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Jackson et al.

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[54] **METHOD OF PROVIDING AN ALUMINUM COATING ON A STEEL SUBSTRATE**

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[30] **Foreign Application Priority Data**

Nov. 3, 1972 United Kingdom.............. 50773/72

[52] **U.S. Cl.**....... **148/11.5 A;** 29/192 CP; 29/196.1; 29/196.2; 29/197; 29/527.2; 75/208 CS; 117/22; 204/37 R; 204/38 S

[51] **Int. Cl.**.................................. **C21d** ; B22f 7/00

[58] **Field of Search**........ 204/37 R, 385, ; 117/201, 117/215, 217, 230, 29, 22; 29/192 GP, 194, 196.1, 196.2, 197, 527.2; 148/11.5 A; 75/208 CS

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[57] **ABSTRACT**

A method of providing a surface of a steel substrate with an aluminum coating, the said method comprising coating the said surface of the steel substrate with a layer of metal, coating the said metal layer with a layer containing aluminium powder, the aluminium powder forming an alloy with the steel substrate at a predetermined elevated temperature, compacting the said metal and powder layers to the substrate, effecting a cold reduction, and effecting a subsequent annealing heat treatment to make the metal and powder layers adhere tightly to the substrate, and thus provide the substrate with the said aluminium coating, the metal layer serving to control nucleation of the said alloy which is formed at the said predetermined elevated temperature.

13 Claims, No Drawings

METHOD OF PROVIDING AN ALUMINUM COATING ON A STEEL SUBSTRATE

This invention concerns a method of providing an aluminium coating on a steel substrate.

If a conventional aluminium coated steel substrate, in which the substrate has aluminium directly coated thereon, is cold reduced and recrystallisation annealed, the annealing temperature is limited by the fact that if a certain temperature is exceeded, then nucleation and growth of a brittle, intermetallic, iron-aluminium alloy will occur and the bond between the aluminium coating and the steel substrate will deteriorate. This temperature is dependent upon the chemical composition of the steel substrate and can be as low as 500°C in the case of some rimming steels. However, it is in practice necessary for the annealing temperature to exceed 500°C if the annealing is to be adequate to compensate for the effects of the cold reduction.

According to one particular aspect of the present invention, there is provided a method of providing a surface of a steel substrate with an aluminium coating, the said method comprising coating the said surface of the steel substrate with a layer of metal, coating the said metal layer with a layer of or containing aluminium powder, the aluminium powder forming an alloy with the steel substrate at a predetermined elevated temperature, compacting the said metal and powder layers to the substrate, effecting a cold reduction, and effecting a subsequent annealing heat treatment to make the metal and powder layers adhere tightly to the substrate and thus provide the substrate with the said aluminium coating, the metal layer serving to control nucleation of the said alloy which is formed at the said predetermined elevated temperature.

If desired, after compacting the said metal and powder layers and before effecting the cold reduction, the compacted substrate may be subjected to an additional heat treatment.

We think that the provision of the said metal layer, which is preferably composed of iron, retards the nucleation of an iron/aluminium alloy layer by raising the temperature below which little or no nucleation occurs.

We think that when nucleation commences, the growth of the alloy from given nucleates is very rapid due to the fast rate of reaction at the raised nucleation temperature. As a result, the risk of blistering and delamination may be reduced. Thus the nucleation appears to be controlled such that the alloy grows in a "toothy" pattern into the aluminium layer, thereby promoting adhesion of the layers to each other.

Thus the present invention enables one to produce in a single continuous manufacturing process a cold reduced aluminium coated steel substrate in which the risk of delamination of the aluminium coating is reduced.

The gauge of the so-coated substrate preferably undergoes a reduction of at least 30 percent in the course of the said cold reduction. Thus the reduction in gauge may be substantially in the range of 50 to 90 percent.

The original substrate may have a gauge in the range 0.1 inch to 0.04 inch.

The annealing heat treatment may be a re-crystallisation anneal which is effected at a temperature within the range of 500° to 550°C.

Preferably compaction is effected by passing the coated substrate between a pair of rollers, and the substrate, prior to passing between the rollers, may be wetted with a liquid which reduces the extent to which the said rollers dislodge the aluminium powder.

The metal layer is preferably an electrolytically deposited layer of iron.

The powder layer may be made up of aluminium particles which are applied to the substrate in an electrostatically charged condition, the average particle size of the aluminium particles not exceeding 40 microns.

Alternatively, the powder layer containing the aluminium powder may contain aluminium powder whose average particle size does not exceed 40 microns and also contains a finely divided silicious material which causes the aluminium powder to flow substantially more readily than it would in the absence of the silicious material, the silicious material constituting not more than 0.5 percent by weight of said powder layer. Thus the silicious material may comprise particles of silica each of which has been provided with an hydrophobic organic coating.

Yet again, the powder layer may be applied to the steel substrate in the form of a slurry. This slurry may be dried before it is compacted to the substrate.

The slurry may contain silica.

Alternatively, the slurry may contain a water soluble cellulose ether.

The invention also comprises a steel substrate provided with an aluminium coating by the method set forth above.

The invention is illustrated in the following Examples.

EXAMPLE I

A mild steel strip to be coated, having a gauge in the range 0.1 inch to 0.04 inch, is wound from a roll thereof and passes at a speed of up to 300 feet per minute through a de-greasing bath where the strip is degreased by a conventional de-greasing liquid. It is then rinsed in cold water whereafter it is pickled in pickling baths. The pickling baths may contain dilute nitric acid, e.g. they may contain 5 percent by weight nitric acid, and in addition may contain 25 grams per litre of urea so as to inhibit the accumulation in the baths of nitrous acid and oxides of nitrogen which if allowed to accumulate would render the baths inactive. Alternatively, the pickling baths may contain sulphuric or hydrochloric acid.

The strip is then rinsed, whereafter it passes successively to two electrolytic plating baths where layers of iron are electrolytically applied to both the opposite surfaces of the strip. Each of the electrolytic plating baths contains an aqueous solution of an iron-salt such as ferrous chloride or ferrous sulphate, when the pickling baths contain hydrochloric acid or sulphuric acid then the waste pickle liquor therefrom may be employed in the electroplating baths.

After passing through the electro-plating baths the strip is rinsed and is then dried. The strip then passes to a powder coating station where one surface of the strip has a solution of sodium (or potassium) silicate sprayed onto it, e.g., in a quantity amounting to 1.5 cc per square foot of the strip, the concentration of the sodium silicate in the said solution being 3 grams per litre.

The strip then passes beneath a feed tray which is arranged to receive a powdered coatant from a hopper. The feed tray has vibratory pulses imparted to it, to cause the particles of powdered coatant to move there-over and to fall onto the adjacent surface of the strip.

The powdered coatant in the hopper consists of a mixture of aluminium powder and silica particles, the silica particles constituting 0.001 percent by weight of the mixture. The aluminium powder may pass a 300 mesh sieve and have an average particle size which does not exceed 40 microns, and preferably does not exceed 30 microns. For example, the average particle size of the aluminium powder may be 20 microns.

Each of the particles of silica has been provided with an hydrophobic organic coating, e.g., of dimethyl chlorosilane. Thus very pure silica produced by flame hydrolysis may be reacted in an inert atmosphere at 400°C with dimethyl chlorosilane and steam so as to produce such coated silica particles. Such coated silica particles are available commercially under the Trade Names "Silica D17" and "Aerosil R972."

The average particle size of the silica particles should preferably not exceed 30 millimicrons and may for example be 22 millimicrons, while the bulk density of the silica should preferably not exceed 40 grams per litre and may for example be 30 grams per litre.

The apparatus constituted by the said feed tray and hopper may for example be as disclosed in British Specification No. 1,094,157 although of course this apparatus is suitable for use with the powdered coatant described above only because the latter comprises the said silica particles.

The strip then passes over further rollers so as to reverse the one of its surfaces which is uppermost. The non-coated surface thus now passes beneath a powder coating station which corresponds to the powder coating station described above, and which is arranged to wet the last-mentioned surface with sodium or potassium silicate solution. The last-mentioned surface then passes under a vibrating feed tray which receives the said powdered coatant from a hopper. As will be appreciated, the strip, after leaving the last-mentioned hopper, has been both wetted and coated on both of its opposite surfaces.

The strip then passes through drying stations each of which incorporate a high frequency heater.

The coated strip is then sprayed at the rate of 3 cc per square foot with a 0.2 percent colloidal solution of sodium carboxymethylcellulose and is thereafter dried, the strip then being passed between a pair of rollers of a rolling mill which compacts the layers of aluminium powder and iron to the steel substrate.

The spraying of the strip with the sodium carboxymethylcellulose reduces the extent to which the said rollers would otherwise dislodge the aluminium powder. Thus there is a reduced tendency for banks of dislodged powder to build up immediately ahead of the rollers and thereby prevent the strip being moved at high speeds.

The compacted strip is then coiled for a sintering heat treatment in which the aluminium and iron layers are caused to adhere tightly to each other and to the steel substrate and thus provide the latter with an aluminium coating. Thus the heat treatment may comprise heating the coil in air for 15 to 20 hours at 300° to 500°C, preferably 350°C, whereby bonding and sintering occurs.

The so-coated steel substrate is then subjected to a cold reduction in gauge in the range of 50 to 70 percent so as to reduce the coated substrate to its final gauge, this being then followed by an annealing heat treatment comprising a re-crystallisation anneal e.g., for 24 hours, at a temperature in the range of 500° to 550°C.

If desired, this annealing heat treatment may be such as to effect the sintering and bonding referred to above, in which case the said sintering heat treatment, which is effected after compaction and coiling may be omitted.

In the course of the said cold reduction, the length of substrate is, of course, correspondingly increased.

Thus assuming that the cold reduction is one of 50 percent, it is necessary to provide an aluminium powder layer having double the thickness required (which may be 0.0015 inch), of the final material.

EXAMPLE II

A hot rolled mild steel strip to be coated, having a gauge of 2.19 mm and a width of 1,000 mm, is wound from a 10 ton coil thereof and de-greased in a conventional hot alkaline de-greasing liquid. It is then rinsed in cold water, after which it is pickled in a pickling bath containing 5 percent by volume of cold hydrochloric acid.

The strip is then rinsed whereafter it passes to an electrolytic plating bath where both the opposite surfaces of the strip are simultaneously plated with 1.75 micron layers of iron. The electrolytic plating bath comprises an aqueous solution containing 100 grams per litre of ferrous chloride tetrahydrate and 10 grams per litre of tri-sodium citrate, the bath being operated at 50°C and 2,700 amps per square metre. The electroplated strip is then rinsed and dried.

The top surface of the electroplated strip is now wetted with 5.0 cc per square metre of a solution containing 8 grams per litre of sodium silicate (e.g., the sodium silicate commercially available as "Crosfields 100 alk grade"). The wetted top surface of the electroplated strip is now coated with 250 grams per square metre of aluminium powder having an average particle size of 25 microns. the powder being applied from a vibrating table through a vibrating wire grid which is electrostatically charged to a voltage of –20 Kv. The passage of the powder particles through the grid causes the particles to be electrostatically charged and thus mutually repelled and then attracted to the strip, which is earthed, to give a uniform, dense coating.

The electroplated strip whose top surface has been so wetted and coated is then passed around rollers to reverse its direction of movement, and the opposite side of the electroplated strip is then similarly wetted with sodium silicate solution and electrostatically coated with a layer of aluminium powder.

The coated strip is then passed through a radiant gas-fired oven to remove moisture, but the aluminium powder continues to adhere to the underside of the coated strip because the sodium silicate acts as a binder. The coated strip then passes through a rolling mill where the powder is compacted to the electroplated steel substrate to form a coherent foil.

This strip is then recoiled and heat-treated in air in a conventional annealing furnace for 16 hours at 350°C. It is then cold reduced to a finished gauge of 0.55 mm on a reversing mill, annealed at 525°C for 16 hours and finally temper rolled.

EXAMPLE III

A mild steel panel, having a gauge in the range of 0.1 inch to 0.04 inch, is degreased, rinsed in cold water, and pickled in nitric acid. The panel is then electroplated with iron in electroplating baths containing an aqueous solution of an iron salt such as ferrous chloride or ferrous sulphate. Thereafter the panel is rinsed and then dried.

The panel is then immersed in and withdrawn at a steady rate from a bath containing an aqueous aluminium powder slurry formed from aluminium powder, of a particle size not exceeding 300 mesh per linear inch, the slurry having the following composition:

Aluminium Powder	400 gms
Water	300 gms
$Na_2O.2\ SiO_2$	1.7 gms
NH_4NO_3	2.4 gms
HNO_3	up to pH = 9.0

Total volume of above slurry 520 mls. The bath thus contains precipated silica in an amount sufficient to give buoyancy to the slurry and confer a degree of thixotropy thereto. By varying the quantities of aluminium powder and silica in the slurry, different viscosities of slurry can be achieved, and this can in turn control the thickness of the coating applied to the panel.

The coated panel is now dried at a temperature of 100°C and is passed between a pair of rollers of a rolling mill which compacts the aluminium powder and electroplated iron to the steel plate, the passage through the said rolling mill producing a reduction in thickness of 5 to 7 percent.

The coated panel is then heated in air at 350°C, whereby bonding and sintering occur, after which the coated panel is subjected to a cold reduction to produce a final foil thickness in the range 38 to 60 microns (0.0015 inch to 0.0023 inch). Finally, the product is given a re-crystallization anneal for 24 hours at a temperature in the range of 500° to 550°C.

The withdrawal of the panel from the slurry bath may be constituted by vertical withdrawal.

Alternatively, instead of immersing the panel in a slurry bath, the slurry, mentioned above may be applied to the panel by a reverse roller coater as in the conventional paint coating of metal strip.

EXAMPLE IV

The procedure is the same as in Example III except that the panel, instead of being immersed in a slurry bath, is sprayed with the slurry by the use of compressed air. The slurry employed is thinner i.e. employs more water, than that of Example III, and may for example, be as follows:

Water	280 grams
$Na_2O.\ 2SiO_2$	1.5 grams
Ammonium nitrate	1.9 grams
Aluminium powder	300 grams
Nitric acid	Present in an amount to adjust the pH of the slurry to 9.0

Such a slurry may be used to build up a coating of any desired thickness, using known spray painting technology.

EXAMPLE V

The procedure is the same as in Example III except that the panel instead of being immersed in a slurry bath, is curtain coated, at a speed of up to 240 ft/minute, with a slurry of the following composition:

Water	400 g
Sodium carboxy methyl cellulose F1000	1 g
Sodium dichromate (inhibitor)	0.4 g
Aluminium powder (the maximum size of whose particles is in the range of 120 to 400 mesh per linear inch)	600 g

(The term F1000 indicates a grade of sodium carboxy methyl cellulose marketed by British Celanese Limited and producing very viscous solutions of low solids content).

The slurry also preferably includes a surfactant such, for example, as an alkyl aryl sulphonate.

If desired, the inhibitor used, instead of being sodium dichromate, could be sodium silicate, sodium chromate, or di-ammonium hydrogen phosphate.

The slurry is made up by first dispersing the water soluble cellulose ether e.g., sodium carboxy methyl cellulose, in the water, and leaving it for an appropriate swelling period. After this the inhibitor is first added, and subsequently the aluminium powder (and the surfactant, if employed).

This particular slurry, after the adjustment of its viscosity by the addition of further water, could also be deposited on the panel by roller coating.

Because of the physical nature of the slurries of Examples III to V, it is not necessary to wet the dried slurries with the sodium carboxy methyl cellulose which is used in Example I to reduce the extent to which the rollers would otherwise dislodge the coating.

We claim:

1. In a method of providing a surface of a steel substrate with an aluminium coating, the said method comprising electroplating the said surface of the steel substrate with a layer of iron, coating the iron layer with a layer containing aluminium powder, and compacting the said iron and powder layers to the substrate, the improvement which consists of subsequently effecting a cold reduction which reduces the gauge of the so-called substrate by at least 30 percent, and effecting a subsequent recrystallisation annealing heat treatment to make the iron and powder layers adhere tightly to the substrate.

2. A method as claimed in claim **1** in which, after compacting the said iron and powder layers and before effecting the cold reduction, the compacted substrate is subjected to an additional heat treatment in the range 300° to 500°C.

3. A method as claimed in claim **1** in which the reduction in gauge is in the range of 50 – 90 percent.

4. A method as claimed in claim **1** in which the original substrate has a gauge in the range 0.1 inch to 0.04 inch.

5. A method as claimed in claim **1** in which the recrystallisation anneal is effected at a temperature within the range of 500° to 550°C.

6. A method as claimed in claim **1** wherein compaction is effected by passing the coated substrate between a pair of rollers, the substrate, prior to passing between the rollers, being wetted with a liquid which reduces the extent to which the said rollers dislodge the aluminium powder.

7. A method as claimed in claim **1** in which the powder layer is made up of aluminium particles which are applied to the substrate in an electrostatically charged condition, the average particle size of the aluminium particles not exceeding 40 microns.

8. A method as claimed in claim **1** in which the powder layer contains aluminium powder whose average particle size does not exceed 40 microns and also contains a finely divided silicious material which causes the aluminium powder to flow substantially more readily than it would in the absence of the silicious material, the silicious material constituting not more than 0.5 percent by weight of the said powder layer.

9. A method as claimed in claim **8** in which the silicious material comprises particles of silica each of which has been provided with an hydrophobic organic coating.

10. A method as claimed in claim **1** in which the powder layer is applied to the steel substrate in the form of a slurry.

11. A method as claimed in claim **10** in which the slurry contains silica.

12. A method as claimed in claim **10** in which the slurry contains a water soluble cellulose ether.

13. A method as claimed in claim **10** in which the slurry contains a chromate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,884,729
DATED : May 20, 1975
INVENTOR(S) : Albert Edward Jackson and Ernest Wayne Williams

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE CLAIMS:

Claim 1, line 8, delete "so-called" and insert --so-coated--

Signed and Sealed this
twentieth **Day of** *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks