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1

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# PROCESS FOR PRODUCING CORROSION-RESISTANT ALUMINUM-COATED IRON SURFACES

Tibor Kenderi, 49 Kelenhegyi ut., Budapest, Hungary

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This application is a continuation-in-part of my copending application Ser. No. 41,794, filed July 11, 1960, now abandoned.

My present invention relates to a process for producing corrosion-resistant aluminum-coated iron surfaces and, more particularly, to an improved method of providing iron bodies or articles, consisting at least in major part of iron, with aluminum coatings for limiting corrosion thereof.

It has been proposed heretofore to provide the surfaces of iron and steel bodies with a coating of aluminum in an effort to ward off corrosion. The aluminum coating is generally applied by dipping the body into a molten metal or by spraying aluminum onto the surface. It has, however, been found to be difficult to provide coatings of this type which were at once thermally stable, well adhering and effective as corrosion-resistant protective layers. Some of these prior-art methods have included the step of heating very thin aluminum layers of 2.5–7.5 micron thickness to temperatures above the melting point of the aluminum for a time period enough to effect a substantially complete alloying between the aluminum coating and the iron-containing substrate. This treatment was preferably carried out in the absence of air or oxidizing media. Other methods included the step of heating of aluminum layers of about 0.2 mm. thickness produced by hot spraying or dipping to temperatures of 800–850° C. for 10–20 minutes; in this case the aluminum coating gets also substantially completely alloyed with the iron substrate. Though the product of these methods showed a quite good corrosion resistance at high temperatures above 300° C. in dry atmospheres, they were not sufficiently resistant to corrosion in humid atmospheres mainly at lower temperatures below 100° C., and the thicker coatings produced by the latter method were not resistant to the usual bending stresses, were brittle and easily cracked and were not capable of withstanding large or rapid temperature fluctuations. It has also been proposed to produce a very thin aluminum layer on the iron surface by vacuum vaporizing and heating this coating in an oxidizing atmosphere to relatively low temperatures of 170–370° C.; this method was only applicable to said very thin and compact vacuum vaporized aluminum layers. Such treatment when applied to the thicker and porous hot sprayed aluminum coating deteriorates rather than improves the corrosion resistance of the coating. The use of coatings produced in accordance with the prior-art methods has, therefore, been quite limited.

It is an object of the present invention to provide an improved process for producing thermally stable, highly adherent nonbrittle protective coatings of aluminum showing excellent corrosion resistance also in humid atmospheres and at temperatures below 100° C. on iron and steel surfaces.

It is another object of the invention to provide iron or steel sheets having such protective coatings.

I have found that several critical factors enter into the production of efficiently corrosion-resistant aluminum coatings on the surfaces of bodies consisting entirely or predominantly of iron. Surprisingly it was discovered that complete alloying of an aluminum layer deposited upon an iron substrate with substantial diffusion of iron

2

into the aluminum layer did not necessarily produce a corrosion-resistant, mechanically and thermally stable surface. These and other critical aspects of the present invention will become more readily apparent hereinafter.

The foregoing objects have been attained, in accordance with the invention, by providing an iron or steel surface, preferably by the usual hot spraying process, with an aluminum layer having a thickness between substantially 0.1 and 0.4 mm. The coated surface is then exposed to heat treatment in an oxidizing atmosphere for strictly defined periods and within a restricted temperature range to obtain an interdiffusion of iron into the aluminum and aluminum into the iron at the interface between the iron and the aluminum protective layer. The resulting alloying of the iron with the aluminum as the iron diffuses into the surface coating is restricted so that alloy formation extends into the aluminum layer to a maximum of approximately two-thirds the thickness of the aluminum layer. It has been found that most advantageous results are obtained when the alloy formation only takes place to a depth of approximately $\frac{1}{10}$ to $\frac{1}{4}$ the thickness of the aluminum layer. By restricting the thickness of the interfacial alloy zone, the characteristic brittleness of prior-art aluminum coatings is, surprisingly, entirely obviated. As opposed to methods which result in alloying beyond the two-third level mentioned above, applicant's method is well-adherent and is able to withstand repeated flexure.

The use of an oxidizing atmosphere in combination with limited alloying is also of vital importance inasmuch as the unalloyed outer portion of the aluminum coating becomes oxidized and is capable of withstanding corrosive environments. Excessive alloying of the aluminum coating with iron renders any oxidation of the residual aluminum of negligeable effect so that corrosive penetration into the surface may occur.

The proper extent of the interfacial alloying and surface oxidation of the aluminum coating can be obtained, in accordance with the present invention, by precise regulation of the heat-treatment temperature and duration. It has been found that effective temperatures must be on the order of or somewhat above the melting point of aluminum, i.e. substantially between 690° C. and 800° C. Best results, however, are obtained when the treatment temperature is between substantially 720° C. and 740° C. The treatment duration should range between 1 and 8 minutes depending upon the temperature employed. It will, of course, be apparent that the shorter durations should be employed when the higher temperatures are used and vice versa.

The proper degree of interfacial alloying and surface oxidation can also be judged from metallographic examination of the aluminum-coated iron surface and especially from microscopic examination of the interfacial cross-section. These techniques are, however, somewhat awkward and an alternative method of judging the proper degree of heat treatment has been devised. Experiments have shown that the color of the exposed surface of the aluminum layer changes in the course of the heat treatment from a bright metallic silver color into a shade of grey. A dark grey or greyish black color is indicative of excessive interfacial alloying while a silvery shade of grey indicates insufficient alloy formation. When the heat treatment proceeds to the proper extent, the exposed surface has a light brownish grey cast. The uniformity and reproducibility of the grey color of the exposed aluminum surface is enhanced when this surface is wetted with paraffin oil or molten paraffin wax. The resulting medium-light grey shade is thus rendered uniform and comparable by visual observation or automatic optical methods.

In fact, the desirable grey color of the exposed aluminum surface may be specified by quantitative photometric measurements. For example, the photometric density value as measured say, by a Pulfrich photometer, which gives an indication of the logarithm of the ratio of the intensity of the illumination ($i_0$), incident upon the exposed grey surface, to the intensity ($i$) reflected therefrom as a photometric density value log

$$\frac{(i_0)}{(i)}$$

should lie between substantially 0.1 and 1.2. Most effective results have been found to be obtained when the photometric density value falls between 0.2 and 1.0. These values correspond to the grey shades of the transparent grey wedge of increasing thickness defined by the German industrial standard DIN 4512 between substantially 0.2 and 1.8, and, preferably, between 0.8 and 1.2.

The use of paraffin wax has been found to have additional advantages in that the wax employed to render the grey surface uniform penetrates into pores in the partially oxidized aluminum coating and thus serves to protect it from chemical deterioration. Other water-repellent impregnants have likewise been found to be suitable in this connection. In addition to hardenable waxy substances, film-forming synthetic resins, such as polyethylenes, polyamides, polyesters or epoxy resins have also been found to be suitable. The waxes include beeswax and carnuba wax in addition to paraffin wax.

Impregnation with paraffin wax can be carried out by cooling the article to a temperature between 200° and 400° C. and then immersing it in a bath of molten paraffin at a temperature of about 100° to 120° C. The article is then removed from the bath and maintained at a somewhat higher temperature, e.g. 100°–200° C., to remove excess paraffin. Polyethylene coatings can be applied by hot spraying the polyethylene solution onto the cold or only limitedly heated workpiece below 200° C. and preferably between 120° and 140° C.

The above and other objects, features and advantages of the present invention will become more readily apparent from the following specific examples:

*Example 1*

Mild-steel sheets having a thickness of approximately 2 mm. were descaled and degreased in the usual manner so as to be substantially free from fatty impurities and oxide film. The surface to be coated was then roughened to render it receptive to the coating metal which was then sprayed by conventional hot-spray techniques onto the roughened surface of the sheet. In this manner aluminum layers of 0.05 and 0.2 mm. in thickness were deposited upon several steel sheets which were then heated to a temperature of 730° C. in an electric furnace under an oxidizing atmosphere. This oxidizing atmosphere was provided by permitting free circulation of air over the aluminum-coated sheets for the duration of the heat treatment, i.e. about 3 minutes.

Sheets provided with the 0.05 mm.-layer of aluminum were found to have a dark-grey color while those provided with the 0.2 mm.-layer had a light brownish-grey appearance. Metallographic examination indicated that the thin coatings of 0.05 mm. had been transformed into an aluminum/iron alloy throughout their cross-section while the fusion of iron into the relatively thick aluminum layer of 0.2 mm. did not extend beyond one-half the thickness of this layer. Corrosion tests showed that the light-grey sheets, i.e. those in which iron diffusion is limited, are resistant to corrosion in humid atmospheres at temperatures above and below the dew point while the darker sheets, i.e. those having complete alloying of iron with the aluminum coating, corroded quickly in humid atmospheres even at temperatures below the dew point. Bending tests indicative of flexibility and permanence of the bond surprisingly showed that the relatively thickly coated samples could be bent around a rod of 15 mm. in diameter through an angle of 180° without rupture of the coating while similar bending of the thinly coated sheets resulted in flaking and cracking of the coating.



*Example 2*

Mild-steel sheets having aluminum layers of approximately 0.2 mm. in thickness were subjected to heat treatment at 690° C. for 6 minutes and 730° C. for 2 minutes, respectively. Both sets of sheets had approximately the same light brownish grey color, only those treated at the lower temperature for longer time being of slightly darker shade. The metallographic examination indicated that in both samples the coating was alloyed with the iron substrate over an interfacial zone whose thickness was only a minor fraction of that of the aluminum layer, again with the interfacial zone of the low-temperature sheet being somewhat wider. Corrosion tests showed that both samples had excellent corrosion resistance in humid atmospheres above and below the dew point and that their coatings were resistant to rupture and flaking during the bending tests.

*Example 3*

When aluminum-coated sheets of the type described in Example 2 were subjected to heat treatment under the following conditions: for 20 min. at 730° C., 10 min. at 760° C., 6 min. at 800° C. and 15 min. at 850° C., the coatings were found to be alloyed with the iron throughout their thickness. The articles were readily corroded in humid atmospheres at temperatures below the dew point and their coatings were easily cracked and flaked during bending tests.

*Example 4*

In a test illustrating the importance of an oxidizing atmosphere, aluminum-coated mild-steel sheets having the aforestated dimensions were heat-treated in nitrogen atmosphere for 5 minutes at 730° C. and for 12 minutes at the same temperature. The sheets treated for the longer period had an appreciably darker grey color than those treated for the lesser period but the aluminum layers of both sheets were substantially denser than those exposed to an oxidizing atmosphere as described in Example 2. The protective layers of the sheets treated in nitrogen atmosphere were sensitive to temperature changes and flaked off when the sheets were bent.

*Example 5*

Mild-steel sheets having a thickness of 2 mm. were coated by spraying with aluminum layers of 0.1 to 0.2 mm. in thickness. These sheets were subjected to heat treatment at 300°, 400° and 500° C. for one minute and five minutes. Metallographic examination indicated that no interfacial alloy zone had been formed on any of these sheets. The sheets also were found to have poor corrosion resistance and poor adherence of the aluminum layer to the substrate.

*Example 6*

A number of mild-steel plates having a thickness of about 1 mm. were provided with a sprayed aluminum layer of a thickness of about 0.15 mm. The samples were heat-treated in oxidizing atmosphere at various temperatures whereupon photomicrographs were taken with a metallographic microscope of the Neophot type at an enlargement of 320×.

From these photomicrographs it may be seen that the interface between the upper aluminum layer and the lower iron substrate is distinct so that only limited adherence of the protective coating to the sheet is possible.

Photomicrographs of specimens heat-treated at 300°, 400°, 500° and 600° C. with treatment times of 10 minutes prove that substantially no alloying or interdiffusion of the two metals has occurred.

However, interfaced zones after heat treatment at 650°, 680°, 700°, 720° and 740° C., respectively, in photomicrographs taken after treatment at less than one minute, reveal that a demonstrable intermingling of the two metals at their interface occurs although without any substantial penetration of the iron into the aluminum; these samples were not capable of withstanding corrosive atmospheres and severe bending stresses. Heat treatment of the samples at temperatures between 690° C. and 800° C. for periods of about 10 to 1 minutes rendered the samples corrosion-resistant and capable of withstanding the bending stresses.

Photomicrographs were taken of specimens heat-treated at 800° and 850° C., respectively, for a period of time less than one minute; this means, however, that taken into consideration the time necessary for heating the samples from about 690° to 800° or 850° C., respectively, and for their cooling down again to about 690° C., the samples were held within the temperature range according to the present invention. All these photomicrographs show a substantial interdiffusion of the two metals with the formation of an alloy zone extending substantially into the aluminum layer but having a width from less than half the thickness of the aluminum layer. These coatings have the high corrosive resistance characterizing the sheets of Example 2 and have excellent bending resistance as measured by a flexing test wherein flaking was examined with a predetermined flexing number. The latter is the number of times the sheets are bent about a 5 mm.-rod. With a flexing number of 6, the specimens heat-treated at 700 and 720° C. for 5 minutes showed little peeling while those treated at temperatures below 690° C. showed substantial flaking.

A specimen heat-treated at a temperature of 800° C. for approximately 15 minutes has an alloy zone approximately equal in thickness to that of the aluminum layer originally applied. The specimen was found to have poor corrosion resistance.

What I claim is:

1. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum having a thickness of about 0.1 to 0.4 mm., and subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 690° and 800° for a period sufficient to form an intermediate alloyed zone between the the aluminum coating and the iron body extending less than substantially two-thirds of the depth of the aluminum layer.

2. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of spray depositing on an iron body a surface layer of aluminum of a thickness of about 0.1 to 0.4 mm., and subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 690° and 800° C. for a minimum time of substantially 1 minute at 690° C. and a maximum time of 8 minutes at 800° C. with intermediate times at intermediate temperatures but for a period and at a temperature sufficient to affect alloying of aluminum layer with the iron body but to a depth less than substantially two thirds of the thickness of said aluminum layer.

3. A process according to claim 2 wherein the heat treatment is effected at a temperature between substantially 720° and 740° C.

4. A process according to claim 2 wherein the aluminum layer is deposited by hot-spraying.

5. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum of a thickness of about 0.1 to 0.4 mm., subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 690° and 800° C., for a period of substantially 1 to 8 minutes and sufficient to form an alloyed zone between the aluminum coating and the iron body extending less than substantially two-thirds of thickness of the aluminum layer, and coating said layer and impregnating its pores with a water-repellent protective layer, selected from the group which consists of hardenable waxes, polyethylenes, polyesters, polyamides and epoxy resins.



6. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum of a thickness of about 0.1 to 0.4 mm., and subjecting said layer to heat treatment in an oxidizing atmosphere at a tempertature between substantially 690° and 800° C. for a period sufficient to change the color of said surface layer to shade of grey characterized by a photometric density value between substantially 0.1 and 1.2 in the cold state of said layer upon treatment thereof by liquid paraffin, said photometric density value being the logarithm of the ratio of the intensity of the illumination incident upon said layer to that of the illumination reflected by it, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body.

7. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum having a thickness between substantially 0.1 and 0.4 mm., and subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 690° and 800° C. for a period sufficient to change the color of said surface layer to a shade of grey characterized by a photometric density value between substantially 0.1 to 1.2 in the cold state of said layer upon treatment thereof by liquid paraffin, said photometric density value being the logarithm of the ratio of intensity of the illumination incident upon said layer to that of the illumination reflected by it, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body.

8. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of spraying on an iron body a surface layer of aluminum having a thickness between substantially 0.1 and 0.4 mm., and subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 720° and 740° C. for a period sufficient to change the color of said surface layer to a shade of grey characterized by a photometric density value between substantially 0.2 and 1.0 in the cold state of said layer upon treatment thereof by liquid paraffin, said photometric density value being the logarithm of the ratio of the intensity of the illumination incident upon said layer to that of the illumination reflected by it, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body.

9. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum of a thickness between substantially 0.1 to 0.4 mm., subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 690° and 800° C. for a period sufficient to change the color of said surface layer to a shade of grey characterized by a photometric density value between substantially 0.1 and 1.2 in the cold state of said layer upon treatment thereof by liquid paraffin, said photometric density value being the logarithm of the ratio of the intensity of illumination incident upon said layer to that of the illumination reflected by it, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body; said treatment by liquid paraffin including the steps of cooling said layer to a temperature below 400° C. and immersing it in a bath of said paraffin heated to a temperature above its melting point whereby said paraffin penetrates into said layer, and subjecting the paraffin-treated layer to a further heat treatment at a temperature higher than that of said bath and below 160° C.

10. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum of a thickness of about 0.1 to 0.4 mm., subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 720° and 740° C. for a period of substantially 1 to 8 minutes and sufficient to form an alloyed zone between the aluminum coating and the iron body extending less than substantially two thirds of the thickness of the aluminum layer, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body, cooling said layer to a temperature below 400° C., immersing it in a bath of paraffin heated to a temperature above its melting point whereby said parrffin penetrates into said layer, and subjecting the paraffin-treated layer to a further heat treatment at a temperature higher than that of said bath and below 160° C.

11. A process for producing corrosion-resistant aluminum-coated iron bodies, comprising the steps of depositing on an iron body a surface layer of aluminum of a thickness of about 0.1 to 0.4 mm., subjecting said layer to heat treatment in an oxidizing atmosphere at a temperature between substantially 720° and 740° C. for a period



of substantially 1 to 8 minutes and sufficient to form an alloyed zone between the aluminum coating and the iron body extending less than substantially two thirds of the thickness of the aluminum layer, thereby rendering said surface layer porous while simultaneously forming a diffuse aluminum-iron interface at the junction of said layer with said body, and coating said layer with a film-forming synthetic resin selected from the group which consists of polyethylenes, polyesters, polyamides and epoxy resins.


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ALFRED L. LEAVITT, *Primary Examiner.*

RALPH S. KENDALL, *Examiner.*