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54 **Method of producing corrosion-resistant coatings on ferrous-base articles.**

57 Hot-dip aluminum-zinc coatings having an aluminum content in excess of about 25% aluminum exhibit a tendency for corrosion flaking, that is, selective corrosion along the interface between the aluminum-zinc overlay and the underlying intermetallic layer. The tendency to such corrosion flaking increases with the aluminum content of the coating. Methods for minimizing this tendency by accelerated cooling of the molten coating as it emerges from the coating bath are ineffective for coatings containing greater than 72% aluminum. It has been found that the addition of 0.04 to 0.32% magnesium in hot-dip aluminum-zinc coating baths will substantially enhance the resistance of the coating to corrosion flaking.

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METHOD OF PRODUCING CORROSION-RESISTANT
COATINGS ON FERROUS-BASE ARTICLES

The present invention relates to the
production of corrosion-resistant coatings on
5 ferrous-base articles.

Hot-dip coated steel articles having a coating
composed principally of various combinations of
aluminum and zinc are known to exhibit an optimum
combination of general corrosion resistance, more
10 durable than zinc coatings, while providing more
galvanic protection to cut edges and areas of
mechanical damage than do hot-dip aluminum coatings.
Thus, a coating bath containing from 25% to 70%
aluminum, balance zinc and silicon is shown in United
15 States Patent Specification No. 3,343,930, and a
coating bath containing from 12 to 24% zinc, optional
amounts of silicon and balance aluminum, is shown in
European Patent Application No. 82306407.6.

It has been shown, however, in United States
20 Patent Specification No. 3,782,909, under certain

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accelerated corrosion tests (in environments containing acidified chlorides) that the coatings containing from 25% to 70% aluminum exhibit a tendency towards "corrosion flaking" in which the aluminum-zinc coating separates along the interface between the intermetallic layer and the aluminum-zinc overlay, even in the absence of any mechanical strain such as bending. The accelerated tests comprise an initial five minute leach with concentrated nitric acid to partially dissolve the zinc-rich materials, rinsing, and then exposure in an acidified salt spray at a pH of 3 and a temperature of 95°F (35°C) for 45 minutes, followed by two hours of drying with compressed air and then 3 1/4 hours holding in the salt spray. The exposure-drying cycle is repeated and the coating is considered stabilized if it survives 100 cycles of the test procedure without exhibiting corrosion flaking. The initial leaching with nitric acid is deemed so severe, that the correlation of the above tests with actual, realistic environment is somewhat questionable. When employing a less severe test, such as ASTM B117-73, the correlatability of which is generally more reliable (although not proven with respect to corrosion flaking), coatings containing about an equal amount of zinc and aluminum do not exhibit corrosion flaking even

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when slowly cooled and thus not stabilized. However, flaking tendency appears to increase as the aluminum concentration of the coating increases. Thus, coatings containing more than about 72% aluminum will exhibit
5 flaking, in the less drastic ASTM test, irrespective of whether they had been stabilized by the rapid cooling. It was found that the resistance to flaking, as evaluated by ASTM B117-73, can significantly be increased by the addition of small amounts of magnesium
10 to the molten aluminum-zinc alloy bath.

According, therefore, to the present invention, there is provided a method of producing corrosion-resistant coatings metallurgically bonded to ferrous-base articles, which comprises dipping a clean
15 surface of said article into a molten bath consisting essentially of, by weight, 72% to 95% Al, up to 3.5% Fe, up to 4% Si, balance Zn for a period at least sufficient to form an aluminum-zinc coating thereon with an interfacial alloy layer portion having a
20 thickness greater than 0.01 mils, said layer resulting from the reaction of the ferrous surface with the bath, removing the coated surface from said bath and cooling the molten coating adhering thereto, wherein resistance to corrosion flaking of the resulting coating is
25 enhanced by adding 0.04 to 0.32% Mg to said molten bath.

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The invention is further described, by way of example, with reference to the accompanying drawing which is a graph showing the effect of small amounts of magnesium on the corrosion flaking of alloy coatings within the range 72 to 95% aluminum (1% Si and balance zinc).

Test samples used for evaluation of corrosion flaking, were prepared by a procedure similar to that described in United States Patent Specification No. 3,393,089. The steel sheet was cleaned in an aqueous silicate solution, annealed in-line under reducing conditions by heating to a temperature of 1475°F (790°C) and cooled to a temperature slightly above bath temperature prior to entry into the coating bath.

The reducing furnace atmosphere was maintained by introducing a hydrogen-nitrogen mixture into a snout just above the bath surface. A baffle was located inside the snout to prevent the incoming cold gases from impinging directly onto the strip. Coating baths were maintained at a temperature of 75 to 100°F (40 to 55°C) above the liquidus temperature for each bath concentration. Air-knives were used to control the thickness of the coating on the strip. For each bath concentration, duplicate runs were employed: (i) in which the average cooling rate over the range of

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solidification was maintained at 25°F/sec.

(14°C/sec.), and (ii) in which said average cooling rate was 15°F/sec. (8°C/sec.) that is, below the critical rate of 20°F/sec. (11°C/sec.) disclosed in

5 U. S. Patent No. 3,343,930.

For coatings containing more than 72% aluminum, less than 4% Si, less than 3.5% Fe, balance Zn, no differences in corrosion flaking tendency were detected, irrespective of the cooling rate employed.

10 Results of the tests performed in accord with the ASTM B117-73 test procedure are reported graphically in the Figure. It may be seen therefrom, with magnesium concentrations of from 0.04 to 0.32% Mg (all percentages by weight), that the flaking tendency of
15 such hot-dip coatings is decreased, and that immunity (in the salt spray environment of ASTM test) is essentially achieved by the addition of 0.07 to 0.28% Mg to such higher Al baths. In this regard, it should be noted that the addition of somewhat similar amounts
20 of Mg to coating baths containing lower amounts of Al, (for example the 25 to 70% Al baths of U. S. Patent No. 3,343,930) would most likely be beneficial in enhancing the resistance to flaking of such lower Al coatings, as well. However, no tests were conducted in this lower

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Al range, since an alternative is already available to the art, that is, the accelerated cooling procedure of U. S. Patent No. 3,782,909.

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CLAIMS:-

1. A method of producing corrosion-resistant coatings metallurgically bonded to ferrous-base articles, which comprises dipping a clean surface of
5 said article into a molten bath consisting essentially, of by weight, 72% to 95% Al, up to 3.5% Fe, up to 4% Si, balance Zn for a period at least sufficient to form an aluminum-zinc coating thereon with an interfacial alloy layer portion having a thickness greater than
10 0.01 mils (0.25 micron), said layer resulting from the reaction of the ferrous surface with the bath, removing the coated surface from said bath and cooling the molten coating adhering thereto, characterized by adding from 0.04 to 0.32% Mg to said molten bath.
- 15 2. A method as claimed in claim 1, characterized in that said ferrous-base article is steel sheet and said sheet is dipped into the bath for a period to form an alloy layer having a thickness less than 0.5 mils (13 microns).
- 20 3. A method as claimed in claim 1 or claim 2, characterized in that said bath contains 12 to 24% Zn, less than 1% silicon, and less than 2.5% iron.
4. A coated product produced by the method of any preceding claim.

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