymers of ethyl acrylate; methacrylates such as polymers and copolymers of methyl methacrylate; epoxy such as the reaction product terephthalic acid and epichlorohydrin; alkyl polymers such as the reaction product of phthalic anhydride with glycerin or linseed oil; urea and melamineformaldehyde polymers; and polyurethane polymers illustrated by the reaction product of polyoxyalkylene glycols with toluene diisocyanate. The polymers illustrated hereinbefore are but a small part of the large number of organopolymeric materials which are adapted for use in the present invention. These materials are given as illustrative of the many known organopolymeric materials which can be used in the present invention and applicant is intended not to be limited thereto.

The foregoing list of organopolymeric materials can be used to form molded or shaped bases having the extractable filler included therein or they can be used to form a base which can be coated with an organopolymeric material containing the extractable filler. The selection of any one material for the formation of a shaped article for electroless plating is dependent on the final characteristics desired in the resultant product.

Many of the foregoing organopolymeric materials can also be utilized as coatings in accordance with the present invention. In general, the organopolymeric material selected for the coating should provide good adhesion to the coated substrate along with suitable physical and chemical properties necessary for the intended use of the final product. The coatings can be applied from solvent solution using such solvent soluble polymers as the acrylates, or by the use of powder coatings or fluidized plastic coating techniques using such polymers as polyvinyl chloride. The coatings can be used with equal effectiveness on non-moldable bases such as wood, stone, glass and preformed ceramics, as well as on moldable bases formed from organopolymeric materials. The coatings can also be used on metallic objects if it is desired to use a metal core for increased structural strength. As is obvious, any of the known methods of applying coatings to base materials along with the attendant coating compositions are intended to be included within the scope of the present invention.

The extractable filler is any material which can be incorporated in the material used to form the article desired to be electrolessly plated and which filler is immiscible in said material, and further, which filler does not degrade or breakdown under the conditions of article formation. The filler can be of an organic or inorganic nature and can be extractable by means of dissolution, volatilization, and, in the case of certain metal salts, by chemical reduction. Preferably, the filler is of such a nature as to be easily included within the base material and is such as to afford easy extraction from the base without extensive chemical treatments, which treatments might damage the base article. Also the filler is preferably in such a form as to provide microporous openings within the surface of the base of a size ranging from about 0.1 to about 1.0 microns.

Illustrative of inorganic fillers and their extracting agents (given in parenthesis) are: sodium, calcium, magnesium-carbonates (acids such as HCl, H_2SO_4, HNO_3), $Al_2O_3 \cdot xH_2O$, (acids such as H_2SO_4), ZnO_2 (acids such as HCl, H_2SO_4, HNO_3), sodium silicates (water), glass in fiber form (HF), antimony hydroxide, and the like. $CaCO_3$ is a preferred inorganic filler.

Illustrative of organic fillers and their extracting agents (given in parenthesis) are: starch (enzyme solution), dimethyl sulfoxide (water), polybutadiene(acetone), polymethyl methacrylate(ketones such as methyl ethyl ketone, esters such as ethyl acetate, aromatic hydrocarbons such as toluene), polyvinyl acetate(alcohols such as ethanol, ketones such as methyl ethyl ketone, esters such as ethyl acetate, aromatic hydrocarbons such as toluene), polyvinyl alcohol (water), copolymers of vinyl chloride/vinyl acetate (ketones such as methyl ethyl ketone), mixtures of polyvinyl alcohol and dimethyl sulfoxide (water), copolymers of vinyl formal and vinyl butyral (esters such as ethyl acetate, ketones such as methyl ethyl ketone and cyclohexanone, alcohols such as butanol, and ethers such as butyl Cellosolve), mixtures of polymethyl methacrylate and polybutadiene (esters such as ethyl acetate, ketones such as methyl ethyl ketone, aromatic hydrocarbons such as toluene), mixture of polymethyl methacrylate and polyethyl acrylate (esters such as ethyl acrylate, ketones such as methyl ethyl ketone), and the like.

Illustrative of agents which can be extracted by volatilization are camphor and iodine.

Illustrative of metal salts which can be reduced in situ to provide metallic particles which can act as catalytic agents for the electroless plating reaction are: nickel carbonate, nickel oxide, iron oxide, and carbonates and oxides of any metals which are catalytic for the plating reaction such as palladium oxide. The surface of the base is treated with an acid to leach out a portion of the metal salt leaving, in the pore, the remaining portion of the salt. Reduction of the remaining portion of the salt can be effected with a strong reducing agent such as concentrated sodium hypophosphite or a borohydride such as methyl, ethyl borane.

Similarly, pores having therein tiny particles of metal such as nickel, iron, copper, and the like which can act as catalytic sites for the electroless plating reaction can be formed by incorporating the powdered metal into the base and partially extracting the same with an acid. Also, metal particles such as nickel, zinc, iron, copper, aluminum and the like can be incorporated in the base and completely leached out of the base with an acid to form the desired pores and the surface then activated utilizing the standard $SnCl_2/PdCl_2$ activation treatment. This activation step can be eliminated with regard to the catalytic metals, e.g., nickel, iron, and copper, by utilizing, in the leaching solution, a complexing agent for the metal such as ammonia and amine complexing agents. A complex of the metal remains within the pores and can be reduced to free metal therein by immersing the base in a strong reducing agent, such as sodium hypophosphite or a borohydride such as methyl, ethyl borane to provide the catalytic sites necessary for electroless plating.

The foregoing are given as illustrative of the numerous fillers which can be utilized in the process of the present invention, and applicant is intended in no way to be limited thereto.

In extracting fillers from organopolymeric materials, it is desirable to accomplish the extraction in the presence of a solvent or swelling agent for the polymer material. It has been found desirable to swell the organopolymeric material used as the base so as to allow the solvent or extracting agent for the filler to enter into and extract the filler from the base. The swelling solvent may be the agent used for extracting the filler material or the swelling solvent can be in admixture with the extracting agent. Less desirably, the polymeric material can be inserted first into a solvent bath therefore and then into a bath of extracting agent. Illustrative of mixed solvent systems for a polymeric surface such as polyvinyl chloride having a filler such as calcium carbonate are methyl ethyl ketone for the polyvinyl chloride and hydrochloric acid for the carbonate filler.

Slight surface roughening might also be necessary in order to expose the included filler for extraction and this can be accomplished by sand blasting, abrading, etc., as it well known to those skilled in the art.

Prior to effecting the electroless plating, it is necessary to thoroughly clean and degrease the substrate in that contaminants thereon can detrimentally affect the adhesion characteristics of the plated metal film. The method of cleaning employed will depend on the nature of the substrate. In the case of plastics, spray washing with a detergent followed by a clear water rinse is effective. If desired, mechanical cleaning, such as sand blasting, can also be used though this is not necessary.

The cleaning operation can be a separate and distinct step in the preparation of the substrate for plating or it can be part of the filler extraction operation. If the filler is an organic solvent-soluble resinous material which is immiscible with the base material, washing in an organic solvent can be sufficient to effect the degreasing and the extraction. In using a volatilizable filler, the use of elevated temperature to effect removal of the filler will also effect removal of surface moisture and other contaminants subject to volatilization.

Following the cleaning step, the base is sensitized, e.g., depositing catalytic metal particles on the surface of the base. Sensitization by chemical reduction generally involves two steps. The first requires the formation of a film or deposits of stannous chloride on the porous surface and within the pores. This is accomplished by the immersion of the base in an acidic stannous chloride solution generally containing about 30 grams of stannous chloride and 10 milliliters of concentrated hydrochloric acid per liter of water. The immersion time need be only a few seconds and slight agitation is recommended to insure complete contact especially in the case of intricately shaped articles. The article is then water washed to remove excess stannous chloride so as to prevent its transfer to and the contamination of the second bath. Two washings of from about 20 to about 30 seconds have been found sufficient to remove any excess stannous chloride without removing the desired surface deposit. In more intricate articles, subsequent washings can be employed if desired to insure sufficient removal of the stannous chloride. The washed article having deposits of stannous chloride thereon is then immersed in a palladium chloride bath. The stannous ions are oxidized to stannic ions and the palladium ions are reduced to free metal. Following this treatment, the base is again washed as before to remove all the stannic ions and any remaining palladium chloride so as not to contaminate the electroless plating bath.

The surface of the base can also be sensitized or pretreated by the inclusion of metal particles in the base material prior to formation or applied to the surface subsequent to formation. Catalytic quantities of electro-conductive material such as nickel, aluminum, iron, cobalt, chromium, and the like in a finely divided state can be compounded into the base material prior to molding and exposed by mechanical abrading. The particles can also be applied by dusting, utilizing, dipping, air blast or other techniques adapted for such application. In the dusting operation, a moistened or sticky surface can facilitate application. This can be accomplished by the application of an adhesive to the surface or by immersing a plastic article in a solvent therefor. Further details of this can be obtained in U.S. Pat. 2,690,401.

Sensitization can also be accomplished by using as the filler a reducible metal salt and reducing the salt situ to form pores in the surface of the base having thereon particles of catalytic metal as discussed hereinbefore. Also, and after filler extraction, the base can be immersed in an electroless nickel plating solution to wet the interior of the pores. The so treated base can then be inserted in a concentrated hypophosphite solution to reduce the nickel ion to free metal within the pores, which metal can then act as the catalytic metal for the electroless plating reaction.

Following the pretreatment of the base, the base is immersed in the electroless plating solution which can be acidic or alkaline. In general, the plating solution is a bath containing the metal to be plated in ion form, a reducing agent and in an acidic solution, a buffer. In an alkaline solution, an agent such as ammonium hydroxide or chloride is used to maintain the pH on the alkaline side. Nickel is generally used as the plating metal in that it provides a good metallic film and can be electrolytically plated following the electroless plating. Other metals such as cobalt, chromium, copper, gold, iron, silver, vanadium and, with proper solutions, alloys such as brass and cobalt-nickel alloys can also be used. For use with the nickel, a reducing agent such as sodium hypophosphite has been found to be effective. Other reducing agents and complexing systems as shown in the art are also useable. The buffering material for the acid solution can be any material which will provide the buffering effect without unduly affecting the plating bath. Mention can be made of soluble salts of short chain aliphatic monocarboxylic acids having an ionization constant (pKa) greater than about 4.5 such as acetic acid, butyric acid, propionic acid and the like. The ratio of reactants in the bath so as to provide a desired ratio of ions therein can be determined for each system so as to provide effective plating. The immersion of the base in the plating bath is for a time sufficient to effect the plating of the desired film on the base. Temperature, agitation and other factors which may affect the plating can be determined in each situation.

Following the application of the initial electrolessly deposited metal film, the base can be subjected to further electroless metal deposition, especially of other metals, or plated electrolytically with such metals as copper, nickel, zinc or chromium. The amount of plating and the type

depends on the final use of the product and the thickness of metal desired on the base. In some instances, it may be required to deposit large amounts of metal on the base to insure that the pores are completely filled and the overall surface of the metal film is flat.

The invention will be illustrated in the examples which follows:

EXAMPLE 1

Plaques for electroless plating are prepared using a medium molecular weight polyvinyl chloride homopolymer (R.V. 2.11) compounded with:

TABLE I

Sample	Filler	Amount in parts/hundred of PVC
1	Polymethyl methacrylate/polyethyl acrylate mixture.	10
	Cis-polybutadiene	10
2	Polymethyl methacrylate/polyethyl acrylate mixture.	10
	Cis-polybutadiene	10
	Calcium carbonate	10
3	ABS (Blendex 401)	20
4	ABS (Blendex 101)	20
	Calcium carbonate	10
5	Cis-polybutadiene	20
	Calcium carbonate	10
	Cis-polybutadiene	20
6	Phenolic antioxidant	
	Calcium carbonate	10

The plaques are pretreated as follows:

TABLE II.—PRETREATMENT

	Temp., ° C.	Time/min.	Cold water rinses
1 Acetone	RT	2	2
2 HNO_3 1:1	65	10	2
3 Hot water	65	5	1
4 Sensitizing, $SnCl_2$	RT	1	2
5 Activation, $PdCl_2$	RT	½	2

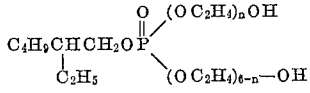
Following pretreatment, the plaques are immersed in an electroless plating solution maintained at 60° C. and at a pH of 5.7 for 10 minutes, the solution having the following composition:

TABLE III

Solution A

	Amount in grams/liter
Nickel fluoborate	42
Sodium hypophosphite	100
Boric acid	20
Acetic acid	16
Glycolic acid	14
Ammonium fluoride	4
Thiourea	p.p.m. 0.3
Wetting agent [1]	0.4

[1] A nonionic surfactant having the formula:



sold under the name of VICTAWET-12

Good adherent nickel plates are obtained on each sample plaque of Table I.

EXAMPLE 2

Plaques of the Sample 3 type of Table I are pretreated under the following conditions:

TABLE IV.—PRETREATMENT

	Temp., ° C.	Time/min.	Cold water rinses
1 Acetone	RT	2	2
2 HNO_3 1:1	65	10	2
3 Electroless nickel Solution A	60	½	1
4 40% Sodium hypophosphite solution	65	2	1

Following pretreatment, the plaques are immersed in electroless nickel plating Solution A for 10 minutes, which solution is maintained at 60° C. Good nickel plates are obtained.

EXAMPLE 3

Plaques are prepared for electroless nickel plating as follows:

TABLE V.—PLAQUES

Sample		Amount by weight, percent
1	PVC (R.V. 2.11)	60
	Cis-polybutadiene	20
	Calcium carbonate	20
2	PVC (R.V. 2.11)	80
	Polyvinyl butyral	20
3	Graft copolymer of polyvinyl chloride and polybutadiene	90 / 10

TABLE VI.—PRETREATMENT AND PLATING CYCLE

	Temp., ° C.	Time/min.	Cold water rinses
1 Alkaline cleaner	60	5	2
2 Methyl ethyl ketone	RT	2	2
3 HNO_3 2:1	60	15	2
4 H_2SO_4 15%	60	10	2
5 HCl 15%	RT	10	2
6 Dilute $SnCl_2$	60	3	1
7 Sensitization, $SnCl_2$	RT	1	2
8 Activation, $PdCl_2$	RT	½	2
9 Electroless nickel plating Solution A	60	10	2

Good plates are obtained on all plaques. Sample plaque No. 2 was subjected to a thermocycle heat stability and adhesion test which encompasses alternate heating and cooling of the plated sample, the upper temperature being 210° F. and the lower temperature being −50° F. Complete particulars on this test can be found at page 540 of the Trans. J. Plastics Inst., June 1967, (Britain). After four thermocycles, no peeling or blistering was observed.

EXAMPLE 4

Plaques are prepared for electroless plating and plated as follows:

TABLE VII.—PLAQUES

Sample		Amount by weight
1	PVC (R.V. 2.11)	100
	ABS (Blendex 401)	100
	PVC (R.V. 2.11)	200
2	ABS (Blendex 401)	40
	Aluminum oxide	20
3	PVC (R.V. 2.11)	100
	Polyvinyl formal	20
4	PVC (R.V. 2.11)	100
	Polyvinyl formal	30
5	PVC (R.V. 2.11)	100
	Polyvinyl formal	40
6	PVC (R.V. 2.11)	100
	Calcium carbonate	20

TABLE VIII.—PRETREATMENT AND PLATING CYCLE

	Temp., ° C.	Time/min.	Cold water rinses
1 Cleaner-mild non-silicated alkaline neutralization 15% H_2SO_4.	60	5	2
2 Methyl ethyl ketone	RT	2	2
3 Etch, CrO_3—H_2SO_4	60	5	2
4 Etch, CrO_3—H_2SO_4—H_3PO_4	RT	2	2
5 Sensitization, $SnCl_2$	RT	1	2
6 Activation, $PdCl_2$	RT	½	2
7 Electroless nickel Solution A	60	10	2

Good plates are obtained on all plaques.

EXAMPLE 5

Polyvinyl chloride plaques are knife coated with one of the following coating compositions and plated as follows:

TABLE IX

	Carrier	Filler	Amount
1	PVC/PVA copolymer (VYHD)	Dimethyl sulfoxide	90/10
1	PVC/PVA copolymer (VYHD)	Polyvinyl methyl ether.	90/10
3	PVC/PVA copolymer (VYHD)	Cis-polybutadiene	90/10
4	PVC/PVA copolymer (VYHD)	Monomethyl ester of a vinyl methyl ether/maleic anhydride copolymer.	90/10

TABLE X.—PRETREATMENT AND PLATING CYCLE

		Temp., ° C.	Time/ min.	Cold water rinses
1	Acetone	RT	2	2
2	HNO_3 1:1	60	2	2
3	Dilute $SnCl_2$ solution	60	2	2
4	Sensitization, $SnCl_2$	RT	1	2
5	Activation, $PdCl_2$	RT	½	2
6	Electroless nickel Solution A	60	10	2

All coated plaques are plated with good nickel plates. Plaques 1 and 2 are provided with a mirror-like uniform and adherent nickel plate. All of the above plaques were subjected to and passed a scratch test and an adhesive tape test. The scratch test is conducted by scribing a line on the surface of the nickel plate and then another line at an acute angle to the first. The test is to determine scratch adhesion by observing the amount of plate removed from the surface at the juncture of the two intersecting scratches. The adhesive tape test (or Scotch tape test) is a further adhesion test which is conducted by adhering a piece of tape over intersecting scratches obtained in the manner described for the scratch test and lifting the tape from the scratched plated surface. The test determines the adherence of the metal plate to the base relative to the adhesive bond of the tape.

EXAMPLE 6

Plaques of polyvinyl chloride are coated with solutions of the following compositions and plated as follows:

TABLE IX

	Carrier	Filler	Solvent	Amount, percent
1	PVC	Dimethyl sulfoxide	(1)	15/1.5
2	PVC	Aluminum oxide	(1)	15/30

[1] (THF=tetrahydrofuran).

TABLE XII.—PRETREATMENT AND PLATING CYCLE

		Temp., ° C.	Time/ min.	Cold water rinses
1	Degrease	65	5	2
2	Acetone	RT	2	2
3	Etch 1:1 HNO_3	65	5	2
4	Neutralize, 15% HCl	RT	2	2
5	Neutralize, dilute $SnCl_2$	65	3	2
6	Sensitization, $SnCl_2$	RT	3	2
7	Activation, $PdCl_2$	RT	3	2
8	Electroless nickel Solution A	60	10	2

Good plates are obtained from all plaques.

What is claimed is:

1. A method for preparing a polyvinyl chloride surface for electroless plating comprising:

(a) admixing a solvent-soluble extractable filler with a polyvinyl chloride;

(b) forming the admixture obtained from step (a) into a shaped article;

(c) immersing said shaped article into a swelling solvent for polyvinyl chloride; and

(d) dissolving said solvent-soluble extractable filler from said shaped article prior to plating to an extent sufficient to provide cavities upon the surface of said shaped article of a size ranging between about 0.1 to 1.0 microns.

2. Method as recited in claim **1** wherein said filler is an inorganic filler.

3. Method as recited in claim **2** wherein said inorganic filler is selected from the group consisting of calcium carbonate and aluminum oxide.

4. Method as recited in claim **1** wherein said filler is an organopolymeric material.

5. Method as recited in claim **4** wherein said organopolymeric material is selected from the group consisting of an acrylonitrile/butadiene/styrene copolymer, polybutadiene, and polyvinyl acetal polymers.

6. Method as recited in claim **1** wherein said surface to be plated is a film of polyvinyl chloride coated on a formed base.

7. The method of claim **1** wherein said swelling solvent is methyl ethyl ketone.

References Cited

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ALFRED L. LEAVITT, Primary Examiner

J. A. BELL, Assistant Examiner

U.S. Cl. X.R.

117—135.5; 156—3; 204—30; 264—49, 343; 117—47 A

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,632,704 Dated January 4, 1972

Inventor(s) Miguel Coll-Palagos

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

Column 8, Example 3, Table V, Sample 3 should read
--Graft Copolymer of polyvinyl chloride 90
and polybutadiene 10 -- ;
Column 9, Example 6, "Table IX" should be changed to
--Table XI-- ;
The following references were not cited and should be inserted therein:

2,686,731	8/1954	Wainer	106 - 288(I)
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3,431,120	3/1969	Weisenberger	117 - 47 (R)
3,466,232	9/1969	Francis et al	204 - 30
3,467,540	9/1969	Shick	117 - 47 (R)

Signed and sealed this 20th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents