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Yamagishi et al.

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[45] **Aug. 6, 1974**

[54] **METHOD OF SURFACE TREATING STEEL PRODUCTS WITH METAL POWDER**

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[22] Filed: **Oct. 4, 1972**

[21] Appl. No.: **294,898**

Related U.S. Application Data

[63] Continuation of Ser. No. 865,885, Oct. 13, 1969, abandoned.

[30] **Foreign Application Priority Data**

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June 23, 1969 Japan 44-49207

[52] **U.S. Cl.** **29/487,** 29/420.5, 29/527.2, 117/131

[51] **Int. Cl.** **B23k 31/02**

[58] **Field of Search** 29/420.5, 527.2, 487; 117/131; 148/6.16; 106/14

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[57] **ABSTRACT**

An aqueous suspension containing a metal powder having a particle size of less than 325 mesh is applied to the surface of a steel product. The coated steel product is than preheated, rolled and post-heated to form a protective coating of said metal.

13 Claims, 4 Drawing Figures

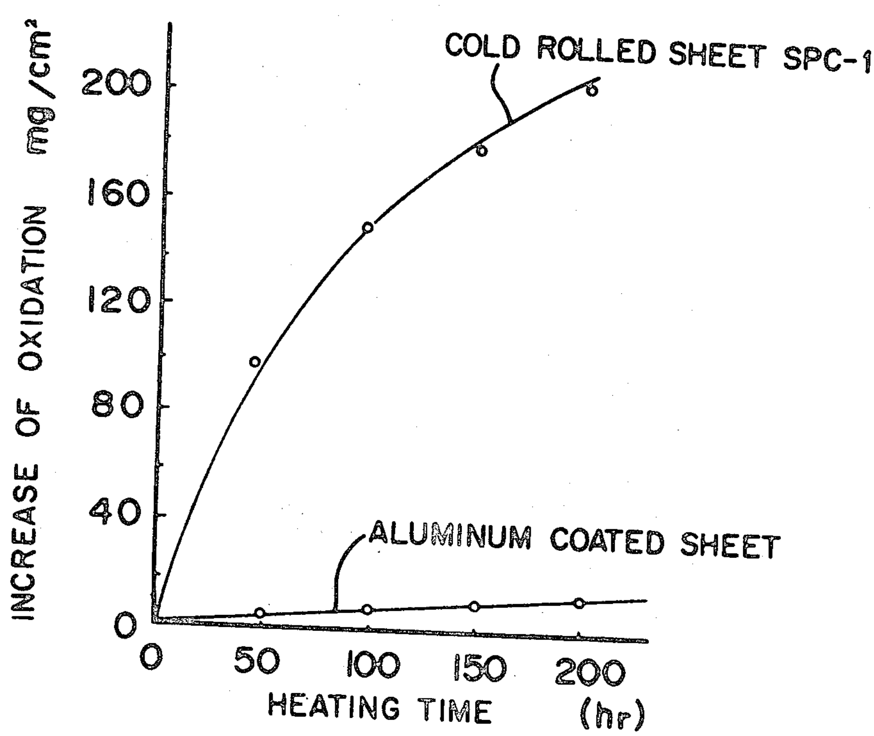


FIG.1

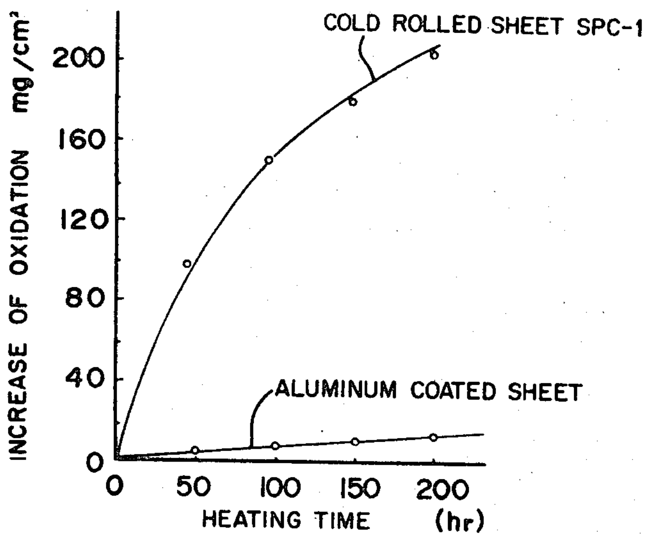
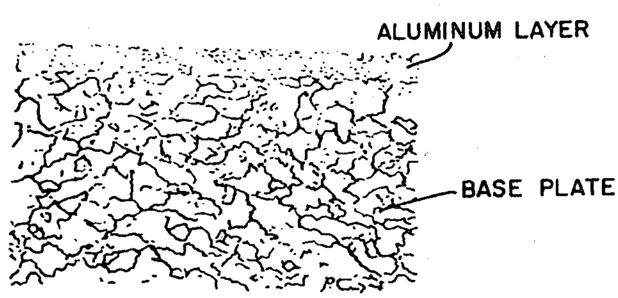


FIG.2



(X 200)

FIG.3

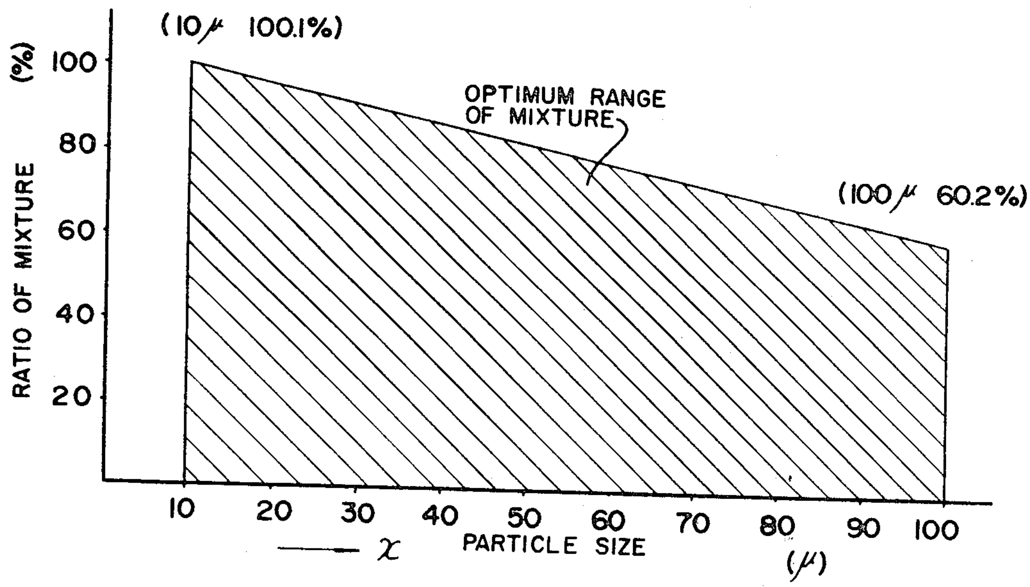
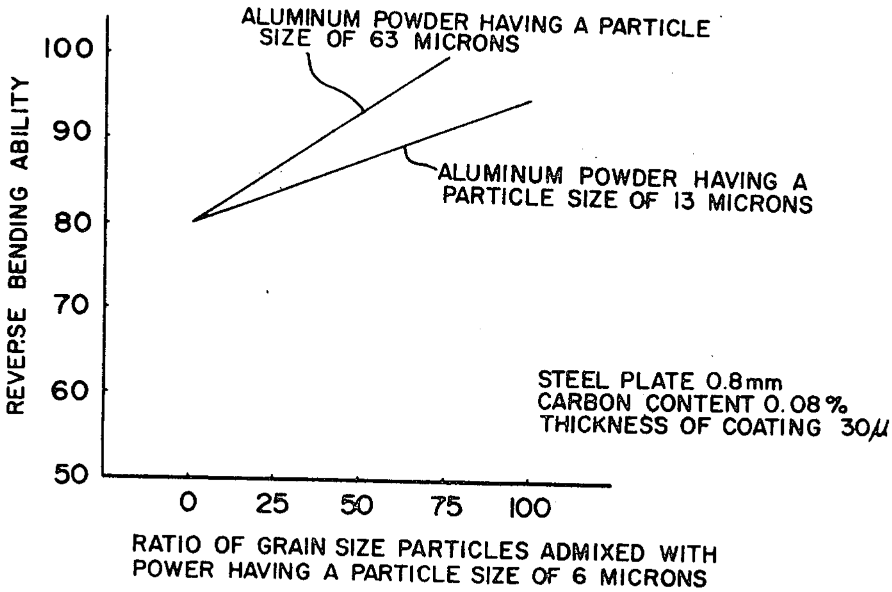

(10μ 100.1%)
OPTIMUM RANGE OF MIXTURE
(100μ 60.2%)
RATIO OF MIXTURE (%)
100
80
60
40
20
10
20
30
40
50
60
70
80
90
100
— x PARTICLE SIZE (μ)

FIG.4


ALUMINUM POWDER HAVING A PARTICLE SIZE OF 63 MICRONS
ALUMINUM POWDER HAVING A PARTICLE SIZE OF 13 MICRONS
REVERSE BENDING ABILITY
100
90
80
70
60
50
STEEL PLATE 0.8mm
CARBON CONTENT 0.08%
THICKNESS OF COATING 30μ
0
25
50
75
100
RATIO OF GRAIN SIZE PARTICLES ADMIXED WITH POWER HAVING A PARTICLE SIZE OF 6 MICRONS

METHOD OF SURFACE TREATING STEEL PRODUCTS WITH METAL POWDER

This is a continuation of U.S. Pat. application Ser. No. 865,885 filed Oct. 13, 1969, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a method of surface treatment wherein a powder of metal is suspended in water and the suspension is applied upon the surface of steel products. The invention is characterized by the utilization of fine metal powder capable of suspending in water. When desired a stabilizer may be incorporated into the suspension.

There are many known processes of surface treatment of steel plates. Among methods of coating the surface of steel plates with aluminum are included the hot dip process, the so-called molten metal spray process wherein molten aluminum is sprayed with a gun, the electrostatic deposition, the electrophoresis, the fused salt electroplating process and the like. However, with the hot dip process it is unavoidable to render brittle by layer of iron-aluminum alloy between the substrate and the coated aluminum layer due to high coating temperature, thus decreasing the formability of the products. Further, such brittle layer results in cracks when the coated products are formed subsequently.

Where the coated layer applied by the molten metal spray method is thin, numerous pin holes are formed in the coated layer to decrease the corrosion resistant property of the products. On the other hand, thick coated layers decrease adhesion of the coated layers to the substrate.

Different from the hot dip process or spray process, recently developed electrostatic deposition and electrophoretic process of aluminum powder can prevent formation of alloy layers and can suitably vary the thickness of the coating thus improving the quality of the products.

However, as the depositing speed of aluminum is low the overall efficiency of surface treating process is also low. Especially with the electrophoretic method, it is necessary to suspend aluminum powder in expensive and dangerous organic solvents. In a special case aluminum powder is admixed with an organic or inorganic binder and the mixture is applied to steel surface by the roll coating method. However, these binders affect the adhesion between the applied aluminum layer and the surface of the steel plates after compaction of aluminum layer. More particularly, where the reduction is not sufficient, proper adhesion cannot be assured so that reduction rate of more than 50 percent is required. Thus, formability after coating of aluminum is greatly reduced.

Further, with these prior methods, not only the heating of steel before rolling must be performed in non-oxidizing atmosphere but also it is necessary to use complicated powder recovery installation because of low rate of deposition of the powder to the steel plates. Thus, these prior process are not yet satisfactory.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a novel method of coating steel products with fine metal powder. Another object of this invention is to provide steel products provided with coatings of metal powder which are smooth, strongly adhere to the steel surface.

Further object of this invention is to provide a novel method of forming protective coatings on steel products without utilizing any special atmosphere and heat treatment apparatus. The invention provides a method of forming on a steel plate a homogenous and beautiful coating layer of excellent formability by the steps of suspending fine metal powder, aluminum powder for example in water, incorporating a slurry stabilizer which also acts as a corrosion preventing agent into the suspension, applying the mixture on the surface of the steel plate, thereafter heating, rolling and reheating.

More particularly, usually a steel strip is payed off from a pay off reel, passed successively through an electrolytic degreasing bath, a pickling bath, scrubber and drier and is then applied with an aluminum coating by a roll coater. The invention is characterized in that the grain size of the aluminum powder supplied to the roll coater is selected to be smaller than 325 mesh. Where aluminum powder of larger grain size is admixed with water and the mixture is applied on the surface of the steel strip by means of the roll coater, the aluminum powder will not be coated uniformly by forming local lumps for example, thus making it difficult to form beautiful and uniform coating. For this reason, it was necessary to use a viscosity increasing agent or a binder. However, such agents adversely affect the adhesion of the coating.

In contrast, incorporation of an aluminum powder of less than 325 mesh eliminates all defects described above and uniformly disperses the aluminum powder in water to provide a slurry mixture having a constituent sufficient to be applied smoothly and readily on the steel surface with a roll coater. Where a suitable ratio of water to aluminum is selected, it is possible to select any desired quality of aluminum to be coated and to precisely adjust the thickness of the coated layer to form continuous coating on the steel surface without utilizing any viscosity increasing agent.

Although the invention is not limited to any type roll coater, it is advantageous to use reverse coater.

Where a slurry of water and aluminum powder is let standstill, the aluminum powder gradually reacts with water or with components contained in water in several or more hours to evolve gas, thus greatly degrading stability, although dependent upon the quality of the water used. For this reason, in accordance with another aspect of this invention, where it is obliged to let standstill for a long period of time before use of the slurry after it has been prepared another additive is incorporated in order to maintain the slurry mixture of water and aluminum powder in an ideal stable condition.

To stabilize the aluminum powder suspended in water, addition of a small quantity of aluminum chloride, aluminum phosphate, alonic acid and the like is effecient but these additives are not desirable because they tend to corrode the surface of the steel plates or exposed portions of the drying furnace, roll coater and the like if it takes a long time before the surface of the steel plate is completely dried after application.

In accordance with this invention as the another additive phytinic acid is incorporated in an amount of about 10 to 1,000 ppm. When phytinic acid is added into water which undergoes reaction within several hours, the slurry becomes stable over 100 hours.

In corporation of phytinic acid not only improves the stability of aluminum powder but aldo prevents rusting of the surface of the steel plate even when it takes a long time before the surface is dried after coating, thus improving process control. It should be understood that the stabilizer utilized in this invention is not limited to phytinic acid alone and that any other equivalent organic acid may be used.

Further object of this invention is to admix metal powders of the same metal but having different mean particle sizes to prepare a slurry to be applied on the surface of steel products in order to provide uniform coating layer and uniform adhesion of the dried metal powder before compaction as well as improved dispersion of metal particles in the slurry. Thus, the major portion of the metal powder has a particle size of less than 10 microns but larger particles are incorporated to improve adhesiveness of the coated metal layer after the final heat treatment. The quantity of larger particles is selected to be in a range not to degrade the stability of the slurry.

According to this invention, metal powder having a mean particle size of less than 10 micron is utilize as the base and a portion thereof is substituted by metal powder having mean particle size of from 10 to 100 microns by a factor of $-4/9\ x + 104.5$ percent, where x represents the particle size of the latter metal powder having mean particle size ranging from 10 to 100 microns. The slurry mixture is then applied on the steel surface and heat treatment, compaction and post-compaction heat treatment are carried out. The metal particles are uniformly dispersed in the slurry and the slurry has excellent adhesion without decreasing easiness of coating operation. More particularly, among metal particles less than 325 mesh, in view of the easiness of coating the slurry containing water and the metal powder and the adhesion of the powder before compaction, it is advantageous to use particles having a grain size of less than 10 microns, preferably of about 6 microns. However, a slurry utilizing metal powder of about 13 microns can also be readily coated with a roll coater. However, where the slurry contains only relatively large particles of about 13 microns, after the slurry has been coated and dried, the metal powder is loosened from the surface of the steel plate by shock and vibration.

The adhesion in terms of reverse bend value (R.B.V.) of coating layers after a series of treating steps is as follows. The R.B.V. of the coating layer consisting of only powder of 6 microns is about 80, whereas that of the coating consisting of powder of 13 microns increases to about 94. We have found that by admixing these two types of metal powder at a proper ratio it is possible to improve the adhesion of the coating after rolling and heat treatment without decreasing the adhesion of the powder after the slurry has been dried. When a powder of larger particle size, for example of 63 microns is mixed with water to form a slurry which is then applied by means of a roll coater the quantity of the powder that can be applied is very small and the powder is not firmly bonded to the surface after drying so that the powder falls off due to small shock or vibration. However, as above described when a suitable quantity of larger particles are incorporated to the powder of 6 microns, the adhesion of the coated layer can be greatly improved over the coating containing only the powder of 6 microns.

In this manner, we have succeeded to improve the adhesion of the coating after being worked by compromising the tendency of falling off of the powder from the surface of steel prior to the rolling operation and the adhesion of the coated metal layer after rolling and heat treatment steps and by utilizing a mixture of powder having a mean particle size of 6 microns and powder of larger size.

Usually, a steel plate coated with aluminum powder is preheated in a preheating furnace in order to increase the rolling speed. Although the preheating temperature is prescribed dependent upon the thickness of the plates, thickness of the coated layer and the heating time, temperatures ranging from 400° to 700° C generally give good results. More particularly, temperatures below 400° C result in blue brittleness causing a brittle plate whereas temperatures above 700° C cause vigorous oxidation of the metal powder thus making it difficult to obtain satisfactory coated layers. In this invention, such preheating can be performed in the atmosphere.

The rolling operation succeeding to the preheating step may be of such extent sufficient to elongate the plate by 2 to 5 percent. This is because that, with elongation of less than 2 percent, the aluminum powder will not be compacted sufficiently, thus forming porous coatings whereas elongation of more than 5 percent increases the brittleness of the plate.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing;

FIG. **1** is a graph to show increase in the weight by oxidation which is obtained by the heat resistance test made on the product of example **1**;

FIG. **2** shows the structure of aluminum coated steel of example 2 magnified 200 times;

FIG. **3** shows a range in which larger particles can be added to powder of 6 microns; and

FIG. **4** is a graph to show the improvement of the adhesion of the coated layer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to have more complete understanding of this invention, following examples are given.

EXAMPLE 1

An aqueous suspension was prepared by admixing a finely divided aluminum powder having a particle size of less than 325 mesh, 80 percent by weight of water and 200 ppm of phytinic acid. The suspension was coated by means of a roll coater upon a cold rolled steel plate of 1.2 mm thick which has been degreased and pickled. The coated steel plate was heated in the atmosphere at a temperature of 650° C for 45 seconds and was then rolled to elongate 5 percent at a rolling speed of 40m/min. After rolling, the plate was heat treated at a temperature of 700° C for 120 seconds.

The aluminum coated steel plate obtained by this method has a uniform and beautiful coating, excellent formability and corrosion resistance. The product showed excellent heat resistance as shown in FIG. **1.**

EXAMPLE 2

The same aqueous suspension as that utilized in example 1 was coated upon a degreased and pickled cold rolled steel plate having a thickness of 0.8 mm at a rate of $80g/m^2$ by means of a roll coater. The coated steel plate was heated in the atmosphere at a temperature of 700° C for 20 seconds and was then cold rolled to elongate 3 percent at a rolling speed of 40m/min. The rolled plate was further heated in the atmosphere at a temperature of 400° C for 3 hours.

The aluminum coated layer formed in this manner on the steel plate had a thickness of 30 microns and no brittle alloy layer was formed as can be noted from a micrograph shown in FIG. 2. Thus the product has excellent deep drawability and corrosion resistance.

It is to be understood that the invention is not limited to steel plate or sheet alone but may equally be applicable to other forms of steel products such as pipes, rods or beams of various cross-sectional configurations. Further, the metal powder is not limited to aluminum alone but may be used powders of zinc, lead, tin, titanium and the like having a particle size of less than 325 mesh. Of course, suitable method of suspending these powders in water and suitable preheating conditions are used.

EXAMPLE 3

This example illustrates the use of a zinc powder. Finely divided zinc powder having a particle size of less than 325 mesh was admixed with water at a ratio of 50 to 400 and 200 ppm of phytinic acid was added to the mixture. The resulted mixture was coated upon a pickled steel plate at a ratio of 120g/m² of the zinc powder. After being heated in the atmosphere at a temperatyre of 400° C for 10 seconds, the steel plate was rolled at a reduction rate of 3 percent. The rolled plate was then heat treated for 1 hour at a temperature of 300° C to obtain a steel plate having a homogenous zinc coating.

Following example show use of powder of 6 microns which is partially substituted by powder of larger particle size by a factor of $-4/9\,x + 104.5$ percent, where x represents the particle size of the powder to be admixed and having a particle size of more than 10 microns, preferably from 10 to 100 microns, and the factor $-4/9\,x + 104.5$ percent shows the maximum permissible percentage of substitution of particles having a particle size of from 10 to 100 microns based on the powder of less 10 microns, such percentage being determined by considering the adhesion of the powder as well as the adhesion of the coating layer after the compaction.

EXAMPLE 4

Aluminum powder having a particle size of 6 microns	10g
Aluminum powder having a particle size of 13 microns	30g
Water	50g

These powders and water were mixed together to form a slurry which was applied with a reverse coater under following conditions.

Iron plate	thickness	0.8mm
	carbon content	0.08%
Quantity of the applied slurry containing aluminum powder		1g/dm² (above 30 microns)
Preheating	In oxidizing atmosphere, 650°C, 30 seconds	
Rolling	40m/min., reduction rate	3%
Post heating	400°C, 3 hours	

Even when particles of 13 microns amounted to 75 percent of the entire particles, different from the coating employing only particles of 13 microns, the particles did not fall off from the coated surface when subjected to shock, thus exhibiting very satisfactory adhesion.

EXAMPLE 5

Aluminum powder having a particle size of 6 microns	20g
Aluminum powder having a particle size of 63 microns	20g
Water	45g

These powders were admixed with water to form a slurry which was applied with a reverse coated under following conditions.

Steel plate	thickness	10mm
	carbon content	0.08%
Quantity of applied slurry containing aluminum powder		1g/dm²
Preheating	In oxidizing atmosphere,	650°C, 40 seconds
Rolling	30m/min., reduction rate	3%
Post heating	400°C, 3 hours	

Similar to example 1, the powder layer prior to compaction had very excellent adhering property. However, when the percentage of the powder having the quantity of particles of 63 microns, exceeded 75 percent of the slurry, such large particles showed a tendency of separation, thus gradually decreasing the adhesion of the dried coating layer. For this reason the particles are fallen off by slight vibration or shock. While utilization of aluminum powder having a particle size of less than 6 microns improves coating facility of the aqueous slurry, such small powder is not advantageous in that it decreases the adhesion of the coating. FIG. 3 shows an appropriate range of the percentage of admixing a powder of 6 microns and powders of larger particle size, with due consideration of uniform dispersion of the particles in the slurry and the adhesion of the powder layer before compaction. FIG. 4 shows the formability of the coating layer from which it will be noted that the formability is improved in proportion to the quantity of incorporation of larger particles.

As above described fine powders of different particle size are suspended in water to form an aqueous slurry and a substance acting as an anti-corrosion agent for steel plates and as a stabilizer of the slurry is added. For this reason steel plates coated with such a slurry do not corrode in water. The slurry is not expensive, dangerous and can be applied at high coating speed with a conventional roll coater with approximately 100 percent of powder utilization, thus eliminating the necessity of installing any powder recovering apparatus.

Further, as the preheating before compaction can be performed in the oxidizing atmosphere.

Since reduction rate of 2 to 5 percent gives satisfactory coating layer, it is possible to provide smooth and beautiful coating layers of excellent corrosion resistance and heat resistance. Although rolled products require post heat treatment to improve the adhesion of the coating layer such heat treatment can be carried out in the atmosphere without utilizing any special heat treating furnace. The temperature and time of the post heat treatment can be suitably varied. Such post heat treatment may be made in or out of the production line.

What we claim is:

1. A method of surface treatment of a steel product with a metal powder characterized by the steps of applying an aqueous slurry on the surface of said steel product, said slurry consisting of water and a metal powder having a particle size of less than 325 mesh suspended therein, prehating the coated steel product at a temperature of 400° to 700° C., rolling the coated steel product at a reduction rate of 2 to 5 percent to cause said metal powder to adhere to the surface of said steel product, and post-heating the resulting steel product at a temperature ranging from 300° to 700° C., said metal being selected from the group consisting of aluminum, zinc, lead, tin and titanium.

2. The method according to claim **1**, wherein said preheating is effected in an oxidizing atmosphere.

3. The method according to claim **1**, wherein said post-heating treatment is carried out in the atmosphere.

4. A method of surface treatment of a steel stock characterized by the steps of applying an aqueous slurry on the surface of said steel stock, said slurry consisting of water and a mixture of metal particles suspended therein, the mixture consisting of metal particles (i) having a mean particle size of less than 10 microns and metal particles (ii) having a mean particle size of from 10 to 100 microns and the maximum percentage of said particles (ii) in said mixture being represented by the factor

$$-4/9X + 104.5 \text{ percent}$$

wherein X represents the particle size of said particles (ii), preheating the coated steel stock at a temperature of 400° to 700° C., rolling the coated steel stock at a reduction rate of 2 to 5 percent to cause said metal powder to adhere to the surface of steel stock and post-heating said coated steel stock at a temperature ranging from 300° to 700° C., to form a stel product coated with an adhered layer of said metal powder, said metal being selected from the group consisting of aluminum, zinc, lead, tin and titanium.

5. The method according to claim **1**, wherein the metal is aluminum.

6. The method according to claim **4**, wherein the metal is aluminum.

7. A method of surface treatment of a steel product with a metal powder characterized by the steps of applying an aqueous slurry on the surface of said steel product, said slurry consisting of water, a metal powder having a particle size of less than 325 mesh suspended therein and a small quantity, sufficient to stabilize said slurry and to inhibit corrosion, of phytic acid, preheating the coated steel product at a temperature of 400° to 700° C., rolling the coated steel product at a reduction rate of 2 to 5 percent to cause said metal powder to adhere to the surface of said steel product, and post-heating the resulting steel product at a temperature ranging from 300° to 700° C., said metal being selected from the group consisting of aluminum, zinc, lead, tin and titanium.

8. The method according to claim **7**, wherein said preheating is effected in an oxidizing atmosphere.

9. The method according to claim **7**, wherein said post-heating treatment is carried out in the atmosphere.

10. A method of surface treatment of a steel stock characterized by the steps of applying an aqueous slurry on the surface of said steel stock, said slurry consisting of water, a mixture of metal particles suspended therein, and a small quantity, sufficient to stabilize said slurry and to inhibit corrosion, of phytic acid, the mixture consisting of metal particles (i) having a mean particle size of less than 10 microns and metal particles (ii) having a mean particle size of from 10 to 100 microns and the maximum percentage of said particles (ii) in said mixture being represented by the factor

$$-4/9X + 104.5 \text{ percent}$$

wherein X represents the particle size of said particles (ii), preheating the coated steel stock at a temperature of 400° to 700° C., rolling the coated steel stock at a reduction rate of 2 to 5 percent to cause said metal powder to adhere to the surface of steel stock and post-heating said coated steel stock at a temperature ranging from 300° to 700° C., to form a steel product coated with an adhered layer of said metal powder, said metal being selected from the group consisting of aluminum, zinc, lead, tin and titanium.

11. The method according to claim **10**, wherein the quantity of said acid is from about 10 to about 1,000 parts per million in said slurry.

12. The method according to claim **7**, wherein the metal is aluminum.

13. The method according to claim **10**, wherein the metal is aluminum.

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