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METAL HYDROXIDE INTERMEDIATE COATING FOR METAL

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ABSTRACT OF THE DISCLOSURE

This specification describes a method of coating elongated steel substrates, e.g., strip, with a powdered coating material, in which a gelatinous, colloidal metal hydroxide is used as a binder. Suitable metal hydroxides include those of aluminium, zinc, nickel, iron, chromium, magnesium and manganese. After deposition of the coating material, the coated substrate is heated to render the coating adherent.

This invention is concerned with a method of coating metal substrates, more particularly metal substrates which can be subjected to rolling, such as sheet, strip, wire or rod, which types of material are hereinafter referred to generally as "substrates in elongated form."

There is an increasing demand at the present time for sheet materials consisting of a metal substrate which is coated on one or both sides with another metal or alloy or with one or more metal oxides, and for metal wire and rod having coatings of these kinds, and it is an object of the present invention to provide an improved process for the production of such coated materials.

According to the present invention we provide a method of coating metal substrates in elongated form which comprises coating the substrate with a colloidal solution of a suitable metal hydroxide, applying a uniform layer of the desired coating material in powder form to the metal hydroxide coating, drying the coated substrate, rolling the substrate to compact the coating, and then heating the coated substrate to an elevated temperature to obtain a tightly adherent coating.

This process is particularly applicable to the formation of metal coatings, for example coatings of aluminium, tin, nickel, brass, zinc, iron and steel and mixtures or alloys of two or more of these or other metals, but can also be used to form coatings of other types, for example coatings of metal oxides such as alumina. When it is desired to obtain a metal alloy coating, a preformed powdered alloy may be used or alternatively the individual constituents of the alloy, in powdered form, may be mixed and the powder mixture applied to the substrate, alloying by inter-diffusion of the constituents taking place during the final heat treatment.

The ability to obtain adherent coatings on metal substrates by this method is due to the use of certain metal hydroxides. Suitable metal hydroxides for this purpose are those which (1) are gelatinous when suitably hydrated and can, in the presence of water, form a colloidal solution, (2) when applied to a metal substrate in the form of such a colloidal solution, are capable of adhering the subsequently applied powder to the substrate sufficiently well, both before and after the drying operation, that the powder is not dislodged to a significant extent by the normal vibrations of a processing line and a rolling mill, and (3) are not deleterious to the rolling and heat treatment and, after the rolling and heat treatment, are not significantly deleterious to the corrosion resistance, formability or appearance of the coated substrate.

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Metal hydroxides which have proved successful include $\text{Al}(\text{OH})_3$; $\text{Zn}(\text{OH})_2$; $\text{Ni}(\text{OH})_2$; $\text{Fe}(\text{OH})_3$; $\text{Cr}(\text{OH})_3$; $\text{Mg}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$, of which $\text{Al}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ are preferred.

In one method of forming the metal hydroxide coating on the substrate, a colloidal solution of the desired metal hydroxide is prepared and applied to the substrate by any suitable coating procedure, such as dipping, roller coating or spraying. The colloidal solution of metal hydroxide may be prepared electrolytically by electrolysis of a dilute aqueous solution of a soluble salt of the metal, the hydroxide of which it is desired to use; the anode should be formed of the same metal. Suitable concentrations of the soluble salt are from 1 to 5 millimoles/litre; nickel chloride can conveniently be used as the soluble nickel salt when it is desired to form a colloidal solution of nickel hydroxide and aluminium nitrate in the case of aluminium hydroxide. The solution is preferably agitated during the course of the electrolysis, for example by means of stirrers immersed in the solution or by continuously circulating the solution through the electrolysis tank.

Electrolysis may be continued until the solution contains a quantity of the desired metal hydroxide appropriate to the particular coating procedure to be used or a more concentrated colloidal solution may be prepared and used as a stock solution, being diluted as required prior to use. In the case of most coating procedures, a suitable concentration of the metal hydroxide is from 2 to 5 grams/litre.

Instead of applying a prepared colloidal solution of the metal hydroxide to the substrate, a coating of colloidal metal hydroxide can be formed directly on the substrate by making the latter the cathode in the above-described electrolysis process. The formation of such coatings can be carried out batchwise or continuously; in the latter case, the substrate in elongated form is passed continuously over a conductor roll or guide and then through the electrolysis tank. The anode length, current density and rate of travel of the substrate should be adjusted so that sufficient metal hydroxide is deposited on the substrate; for example where it is desired to form a nickel hydroxide coating on steel strip using an aqueous solution containing from 1 to 2 millimoles of nickel chloride per litre, a strip speed of 50 feet/minute, an anode length of 6 feet (the anode having the same width as the strip and being arranged parallel to the latter), a current density of from 5 to 10 amps./sq. ft. will give a suitable deposit of the hydroxide.

Whichever method of forming the metal hydroxide coating is used, we find that, in general, adequate powder adhesion, both before compaction and after the final heat treatment, is obtained with a metal hydroxide coating weight of from 0.5×10^{-5} to 5×10^{-5} grams per sq. cm. of substrate surface. It is preferred to use lower coating weights within this range in the case of nickel hydroxide, the preferred range for this hydroxide being from 0.6×10^{-5} to 0.9×10^{-5} gms./sq. cm., and higher coating weights within the broad range in the case of aluminium hydroxide, the preferred range for the latter hydroxide being from 1.5×10^{-5} to 4×10^{-5} gms./sq. cm. The preferred nickel hydroxide coating weight can be obtained, for example, by applying a colloidal solution containing from 2 to 3 gms./litre of nickel hydroxide to the substrate in such a way, for example by dipping followed by light squeegeeing, as to leave 30 ml./sq. metre of the solution on the substrate.

After coating the substrate with the metal hydroxide, the powder which is to form the coating can be applied to the substrate in any way which enables a substantially uniform rate of coating, in terms of weight of powder per

unit area of substrate surface, to be obtained. One method of applying the powder to substrates in the form of sheet or strip involves the use of a rotating metering roll as described in British patent specification No. 1,035,256, the disclosure of which is incorporated herein by way of reference; with this arrangement the rate of application of the powder can be varied by varying the speed of rotation of the roll. Powder deposition may also be effected by electrostatic deposition from a gaseous suspension of the powder particles.

After application of the powder, the coated substrate is dried and then rolled. Suitable temperatures for drying are, for example, from 100° to 300° C. The rolling pressure required to obtain adequate compaction will depend upon such factors as the nature of the powder coating, the hardness of the substrate and the diameter of the rolls. In many cases rolling to obtain an extension of form ½ to 5% is suitable; it is usually desirable to roll the coated substrate while it is still hot from the drying step. A heat treatment is then effected to obtain maximum adhesion of the coating. In most cases, this heat treatment is preferably such as to cause sintering of the coating particles and may be carried out at a relatively low temperature for an extended period of time or at a temperature only a little below the melting point of the coating material for a short period, for example of a few seconds. When

amps./sq. decimetre for about 5 hours using a steel cathode and a nickel anode. Throughout the electrolysis, the solution was circulated by a pump. The colloidal solution of nickel hydroxide obtained was used as a stock solution and was diluted as required to give the nickel hydroxide concentrations mentioned below.

Steel samples 22 cm. x 10 cm. were cathodically degreased in aqueous sodium hydroxide solution, dried and weighed. The samples were then dipped into the colloidal solution, allowed to drain for 60 seconds and aluminium powder deposited from a metering roll apparatus as shown in FIGURE 2 of the aforementioned British patent specification No. 1,035,256. The coating was dried at 100° C., the sample weighed and then clamped at each end with the plane of the sample vertical in an apparatus which included a vertical slide for a weight which could be dropped on to the edge of the sample; a weight of 125 grams was used and it was dropped from a height of 300 cm. The sample was then reweighed and hence the weight of powder removed by the impact determined. This procedure was repeated for solutions of nickel hydroxide of various concentrations.

Knowing the hydroxide content of the colloidal solution and the weight of liquid entrained on the sample, the amount of hydroxide in the coating was calculated. The results obtained were as follows:

Conc. Ni(OH) ₂ in Sol., gm./litre	Wt. of Liq. Entrained on Sample, gm.	Ni(OH) ₂ Conc. on Sample, gm./cm. ²	Wt. of Powder Deposited, gm.	Coating Thickness, microns	Wt. Removed by Impact, gm.	Percent Powder Removed by Impact
3	0.6	0.85×10 ⁻⁵	1.5	25	0.05	3
3	0.6	0.85×10 ⁻⁵	1.7	28	0.15	9
2.75	0.6	0.8×10 ⁻⁵	1.5	25	0.10	7
2.75	0.6	0.8×10 ⁻⁵	2.0	33	0.25	12
2.5	0.6	0.7×10 ⁻⁵	1.0	25	0.10	7
2.5	0.6	0.7×10 ⁻⁵	1.75	29	0.20	11
2.0	0.6	0.6×10 ⁻⁵	1.5	25	0.20	14
2.0	0.6	0.6×10 ⁻⁵	2.0	33	0.5	25
1.5	0.6	0.45×10 ⁻⁵	1.5	25	1.0	60
1.5	0.6	0.45×10 ⁻⁵	1.7	28	1.5	88
1.0	0.6	0.3×10 ⁻⁵	1.5	25	1.2	80
1.0	0.6	0.3×10 ⁻⁵	2.0	33	1.8	90

aluminium powder is used as the coating material, suitable heat treatments are, for example, 10–15 hours at 250° C., 30 minutes at 500° C., or a few seconds at 600–650° C. If the coating is liable to undergo undesirable oxidation at the temperature of the heat treatment, it should be carried out in a non-oxidising atmosphere.

The process is well adapted for the continuous treatment of substrates in continuous form, such as strip and wire, since all the steps of the process can be carried out rapidly and, therefore, in line. If a long heating schedule is preferred for the final step, the coated strip or wire can be coiled after rolling and the heat treatment carried out in coil.

Coatings produced by this process are firmly adherent and the coated substrates can be severely deformed, for example by being bent flat through 180°, without damage or delamination of the coating taking place.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

Example 1

An aqueous solution containing 1 millimole nickel chloride per litre was electrolysed at a current density of 0.5

It is considered that where not more than 25% of the powder coating is removed by the test described above, the coating is sufficiently adherent to withstand the vibration of a commercial continuous coating line.

The samples coated as described were then compacted by passing them through compacting rolls which applied a load of 4 tons/inch width and caused an extension of 3% and were then heated to 500° C. for 30 minutes.

In all cases, that is with all the coating weights of nickel hydroxide and aluminium powder specified in the foregoing table, tightly bonded aluminium coatings were obtained. The coated samples were bent flat through 180° and no damage to or delamination of the coatings was observed.

Example 2

Example 1 was repeated but using a colloidal solution of aluminium hydroxide. This was prepared as described in Example 1, the nickel chloride being replaced by 1 millimole per litre of aluminium nitrate and the nickel anode by an aluminium anode.

The results obtained were as follows:

Conc. Al(OH) ₃ in Sol., gm./litre	Wt. of Liq. Entrained on Sample, gm.	Al(OH) ₃ Conc. on Sample, gm./cm. ²	Wt. of Powder Deposited, gm.	Coating Thickness, microns	Wt. of Powder Removed by Impact, gm.	Percent Powder Removed by Impact
5	0.6	1.5×10 ⁻⁵	1.5	25	0.35	23
5	0.6	1.5×10 ⁻⁵	1.75	30	0.9	51
2	0.6	0.6×10 ⁻⁵	1.5	25	0.63	42
2	0.6	0.6×10 ⁻⁵	2.2	35	1.25	57

The coated samples were then compacted by passing them through compacting rolls which applied a load of 4 tons/inch width and caused an extension of 4% and

were then heated to 500° C. for 30 minutes. In all cases, that is with all the coating weights of aluminium hydroxide and aluminium powder specified in the foregoing table, bonded aluminium coatings which withstood the deformation test described in Example 1, were obtained.

Steel sheets have also been coated with nickel and with zinc using a procedure as described in Example 1. In the case of coating with nickel powder, suitable rolling loads were found to be from 12 to 15 tons/inch width and a suitable heat treatment, 5 hours at 700° C. or 2 minutes at 1000° C. In the case of coating with zinc powder, a suitable rolling load was found to be 4 tons/inch width and a suitable heat treatment, 30 minutes at 350° C. In the case of these two coating metals also, the coated sheet could be bent flat through 180° without damage or delamination of the coating taking place.

In the foregoing examples we have described a pretreatment of the substrate which comprises cathodic degreasing and this or another cleaning operation will normally always be necessary. We have also found that adhesion of the coating is improved by pickling the substrate in dilute nitric acid or other strong oxidising acid prior to applying the metal hydroxide. A suitable treatment is, for example, dipping for 30 seconds in 5% by volume aqueous nitric acid.

I claim:

1. A method of coating steel substrates in elongated form, which comprises coating the substrate with a colloidal solution of a metal hydroxide selected from the group consisting of $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$, applying a uniform layer of the desired coating material selected from the group consisting of aluminum, tin, nickel, brass, zinc, iron and steel mixtures of said metals, alloys of said metals and oxides of said metals in powder form to the metal hydroxide coating, drying the coated substrate, rolling the substrate to compact the coating, and then heating the coated substrate to an elevated temperature to obtain a tightly adherent coating, said coating material being selected from the group consisting of metals, metal alloys, and metal oxides.

2. A method according to claim 1, in which the substrate is coated with from 0.5×10^{-5} to 5×10^{-5} gm. of metal hydroxide per square centimetre of substrate surface.

3. A method according to claim 1, in which the metal

hydroxide coating is formed by dipping the substrate in an aqueous colloidal solution of the metal hydroxide containing from 2 to 5 gms./litre of the metal hydroxide and then lightly squeegeeing the substrate.

4. A method according to claim 1, in which the metal hydroxide is nickel hydroxide and the substrate is coated with from 0.6×10^{-5} to 0.9×10^{-5} gm. of nickel hydroxide per square centimetre of substrate surface.

5. A method according to claim 1, in which the metal hydroxide is aluminium hydroxide and the substrate is coated with from 1.5×10^{-5} to 4×10^{-5} gm. of aluminium hydroxide per square centimetre of substrate surface.

6. A method according to claim 1, in which the coated substrate is dried at a temperature of from 100° to 300° C.

7. A method according to claim 1, in which rolling is effected under such pressure that an extension of from 0.5 to 5% of the substrate is effected.

8. A method according to claim 1, in which rolling is effected at the drying temperature.

9. A method according to claim 1, in which the final heat treatment is such as to effect sintering of the powdered coating material.

10. A method according to claim 8, in which the coating material is aluminium powder and the final heat treatment comprises heating at from 250° C. to 500° C. for from 15 hours to 30 minutes.

11. A method according to claim 1, in which, after rolling, the coated substrate is coiled and the final heat treatment is effected in coil.

12. A method according to claim 1, in which prior to applying the metal hydroxide to the substrate, the latter is pickled in dilute nitric acid.

13. A method as claimed in claim 1 in which said coating material is selected from the group of metals consisting of aluminum, tin, nickel, brass, zinc, iron, and steel, mixtures of said metals, alloys of said metals, and oxides of said metals.

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