

Sept. 26, 1967

A. R. BORZILLO ET AL

3,343,930

FERROUS METAL ARTICLE COATED WITH AN ALUMINUM ZINC ALLOY

Filed July 14, 1964

3 Sheets-Sheet 1

Fig. 1

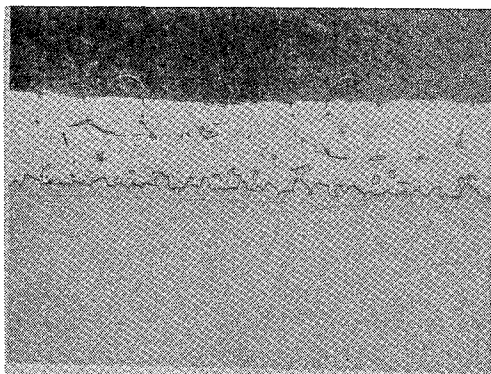
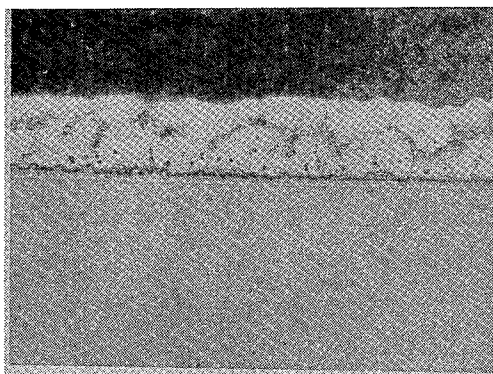


Fig. 2

INVENTORS

Angelo R. Borzillo

James B. Horton

Sept. 26, 1967

A. R. BORZILLO ETAL

3,343,930

FERROUS METAL ARTICLE COATED WITH AN ALUMINUM ZINC ALLOY

Filed July 14, 1964

3 Sheets-Sheet 2

Fig. 3

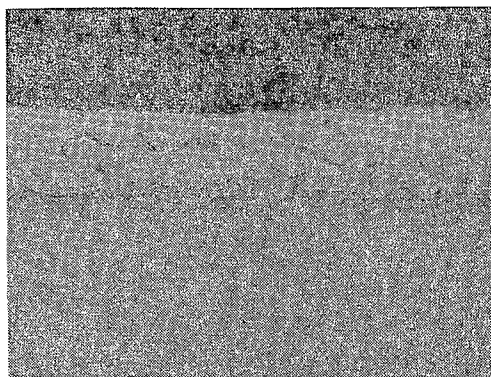
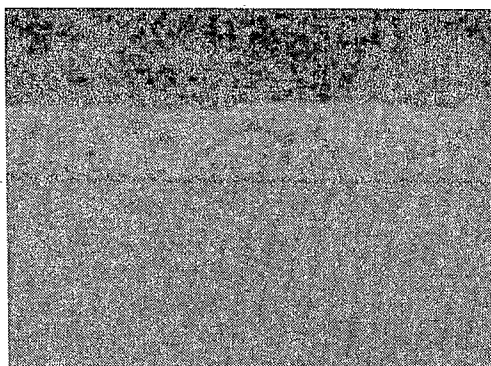


Fig. 4

INVENTORS

Angelo R. Borzillo

James B. Horton

Sept. 26, 1967

A. R. BORZILLO ET AL

3,343,930

FERROUS METAL ARTICLE COATED WITH AN ALUMINUM ZINC ALLOY

Filed July 14, 1964

3 Sheets-Sheet 3

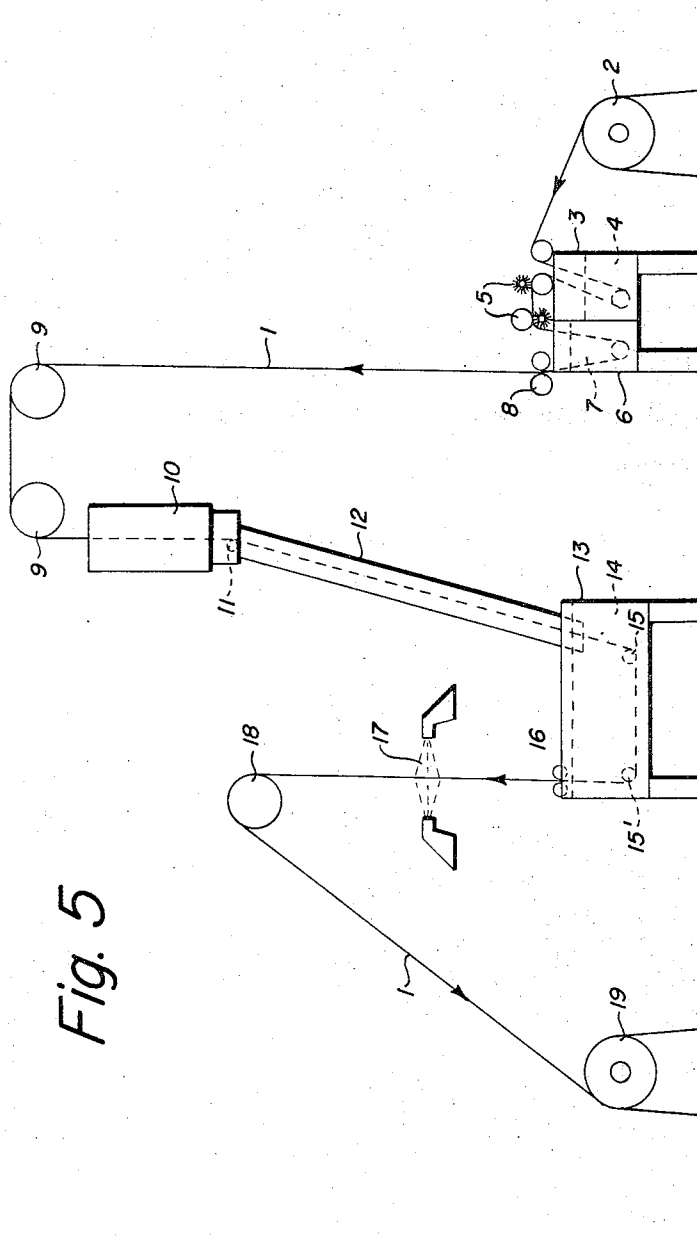


Fig. 5

INVENTORS

Angelo R. Borzillo

James B. Horton

1

3,343,930

FERROUS METAL ARTICLE COATED WITH AN ALUMINUM ZINC ALLOY

Angelo R. Borzillo, Allentown, and James B. Horton, Bethlehem, Pa., assignors to Bethlehem Steel Company, a corporation of Pennsylvania
Filed July 14, 1964, Ser. No. 382,595
9 Claims. (Cl. 29—196.2)

This invention relates to zinc-aluminum coatings on ferrous surfaces, and more particularly to zinc-aluminum protective coatings on steel surfaces which coatings are ductile, corrosion resistant and tightly adherent to said surfaces.

In the protection of ferrous surfaces from corrosive media, it is common practice to coat the ferrous metal surface with a non-ferrous metal, by immersion in a molten bath of the coating metal or by other methods. These coatings should not only be protective, but they should be ductile and tightly adherent as well, and should have a smooth, pleasing appearance.

Many metals have been used in the past as a protective coating for ferrous surfaces, such metals including tin, zinc,terne metal, nickel, chromium, cadmium, copper, aluminum, bronze and lead. One of the most commonly used coating metals is zinc, partly because of its relatively low cost, and partly because of its higher position in the electromotive series relative to iron. However, for many applications, zinc coatings do not have adequate resistance to corrosion. The search for metallic coatings which will combine high protective power, ductility, adherence, good appearance and low cost is a continuing one.

Accordingly it is an object of this invention to provide a ferrous base having thereon a metallic coating which is highly corrosion-resistant.

Another object of this invention is to provide metallic coatings on ferrous base stock, which coatings are metallurgically bonded to the base stock.

Another object of this invention is to provide a ferrous base which has a metallic coating thereon and in which the iron-bearing alloy layer at the interface between coating and base metal is thin and uniform.

A further object is to provide a ferrous base having a metallic coating thereon characterized by good appearance and formability.

An additional object is to provide a ferrous base with a metallic coating which is ductile and firmly adherent.

Another object is to provide a method for producing said coated product.

We have discovered that the foregoing objects can be attained by providing a ferrous base which has metallurgically bonded thereto a coating consisting essentially of from 25% to 70% aluminum, with the balance substantially zinc.

Our product is characterized by the fact that the iron-bearing alloy layer at the interface of the ferrous base and the coating is thin and uniform.

Briefly, the method by which our new product is obtained broadly comprises applying to a ferrous base, such as strip, the surface of which is substantially free from oxides and other contaminants, a coating consisting essentially of 25% to 70% aluminum, balance zinc, the coating being applied in such a manner as to result in a thin and uniform iron-bearing alloy layer at the interface between the base and the coating.

This invention has particular applicability for the coating of steel strip and wire. Heavy alloying at the interface of steel strip and a non-ferrous protective coating metal promotes cracks in the coating upon subsequent deformation of the coated product. In addition, with strip of thin gages, heavy alloying of coating metal with iron of the

2

strip results in a large proportionate loss of base metal, thus weakening the base metal itself. Then too, heavy alloying at the interface at times results in an uneven coating, the surface appearance of which leaves much to be desired.

The coated product of our invention and a preferred method, by which the coating may be applied to a ferrous base, will be described with reference to the following drawings.

FIG. 1 is a reproduction of a photomicrograph of a cross section of a coated steel strip embodying our invention, the coating containing approximately 25% aluminum, and approximately 74% zinc.

FIG. 2 is a reproduction of a photomicrograph of a cross section of a coated steel strip embodying our invention, the coating containing approximately 35% aluminum, and approximately 64% zinc.

FIG. 3 is a reproduction of a photomicrograph of a cross section of a coated steel strip embodying our invention, the coating containing approximately 54% aluminum, and approximately 44.5% zinc.

FIG. 4 is a reproduction of a photomicrograph of a cross section of a coated steel strip embodying our invention, the coating containing approximately 70% aluminum, and approximately 28% zinc.

FIG. 5 is a diagrammatic side elevation of a preferred embodiment of apparatus for producing the product of this invention.

A preferred method of coating a ferrous base, e.g. steel strip, is as follows. The strip is first passed through a cleaning solution which removes grease and dirt from the surface thereof. The cleaned strip is then introduced into a furnace and heated to a temperature approximately that of the coating bath. The strip is then passed through a protective atmosphere directly into a bath of molten metal consisting essentially of 25% to 70% aluminum, balance zinc. The temperature of the bath is maintained slightly above the melting point of the metal, the exact temperature depending, of course, upon the relative amounts of aluminum and zinc in the bath.

Strip speeds and bath immersion times are similar to those used in continuous galvanizing.

Following is a specific example of our preferred method.

Referring to FIG. 5, a strip 1 of 28 gage rimmed steel, having a carbon content of 0.06%, a manganese content of 0.31%, and other elements customarily found in rimmed strip steel, was fed from pay-off reel 2 to cleaning tank 3 containing an aqueous solution 4 (approximately 4 oz./gal.) of Pennsalt No. 30, a standard alkaline cleaning solution for steel strip. The cleaning solution was maintained at a temperature of approximately 180–200° F. The cleaned strip was scrubbed at scrubbers 5, and rinsed in tank 6 with water rinse 7. From the rinse tank 6, the strip was led through rubber squeegee rolls 8, over rolls 9 and downwardly through a furnace 10, where the strip was heated to a temperature of approximately 1200° F. The furnace was heated by the products of combustion of natural gas and air in the ratio of 1 to 8. From the furnace, the strip was led around positioning roll 11, through a holding chamber 12 where its temperature fell to approximately 800° F. An atmosphere of 99% hydrogen was maintained in the holding chamber 12 to protect the strip from oxidation prior to its entry into the coating pot 13. After entering pot 13, the strip was passed through a molten bath 14, by way of sinker rolls 15 and 15'. This bath was maintained at a temperature of 1060° F. Upon leaving the bath, the strip was passed between a pair of smooth low carbon steel exit rolls 16. An air-blast 17 was used to chill the coating as the strip passed vertically to roll 18, and then take-up reel 19. The speed of the

3

strip was approximately 45 feet per minute and the time of immersion in the coating bath was about 4 seconds. The total coating thickness, which includes the coating on the two sides of the thus-coated strip, averaged 0.00197 inch.

In preparing the molten bath, 99.50% minimum Al grade aluminum was used. This material had the following analysis:

	Percent
Aluminum -----	99.65
Iron -----	0.19
Silicon -----	0.13
Manganese -----	0.01
Zinc -----	0.01
Vanadium -----	0.01
Cadmium -----	0.02
Sodium -----	0.001

The zinc employed for the molten mixture had a specified zinc purity of better than 99.99%.

Silicon was added to the bath in the form of an aluminum alloy. This material analyzed as follows:

	Percent
Silicon -----	12.00
Iron -----	0.33
Aluminum -----	Balance

These ingredients were combined in such proportions that the bath analyzed approximately 35% aluminum, 64% zinc, and 1% silicon.

A photomicrograph taken at 500 magnifications, of a cross section of the coated product, made by the method of the example, is reproduced in FIG. 2. The alloy layer between the coating and base metal is so thin as to be almost indistinguishable at 500 magnifications.

FIG. 1 is a reproduction of a photomicrograph, also at 500 magnifications, of a cross section of another coated product of our invention wherein carbon steel strip was coated by the process above described in a bath analyzing approximately 25% aluminum, 74% zinc and 0.77% silicon. In this sample, there is no distinguishable alloy formation of iron with coating metal.

As the aluminum content in the coating is increased above 35%, there is evidence of a small amount of interfacial alloy layer. But even when the aluminum represents 70% of the alloy coating, the iron-bearing alloy at the interface is uniform and thin. The thinness and uniformity of the interfacial alloy occurring with the higher ranges of aluminum can be observed in FIGURES 3 and 4, each of which is a photomicrograph, at 500 magnifications, of a cross section of a similar steel, coated by the process above described. In FIG. 3, the bath, from which the coated product was made, analyzed approximately 54% aluminum, 44.5% zinc and 1.5% silicon, while in FIG. 4 the coating bath had an analysis of approximately 70% aluminum, 28% zinc and 2% silicon.

All of the samples shown in FIGURES 1-4 were etched in a solution of 95% amyl alcohol, 5% nitric acid, for five seconds.

By thin iron-bearing alloy layer is meant a layer at the interface having an average thickness not greater than about 0.25 mil, excluding localized projections. However, our invention, in its broad aspects, is not limited to an alloy layer of this thinness, for in some applications it may be possible to tolerate a layer of greater thickness.

By uniform is meant a layer surface which is substantially flat (for a flat substrate) but which may include localized projections into the zinc-aluminum coating, as shown, for example, in FIGS. 3 and 4.

The operating temperature of the molten coating bath will ordinarily range from about 975° F. to 1220° F., depending on the amount of aluminum in the alloy, the temperature increasing with increasing aluminum content.

Specific examples of preferred bath temperatures for

4

varying aluminum contents are set forth in the following examples:

Aluminum (percent):	Approximate bath temperature (° F.)
25 -----	995
35 -----	1060
45 -----	1120
54 -----	1155
70 -----	1205

Coatings made as above described are metallurgically bonded to the ferrous base.

Our coated products have many favorable properties, as will be apparent from the following data based on coatings produced by the method above described.

In the entire coating range of 25% to 70% aluminum, the coated products of this invention show an advantage over continuously galvanized products in the salt spray test of the order of approximately 3 to 1, up to 8 to 1. The salt spray test is performed according to A.S.T.M. Method B117-62.

Typical results (average of four 4" x 6" test specimens with protected edges) for salt spray tests are set forth in the following table for a galvanized steel sheet, and for steel sheets coated with zinc-aluminum coatings according to the invention.

TABLE I

Type of coating:	Hours to first (1%) rust per mil of coating thickness
(1) Continuous galvanized -----	325
(2) Zinc-aluminum coating containing approximately 25% Al -----	2290
(3) Same as (2) with approximately 35% Al -----	3234
(4) Same as (2) with approximately 45% Al -----	¹ >3805
(5) Same as (2) with 54% Al -----	¹ >3405
(6) Same as (2) with 70% Al -----	940

¹ Tests not completed.

Appearancewise, the coated products of the invention exhibit a small spangle. This property is highly desirable in many operations, where additional surface treatment, such as the application of paint, is required. In the coating range of from about 25% to 45% aluminum content, the surface of the product has an exceptionally smooth, white lustre.

In the so-called muffler test, the corrosion resistance of the products of our invention, within the coating range of 25% to 70% aluminum content, is far and above that which can be met with galvanized products.

The muffler test referred to is that known as Muffler Condensate Test. In the test, coated specimens, 2 inches by 4 inches, are dipped into an aqueous solution of 0.05 normal sulfuric acid and 0.01 normal hydrobromic acid for 8 seconds at a solution temperature of 180° F. The specimens are removed at the end of the 8 second immersion period, and suspended in the vapors of the immersion solution for the remainder of one hour. The procedure is repeated every hour for 20 hours, after which the specimens are heated in a laboratory furnace for 2 hours at 500° F. to complete what is referred to as a one-day cycle. Specimens are examined visually after each one-day cycle for start of rusting (disregarding the rusting of the sheared edges of the specimens). The complete test comprises 13 one-day cycles.

Test results from the muffler test are shown in Table II, which follows:

TABLE II

Type of coating:	Cycles for start of rusting of steel base *
(1) Continuous galvanized -----	6
(2) Zinc-aluminum coating containing approximately 25% Al -----	12-13
(3) Same as (2) with approximately 35% Al -----	13

5
TABLE II—Continued

Type of coating:	Cycles for start of rusting of steel base *
(4) Same as (2) with approximately 45% Al -----	13
(5) Same as (2) with approximately 54% Al -----	13
(6) Same as (2) with approximately 70% Al -----	13

* Rusting of sheared edges of specimens disregarded.

The products of our invention in the entire range from 25% to 70% aluminum in the coating, meet A.S.T.M. Specification No. A93-59T for bend test requirements. Further, in the demanding flat lockseam test, the products of our invention showed no flaking at any aluminum concentration in the coating of from 25% to 45%. The 70% aluminum coating showed slight localized flaking.

Furthermore, the products of our invention having coatings in the range between 25% and 45% aluminum showed only slight cracking when bent 180° flat on themselves.

The ductility and adherence of the coatings of the products of our invention, over the entire range of aluminum content (25% to 70% aluminum) are such that the said products can withstand commercial forming such as corrugating, bending, etc. without significant cracking or flaking.

Our improved coating may also be applied by what may be referred to as a roll-bonding procedure. As an example of this method, the surface of a low carbon steel sheet was roughened by acid etching. A thin layer of tridecyl alcohol was applied to the surface of the sheet. The sheet was then coated with a mixture comprising zinc powder (75%) and aluminum powder (25%), the alcohol serving to promote initial adherence of the powder to the sheet. The sheet, with the powder coating thereon, was passed through pressure rolls to compact the powder on the sheet, and was then heated at 750° F. for a period of about five minutes to bond the coating to the sheet. This method is described more fully in an application by Edward H. Mayer and Hilton N. Rahn, filed concurrently herewith.

As far as is presently known, silicon is required in producing the product of our invention by the hot dip process. We have found that the presence of silicon in the bath promotes the formation of an adherent coating, suppresses the formation of an iron-bearing alloy layer at the interface between the strip and the coating, and assures that the alloy layer which is formed is thin and uniform. We have further found that the silicon content of the bath should be not less than 0.5%, and preferably about 3%, of the aluminum content. More silicon may be used if desired. Silicon will also be present in the coating. However, the silicon content of the coating does not, so far as we can determine, have any effect on the corrosion resistance of the coated product. Silicon is not essential to the roll bonding process.

To recapitulate, we have found that our zinc-aluminum coated ferrous products, wherein the aluminum content represents from 25% to 70% of the total coating, exhibit corrosion resistance properties superior to those of continuously galvanized products. Within this broad range, coatings having an aluminum content between 25% and 45% of the total coatings are characterized by their ductility and freedom from flaking, when subjected to severe forming operations; while coatings having an aluminum content between 40% and 60% of the total coating are characterized by their remarkable corrosion resistance, which is far superior to that of galvanized coatings, although at some slight loss of formability at the high end of the aluminum ranges.

Examples of articles, other than steel strip, for which the above-described zinc-aluminum coatings would find ready application, are steel wire, hardware and structural shapes.

While the coatings of the products of our invention consist essentially of the metals zinc and aluminum, other substances which do not materially detract from the novel and basic properties of our invention may be present either as impurities or as deliberate additions. For example, the coating may contain up to 0.3% chromium for control of intergranular corrosion.

By the term "consisting essentially of" we do not wish to exclude the presence of such substances.

All percentages shown herein, which relate to bath or coating components, represent weight percent.

We claim:

1. A ferrous base having a ductile, adherent, corrosion-resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 70% aluminum, balance zinc.

2. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 45% aluminum, balance zinc.

3. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 40% to 60% aluminum, balance zinc.

4. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 70% aluminum, silicon in an amount not less than 0.5% of the aluminum content, balance zinc.

5. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 45% aluminum, silicon in an amount not less than 0.5% of the aluminum content, balance zinc.

6. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 40% to 60% aluminum, silicon in an amount not less than 0.5% of the aluminum content, balance zinc.

7. A ferrous base having a ductile, adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 70% aluminum, balance zinc, the iron-bearing alloy layer at the interface between the ferrous base and the coating being thin and uniform.

8. A ferrous base having an adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 25% to 45% aluminum, balance zinc, the iron-bearing alloy layer at the interface between the ferrous base and the coating being thin and uniform.

9. A ferrous base having an adherent, corrosion resistant coating metallurgically bonded thereto, said coating consisting essentially of 40% to 60% aluminum, balance zinc, the iron-bearing alloy layer at the interface between the ferrous base and the coating being thin and uniform.

References Cited

UNITED STATES PATENTS

2,126,244	8/1938	Cook -----	29—196.5
2,196,034	4/1940	Schulzo -----	75—178.6
2,870,008	1/1959	Neu -----	75—146 X
3,190,768	6/1965	Wright -----	29—196.5 X

HYLAND BIZOT, *Primary Examiner.*

UNITED STATES PATENT OFFICE
Certificate of Correction

Patent No. 3,343,930

September 26, 1967

Angelo R. Borzillo et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawings, Sheet 1, strike out FIGS. 1 and 2 and insert instead the following:

Fig. 1

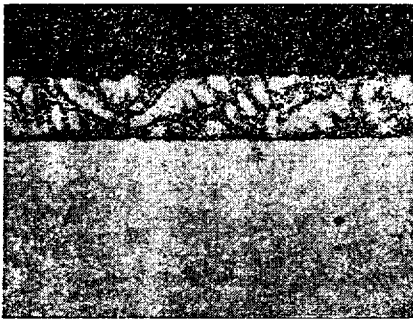
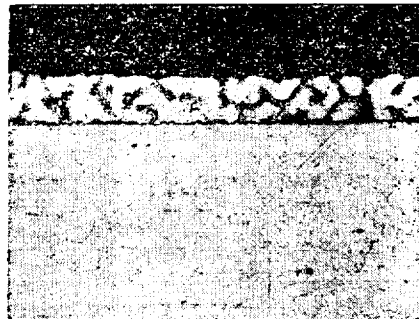


Fig. 2



in the heading to the printed specification, lines 4 to 6, for "Angelo R. Borzillo, Allentown, and James B. Horton, Bethlehem, Pa., assignors to Bethlehem Steel Company, a corporation of Pennsylvania" read—Angelo R. Borzillo, Bethlehem, and James B. Horton, Allentown, Pa., assignors, by mesne assignments, to Bethlehem Steel Corporation, a corporation of Delaware—.

Signed and sealed this 11th day of March 1969.

[SEAL]

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer.

EDWARD J. BRENNER,
Commissioner of Patents.