



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

APR 2 1967
Langley

REPLY TO
ATTN OF: GP

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for
Patent Matters

SUBJECT: Announcement of NASA-Owned U. S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code USI, the attached NASA-owned U. S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U. S. Patent No. : 3468765

Government or
Corporate Employee : Government

Supplementary Corporate
Source (if applicable) : N/A

NASA Patent Case No. : XLA-08966-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Yes No

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the Specification, following the words "... with respect to an invention of . . ."

Dorothy J. Jackson
Dorothy J. Jackson

N71-25903

Enclosure
Copy of Patent cited above

XLA-08966-1

Sept. 23, 1969

J. C. McCONNELL

3,468,765

METHOD OF PLATING COPPER ON ALUMINUM

Filed Aug. 4, 1966

FACILITY FORM 602
 (ACQUISITION NUMBER) **N71-25903** (THRU) _____
 (CODE) *00* (CATEGORY) _____
 (PAGES) *2*
 (NASA CR OR TMX OR AD NUMBER) _____

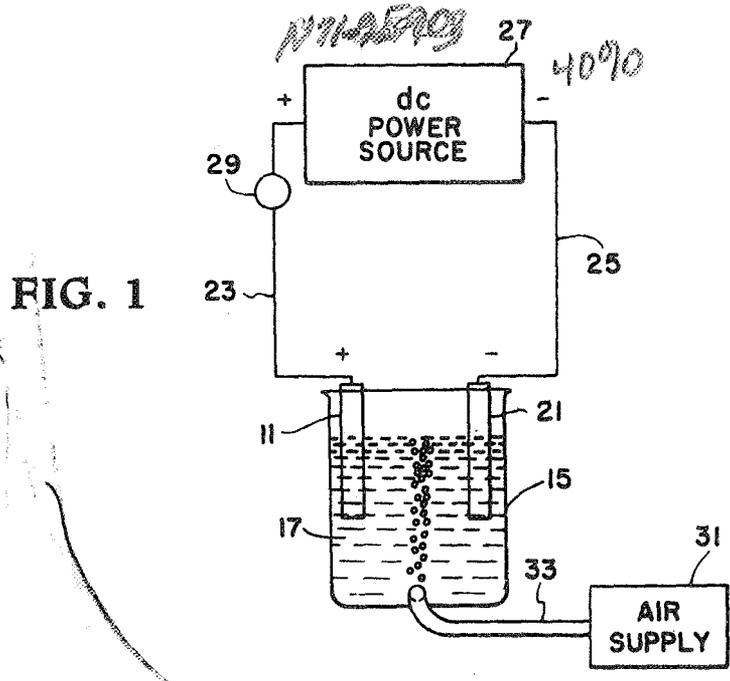


FIG. 1

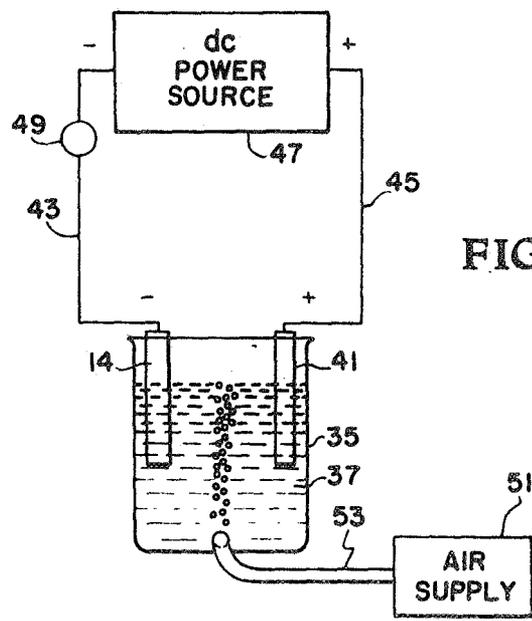


FIG. 2

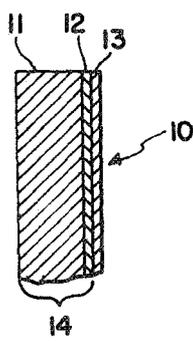


FIG. 3

INVENTOR
JAMES C. McCONNELL

J. C. McConnell

Wallace J. Nelson
ATTORNEYS

BY

(15/2)

1

3,468,765

METHOD OF PLATING COPPER ON ALUMINUM
James C. McConnell, Wallops Island, Va., assignor to the United States of America as represented by the Administrator of the National Aeronautics and Space Administration

Filed Aug. 4, 1966, Ser. No. 570,678
Int. Cl. C23b 5/20

U.S. Cl. 204—33

4 Claims

ABSTRACT OF THE DISCLOSURE

A method of recovering an aluminum article having a thin copper plating with excellent adhesion characteristics thereon comprising degreasing the aluminum surface, anodizing the clean surface in a phosphoric acid solution, washing with water and live-entry transferring the wet aluminum substrate to an aqueous acid-copper plating tank under controlled conditions.

The invention described herein was made by an employee of the United States Government and may be manufactured or used by or for the Government without the payment of any royalties thereon or therefor.

This invention relates generally to a method of plating copper on aluminum and relates with particularity to a method of providing an aluminum surface with a copper coating to permit structural aluminum bodies to be soldered by conventional soldering operations.

There are numerous potential industrial applications for lightweight economical aluminum products to be used as replacements for heavier and more costly metal structures. For example, aluminum could be used in electronic products such as bus bars, switch gears, microwave fittings and terminal boards as a replacement for copper as now generally used for these products; in the automotive industry, bumper guards, tire molds, trim, pistons and cylinders could readily be made from aluminum as could numerous screws, nuts, bolts, window and door hardware, household appliances, jewelry, and beverage cans. Although aluminum has been used in some of these applications, the use thereof has been somewhat restricted due to the expensive and complicated soldering techniques required to attach aluminum bodies to other metal surfaces. Thus, if an aluminum body could be provided with a thin copper plating which is easily soldered by conventional and inexpensive techniques, the universal utility and the lightweight structural strength characteristics, inherent in aluminum products, could be employed in industrial and space applications.

At present, the zincate process is used for most commercial electroplating on aluminum substrates. In this prior art process, a clean aluminum part is immersed in a strong alkali solution containing zinc salts. As the oxide dissolves, the aluminum is coated with a thin zinc film. The zinc film is then copperplated from a highly basic copper cyanide solution. One major disadvantage of the zincate process is the tendency of the copper plating to blister or peel upon heating as when copper is applied to a part that must have an electrical connection soldered to it. Another major disadvantage is metal removal during the zinc-coating part of the process. That is, parts with sharp corners or close tolerances, such as threaded parts, may be unusable because of metal removal caused by the highly basic zinc-coating procedure. The present invention combines all of the advantageous features of the

2

zincate process while eliminating many of the disadvantages thereof.

Accordingly, it is an object of the present invention to provide a new and novel method of plating copper on aluminum.

Another object of the present invention is to copper-plate an aluminum article with the copper plating being free of blisters and peeling upon heating.

A further object of the present invention is a method of providing a copper plating protective coating to an aluminum article.

Another object of the present invention is a method of improving the electrical conductivity of aluminum by providing a thin copper plating thereon.

A further object of the present invention is to provide a copper plating on an aluminum substrate with no adverse alteration of the physical shape of the substrate being effected during the plating operation.

Another object of the present invention is to provide a copper plating on aluminum in which the bending characteristics of the aluminum are retained and the electrical conductivity is increased.

Yet another object of the present invention is a method of copper plating aluminum and aluminum alloys for maximum adhesion and to permit soldering of the plated article by conventional soldering techniques while retaining the structural advantages of strength, lightness, ease of fabrication, and the like, normally associated with aluminum.

According to the present invention, the foregoing and other objects are obtained by providing the aluminum to be plated, cleaning the aluminum surface with a non-alkali cleaner, anodizing the clean aluminum surface in a phosphoric acid solution, thoroughly rinsing the acid from the aluminum substrate with cold distilled water and immediately transferring the aluminum substrate, while wet, to an acid-copper plating tank in which the power has previously been turned on. After plating, the plated aluminum is removed from the copper plating tank and dried with a blast of hot air to thereby recover an aluminum article having a thin copper plating with excellent adhesion characteristics thereon.

A more complete appreciation of the invention and many of the attendant advantages thereof will be more clearly understood by reference to the following detailed description when taken in connection with the drawings wherein:

FIG. 1 is a schematic representation of the apparatus employed in the anodizing procedure of the present invention;

FIG. 2 is a schematic representation of the plating procedure employed in the present invention; and

FIG. 3 is a sectional schematic view of an aluminum substrate provided with a copper plating by the method of the present invention.

Referring now to the drawings, FIG. 3 shows a sectional representation of a plated article prepared in accordance with the present invention as designated generally by reference numeral 10. Plated article 10 includes aluminum 11, an aluminum oxide substrate 12 and an outer or exposed plating layer 13 as prepared in accordance with the present invention. Inasmuch as the plated copper has strong adherence characteristics to the aluminum substrate the plated article 10 may be soldered by conventional techniques to any suitable electrical connection, metallic structural component, or the like.

Referring now more particularly to FIG. 1, the anodiz-

ing apparatus, including anodizing tank 15 containing the anodizing electrolyte 17 therein, is shown. The aluminum article or specimen 11 to be coated, is suitably attached and maintained immersed in an anodizing electrolyte 17 in a conventional manner and serves as the anode of the anodizing circuit. Any portions of the aluminum 11 that are not desired to be anodized and copper plated are masked off by a suitable and conventional masking technique or otherwise maintained out of contact with the anodizing electrolyte. This masking may be readily accomplished, for example, by spraying the area that is not to be copper plated with a clear acrylic lacquer. The cathode in the anodizing process is made up of a stainless steel element as designated by reference numeral 21 which is also immersed in the anodizing electrolyte 17. Suitable electrical connectors 23 and 25 connect aluminum anode 11 and stainless steel cathode 21, respectively, with a suitable voltage-controllable direct current power source as schematically shown and designated by reference numeral 27. A conventional ammeter 29 is provided in the circuit for measuring the current flow as will be more fully explained hereinafter. A suitable air-agitating device which includes pressurized air supply 31 is provided in fluid connection, by way of conduit 33, with the base of anodizing tank 15.

Referring more particularly to FIG. 2, the schematic representation of the apparatus for performing the copper plating step will now be described. Copper plating tank 35 contains a quantity of the copper plating electrolyte 37 therein and in which is disposed the anodized aluminum cathode 14 and a copper anode 41. Cathode 14 comprises the aluminum article 11 and the aluminum oxide layer 12 (FIG. 3) that is formed by the anodizing as described hereinbefore. Electric leads 43 and 45 connect, respectively, the aluminum cathode 14 and the copper anode 41 to a suitable voltage-controllable direct current power source 47. A current measuring ammeter 49 is also provided in the circuit. Air-agitation during the plating operation is provided by pressurized air supply 51 which is in fluid connection with tank 35 by way of conduit 53.

OPERATION

In operation, the aluminum 11 to be coated is first thoroughly cleaned to remove any foreign particles and oxide film appearing thereon by immersing the substrate in a non-alkali cleaner such for example, a 5% hydrofluoric acid bath, prior to being placed in the anodizing tank as shown in FIG. 1. One anodizing electrolyte 17 employed in a specific example of the present invention was a 25% volume solution of 85% phosphoric acid in distilled water, although other concentrations of the acid are considered within the scope of the invention. The aluminum is then anodized sufficiently to provide an anodized layer over the portions of the aluminum that are desired to be plated. An anodizing time of approximately six minutes in this solution, while maintaining a current density of 3-4 amperes per square foot of substrate, and an anodizing electrolyte temperature of approximately the same as that of room temperature appears adequate for most operations to provide an adequate anodized layer on the aluminum.

The anodizing current may be varied anywhere from three up to twenty amperes per square foot and the anodizing time varied from two to ten minutes, as so desired, with increases in current density resulting in a decrease in the anodizing time. Variations in the anodizing coating do not appear to be caused by temperature change of the anodizing electrolyte and, accordingly, room temperature appears the most practical temperature to use in application of the present invention.

After anodizing, the aluminum substrate is removed from anodizing tank 15 and thoroughly rinsed in cold distilled water. After rinsing, the anodized aluminum substrate is immediately transferred to the acid copper plating tank 35 in which power supply 47 has previously been

turned on. The copper plating electrolyte 37 in tank 35 comprises copper sulfate, 33 ounces/gal., sulfuric acid, 1.5 ounces/gal., thiourea, 0.0001 ounce/gal., and a suitable wetting agent, such for example the commercially available Alconox, 0.027 ounce/gal. Other suitable detergent type wetting agents may be employed as so desired. In the plating operation it was found that at room temperature, in order to adequately cover the anodized surface before it dissolved the anodized layer, a high initial current density of approximately 50 amperes per square foot of substrate be employed for approximately the first two minutes of copper plating time. The current is then lowered to yield a current density of approximately 10 amperes per square foot for at least five minutes to effect an adequate copper plate coating for the aluminum substrate. Additional plating time increases the thickness of copper plating but appears unnecessary for most soldering operations.

Technical grade copper sulphate is employed in the copper plating electrolyte and commercially available concentrated sulfuric acid is employed for the acid used therein. After plating, the plated substrate is removed from the copper plating tank and dried with a blast of hot air to recover the copper plated end product. As mentioned hereinbefore, suitable agitation is provided in both the anodizing and the copper plating tanks by a pressurized air supply leading to the base of the respective tanks by suitable conduits.

After drying the plated aluminum article 10 (FIG. 3) may be readily soldered to solid copper wire, other plated aluminum substrates, and the like, by a conventional flux-cored tin base solder and using manual soldering techniques. Also, due to the thick porous nature of the copper obtained, the plating bond with the aluminum is very strong and aids in plating other metals, such for example nickel, chromium, and silver onto the copper surface. As is well known, chromium plating on aluminum or steel is usually accomplished by first plating a thin layer of copper on the part followed by the heavier plating of chromium for corrosion protection and appearances.

As mentioned hereinbefore, the copper plated article prepared by the present process showed no tendency to blister or peel upon heating as when soldering electrical connections and the like to the plated surface. This proved a major advantage over the well-known zincate process presently being used by industry for copper plating aluminum surfaces. In addition, parts with sharp corners or close tolerances such as threaded parts may be coated by the present process without the danger of metal removal that is experienced by the highly basic zinc coating process.

In addition to commercially pure aluminum, 1100-H-14, four alloy groups giving a representative sample of aluminum alloys have also been tested by the present process. These alloys are 2219-T87, 5052-0, 6071-T6, and 7106-T3. The process was also tested using both sheet aluminum and aluminum castings with satisfactory results being obtained in plating adherence and soldering techniques in both instances.

Some agitation of the anodizing and plating solutions appears to be a very important necessity in the process of the present invention. The desired agitation rate for each application of the present invention will vary with bath size, work size, and geometry of the substrate being plated. Too violent agitation may cause streaking while no agitation causes "burning" of the substrate during anodizing.

Due to the superior adhesion of the copper plate to the aluminum substrate, when applied by the present process, this invention can be utilized to considerable advantage in plating aluminum with precious metal for decorative or technical purposes, plating aluminum with nickel, chromium, and the like, for corrosion protection, surface hardness, or other technical reasons. In addition, the present invention provides a satisfactory base for coloring by oxide methods and other processes where it is necessary or desirable to obtain special effects such as flat black as em-

5

ployed in optics. Each of these well-known industrial processes are more readily accomplished where a copper plating surface is previously applied to the aluminum base.

Additionally, the present process will find utility in the electro-forming when utilizing aluminum mandrels, as a primer for certain organic coatings, paints, plastics and the like, for masking purposes in heat treating, anodizing, spot plating, welding and the like. This process could also be useful in fabrication of optical mirrors, especially where it is desired to use aluminum castings or structures. This copper plating process constitutes an excellent base for the plating of silver, nickel, chromium and the like which suggests an improvement in the quality of present day plated equipment. As mentioned hereinbefore one of the primary advantages of the present invention is the absence of any blistering or peeling during thermal shock such as encountered during soldering of copper wires and the like to the plated structure which clearly indicates improved adhesion of the coating over any known prior art coating technique. Also, since no adverse alteration of the physical size of anodizing of the aluminum has been noted the entire process of the present invention becomes both controllable and predictable. It therefore follows that the close tolerances can be held which is an extremely important aspect, for example, in the field of instrumentation. In addition to the other advantages of the present invention, it is noteworthy to mention that the bending characteristics of the aluminum are retained after copper plating according to the present invention and the electrical conductivity remains high or is increased due to the nature of the copper deposit.

With the recent development of such high strength aluminum alloys as the 2219 and the 7106 alloys studied during the development of this invention, items such as bumper guards, hydraulic parts, and small forgings could quite possibly be made of aluminum rather than steel which is now being used. These parts could be plated first with a flash of copper and then with decorative or hard chrome whichever is applicable. In addition, commercial plants using large amounts of electricity have previously tried aluminum for the construction of bus bars but have discontinued it because the problems encountered in aluminum oxide layers formed at the connection of the bus bars. That is, bus bars jointed by bolting or riveting have not proven satisfactory because of the buildup of the oxide corrosion products between the joints. However, by use of the present invention the bus bars could be made of aluminum and plated with copper by the phosphate-anodizing process of the present invention and successfully joined by soldering. When formed in this manner, the aluminum surface would be protected against oxidation and considerable cost and weight savings would be experienced in the manufacture of large industrial bus bars.

Test specimens plated by the present invention showed no evidence of flaking during bend testing, no evidence of blistering or peeling, when bake-tested at 350° F. for thirty minutes, and no blistering when soldered to copper wires by conventional soldering techniques. When wire, soldered to a copper-plated aluminum substrate prepared by the present inventive process, was tension tested, either the wire failed or the wire ripped loose from the solder. The copper-aluminum bond never failed during such tension testing.

Although the invention has been described in connection

6

with a specific process, there are obviously numerous modifications and variations that will be apparent to those skilled in the art within the light of the above teachings.

It is therefore to be understood that the invention may be practiced otherwise than as specifically described.

What is claimed and desired to be protected by Letters Patent of the United States is:

1. A method of applying copper plate to an aluminum substrate comprising:

- cleaning the aluminum surface with a non-alkali cleaner, anodizing the clean aluminum surface in an aqueous phosphoric acid solution, rinsing the anodized surface in cold distilled water, immediately live-entry transferring the wet aluminum surface to an aqueous acid-copper plating tank containing a copper plating solution, said copper plating tank solution being at approximately room temperature with the current density employed being initially set at approximately 50 amperes per square foot of substrate and maintained at this level for approximately two minutes and thereafter the current density being lowered and maintained at approximately 10 amperes per square foot of substrate during the remaining electroplating time, and drying and recovering the copper plated aluminum substrate.

2. The method of claim 1 wherein said copper plating solution is agitated at a controlled rate during anodizing of said substrate.

3. The method of claim 2 wherein a flow of air is bubbled through said copper plating solution to effect said agitation.

4. The method of claim 1 wherein said copper plating tank contains an electrolyte consisting essentially of:

	Oz./gal.
Copper sulphate	33
Sulfuric acid	1.5
Thiourea	0.0001
Wetting agent (detergent type)	0.027

References Cited

UNITED STATES PATENTS

1,971,761	8/1934	Travers	204—42
3,189,532	6/1965	Chow et al.	204—35 XR
2,999,771	9/1961	Gaynes	204—15 XR

OTHER REFERENCES

- Bengston, Helmer: "Methods of Preparation of Aluminum for Electrodeposition," The Electrochemical Society, preprint 88-25, pp. 273-276, 1945.
- Lowenheim, Frederick A.: "Modern Electroplating," pp. 176-181, 1963.
- Wernick, S., et al.: "Surface Treatment of Aluminum," pp. 594-602, 1964.
- Graham, A. K.: "Electroplating Engineering Handbook," pp. 599-601, 1955.

HOWARD S. WILLIAMS, Primary Examiner
G. L. KAPLAN, Assistant Examiner

U.S. Cl. X.R.

204—35, 42, 58