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# 3,489,657 PROCESS FOR PRODUCING SOLDERABLE

ALUMINUM MATERIALS
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### ABSTRACT OF THE DISCLOSURE

A process for producing solderable aluminum materials is disclosed. The process comprises depositing upon an aluminum surface a first layer consisting essentially of a relatively thin layer of tin, a second layer consisting essentially of a tin-copper alloy, a third layer of nickel having a thickness from about  $25\times10^{-6}$  inches to about  $50\times10^{-6}$  inches and a fourth layer of solderable metallic material.

### BACKGROUND OF THE INVENTION

This invention relates to materials having an aluminum surface. More particularly it relates to a process for rendering these materials solderable.

Aluminum materials that are made from either solid aluminum or clad with an aluminum layer are difficult to solder. Solderability characteristics of these materials can be improved by processes heretofore known. These processes generally are time-consuming techniques and employ relatively expensive materials. Furthermore, in most instances, the thickness of the materials that are added to make the aluminum surfaces solderable adds considerable weight to the aluminum material. This additional weight often offsets the weight advantage that materials employing aluminum offer over comparable materials of construction. For example, one method heretofore known involved two separate immersion steps in a sodium zincate solution. After the first immersion step the zinc deposit is removed with nitric acid. After the second zinc immersion step, the material is electroplated with copper to a thickness of a copper deposit of about 200×10-6 inches followed by rinsing, neutralization, then a second coating of copper to a thickness of about  $300\times10^{-6}$  inches, rinsing, neutralization, and a third coating of copper to a thickness of from about  $50 \times 10^{-6}$ to about 100×10-6 inches, then followed by a silver plating step, during which from about  $200 \times 10^{-6}$  to about  $300 \times 10^{-6}$  inches of silver is deposited upon the copper. After the foregoing plating steps, the last step is a heat treatment step wherein the coated material is heated at 55 about 370° F. for 25 minutes to an hour. While the aluminum material is solderable, it can be seen from the above description multitudinous coating steps including two zinc coating steps, three copper coating steps, one silver coating step and a relatively long heat treatment 60 step are required to achieve a solderable aluminum surface. Furthermore, the total thickness of the layers of additional materials are at least about  $750 \times 10^{-6}$  inches. A significant increase occurs by the addition of a relatively thick coating. In many instances the materials having these thick coatings are rendered less ductile and will tend to flake off under severe stresses such as those that are produced during bending or flexing. It is believed, therefore, that a process that is simpler than those heretofore used for rendering aluminum surfaces solderable 70 and that employs less expensive raw materials would be an advancement in the art.

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### SUMMARY OF THE INVENTION

In accordance with one aspect of this invention, there is provided a process for rendering an aluminum material solderable, which process comprises depositing over the aluminum surface, a first layer of tin, a second layer of a copper-tin alloy, a third layer of nickel having a thickness of from about  $25\times10^{-6}$  inches to about  $50\times10^{-6}$  inches and a fourth layer of a solderable metallic material. The preferred aspects of this invention also comprise the preferred methods of deposition of the various layers and the preferred solderable materials.

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above description of the invention.

# DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention enables the use of relatively inexpensive raw materials for rendering the aluminum materials solderable. Additionally, when the various metallic layers are deposited by the preferred methods, a relatively short period of time is consumed in the process. Furthermore, not only do the treated aluminum materials exhibit excellent solderability characteristics, the materials are very ductile and can be bent and flexed without any flaking of the layers that have been applied.

As has been mentioned previous, the first step in the process of this invention is the deposition of a first layer of tin. Although any method that will deposit a relatively thin layer of tin upon the aluminum surface of the material can be used, one of the preferred methods is to use an immersion step wherein the thin layer of tin is deposited in a few seconds by immersing the material in an aqueous solution containing Sn<sup>+4</sup> ions. If desired, however, the thin tin layer can be deposited by electrodeposition techniques. The details of both the immersion and electrodeposition techniques are known to those skilled in the art.

In most instances the tin layer is quite thin, that is below about  $3\times10^{-6}$  inches and it is often difficult to determine the exact thickness of the tin layer. An average thickness is generally calculated from the resulting weight gain of a sample of material after it has been in contact with an aqueous solution containing stannate ions and has generally been found to be at least about  $1 \times 10^{-6}$  inches. It is believed that the thickness of the tin layer is not critical since a suitable layer is deposited almost instantly when the aluminum is contacted with the above described solutions. The concentration of Sn+4 ions, pH, temperature and other operating variables are well known to those skilled in the art of tin plating. In most instances the time periods used for the deposition of the various layers will be minimized since short deposition times maximize the production rate.

After the relatively thin tin layer is deposited upon the aluminum surface, a tin-copper alloy is deposited upon the tin layer. A layer having a thickness of at least about  $3\times 10^{-6}$  inches is generally used, with thickness of from about  $3\times 10^{-6}$  to about  $10\times 10^{-6}$  inches being preferred. In most instances it will be preferred to deposit the tin-copper alloy by electroplating. Generally an electroplating bath is used containing copper and stannate ions. In most instances the concentration of tin  $(Sn^{+4}$  basis) in the bath will be maintained within the range of from about 20 grams/liter to about 60 g./liter and the concentration of copper  $(Cu^{+2}$  basis) will be maintained within the range of from about 3 grams/liter to about 12 g./liter. Although the concentrations of the elements in the baths can vary outside the range given above and some of the ad-

vantages of this invention can be achieved, in some instances the quality of the product can be lower, therefore, the foregoing ranges are preferred. Although it is preferred to use an electroplating bath as above described to deposit the tin-copper alloy (generally containing between about 30% and 70% tin) other methods can be used such as multiple immersion, electroplating using a consumable electrode and the like, if desired. In most instances, however, the optimum production rate and quality is obtained when the preferred method is used.

The third step involves the deposition of a nickel layer over the tin-copper alloy layer. It has been found that the thickness of the nickel layer should be from about  $25\times10^{-6}$  inches to about  $50\times10^{-6}$  inches, with thicknesses of from about  $35 \times 10^{-6}$  inches to about  $45 \times 10^{-6}$ inches being preferred. Use of lower thickness, that is less than  $25 \times 10^{-6}$  inches, results in only slight improvements in solderability characteristics. Materials having a thickness of the nickel layer greater than about  $50 \times 10^{-6}$ inches tend to flake.

While any method for depositing the layer of nickel having the foregoing thickness can be used and the benefits of this invention can be achieved, electroplating is the preferred method. One suitable method of deposition is to use a bath which contains nickel ions. If desired, 25 however, a consumable electrode of nickel can be used as the nickel source. In most instances, preferred production rates are achieved when electroplating solutions are used having a concentration of about 100 to 200 grams/liter (Ni<sup>+2</sup> basis).

As can be appreciated, the time required to obtain the desired thickness of nickel will be dependent upon several factors, such as concentration of nickel in the bath, the current density used, the type of aluminum material being plated and the like, in most instances the 35 time will be relatively short, that is, below about 5 minutes and in many instances only a few seconds.

Since the time periods to obtain the layer is relatively short in each instance, the process as described herein is particularly suited for the continuous production of large 40 volumes of materials such as aluminum wire and small thickness aluminum strip.

After the nickel layer is deposited any method can be used to deposit the solderable material over the surface, however, as described herein, it is preferred to use electroplating. Although any solderable material can be used as the fourth layer, a layer of tin or a layer of tin-lead alloy is preferred. If a tin-lead alloy is desired, use of a fluoroborate bath containing the proper concentrations of tin and lead is the preferred method of electroplating. When the relative pure metals such as tin are deposited on the nickel layer, the thickness of the metal layer will be less thick than the nickel layer, however, the thickness will increase if a tin-lead alloy is employed as a solderable material. For example, tin layers can be as low as 50×10<sup>-6</sup> inches whereas when a 60:40 tin-lead alloy is used the thickness is generally from  $50 \times 10^{-6}$  to about 500×10-6 inches. If a tin-lead solder is used it is preferred to use a solder having a 60:40 ratio of tin to lead. Other solderable materials such as copper, other alloys such as copper-tin, copper-zinc, silver-copper-zinc, silverzinc-cadmium can be used. The type of solderable material is not critical, however, the material should be such that when the material is subjected to heat, then soldered and subsequently broken at the solder joint, a fractured segment shows that the fracture occurs in the solder joint rather than in the metal.

The current density used during the electroplating of solderable material will be dependent upon the size of the material, the procedure for depositing the layer and 70 the time requirements in the individual process.

In any event, the material produced has excellent solderability characteristics and the process is adaptable for the production of aluminum wire, plate, aluminum clad or plated materials. The resulting treated material 75 Example I, excellent results are attained.

has a weight advantage over comparable materials of construction such as copper. Furthermore, it is to be noted that the materials which are used in the present invention are relatively inexpensive when compared to the raw materials used in the processes heretofore known.

To further illustrate the preferred embodiments of this invention, the following detailed examples are presented. All parts, proportions and percentages are by weight unless otherwise indicated.

## EXAMPLE I

A sample of .032 inch diameter aluminum wire is cleansed to remove the aluminum oxide coating by standard techniques employing an alkali cleanser followed by immersion in a 50% nitric acid solution. The cleansed aluminum is immersed for less than about 10 seconds in an aqueous solution containing potassium stannate and potassium hydroxide at concentrations of about 45 g./liter (Sn<sup>+4</sup> basis) and about 7 g./liter (KOH basis) respectively. A relatively uniform thin plate of tin is deposited upon the aluminum wire.

The plated aluminum wire is then immersed in a basic aqueous solution containing stannate and copper ions along with potassium cyanide. The concentrations of stannate and copper ions are about 40 g./liter (Sn<sup>+4</sup> basis) and about 8.9 g./liter (Cu<sup>+</sup> basis). The concentration of free KCN in the aqueous solution is about 27 g./liters. A current density of about 300 amperes/sq. ft. is supplied to the wire for about 15 seconds and a copper-tin alloy plate thickness of about  $5 \times 10^{-6}$  inches is deposited on the tin plate.

After the above two plating operations, the wire is transferred to an aqueous bath containing nickel sulfamate, nickel chloride and boric acid. The concentration of nickel ion in the bath is about 140 g./liter (Ni+2 basis). A current density of about 800 amperes/ft.2 is supplied to the wire for about 15 seconds and a nickel plate having a thickness of about  $40 \times 10^{-6}$  inches is plated over the tin-copper alloy plate.

After the nickel plate is deposited, a layer of 50:50 (tin:lead) solder is deposited upon the wire using a current density of about 80 amperes per sq. ft. A solder layer thickness of about 380×10<sup>-6</sup> inches is deposited in about one minute.

The wire containing the solder layer is subjected to soldering tests and found to produce excellent joints when a solder having a tin to lead ratio of about 60:40 is used to solder the wire of this example to other materials of construction. A solder joint, soldered at 450° F. in 10 seconds, and subjected to breaking stress breaks across the solder and not at the aluminum. The layers do not flake off the aluminum even after repeated bending and flexing.

## EXAMPLE II

An aluminum wire having a diameter of about 0.0641 inch (14 gauge) is subjected to essentially the same conditions as in Example I to obtain the cleansing, tin plating and tin-copper alloy plating steps, except that a single solution is prepared for the tin plating step (immersion) 60 and the tin-copper alloy plating step (electrodeposition). Similar thicknesses of tin and tin-copper alloy layers are obtained as in Example I.

The wire, after the two layers are deposited, is immersed in an aqueous solution containing a concentration of 65 nickel of about 140 g./liter (Ni+2 basis) and at a pH of about 4 and about 130° F. to a current density of about 110 amperes/ft. is applied to the wire for a sufficient time to deposit a layer of nickel of about  $40 \times 10^{-6}$  inches thick upon the tin-copper alloy layer.

After the nickel layer is deposited, the wire is electroplated with a layer of tin having a thickness of  $10 \times 10^{-6}$ inches. An aqueous electroplating bath containing a concentration of stannate ions of about 60 g./liters is used.

When the wire is subjected to similar solderability as in

Substantially similar results are obtained when other water-soluble copper, tin and nickel sources are substituted in substantially stoichiometric amounts for the water-soluble copper, tin and nickel sources of this example. Additionally, similar solderability results are achieved when relatively thin aluminum sheet is substituted for the wire of the above examples. Best results are obtained when aluminum plate has a thickness from about 0.004 inch to about 0.1 inch.

While there has been shown and described what is at 10 present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined in the appended claims.

We claim:

- 1. A process for rendering a material having an aluminum surface solderable comprising:
  - (a) depositing upon said aluminum surface a relatively thin first layer consisting essentially of tin;
  - (b) depositing upon said first layer a second layer consisting essentially of a tin-copper alloy and having a thickness of at least about  $3 \times 10^{-6}$  inches;
  - (c) depositing upon said second layer, a third layer of from about  $25 \times 10^{-6}$  to about  $50 \times 10^{-6}$  inches;
  - (d) depositing upon said nickel layer, a layer of a solderable material selected from the group consisting of tin, copper and alloys selected from the group consisting of copper-tin, copper-zinc, silver-copper- 30 zinc and silver-zinc-cadmium.
- 2. A process according to claim 1 wherein said first layer is deposited by immersing said material in an aqueous solution containing stannate ions for at least about 5 seconds.

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- 3. A process according to claim 2 wherein said second layer is deposited by electroplating using a bath containing copper and stannate ions.
- 4. A process according to claim 3 wherein said solderable material is selected from the group consisting of tin and tin-lead alloys and where said layer has a thickness of from about  $5\times10^{-6}$  to about  $500\times10^{-6}$  inches.
  - 5. A process according to claim 1 wherein said nickel layer is deposited by electroplating.
- 6. A process according to claim 5 wherein said first layer is deposited by immersing said material in an aqueous solution containing stannate ions for at least about 5
- 7. A process according to claim 6 wherein the thickness 15 of said nickel layer is from about  $35 \times 10^{-6}$  inches to about  $45 \times 10^{-6}$  inches.
- 8. A process according to claim 6 wherein said solderable material is selected from the group consisting of tin and tin-lead alloys and where said layer has a thickness of from about  $5\times10^{-6}$  to about  $500\times10^{-6}$  inches.
  - 9. A process according to claim 8 wherein said second layer is deposited by electroplating using a bath containing copper and stannate ions.
- 10. A process according to claim 9 wherein the thickconsisting essentially of nickel and having a thickness 25 ness of said nickel layer is from about 35×10-6 inches to about  $45 \times 10^{-6}$  inches.

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