June 30, 1936. A. O. RODRIGUEZ 2,046,036

METHOD OF COATING FERROUS BODIES WITH OTHER METALS

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FIG. 1

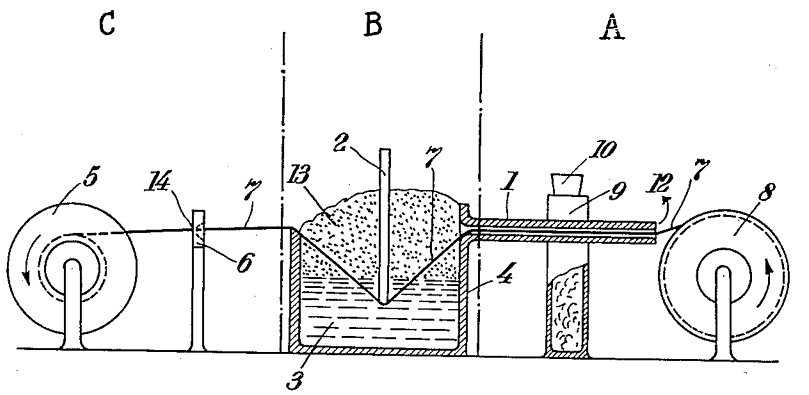
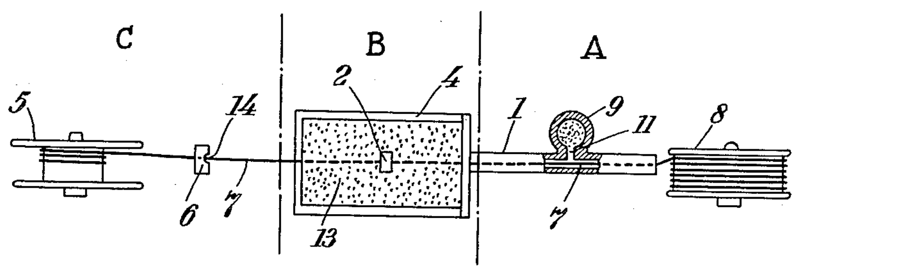


FIG. 2



Inventor:
Anselmo O. Rodriguez
By Hoguet Neary
His Attorneys

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METHOD OF COATING FERROUS BODIES WITH OTHER METALS

Anselmo Ortiz Rodriguez, Valverde-Leganes Badajoz, Spain

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Some of the methods previously used for coating ferrous bodies with other metals, such as tin, zinc, etc., by heat, consist essentially in causing the said bodies, previously deoxidized by being passed through acid baths, to pass through and be wetted by the molten metal contained in a crucible.

These methods have the following disadvantages:

The acid baths remove the oxides of iron, but the ferrous bodies, after passing through them, contain impurities on their surfaces, which the acids have not removed, such as carbon, residual moisture, occluded air, etc. The carbon does not solder with the metals used for coatings, and the oxygen of air or occluded water produces oxides that remain incrusted in the coatings. The consequence is that the metallic layers obtained are not continuous, but show pores or gaps that impair the quality of the coating.

In the case in which the coating comprises a metal with the characteristics of aluminium, these superficial impurities of the ferrous body prevent the adherence of any coating and are the cause of the failure of the many attempts made to cover ferrous objects with aluminium.

In these prior methods ferrous objects enter the bath of molten metal at a very low temperature, and must be heated to the temperature necessary for union by remaining for a more or less long time in the mass of molten metal. When working with metals of high melting point, like zinc or aluminium, or with objects of a relatively large mass or thickness, or when it is desired to increase the output of the plant, the bath of molten metal must be of extraordinary size, and furnaces of large dimensions are required in order to hold the considerable quantity of metal. These furnaces are costly to install and repair, and they are expensive to operate because of the great waste of heat radiated from their large surfaces.

I have found that metallized ferrous products without the aforesaid disadvantages, and in which all the impurities present on the surface of the objects that hinder or prevent perfect metallization are completely removed, may be obtained by plunging the ferrous object into the bath with the object at a temperature as high as desired, whereby the following advantages are obtained.

1. Because the ferrous object enters the bath with its surface free from impurities of all kinds and therefore a surface of pure iron, a perfect continuous soldering is obtained and a coating is produced without pores, oxides or gaps, and therefore of better quality.

2. Because the ferrous object enters the bath at a temperature very near that of the bath, the latter is not cooled, and the object does not need to stay in the mass of the metal more than the time necessary for it to be wetted thereby. Thus, both the size and the number of baths of molten metal are greatly reduced, and a similar reduction is effected in the cost of the crucibles, the quantity of metal necessary, the cost of repairs and renewals, the radiant surface, etc.

3. The output of coated metal may be increased by lengthening the time of the preliminary treatment at high temperatures, without the necessity of increasing the length or number of the baths of metal. Because the cost of installation and operation for the preliminary treatment is small, a production much higher than that secured by modern plants can be obtained at a small cost, and thereby a great increase in the output is secured with the same mechanical equipment as exists at present.

Hereinafter and by way of example the process is described as it may be applied to the production of aluminium-coated ferrous bodies susceptible of being mechanically produced in a continuous manner, such as wire, strips, sheets, etc.

First, the rolls or bundles of wire, strips or sheets must be cleaned as effectively as possible to remove from their surface the oxides and other impurities, such as grease, etc. For example, they are treated with acid and alkaline solutions, in the usual way, followed by washing and drying. They are then fitted into any mechanical device that causes them to pass in a continuous, uniform and constant manner, through a furnace or apparatus that is the subject of this invention.

This furnace or apparatus is composed of three parts or zones, through which the wire, strip or sheet must pass successively and in the same order as described.

A. Purifying and heating part or zone.
B. Metallization part or zone.
C. Cooling part or zone.

Referring to the attached drawing, Figures 1 and 2 show these parts schematically.

The purifying and heating zone is composed of a hollow body, 1, which may be a tube, and the retort 9; they must be of material that is both fire-proof and impervious to the gases passing through them, and are joined hermetically to and in communication with the zone B, which is composed of the metal or alloy 3, maintained in a liquid state in the crucible 4.

The cooling zone C is the space included between the surface of the bath and the drawing roller 5. In this zone is the wiper 6, consisting essentially of a metallic member having an orifice 14, through which passes the wire, strip or sheet.

Parts A or B are maintained, by any source of heat, at the temperatures to be specified later, and are fixed in the interior of a furnace of refractory material.

In the system formed by the three foregoing parts, the wire, strip or sheet 7, coming from the reel 8, enters the hollow body 1.

To remove the impurities from the ferrous object, it is passed through an atmosphere of gases or vapours that circulate continuously through the interior of the body 1 and are produced within or outside of that body by any process.

The chemical nature of these gases or vapours must be such that they combine with the impurities of the wire, strip or sheet, forming compounds which are volatile at the temperature of the zone A, in order that they may be continuously eliminated from this zone in a state of vapour and do not form deposits, the accumulation of which would impede the efficient working of the system.

Ammonium chloride (NH_4Cl) vapours, at red heat or at 500° to 700° C. are found to be particularly advantageous in practice.

The ammonium chloride may be introduced into the apparatus by any process, for instance, in a solid state into the interior of the retort 9, by raising the plug 10.

The temperature of the retort 9 must be so graduated as to generate a continuous emission, as regular as possible, of the NH_4Cl vapours.

The vapours of NH_4Cl leave the retort through the conduit 11, which likewise communicates with the hollow body 1, through which they circulate continuously and issue at the open end 12.

At a temperature of 500° to 700° C. corresponding to that of the hollow body 1, a reaction is set up between the NH_4Cl vapours and the iron of the wire, strip or sheet, according to the equation:

$$2NH_4Cl+Fe=FeCl_2+2NH_3+H_2 \text{ (Equation I)}$$

The ammonia in a nascent state combines with the carbon of the ferrous material used according to the equation:

$$2NH_3+C=NH_4CN+H_2 \text{ (Equation II)}$$

This ammonium cyanide, in conjunction with the nascent hydrogen produced in the process as represented by both the preceding reactions and with the excess of ammonia not combined with the carbon—all of which are reducing substances in the operating conditions—combines rapidly with the small quantity of oxygen that the wire, strip or sheet may contain, whether in the form of residues of oxides not dissolved in the acids or of occluded air, forming water that is eliminated in the gaseous current.

At the red-heat temperature of the hollow body 1, the chloride or chlorides of iron formed according to the Equation I are maintained in a state of vapour and do not condense upon the walls of the hollow body 1, but are eliminated together with the other vapours or gases through the open end 12.

The section of the hollow body 1 must be formed according to the section of the wire, strip or sheet or other continuous ferrous body which is to be coated with aluminium, and in such a way that an empty space is left around the ferrous object. This space must be as small as possible to facilitate the transfer of heat to the ferrous object, and yet sufficiently ample for the gases and vapours to circulate and bathe it easily.

This section can also be formed so as to allow several continuous ferrous objects to circulate through it simultaneously, for instance, several wires, strips or sheets at the same time.

Instead of ammonium chloride, its components, hydrochloric acid and ammonia may be employed mixed in such proportions as to produce ammonium chloride in a quantity sufficient to remove the impurities from the ferrous surface.

Simultaneously with the foregoing chemical treatment, the wire, strip or sheet becomes heated by passing through the region or zone A at red heat. The increase in temperature that the ferrous object acquires by passing at a constant speed through this zone, depends on the time it remains therein. This time should be such that, when the ferrous object leaves the zone in order to enter the molten metal bath, its temperature shall be that necessary to unite rapidly with the molten metal when wetted by it, and without requiring it to pass through a considerable mass of the metal as is required in the known methods of metal coating by heat.

Several methods can be used to increase the time during which the object remains in zone A. In practice, good results can be obtained if the time of heating is increased by increasing the length of zone A. If the speed of passage of the object is increased, there will result an increase in the production per hour.

The wire, strip or sheet, with its surface free from impurities, and at a temperature approximating that of the metallic bath, leaves the body 1 and enters the zone B, or the aluminium-coating zone.

This part of the apparatus comprises essentially a receptacle or crucible 4 containing the aluminium or aluminium alloy 3 in a molten state.

To prevent the oxidizing of the wire, strip or sheet between its exit from the hollow body 1 and its entrance into the mass of metallic bath, several methods may be used. For example, devices may be employed which maintain an atmosphere of the NH_4Cl vapours around the wire, strip or sheet until it penetrates into the metal bath; protecting materials, such as reducing or inert bodies 13, in a powdered or liquid state, that prevent air from reaching the wire, strip or sheet may be used; or inert or reducing gases may be employed.

The wire, strip or sheet, guided by the plunger 2, comes out from the bath of aluminium or aluminium alloy coated with a continuous film of molten metal, and enters the cooling zone C.

In this zone, the liquid film quickly solidifies, and the combination of the metals of the film with the iron base is quickly interrupted. At the same time, the oxide impurities that may have come from the metallic bath are removed from the surface, and the coating is smoothed.

Many devices may be used for this purpose. In practice, good results are obtained by using a metallic member 6 provided with an opening 14, like a wire drawer, through which passes the wire, strip or sheet. The opening of the wire-drawer should be of a section slightly larger than that of the wire, strip or sheet; and the member may radiate heat at such a rate that the aluminium or aluminium alloy carried along by the wire, strip or sheet is kept in the said space in a pasty state and the wire strip or sheet slips through it. Thus, in the end, it may be said to constitute a device for smoothing out of aluminium or aluminium alloy, proceeding from the metal bath.

The metals that may be employed in a molten state for obtaining metallic coatings on ferrous objects, in accordance with this process, may vary; it should be understood that this invention refers to the process, independently of what metals or alloys may be adopted. The explanation of what has been done with the aluminium has only been given by way of example.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of ammonium chloride at a temperature ranging from 500° C. to 700° C., and then applying thereto a coating of molten metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc.

2. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of ammonium chloride at a temperature ranging from 500° C. to 700° C., passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is not in contact with the ammonium chloride, and then smoothing and cooling.

3. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of hydrochloric acid and ammonia at a temperature ranging from 500° C. to 700° C. and in proportions to produce ammonium chloride in a quantity sufficient to remove the impurities from the surface of the ferrous body, passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is not in contact with the hydrochloric acid and ammonia and then smoothing and cooling.

4. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of ammonium chloride at a temperature ranging from 500° C. to 700° C., passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is separated from contact with the ammonium chloride vapors by a mass of protecting material in a powdered state, and then smoothing and cooling.

5. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of hydrochloric acid and ammonia at a temperature ranging from 500° C. to 700° C. and in proportions to produce ammonium chloride in a quantity sufficient to remove the impurities from the surface of the ferrous body, passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is separated from contact with the vapors of the hydrochloric acid and ammonia by a mass of protecting material in a powdered state, and then smoothing and cooling.

6. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of ammonium chloride at a temperature ranging from 500° C. to 700° C., passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is not in contact with the ammonium chloride, and then cooling said body and smoothing the coating thereon, said smoothing step being carried on by passing the coated body in wiping contact with a body of said coating metal in a pasty state.

7. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of hydrochloric acid and ammonia at a temperature ranging from 500° C. to 700° C., and in proportions to produce ammonium chloride in a quantity sufficient to remove the impurities from the surface of the ferrous body, passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is not in contact with the hydrochloric acid and ammonia, and then cooling said body and smoothing the coating thereon, said smoothing step being carried on by passing the coated body in wiping contact with a body of said coating metal in a pasty state.

8. A method of coating a ferrous body with a metal, which consists of subjecting the said body to an atmosphere of vapors of ammonium chloride at a temperature ranging from 500° C. to 700° C., passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is separated from contact with the ammonium chloride vapors by a mass of protecting material in a powdered state, and then cooling said body and smoothing the coating thereon, said smoothing step being carried on by passing the coated body in wiping contact with a body of said coating metal in a pasty state.

9. A method of coating a ferrous body with a metal, which consists in subjecting said body to an atmosphere of vapors of hydrochloric acid and ammonia at a temperature ranging from 500° C. to 700° C., and in proportions to produce ammonium chloride in a quantity sufficient to remove the impurities from the surface of the ferrous body, passing said body through a bath of molten coating metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, the surface of which is separated from contact with the vapors of the hydrochloric acid and ammonia by a mass of protecting material in a powdered state, and then cooling said body and smoothing the coating thereon, said smoothing step being carried on by passing the coated body in wiping contact with a body of said coating metal in a pasty state.

10. A method of coating a ferrous body with a metal, which consists in simultaneously and chemically decarburizing and deoxidizing the surface of the ferrous body at a temperature varying from 500° C. to 700° C. to remove all of the impurities on the surface of the body that prevent perfect metallization, removing in vaporous form the reaction products formed by the decarburizing and deoxidizing, and then applying to the surface of said ferrous body, while it is in a decarburized and deoxidized state and free from oxides and impurities, a molten coating of metal selected from the group consisting of aluminum, aluminum alloys, tin and zinc, whereby a continuous soldering on a surface of pure iron and a coating without pores, oxides or gaps is obtained.

ANSELMO ORTIZ RODRIGUEZ.