Patented Feb. 20, 1945

2,370,108

UNITED STATES PATENT OFFICE

2,370,108

METHOD OF MAKING BIMETAL BOND

Robert D. Pike, Piedmont, Calif.

No Drawing. Application August 7, 1939, Serial No. 288,831

4 Claims. (Cl. 204—34)

The present invention relates to the bonding together of metals of widely different characteristics such as ferrous metals and certain non-ferrous metals and particularly to preparation of the ferrous metal for electro-deposition of the other metal thereon to form an extremely strong bond.

An example of a metal bond which is frequently required to have great strength is that between copper and iron or steel, and the present invention will be described in its application to such metals; but the description is not to be taken as limiting the invention to specific metals named, as the possibility of applying the invention to bonds between other metals will be apparent.

It is common practice to deposit copper on iron or steel by electro-deposition for the purpose of forming a thin plating of the copper, and even to build up a relatively thick layer of copper upon the surface of the iron or steel. Electro-deposition to form a bi-metal bond is desirable because it results in the deposit on the steel of copper in a very pure state. A deposit of pure copper is advantageous because the metal retains its softness, its high degree of thermal and electrical conductivity, and other qualities of the pure metal which are valued for different uses and which are often lost in other methods of bonding wherein there is more or less alloying of the metals bonded. The bond formed by ordinary electro-deposition of copper upon steel is sufficiently strong for ordinary purposes of electro-plating practice where a thin layer only of the electro-deposited metal is required. Where the metal is deposited in thicker layers, however, and particularly where working or bending of the metal is to take place after the bond has been made, the bond frequently fails, and it is the object of the present invention to provide a method for producing a strong bond between iron or steel and copper, and to produce a bond wherein the copper may be electrically deposited to considerable thickness, and which will be so strong that the two metals may not be separated by mechanical means but will act, upon being bent and subjected to other strains, substantially as one metal.

A further object is to provide a method of preparing a ferrous metal for the reception of an electro-deposited non-ferrous metal thereon which will result in an unusually strong bond between the metals.

A further object is to provide an exceptionally strong bi-metal bond in which there is no alloying of the two metals bonded.

A still further object is to provide a method of making a strong bond between copper and steel in which the copper retains a very high degree of purity and thus retains its softness, conductivity, and other native characteristics.

I have discovered that ordinary methods of electro-deposition of copper upon steel do not result in a bond which may be termed integral or sufficiently strong to permit of its being subjected to severe strain without separation. By severe strain I mean, for example, cold bending of a bi-metal strip made by hammering to form a flat bend through 180°. The reason for the failure of the ordinary bond when subjected to a test of this kind is apparently due to the fact that the steel is not properly cleaned before the copper is deposited thereon. I have found that in current practice of pickling and cleaning of steel, a certain amount of hydrogen is adsorbed or absorbed on the surface of the steel. The presence of this hydrogen is of course indiscernable to the eye, and though the steel appears perfectly clean and bright, it carries this coat of adsorbed or absorbed hydrogen which prevents a full molecular joining of copper when it is electrically deposited thereon, resulting in a bond between the two metals which is readily disrupted by severe working or bending stresses.

According to present practice, when copper is to be electro-deposited directly upon iron or steel, the steel is first plated with a thin layer or strike of copper in a so-called copper cyanide plating bath. When copper is deposited from such a bath, some hydrogen is also electro-deposited with it, and if the surface of the steel already contains adsorbed or absorbed hydrogen, this condition is accentuated with the result that an infinitesimally thin layer of hydrogen is interposed between the copper and the steel, preventing the desired full molecular joining of the two metals. The purpose of this initial thin plating of strongly adherent copper which is effected in the copper cyanide plating bath is to provide a copper surface on the steel upon which the desired relatively thick layer of copper may be built up by electro-deposition. This thick layer is ordinarily deposited in an acid copper sulphate plating bath of well-known composition in which the piece to be plated is placed, after it has been removed from the cyanide plating bath, and after it has been washed with water. According to this method, copper may be deposited, as is well-known, to any desired thickness at high cur-

rent efficiency, or the thick layer of copper may be deposited from a cyanide plating bath of suitable well-known composition for this purpose, or from other suitable electrolytes. In many cases a thick coating of nickel from suitable well-known electrolyte is employed in place of both the initial and thick coatings of copper. Hydrogen is deposited with nickel in the same manner that it is with copper, but the present invention is just as effective in eliminating the hydrogen and producing a stronger bond with the use of either metal. Practice of the present invention completely overcomes the effect of adsorbed or absorbed hydrogen on the steel by substituting oxygen as the adsorbed or absorbed gas before the steel is placed in the plating bath.

As an example of a practical application of the invention, blue annealed steel sheets to which copper is to be bonded are de-greased by any conventional means and then placed in a hot acid pickling bath to effect removal of scale. These sheets, after having been pickled in any solution conventionally used for this purpose, may present a clean metallic appearance to the eye, although their surfaces contain adsorbed or absorbed hydrogen. In order to remove this hydrogen and to present a surface better adapted to a firm bond with an electro-deposited metal, the sheets are placed as anodes in a hot alkaline bath, say 190 to 200° F., at a current density of 4 amps. per square foot for a period of five to ten minutes, or until a film of brown iron oxide appears on the steel. The formation of this film of oxide is evidence not only that the hydrogen has been removed from the surface of the sheets but also that an excess of oxygen has been present for some time under anodic conditions resulting in the formation of actual oxide of iron and also in the adsorption and absorption of oxygen itself by the steel. The iron oxide so deposited is loosely adherent to the surface of the steel and must be cleaned off prior to the plating operation. Vigorous brushing, for example, with wire brushes will suffice to remove the oxide, or it may be removed if desired by a high pressure needle water spray or by other suitable mechanical means.

Next the steel is etched, as is common practice, by immersion for 30 to 60 seconds as an anode, for example, in a 55° Bé. bath of sulphuric acid at a current density of about 8 amps. per square foot. This etching step may, as is well-known, be employed prior to electro-deposition and, while it serves to an extent to produce a better bond between the steel and the electrically deposited metal, it is insufficient, if hydrogen is present on the surface of the steel, to produce a bond comparing in strength with that of the present invention. After removal from the sulphuric acid etching bath or its equivalent, the plates may be stored, until the time for placing them in the cyanide copper plating bath, in a solution of about 10% sodium cyanide. They will preferably remain in the cyanide copper plating bath for a period of about 5 to 10 minutes at a current density of 4 to 8 amps. per square foot under bath conditions yielding a cathodic current efficiency of 30 to 50 per cent, under which conditions considerable gassing takes place on the cathodes. They are then removed, rinsed in water, and placed in the acid sulphate plating bath.

The steel is left in the acid sulphate bath for a length of time determined by the thickness of the copper desired to be plated thereon. If a thick plate of copper is desired only on one side of the sheet or on certain portions of the sheet, they may be removed from the bath and the areas where the copper is not required may be coated with a conventional stop-off lacquer. Sheets of steel with copper bonded thereto in the manner above described have been subjected to flat cold bending through 180° by hammering, either with the copper layer on the inside or on the outside without disrupting the bond between the copper and the steel. The extremely strong bond resulting from the practice of the method set forth above is apparently due to the fact that the hydrogen has been removed from the surface of the steel and replaced by oxygen before the first layer of copper, nickel, or other equivalent non-ferrous metal as the case may be, is deposited thereon. When the hydrogen is deposited on the cathode at the beginning of the initial plating operation, it is in nascent condition and reacts with the adsorbed or absorbed oxygen on the steel surface forming water. This reaction leaves the surface of the steel in a perfectly clean condition and substantially free from adsorbed gases. In this condition of the steel, the copper or other metal deposited thereon forms a molecular contact or junction with the steel far superior to that which is possible when hydrogen is present on its surface. After electro-deposition of the copper or other metal to the desired thickness or slightly greater than that thickness, it may be mechanically milled or otherwise machined to present a smooth surface and uniform thickness. If it is desired to obtain the full softness of the copper or other metal, the bi-metal sheets may be annealed, and annealing also effects removal of any residual gas from the bond which may possibly have escape removal at the start of the initial plating bath in the manner set forth above. Annealing may be satisfactorily accomplished at a temperature of 1000 to 1750° F. in a reducing atmosphere for about a half hour. The bonded sheets may then be worked or shaped hot or cold suitable to any purpose for which they are to be used.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. The method comprising integrally bonding a non-ferrous metal to an iron base and forming a composite unit capable of withstanding hot and cold working without separation, comprising removing scale from said iron base, subjecting the latter as an anode to electrolytic action in a hot alkaline bath having a temperature not exceeding approximately 200° F. at a current density of about 4 amps. per square foot for 5 to 10 minutes until a loosely adherent film of iron oxide is produced on the iron base, mechanically removing said film from the base, etching the so-treated iron base by treating said iron base with acid, as an anode, to prevent hydrogen formation on the surface thereof, and depositing by electrodeposition an integrally bonded coating of a non-ferrous metal on the iron base.

2. The method comprising integrally bonding copper to an iron base and forming a composite unit capable of withstanding hot and cold working without separation, comprising removing scale from said iron base, subjecting the latter as an anode to electrolytic action in a hot alkaline bath having a temperature not exceeding approximately 200° F. at a current density of about 4 amps. per square foot for 5 to 10 minutes until a loosely adherent film of iron

oxide is produced on the iron base, mechanically removing said film from the base, etching the so-treated iron base by treating said iron base with acid, as an anode, to prevent hydrogen formation on the surface thereof, and depositing by electrodeposition an integrally bonded coating of copper on the iron base.

3. The method comprising integrally bonding a non-ferrous metal to an iron base and forming a composite unit capable of withstanding hot and cold working without separation, comprising removing scale from said iron base, subjecting the latter as an anode to electrolytic action in a hot alkaline bath having a temperature not exceeding approximately 200° F. at a current density of about 4 amps. per square foot for 5 to 10 minutes until a loosely adherent film of iron oxide is produced on the iron base, mechanically removing said film from the base, etching the so-treated iron base by treating said iron base with acid, as an anode, to prevent hydrogen formation on the surface thereof, depositing by electrodeposition an integrally bonded coating of a non-ferrous metal on the iron base, and annealing the composite unit at a temperature varying between 1000° and 1750° F. in a reducing atmosphere to remove any gaseous compounds from between the iron base and its coating.

4. The method comprising integrally bonding copper to an iron base and forming a composite unit capable of withstanding hot and cold working without separation, comprising removing scale from said iron base, subjecting the latter as an anode to electrolytic action in a hot alkaline bath having a temperature not exceeding approximately 200° F. at a current density of about 4 amps. per square foot for 5 to 10 minutes until a loosely adherent film of iron oxide is produced on the iron base, mechanically removing said film from the base, etching the so-treated iron base by treating said iron base with acid, as an anode, to prevent hydrogen formation on the surface thereof, depositing by electrodeposition an integrally bonded coating of copper on the iron base, and annealing the composite unit at a temperature varying between 1000° and 1750° F. in a reducing atmosphere to remove any gaseous compounds from between the iron base and its coating of copper.

ROBERT D. PIKE.