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PLATING NICKEL ON ALUMINUM

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The present invention relates to an improved method for plating nickel on aluminum and more particularly, to an improved method of nickel plating on aluminum that forms a plated aluminum base upon which any subsequent metal can be plated with firm adherent adhesion.

The old methods of plating on aluminum require that first, a layer of zinc be put on the aluminum either by immersion or by electrodeposition, then secondly, followed by a layer of electrodeposited copper. After these two layers of metals have been put on the aluminum, then the desired finish metal may be deposited over the zinc-copper coated aluminum. The disadvantages of the old method are that two metals must be plated on the aluminum before a desired finish metal may be plated. Further, the plating of the zinc coating, especially by the immersion method, must be controlled within very narrow limits or blisters will occur during the copper plating as well as any subsequent plating. Also, the copper bath, which is cyanide in nature, must be kept below a maximum limit in free cyanide. If the finish metal is a metal that must be plated from a molten salt bath, the zinc, which has a low melting point will be melted and become a liquid, thus no longer giving protection to the aluminum for electrodepositing the finished metal. The results of plating on zinc-copper coated aluminum in a molten salt bath above the temperature at which zinc melts, will give blistered non-adherent deposits of the finish metal.

The method of the invention described herein corrects these deficiencies of the prior art. Broadly, a new method of obtaining electrodeposits on aluminum with excellent adhesion has been developed. This method consists of producing a thin coating of nickel on the surface of the aluminum, then heat treating the nickel-clad aluminum, which forms a suitable base upon which any subsequent metal can be plated with perfect adhesion. The details of the process will be more clearly defined hereinafter.

There are many advantages to this invention; some of the most outstanding are described in the following. Only one underlaying metal is plated on the aluminum before the desired finish metal. There are no rigid controls on the dips and plating bath. Excellent adhesion is always assured because of the fusion of the nickel and the aluminum. Nickel is a high melting metal, thus when nickel is used as the underlaying metal a subsequent finish can be given that is plated from a molten salt bath.

The principal object of the present invention is to provide a method of plating on aluminum in which nickel is used instead of the zinc and copper platings as the underlaying metal plating between aluminum and the finished metal.

Another object of the invention is to provide a method of plating nickel on aluminum in which the nickel is fused with the aluminum before the finish plate is applied to give maximum adhesion which has never before been obtained with plated metals on aluminum.

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Other objects and advantages will become apparent as the description proceeds.

Since the applications of electroplated aluminum are manifold and continually increasing, a great deal of interest has been created in the development of methods for plating on aluminum. Some of the applications for metallic coatings on aluminum are to decrease contact resistance, to improve surface conductivity, to improve solderability, to reduce friction, to facilitate the bonding of rubber, and to increase wear resistance.

Decorative finishes on aluminum have found wide usage in household appliances and in the jewelry industry. In general, plated aluminum of good quality has found wide application in all industries because of its relative economy, attractive finish, strength and lightness.

The plating of aluminum can generally be divided into two broad categories. The first is chemical etching, in which the aluminum article is chemically-etched and a subsequent metal is deposited on the conditioned surface either by immersion or by electrodeposition. The second, which is no concern here, includes the various anodizing processes which produce an oxide coating upon which subsequent metals can be deposited. Of the different methods of plating on aluminum, only a few procedures have merit. Most give only fair results or are impractical or uneconomical.

One of the most practical and economically-sound methods of plating on aluminum is, categorically, a chemical-etching process. Various degrees of the chemical-etching process are used more often throughout industry than any other process because of the low-operating cost of the etch bath as compared to the high power cost for operating anodizing baths. The method explained herein consists of chemically-etching and then electrodepositing nickel on the aluminum.

Several methods of plating on aluminum were evaluated to determine the best technique for obtaining good adhesion between the plated metal and the aluminum. One of the first methods approached was the familiar zincate. In the hands of those who are skilled in the art of plating on aluminum, the method works with good success; however, in production-type operations, the method is not consistent because of the different procedures and the high degree of skill that must be utilized when the different alloys of aluminum are encountered.

A modification of the zincate method was investigated and found to give more consistent results. This procedure consists of the standard process for cleaning aluminum i.e., degrease, alkaline etch, deoxidize. After the deoxidation treatment, the aluminum article is given a dip in fluoroboric acid. A thin film of zinc is then electrodeposited on the aluminum from a standard alkaline zinc bath. An improvement over the normal zincate procedure was observed; however, the procedure did not fulfill the requirements of consistent firm adhesion and suitability for production processing.

Since none of the methods investigated, using zinc as an intermediate coating between aluminum and subsequent electrodeposits, gave the results desired, further investigation was carried out. This led to the use of a method developed in Cambridge, England, by Dr. J. M. Bryan. It consisted of placing the aluminum article in an etch which consisted of dextrin, water and trichloroacetic acid, rinsing in acetone, and plating nickel on the etched surface from a nickel sulfate bath. Dr. Bryan's procedure was found to be an improvement over the zinc coating methods; but, because of the high cost of the etch bath and, in some cases, the poor adhesion of the nickel to the aluminum, the method was not accepted as the best. However, there were some alternate procedures

developed from this method which later led to the development of the present method. It was found that, after etching, tin, rhodium, and chromium could be plated directly on the etched surface of the aluminum just as the nickel had been plated in other instances. The plated metals of the pieces processed appeared to have good adhesion to the aluminum.

Although this alternative method offered some satisfaction, it was felt that further improvement in the adhesion characteristic of the plating could be obtained if the deposited metal were fused with the aluminum. To accomplish this fusing operation, the plated aluminum was subjected to a furnace temperature of 800° F. to 1050° F. for five minutes. As an example, nickel could be the plated metal and the aluminum prepared and processed by the following operations:

- (1) Degrease.
- (2) Etch.
- (3) Nickel strike 0.0001" to 0.0005" thick.
- (4) Heat treat at a furnace temperature of 800–1050° F. for approximately five minutes. The temperature depends on the aluminum alloy.
- (5) Clean.
- (6) Plate any desired metal.

The degreasing step removes oils and organic contamination on the surface of the aluminum. This may be accomplished by vapor degreasing or by soaking the aluminum in any solvent ordinarily used for this purpose.

The etching operation involves the use of two types of etches. The aluminum article is first etched in a 10% by volume solution of hydrofluoric acid (48–52%) for 10 to 15 seconds. The article is then rinsed and transferred to a second etch of 50% hydrochloric acid containing 9 to 10 g./l. of manganous sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). The etching time varies from 10 to 80 seconds, depending upon the aluminum alloy.

For the light alloys of aluminum, an etching time of 20 to 30 seconds is usually sufficient. For some die and sand castings, a more severe etch than hydrofluoric acid and water may be needed. In such cases, an etch which consists of 3 parts of nitric acid and one part of hydrofluoric acid may be substituted. After the aluminum article has been given the two etching treatments, it is dip rinsed and transferred to the nickel bath.

The nickel plate is obtained from a nickel bath of the following composition:

	Oz./gal.
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	19
Magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	10
Ammonium chloride	2
Water	95
Boric acid	2

The aluminum article is made the cathode and plated at 15 amp./sq. ft. for approximately 10 minutes to obtain the desired thickness of the nickel plate which ranges from 0.0001" to 0.0005" thick.

It is presumed that during the heat-treating process some of the nickel diffuses into the aluminum, and, because of the high surface energy of the nickel, readily agglomerates into islands. The temperature during the heat treatment should be between 800–1050° F. for the islands to form. Several temperatures were investigated to determine at which points the islands would form. Since each different alloy of aluminum will have a different melting point and will, therefore, form islands at different temperatures, it was found that the islands always form when the temperature range is 800–1050° F.

The formation of the aluminum nickel alloy and the formation of the islands provides a suitable surface upon which other metals may be electrodeposited. Metals plated on this surface have improved adhesion around the regions of the islands. However, if the heat treatment is carried out in air, a thin layer of oxide is formed on the surface of the article. Before subsequent plating can be

accomplished the oxide must be removed by giving the article a reverse current treatment in 25% sulfuric acid solution. If the nickel-plated aluminum is heat treated in the non-oxidizing atmosphere, oxidizing atmosphere, oxidization is minimized and the article need only be dipped in a 25% sulfuric acid solution for a few seconds to activate the surface before subsequent plating is carried out.

If the time in the hydrochloric acid etch is controlled very closely with each different type of alloy used, the heat treatment step may be omitted and fair adhesion of the nickel and aluminum will be obtained. It was found that with 24 ST aluminum good adhesion could be obtained using an etch time of 18–22 seconds. However, if the best adhesion is to be obtained in every case and, if the process is to be reproducible, the heat treatment step is essential.

As a more specific illustration of the present invention, reference is made to the following examples:

Example 1

- (1) Degrease the aluminum with trichloroethylene vapors, acetone or any organic solution commonly used for this purpose.
- (2) Cold water rinse.
- (3) Dip for 10–15 seconds in one part of hydrofluoric acid to nine parts of water.
- (4) Cold water rinse.
- (5) Dip in a 50% solution of hydrochloric acid containing 9.0 to 10.0 g./l. of manganous sulfate for 10–60 seconds. This time depends upon the alloy of aluminum and must be worked out for each alloy.
- (6) Cold water rinse.
- (7) Plate in the following aqueous nickel bath at 15 amperes/sq. ft. for 10–20 minutes:
19 oz./gal. nickel sulfate.
10 oz./gal. manganous sulfate.
2 oz./gal. ammonium chloride.
2 oz./gal. boric acid.
- (8) Rinse and air blast part dry.
- (9) Place in an oven at 1000° F. for 2.5–5 minutes.

To insure the best adhesion of the nickel to the aluminum, the nickel coated aluminum is placed in the oven at 1000° F. for 2.5–5 minutes in which time the under coat of the nickel is fused into the aluminum. During this fusion a light blue oxide is formed on the nickel which must be removed before any subsequent plating may be carried out on the fused nickel-coated aluminum. This oxide is removed by the following method:

- (1) Anodic alkali clean for 30–45 seconds at 4V in 3 oz./gal. sodium hydroxide, 2 oz./gal. sodium carbonate.
- (2) Rinse.
- (3) Reverse current clean in 25% sulfuric acid at 4V using lead cathode until the blue oxide is removed. Approximate time is 60–70 seconds.
- (4) Rinse and plate any desired metal.

Example 2

This example illustrates a method of plating 24 ST aluminum.

- (1) Degrease the aluminum with trichloroethylene vapors, acetone or any organic solution commonly used for this purpose.
- (2) Cold water rinse.
- (3) Dip for 10 to 12 seconds in one part of hydrofluoric acid to nine parts of water.
- (4) Cold water rinse.
- (5) Dip in a 50% solution of hydrochloric acid containing 9 to 10 g./l. of manganous sulfate for 18–22 seconds.
- (6) Cold water rinse.
- (7) Plate in the following aqueous nickel bath at 15 amperes/sq. ft. for 10–20 minutes:
19 oz./gal. nickel sulfate.

- 10 oz./gal. manganous sulfate.
- 2 oz./gal. ammonium chloride.
- 2 oz./gal. boric acid.
- (8) Rinse and air blast part dry.
- (9) Place in an oven at 900° to 1000° F. for 3 to 10 minutes.
- (10) Remove the oxide as outlined hereinabove under the removal of oxide method.
- (11) Plate prepared aluminum sample with gold from any type of conventional gold plating solution; an example is cited as:
 - 40 g./l. potassium bold cyanide.
 - 29 g./l. potassium cyanide.
 - 40 g./l. potassium tartrate.
 - 3 g./l. potassium hydroxide.
 - 10 g./l. potassium carbonate.

Example 3

This example illustrates a method for plating on Alcoa No. 38D aluminum.

- (1) Degrease the aluminum with trichloroethylene vapors, acetone or any organic solution commonly used for this purpose.
- (2) Cold water rinse.
- (3) Etch for 8-12 seconds in one part of hydrofluoric acid to 9 parts of water.
- (4) Cold water rinse.
- (5) Dip in a 50% solution of hydrochloric acid containing 9 to 10 g./l. of manganous sulfate for 10 to 15 seconds.
- (6) Cold water rinse.
- (7) Plate in the following aqueous nickel bath at 15 amperes/sq. ft. for 10-20 minutes:
 - 19 oz./gal. nickel sulfate.
 - 10 oz./gal. manganous sulfate.
 - 2 oz./gal. ammonium chloride.
 - 2 oz./gal. boric acid.
- (8) Rinse and air blast part dry.
- (9) Heat in an 800° to 950° F. oven for 5 to 15 minutes while passing a pure hydrogen atmosphere or an atmosphere comprising principally hydrogen and the remainder is argon or any inert gas.
- (10) Dip in a dilute solution of hydrochloric acid.
- (11) Plate any desired metal; an example is chromium from a chromic acid solution.

Over 50 samples of aluminum of varying alloy composition, specifically 24ST, 3S, and sand castings, were treated as outlined above, including the heat treatment step. After the prepared samples had been activated, copper (acid and cyanide), chromium, nickel, zinc, cadmium, gold, tin, and solder were plated on the conditioned surface. After these metals had been plated on the aluminum samples, they were subjected to the following tests to evaluate the adhesion. Some samples were heated to 600° C. for 30 minutes; some were dipped in a 500° F. oil bath for 10 minutes; some were given bend tests; and others were left untouched in the laboratory for six months. In no case did the samples show any degree of blistering, peeling, or other evidences of poor adhesion.

In summary it may be stated that several methods of plating on aluminum were evaluated to establish a method which would give perfect adhesion between the plated metal and the aluminum and, to a lesser extent, a method which could be utilized by the general type of plating personnel. The familiar zincate process was evaluated but did not give the desired results unless used by skilled personnel. A modification of the zincate process was investigated and found to give more consistent results than the normal zincate method. However, this method did not fulfill the requirements desired. A method which was developed in England of putting nickel on aluminum, instead of zinc, was investigated and found to be a great improvement over the zinc coating methods.

This process, too, was not acceptable because of high operating cost and because perfect adhesion was not obtained in every case.

Although the above nickel process appeared to be satisfactory, a method was developed which would be acceptable in every case. This method consisted of etching the aluminum article in a hydrofluoric acid solution, in a hydrochloric acid and manganous sulfate solution, nickel plating, heat treating, and then subsequent plating a desired metal. It was found that this process, in every case, produced firm adherent coatings on varying alloys of aluminum.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefor particularly point out and distinctly claim as our invention:

1. In a method of depositing an electroplate of a nickel group metal upon articles of aluminum and aluminum-base alloys, the steps which include degreasing the article; rinsing in water; subjecting the article to two etching actions, the first, dipping in hydrofluoric acid, rinsing in water, and the second, dipping in a solution of hydrochloric acid containing manganous sulfate, the total etching time varying from 10 to 80 seconds, rinsing in water; cathodically treating the article in an aqueous nickel bath comprising nickel sulfate, magnesium sulfate, ammonium chloride, and boric acid and subjecting the bath to a current density of circa 15 amperes per square foot for a period of approximately 10 minutes, electrodepositing a layer of nickel on the article and controlling the electrodeposition to produce a thickness which ranges from 0.0001 inch to 0.0005 inch; rinsing in water and then partially drying with an air blast; heat treating the composite plated article at a temperature of about 1000° F. for a period of 2½ to 5 minutes; then removing the light blue oxide that forms thereon during the heat treating step by anodically treating the composite plated article in a solution of sodium hydroxide and sodium carbonate; rinsing in water; subjecting the composite plated article to a reverse current treatment in sulfuric acid; rinsing in water; and thereafter electrically depositing a metal upon the composite plated article other than nickel.

2. In a method of depositing an electroplate of a nickel group metal upon articles of aluminum and aluminum-base alloys, the steps which include degreasing the article; subjecting the article to two etching actions, the first, dipping in a 10% by volume solution of 48-52% hydrofluoric acid, and the second, dipping in a solution of 50% hydrochloric acid containing 9 to 10 grams per liter of manganous sulfate, the total etching time varying from 10 to 80 seconds, depending upon the aluminum alloy; cathodically treating the article in an aqueous nickel bath comprising 19 ounces per gallon of nickel sulfate, 10 ounces per gallon of magnesium sulfate, 2 ounces per gallon of ammonium chloride, and 2 ounces per gallon of boric acid and subjecting the bath to a current density of 15 amperes per square foot for a period of approximately 10 minutes, electrodepositing a layer of nickel on the article and controlling the electrodeposition to produce a thickness which ranges from 0.0001 inch to 0.0005 inch; and then partially drying with an air blast; heat treating the composite plated article in an oven at a temperature of about 1000° F. for a period of 2½ to 5 minutes; then removing the light blue oxide that forms thereon during the heat treating step by anodically treating the composite plated article for a period of 30 to 45 seconds at 4 volts in a solution of 3 ounces per gallon of sodium hydroxide and 2 ounces per gallon of sodium carbonate; subjecting the composite plated article to a reverse current treatment in 25% sulfuric acid for the period of approximately 60 to 70 seconds at 4

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volts; and thereafter electrically depositing a metal upon the composite plated article other than nickel.

3. In a method of depositing an electroplate of a nickel group metal upon articles of aluminum and aluminum-base alloys, the steps which include degreasing the article with trichlorethylene vapors; rinsing in water; subjecting the article to two etching actions, the first, dipping in a 10% by volume solution of 48-52% hydrofluoric acid, rinsing in water, and the second, dipping in a solution of 50% hydrochloric acid containing 9 to 10 gallons per liter of manganous sulfate, the total etching time varying from 10 to 80 seconds, depending upon the aluminum alloy; rinsing in water; cathodically treating the article in an aqueous nickel bath comprising 19 ounces per gallon of nickel sulfate, 10 ounces per gallon of magnesium sulfate, 2 ounces per gallon of ammonium chloride, and 2 ounces per gallon of boric acid, electrodepositing a layer of nickel on the article and controlling the electrodeposition to produce a thickness which ranges from 0.0001 inch to 0.0005 inch; rinsing in water and then partially drying with an air blast; heat treating the

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composite plated article in an oven at a temperature of about 1000° F. for a period of about 5 minutes; then removing the light blue oxide that forms thereon during the heat treating step by anodically treating the composite plated articles for a period of 30 to 45 seconds at 4 volts in a solution of 3 ounces per gallon of sodium hydroxide and 2 ounces per gallon of sodium carbonate; rinsing in water; subjecting the composite plated article to a reverse current treatment in 25% sulfuric acid for the period of approximately 60 to 70 seconds at 4 volts; rinsing in water; and plating the article with gold from a basic gold plating solution.

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