United States Patent Office 3,726,771 Patented Apr. 10, 1973

3,726,771

PROCESS FOR CHEMICAL NICKEL PLATING OF ALUMINUM AND ITS ALLOYS

Miguel Coll-Palagos, Rye, N.Y., assignor to Stauffer Chemical Company, New York, N.Y.

No Drawing. Continuation of abandoned application Ser. No. 687,428, Dec. 4, 1967. This application Nov. 23, 1970, Ser. No. 92,167

Int. Cl. C23b *1/00*; C23f *1/00*; B32b *15/04*

U.S. Cl. 204—38 B 9 Claims

ABSTRACT OF THE DISCLOSURE

Aluminum and its alloys can be electrolessly plated by first degreasing and cleaning the aluminum surface, etching the degreased and cleaned surface wih hydrofluoric acid followed by immersing the base or surface in an acidic electroless plating solution containing nickel ions, hypophosphite ions, fluoborate and/or sulfamate ions, glycolate ions and a small amount of fluoride ions. The pH of the solution is within the range of 5.3 to 7.

This application is a streamlined continuation of application Ser. No. 687,428 filed Dec. 4, 1967, now abandoned.

The present invention relates to improved processes for the chemical nickel plating of aluminum and its alloys and to the baths employed in such processes.

Aluminum is being used extensively as a base material for decorative objects by anodizing and subsequent coloring or by surfacing the aluminum with an electrodeposited metal plate of chromium, nickel, copper, brass, silver, tin, gold or modifications thereof. Decorative finishes are usually provided by plating with chromium, silver and gold. The modification of the aluminum surface for other purposes is also accomplished by electroplating such as by the use of silver on electrical equipment to improve surface conductivity; the use of brass to facilitate bonding of rubber to aluminum; the use of copper, nickel or tin for assembly by soft soldering; chromium to reduce friction and obtain increased resistance to wear; zinc to threaded parts where organic lubricants are not permissible and tin to reduce friction on bearing surfaces. Because of the lightness of aluminum, its low cost, its corrosion resistance and easy formability, aluminum is a desirable choice for a base material. However, aluminum cannot be effectively electroplated directly. Chromium, gold, copper, and tin do not adhere strongly to aluminum but they do adhere to an intermediate layer of nickel. However, and due to the ever-present natural aluminum oxide film on the surface of the aluminum and due to the metallurgical structure of the aluminum itself, nickel also cannot be easily electroplated on aluminum. In order to commercially adopt aluminum to electroplating, the aluminum is required to be extensively pretreated prior to plating. One such pretreatment is by the use of the zincate or zinc immersion technique whereby the aluminum oxide is replaced by zinc. The aluminum can then be plated electrolytically with nickel to provide the base for chrome or other metallic plates.

In an attempt to eliminate this intermediate zincate coating procedure, the prior art has attempted to deposit the nickel plate directly on the aluminum using the chemical reduction or electroless nickel plating procedure. The

process of depositing a nickel plate electrolessly comprises the basic steps of immersing a body having a catalytic surface into a plating solution containing nickel ions in reducible form and a reducing agent such as a hypophosphite. The nickel ions are reduced to free metal at the catalytic surface and the hypophosphite is oxidized to orthophosphite. However, the procedure is fraught with problems.

The general electroless plating process for aluminum is set forth in the ASTM Symposium on Nickel Plating (STP No. 265) at page 34 and encompasses the following steps: (1) degrease; (2) clean; (3) rinse; (4) acid dip; (5) rinse; and (6) plate. The first three steps are to insure that the surface of the aluminum be thoroughly clean. Otherwise, the quality of the plate and its adhesion to the base are adversely affected. The acid dip pretreatment is essential to remove the natural aluminum oxide layer and to effectively expose a catalytic surface on the aluminum. Aluminum in its pure state is catalytic for the purpose of the electroless plating process whereas aluminum oxide is not. Therefore, the aluminum oxide must be removed and the surface of the aluminum must be inhibited from oxidation for a period of time sufficient to obtain an initial layer of electrolessly deposited nickel. Complete removal of the oxide layer is essential to good adhesion, brightness and quality of the nickel plate. Past procedures for effecting removal of the oxide layer have included pickling of the aluminum in hydrochloric acid followed by scum removal in an extremely dilute hydrofluoric/nitric acid cleansing bath (2,694,017). Scum removal has also been effected by chromic/sulfuric acid treatments. These treatments are undesirable in that they tend to provide ions on the surface of the object to be plated which are carried over into the plating bath, which are carried over into the plating both, which ions are adverse to the plating solution.

Electrolyess plating solutions for aluminum exhibit stability problems in that they tend to decompose rapidly in use. In order to overcome this, the prior art has suggested adding nitrate ions to the plating solution (2,694,017). The patent teaches that the addition of nitrate ions stabilizes the plating solution by passivating the aluminum surface. This decreases the plating rate so that fluoride ions must be added to the solution in order to increase the plating rate. This requires adjustment of the ion concentrations in the solution in order to maintain solution stability, plating rate and plating characteristics.

It has also been found that the known electroless plating solution without nitrate ions provides a nickel plate which is "passive" and cannot be effectively electroplated thereafter with a good, bright, adherent plate without treating the nickel to activate it. Activation of the passive nickel can be accomplished by extensive chemical treatment and the activation is necessary in order to obtain not only a good plate but a plate which is adherent to the nickel. The use of nitrate ions as suggested in the prior art tends to further increase the proclivity of the electroless plating solution to provide a passive nickel plate on the aluminum surface.

It has now been found that aluminum can be easily and effectively plated with nickel electrolessly without extensive pretreatments, which nickel is characterized by good adesion to the aluminum base and which is sufficiently active to allow for direct electrolytic plating without extensive chemical treatments to activate the nickel.

In accordance with the present inventon, an aluminum or aluminum alloy surface can be effectively nickel plated electrolessly by degreasing and cleaning the surface, immersing the cleaned and degreased surface in an aqueous solution of hydrofluoric acid followed by immersing the so treated surface in an electroless plating solution containing nickel ions, hypophosphite ions, fluoborate and/or sulfamate ions and a small amount of fluoride ions. The nickel plate is highly adherent to the aluminum base and is in an active state so as to allow direct electrolytic plating with other metals such as chromium.

In theory, the hydrofluoric acid treatment of the aluminum removes aluminum oxide from the surface of the base and temporarily inhibits the oxidation reaction of the aluminum so as to prevent further formation of aluminum oxides. The hydrofluoric acid also etches the surface of the aluminum so as to provide adhesion sites for the electrolessly deposited nickel. The use of the single step which can be accomplished at room temperature and in a short period of time provides not only the catalytic surface necessary for plating but also improves the adhesion of the nickel plate to the base. The use of the electroless plating solution having the fluoborate and/or sulfamate ions, and the fluoride ions provides an electroless nickel plate which is sufficiently activated so as to allow for direct electrolytic deposition of other metallic materials such as chrome. Also, the electroless plating solution is sufficiently stable so that the activity of the aluminum does not induce plating solution instability, thereby avoiding the necessity of including nitrate ions in the solution as taught by the prior art. The foregoing is theory and applicant is intended not to be bound thereby.

The process of the present invention can be utilized to plate any type of aluminum and its alloys. The aluminum can contain any of the known impurities such as copper, manganese, silicon, magnesium, zinc and the like, and can be cast, wrought, extruded, or in any form desired to be plated. Illustrative of the various types of aluminum and its alloys which can be plated are 2024, 3003, 5052, 5252, 5254, 5357, 5457, 5557, 6061, 6063, 7075, etc. These are given as illustrative and are in no way intended to be inclusive of all such aluminum materials which can be plated.

In utilizing the present invention with aluminum having a high degree of silicate content, it is more desirable to use an alternate procedure which comprises anodizing the aluminum using conventional anodizing techniques to provide a porous surface, followed by activating the anodized surface to make it catalytically active. This activation is necessary since the anodization provides a surface on the aluminum which is catalytically inactive in the electroless plating bath. The activation can be accomplished by using one of the known methods of activating electrically non-conductive surfaces for electroless plating such as by immersing the aluminum in a solution of stannous chloride followed by immersing the base in a solution of palladium chloride. Also, and by using the solution of the present invention, the stannous chloride treatment can be omitted. The anodized aluminum can be immersed in a very dilute solution of palladium chloride and, after water rinsing, then placed into the electroless nickel plating solution. The palladium catalytic sites necessary for electroless plating are formed in situ.

With respect to the compositions of the electroless plating bath, it essentially comprises an aqueous acidic solution containing nickel cations, hypophosphite anions, fluoborate and/or sulfamate anions and a small quantity of fluoride anions. The solution can be formed by dissolving a soluble nickel salt, preferably nickel fluoborate and/or nickel sufamate, in an acidic aqueous solution followed by adding hypophosphite ions derived from such compounds as sodium, potassium, magnesium, hypophosphite or combinations thereof. The fluoride anions can be derived from salts, such as sodium, and potassium fluoride, or by the use of hydrofluoric acid. In order to maintain

the stabilility of the bath, glycolate ions generally are added by means of glycolic acid, acetate ions are added by acetic acid; a buffer in the form of boric acid; and a small quantity of a plating rate accelerator in the form of thiourea are also added to the solution. A more complete description of the plating solution is set forth in U.S. Pat. 3,667,972, which patent is a streamlined continuation of copending application of Miguel Coll-Palagos, Ser. No. 687,470 and now abandoned.

For effective plating of aluminum, the surface must be degreased and cleaned. Any known method for effecting this can be used in accordance with the invention. Illustrative of one such method is the immersion of the aluminum base in a solution containing 2% sodium hydroxide and 4 grams per liter sodium gluconate at about 60° C. Any other cleaning process which will effectively clean the surface can also be utilized. In order to prevent any carry-over of impurities from the cleaning step into the hydrofluoric acid bath, the cleaned object is preferably rinsed twice in water. The cleaned and rinsed article is then etched in an aqueous solution of hydrofluoric acid. The etching solution can contain from about 3% to about 8% hydrofluoric acid but preferably the etching solution is a 5% solution of hydrofluoric acid. This can be accomplished at room temperature though the rate of etching can be increased by increasing the temperature. The etching at room temperature is preferably conducted for at least thirty seconds to a maximum of about two minutes. The etched surface is again preferably double rinsed in cold water to prevent carry-over of impurities from the etching bath into the next step of the process. The etched base is then immersed in the electroless nickel plating bath for a time sufficient to provide the desired nickel plate on the surface of the aluminum. At about 40° C., about 10 minutes, and at 60° C., about 5 minutes are required to deposit a sufficient amount of electroless nickel to allow for further electrolytic plating with such systems as Cu/Ni/Cr, Ni/Ni/Cr, or chrome. Selection of temperature and plating time will be determinative of the amount of plate deposited on the aluminum and this selection can be made by one skilled in the art.

Following the electroless plating, the surface is rinsed and, to insure complete cleanliness, the electroless plated nickel is treated in a mild HCl/H_2SO_4 acid bath prior to insertion of the plate in an electrolytic bath. Standard chrome plating solutions containing chromic acid, sulfate ions at standard temperatures using standard current densities can be used. If desired, and for leveling purposes, the electroless nickel can be electroplated with copper, followed by electrolytically depositing bright nickel, followed by the chrome plating, as is well known in the electrolytic plating art.

The invention is further illustrated in the example which follows.

EXAMPLE 1

Plates of aluminum are prepared and plated with electroless nickel as follows:

PRETREATMENT

	Temp. (° C.)	Time	Water rinses [1]
Immerse in 2% NaOH solution containing 4 grams/liter sodium gluconate.	60	30 sec	1 CWR
Repeat step 1	60	30 sec	2 CWR
Immerse in 5% HF solution	RT	1 min	2 CWR

[1] CWR=cold water rinse.

Following pretreatment, the aluminum is electrolessly plated by immersing for 10 minutes in an electroless plating solution maintained at 60° C. and having a pH within the range of 5.5 to 7.

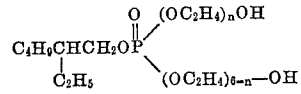
Aluminum alloys 3003, 5052, 5252, 5357, 5457, 5557, and 6063 are effectively plated with a uniform and adherent nickel plate using any of the five following electroless nickel plating solutions (the composition of these alloys

and those given hereinbefore are set forth in the Alcoa Aluminum Handbook, 1962 (c) Alcoa):

TABLE I

Components	Solution A	B	C	D	E
Nickel fluoborate, g./l.	42	-------	22	63	84
Nickel sulfamate, g./l.	-------	52	26	-------	-------
Sodium hypophosphite, g./l.	100	100	100	150	100
Boric acid, g./l.	20	20	20	30	40
Acetic acid (glacial) g./l.	16	16	16	16.8	-------
Glycolic acid, g./l.	14	14	14	31.5	35
Ammonium fluoride, g./l.	4	4	4	9	6
Thiourea, p.p.m.	0.3	0.3	0.3	-------	0.3
Wetting agent,[1] g./l.	0.4	0.4	0.4	0.6	0.2

[1] Nonionic wetting agent of the formula:



sold as Victawet 12.

The invention is defined in the claims which follow.

What is claimed is:

1. The method for chemically plating with nickel an aluminum or aluminum alloy surface consisting essentially of degreasing and cleaning the aluminum surface, immersing the degreased and cleaned surface in an aqueous solution containing from about 3 to about 8% hydrofluoric acid, followed by immersing the so-treated base in an acidic electroless plating solution consisting essentially of:

	Amount in grams/liter
Nickel ion	1 to 40
Hypophosphite ion	50 to 150
Fluoborate ion or sulfamate ion ----per nickel ion--	2
Borate ion	15 to 50
Glycolate ion	7 to 21
Acetate ion	10 to 25
Ammonium fluoride	2 to 10

Thiourea, 0.2 to 0.8 p.p.m.

said electroless plating solution having a pH in the range from about 5.3 to about 7.

2. The method as recited in claim 1 wherein said ion is fluoborate.

3. The method as recited in claim 1 wherein said ion is sulfamate.

4. The method as recited in claim 1 wherein said nickel ions are provided by using nickel fluoborate.

5. The method as recited in claim 1 wherein said cleaned and degreased surface is immersed in an aqueous solution containing about 3% to about 8% hydrofluoric acid for a period of time ranging from 30 seconds to 2 minutes at room temperature.

6. The method for chromium plating aluminum which comprises degreasing and cleaning the aluminum surface, immersing the degreased and cleaned surface in an aqueous solution containing about 3% to about 8% hydrofluoric acid, followed by immersing the so-treated base in an acidic electroless plating solution consisting essentially of:

	Amount of grams/liter
Nickel ions	1 to 40
Hypophosphite ions	50 to 150
Fluoborate ions or sulfate ions ----per nickel ion--	2
Borate ion	15 to 50
Glycolate ion	7 to 21
Acetate ion	10 to 25
Ammonium fluoride	2 to 10

Thiourea, 0.2 to 0.8 p.p.m.

said electroless plating solution having a pH in the range from about 5.3 to about 7, followed by electrolytically depositing a layer of chromium on said base by the use of an electrolytic chromium plating bath.

7. The method as recited in claim 6 wherein said surface is immersed in said 3% to 8% hydrofluoric acid solution for a period of time ranging from about 30 seconds to about 2 minutes at room temperature.

8. The method as recited in claim 6 wherein said ion is fluoborate.

9. The method as recited in claim 6 wherein said ion is sulfamate.

References Cited

UNITED STATES PATENTS

2,580,773	1/1952	Heiman	117—130
3,152,009	10/1964	DeLong	106—1
3,338,741	8/1967	Katz	117—130
2,746,136	5/1956	Richand	204—38 B
3,211,578	10/1965	Gutzeit	106—1
2,694,017	11/1954	Rescham	117—50
3,370,974	2/1968	Hepfer	117—47
3,378,400	4/1968	Sickles	117—160
3,432,338	3/1969	Sickles	117—130

JOHN H. MACK, Primary Examiner

T. TUFARIELLO, Assistant Examiner

U.S. Cl. X.R.

106—1; 117—50, 130 E; 204—33