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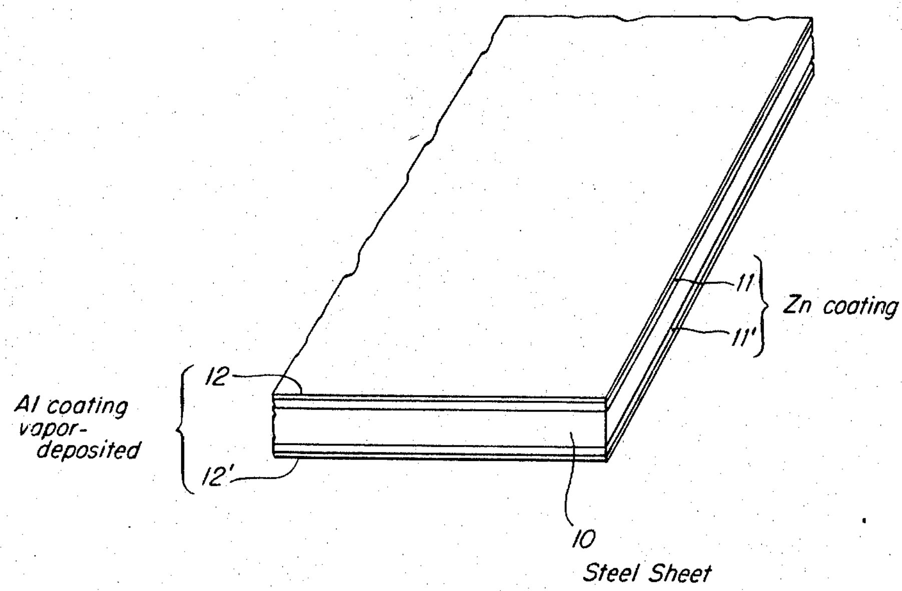

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ZINC-COATED STEEL WITH VAPOR-DEPOSITED ALUMINUM OVERLAY AND METHOD OF PRODUCING SAME

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ABSTRACT OF THE DISCLOSURE

A zinc-coated steel article with a vapor-deposited aluminum overlay is produced by applying to a steel surface an adherent coating of zinc, and thereafter applying a coating of aluminum to the zinc-coated steel surface by depositing aluminum vapor thereon.

This invention relates to the manufacture of zinc-coated steel articles. In particular, it is directed to methods of producing on a steel surface a zinc coating having improved corrosion resistance, and also to the resulting articles, such as steel sheet carrying an adherent corrosion-resistant coating.

The coating of sheet steel and other steel articles with zinc, as by hot-dip galvanizing, electroplating or vapor deposition, is widely employed as a steel surface-treating operation. Zinc-coated steel sheet, meaning strip or other sheet of steel, whether cold rolled or hot rolled, has distinct advantages in many fields of use, particularly in avoiding or reducing corrosion or like deterioration of the steel surface. As is well known, zinc protects steel galvanically, i.e., in a corroding medium the zinc will preferentially corrode; in any given corroding medium the protection which the zinc affords the steel is a function of its thickness.

Under severe conditions (as for example in exposure to salt spray) the zinc is rapidly consumed, and accordingly the protection afforded by the coating against corrosion, in the case of conventional zinc coatings, may be relatively short-lived. In other words, under such conditions conventionally zinc-coated steel articles may exhibit substantial corrosion after comparatively brief periods of exposure.

An object of the present invention is to improve the resistance to corrosion of zinc-coated steel articles and in particular to increase the duration of effective protection against corrosion afforded by zinc coatings on steel surfaces. Another object is to provide methods of producing zinc coatings on steel, affording coatings having improved corrosion resistance. A further object is to provide zinc-coated steel articles having superior corrosion-resistant properties.

To these and other ends, the method of the invention in a broad sense contemplates establishing an adherent coating of zinc on a steel substrate, e.g., in conventional manner, and thereafter applying to the zinc-coated surface a further, thin coating or overlay of aluminum by depositing aluminum vapor thereon. It is found that zinc-coated steel articles thus produced, i.e., having a thin vapor-deposited aluminum overlay, exhibit greatly enhanced resistance to corrosion and in particular that the duration of effective protection against corrosion afforded by the zinc coating is very materially increased, as compared to that afforded by conventional zinc coatings of equivalent thickness. This improvement in corrosion resistance is presently believed to be due to some effect of the aluminum overlay in sealing the pores which exist in zinc coatings and/or otherwise serving to make the zinc surface less active thereby to retard the consumption of zinc under corrosive conditions.

In the practice of the present method, the step of applying the zinc coating may itself, as stated, be entirely conventional. Thus, for example, the zinc coating may be established on the steel substrate by hot-dip galvanizing or by electroplating. In hot-dip galvanizing, the steel surface, suitably cleaned, is immersed in a body of molten zinc to establish on the surface a zinc layer that solidifies (after the surface is withdrawn from the zinc bath) as a coating adherent thereto. Electroplating of zinc involves immersing the steel surface (after thorough cleaning thereof) in an appropriate electrolytic bath, e.g., containing zinc sulfate, and passing direct electric current through the bath, to plate an adherent coating of zinc onto the surface. The resultant zinc coating as prepared by either procedure may be wholly conventional in character, e.g., a conventional hot-dip galvanized or electroplated zinc coating on steel, and may have a thickness (for example) of the order of 20 to 1,500 microinches (one microinch being 10^{-6} inch), or more depending upon conditions of operation of a zinc-applying step. Both hot-dip galvanizing and electroplating operations as contemplated herein, including surface precleaning steps and selection of conditions to produce a desired coating thickness, are well-known in the art and accordingly need not be described in detail.

Following the application of the zinc coating, however produced, a further coating, of aluminum metal, is applied to the zinc-coated steel surface by vapor deposition. This vapor deposition step may be performed in accordance with conventional vacuum metalizing techniques for depositing aluminum from vapor on a metal substrate. Thus, the deposition may take place in a standard vacuum system for the vapor deposition of metals having a vacuum chamber, into which the steel is passed after coating with zinc. To achieve desired adherence of the aluminum layer, the zinc-coated steel surface as introduced to the chamber must be thoroughly clean and dry; accordingly, between the steps of applying the zinc and aluminum coatings, the surface may be cleaned or rinsed and dried, again in accordance with conventional procedures for preparing metal substrates for vacuum metalizing. For the vapor-depositing operation, the vacuum chamber is evacuated and maintained at a relatively high vacuum, of the order of a half micron or less of mercury, and aluminum from a clean and uncontaminated source is evaporated, by heating the source, to produce aluminum vapor in the chamber. The vapor condenses or deposits on the zinc-coated surface as an adherent solid film of aluminum overlying the zinc coating, the thickness of this film being determined by the rate of vapor deposition and duration of exposure of the surface thereto.

One specific example of a vacuum-metalizing technique, suitable for use in depositing the aluminum coating in the present method, is that described in United States Patent No. 2,959,494 as employed to deposit aluminum from vapor on a bare steel substrate. This procedure may be performed in a vacuum system consisting of a vacuum metallizer and a vacuum chamber. In the step of deposition of aluminum, the vacuum chamber is evacuated prior to aluminum deposition by a four stage procedure which includes a first step of rough pumping to a vacuum of 200 microns of mercury. The vacuum is then further reduced by the use of diffusion pumps. The residual atmosphere remaining after a pump-down must not contain organic vapors. A high voltage discharge step provides good adherence of the aluminum coating on the substrate; this is effected while the vacuum chamber is being evacuated with the diffusion pumps. The surface of the substrate is degassed by a high voltage discharge. After the high voltage discharge, the fourth step of the pump-down procedure carries the vacuum to about 0.5 micron of pressure. Aluminum is then vaporized from a suitably heated surface to which metallic aluminum is supplied. Alternatively, the aluminum may be vaporized by means of an electron beam, e.g. utilizing electron-beam vaporizing apparatus and techniques as known in the art, wherein the aluminum source is positioned in a vacuum chamber in the path of a beam of electrons from a suitable electron source with appropriate voltage applied between the electron source and the aluminum source, so that the electron beam vaporizes aluminum from the latter source for deposition on the substrate to be coated.

An alternative example of a vacuum-metalizing technique suitable for depositing aluminum from vapor on the zinc-coated steel surface in the present method is that described in United States Patent No. 3,117,887, wherein a strip of sheet metal substrate to be coated is continuously advanced through a vacuum chamber past a vertical plate or block which is maintained at aluminum-vaporizing temperature by electrical resistance heating, i.e. by passage of electric current therethrough. Aluminum in wire form is fed into contact with the upper part of a vertical surface of the heated block (such surface being parallel to and facing the metal substrate surface to be coated); the aluminum melts and flows down over the vertical block surface and evaporates therefrom as a vapor which deposits on the substrate.

The product of the invention, as obtained by the described method, is a zinc-coated steel article (of sheet, strip or other form) having a thin, continuous vapor-deposited outer coating of aluminum. The integrity of the zinc coating is maintained through the aluminum deposition step; i.e. in the final product the zinc layer has integrity as a zinc coating and indeed is itself a conventional adherent coating of zinc as heretofore employed for protection of steel surfaces against corrosion. The vapor-deposited aluminum coating overlies this zinc coating and adheres thereto. A presently preferred range of values of thickness for the vapor-deposited aluminum overlay is between about 5 microinches and about 100 microinches, a thickness of at least about 15 microinches being presently considered particularly advantageous and a range of between about 30 and about 60 microinches being especially preferred. The aluminum coating thickness may exceed 100 microinches if desired, the latter value representing a preferred upper limit from the standpoint of economy.

After the zinc and aluminum coatings have been applied as described above, the coated steel surface may, if desired, optionally be treated with a chromite solution, in accordance with conventional procedures as presently used for treating zinc coatings to prevent white rust, and for treating aluminum coatings to promote paint adherence. Many such chromate solutions are well-known in the art and commercially available; by way of specific example, the zinc-coated steel surface bearing the aluminum overlay may be treated with Iridite Solution 14–9, which is manufactured by Allied Research Products, Inc., and is believed to be basically a potassium dichromate solution. This chromate treatment in certain instances appears to enhance the corrosion resistance of the coated surface to some extent, but is not necessary to the attainment of the advantages of the invention and thus may be omitted.

The effect of the aluminum overlay on the corrosion-resistant properties of zinc-coated steel has been ascertained by testing, for resistance to corrosion under exposure to salt spray, zinc-coated steel panels (including both hot-dip galvanized and electroplated zinc-coated panels) prepared and coated with a vapor-deposited overlay of aluminum in accordance with the invention. The samples tested included panels having aluminum coatings 15, 30, 45 and 60 microinches thick, deposited over zinc coatings of various thicknesses ranging from less than 50 microinches to more than 950 microinches. Some of these panels were treated, i.e. before testing, with a chromate solution as described above; others were untreated. Results of the tests were compared with results of similar tests on panels having conventional hot-dip galvanized or electroplated zinc coatings of like thickness but no aluminum overlay.

The testing procedure used was a standard ASTM test method (specification No. B117–62) for resistance to corrosion under salt spray, wherein the panel under test is continuously exposed to salt spray until red rust develops on the panel surface, the resistance to corrosion being determined by the duration of exposure and the proportion of the panel surface covered with red rust as appraised by visual inspection. In the present tests, each of the panels was exposed to salt spray until 10% of the panel surface was covered with red rust; the exposure time required to produce this 10% red rust condition served as a measure of the resistance of the panel to corrosion.

These tests demonstrated that for all the thicknesses of zinc and aluminum coatings tested, the presence of the aluminum overlay greatly increased the time required for zinc-coated steel panels to reach 10% coverage with red rust under exposure to salt spray, as compared with panels having zinc coatings of the same thickness but no coating of aluminum. Thus, for panels without aluminum overlay having zinc coatings up to about 175 microinches thick, the exposure time required to exceed 10% red rust was well under 100 hours, and ordinarily less, i.e. 50 hours or so. In contrast, a series of 18 panels having zinc coatings in the same thickness range with aluminum overlays 15 to 60 microinches thick all required more than 100 hours to reach 10% red rust, and a majority of these samples required more than 200 hours, even in some cases above 350 hours, to reach 10% red rust. Again, in the case of panels without aluminum overlay having zinc coatings 300 to 700 microinches thick, the exposure times necessary to attain 10% red rust were less than 200 hours; a series of 18 panels having zinc coatings in the latter thickness range and aluminum coatings 15 to 60 microinches thick all required more than 300 hours of exposure to reach 10% red rust, and for 15 of these panels having aluminum overlays 30 to 60 microinches thick the exposure times to 10% red rust ranged from 600 to 1,200 hours. The longest exposure times (900–1,200 hours) in this series were achieved with panels having a zinc thickness of between about 450 and 650 microinches and an aluminum thickness of 30 to 60 microinches, treated with chromate before testing, although exposure times well above 600 hours were also achieved with panels having an aluminum thickness (over zinc) in the latter range, without chromate treatment.

It will therefore be appreciated that a principal advantage of the present invention is in greatly enhancing the protection against corrosion afforded by zinc coatings on steel. As shown in the foregoing tests, by the provision of a thin (5–100 microinch) vapor-deposited aluminum overlay on a zinc coating in accordance with the invention the duration of effective protection afforded by the coating can be increased by 100 to several hundred hours, i.e. in many cases by a factor of two, three or even more over the duration of protection afforded by zinc coatings without aluminum overlay. The remarkable enhancement of corrosion resistance of zinc-coated steel thus achieved is not fully explained, especially since vapor-deposited aluminum alone on a bare steel substrate affords very little protection against salt spray; for example, steel having a 30-microinch vapor-deposited aluminum coating (with no zinc coating) requires only about 10 hours of exposure to salt spray to reach 10% red rust. In other words, then, the salt spray resistance of zinc-coated steel with a vapor-deposited aluminum outer coating is much more than a mere additive function of the protection afforded by either coating alone.

While aluminum layers 15 to 60 microinches thick were used in the foregoing tests, and represent presently preferred values of thickness for the aluminum overlay on the zinc-coated articles of the invention, the advantages of the invention may be realized with even thinner coatings of aluminum. For example, steel panels coated with 15 and 30 microinches of zinc and further coated with a vapor-deposited flash of aluminum (3 microinches) were found to exhibit improved resistance to corrosion in a humidity cabinet, over samples coated with an equal thickness of zinc but having no aluminum overlay.

Although the method of the invention has been described above as including the application of a zinc coating by conventional electroplating or hot-dip galvanizing procedures, other operations for applying zinc coatings to steel surfaces may also be employed, followed by vapor-deposition of aluminum, with like advantages in improving the corrosion resistance of such zinc coatings. For example, the zinc coating may itself be applied to the steel surface by vapor deposition. One especially effective procedure for depositing zinc on steel from vapor is described in the copending application of the present applicants, Ser. No. 423,249, filed Jan. 4, 1965, and now abandoned. In the latter procedure, the steel surface (after appropriate cleaning) is first coated with a thin adherent layer of copper or other metal selected from a specific class of metals in the upper range of the electromotive force series, namely gold, silver and copper, brass being also deemed a member of the named group in that the latter is an alloy consisting essentially of copper and zinc wherein copper predominates. This coating may be applied e.g. by ionic deposition from an aqueous medium or by electroplating and is followed by a vacuum metalizing deposition of zinc from vapor on the treated surface. The first-mentioned coating serves to enhance the adherence of the vapor-deposited zinc, which may be applied for example by directing zinc vapor onto the surface in a vacuum chamber. The zinc vapor may be produced in any convenient manner, for example by electron-beam vaporization as described above for vaporization of aluminum.

In the use of this latter procedure in the method of the present invention, the steel article bearing the vapor-deposited zinc coating is subjected to a further vacuum metalizing step for deposition of aluminum from vapor to provide an aluminum overlay, in the same manner as described above. Again, this aluminum overlay is found to afford the aforementioned advantages in providing far superior resistance to corrosion of the vapor deposited zinc coating.

The accompanying drawing shows, for illustration of the novel products and also to indicate the nature of the process, a diagrammatic, perspective, enlarged view of a portion of a steel sheet produced with a zinc coating on both sides in accordance with the invention.

Thus, in the drawing, the body of the steel sheet 10, which may be cold rolled strip, is first coated, e.g. by hot-dip galvanizing, electroplating, or vapor deposition, with an adherent layer of zinc 11, 11′ on its opposite faces. Thereafter, aluminum coatings 12, 12′ are applied by vapor deposition of aluminum in a vacuum. The zinc layer may be, for example, from 20×10^{-6} inch to $1{,}500\times10^{-6}$ inch or more in thickness, while the aluminum overlay may be, for example from 5×10^{-6} inch to 100×10^{-6} inch in thickness. If desired, one of the aluminum coatings may be omitted, as by simply directing vapor onto one face of the sheet during its passage through the vacuum chamber, and also one of the zinc coatings may be omitted, to provide a steel sheet having only one coated surface. Again, the sheet may be coated with thicker coatings on one side than on the other for use where the two surfaces of the product are exposed to differing corrosion conditions, e.g. as in automobile bodies wherein one side of the sheet is painted and the other is exposed to corrosive material such as salt splashed up from roadways.

By way of further and more specific illustration of the invention reference may be had to the following specific examples:

Example I

Each of a series of cold-rolled steel panels was alkali cleaned in a solution containing 40 g./liter of sodium carbonate, 30 g./liter of trisodium phosphate and 20 g./liter of sodium hydroxide. The temperature of the cleaner was maintained at 200° F. and the steel panels were cleaned cathodically at 50 amperes per square foor for one minute. The panels were then rinsed, pickled in muriatic acid for 30 seconds, rinsed again and zinc plated in a bath containing 90 g./liter of zinc (as sulfate) and 30 g./liter $(NH_4)_2SO_4$, the bath having a pH of 3.0 and a temperature of 80° F., at a current density of 20 amp./ft.^{2}. Plating times were adjusted to give zinc coatings of 25, 50, 100 and 150 microinches on different panels. After zinc plating the samples were rinsed and dried. Thereafter, some of the samples were placed in a vacuum chamber, the air was evacuated, and these samples were plated with vapor deposited aluminum. The aluminum was deposited under a vacuum (i.e. pressure) of 0.1 micron by placing an aluminum clip on a tungsten filament and heating the filament to vaporize the aluminum, the aluminum being evaporated at a temperature of about 1370° C. The thickness of the aluminum overlay thus produced, on various samples, was 15 and 30 microinches.

In addition, several samples were prepared in which aluminum vapor was deposited directly on bare steel, with no zinc coating.

Samples of the zinc-coated steel without aluminum overlay, of the aluminum-coated steel without zinc and of the aluminum over zinc on steel were placed in a salt spray atmosphere and tested to determine their resistance to corrosion by duration of exposure and extent of red rust produced. Results are summarized in the following table:

Zn thickness (microinches)	Al thickness (microinches)	Total coating thickness (microinches)	Exposure time (hrs.)	Red Rust, Percent
40	None	40	6	50
65	None	65	6	15
115	None	115	6	10
165	None	165	12	20
None	15	15	6	50
None	30	30	12	25
150	15	165	48	20
100	30	130	114	10

As indicated in the table, samples of zinc coated steel without aluminum overlay having zinc thickness up to 165 microinches reached a condition of 10% or greater coverage with red rust in six hours, or 20% in twelve hours. Samples of aluminum-coated steel without zinc reached a condition of 25% to 50% red rust coverage in six to twelve hours. However, the samples prepared in accordance with the present invention, having an aluminum overlay on a zinc coating, attained only 10% to 20% red rust coverage in 48 to 114 hours, i.e. these latter samples exhibited very markedly improved resistance to corrosion. Thus, whereas a zinc coated panel without aluminum having zinc thickness of 165 microinches reached 20% red rust in 12 hours, and an aluminum coated panel without zinc having an aluminum thickness of 15 microinches reached 50% red rust in six hours, a panel coated with 150 microinches of zinc and 15 microinches of vapor deposited aluminum (for a total coating thickness of 165 microinches) reached only 20% red rust in 48 hours. Again, a panel having a 100 microinch zinc coating and a 30 microinch aluminum coating reached only 10% red rust in 114 hours whereas a panel having a 115 microinch thick zinc coating without aluminum reached 10% red rust in six hours and a panel bearing 30 microinches of aluminum without zinc reached 25% red rust in twelve hours.

Example II

Five zinc-coated steel panels prepared by hot dip galvanizing and having a zinc coating thickness of 800 microinches were cleaned with an alkaline scrubber-type cleaning line and thereafter further coated with 45 microinches of aluminum by vapor deposition over the zinc surfaces. The aluminum was deposited under a vacuum (i.e. pressure) of 0.1 micron at a rate of 0.03 lb./ft.^{2} per minute, the aluminum being evaporated at a temperature of about 1370° C. These samples and five similar steel panels having hot-dip galvanized zinc coatings of the same thickness but no aluminum overlay, were then exposed to salt spray until 10% red rust coverage was attained. For the five galvanized panels without aluminum overlay, the average exposure time required to reach 10% red rust was 264 hours; for the five panels having the aluminum layer, the average time required to reach 10% red rust condition was 840 hours.

We claim:

1. A method of producing a zinc-coated steel article with a vapor deposited aluminum overlay, comprising applying to a steel surface an adherent coating of zinc, and thereafter applying a coating of aluminum to the zinc-coated steel surface by depositing aluminum vapor thereon.

2. A method according to claim **1**, wherein said step of applying said zinc coating comprises electroplating zinc on the steel surface.

3. A method according to claim **1**, wherein said step of applying said zinc coating comprises immersing said steel surface in molten zinc.

4. A method according to claim **1**, wherein said step of applying said zinc coating comprises directing zinc vapor onto said steel surface to establish an adherent vapor-deposited zinc coating thereon.

5. A method of producing a zinc-coated steel article with a vapor deposited aluminum overlay, comprising applying to a steel surface an adherent coating of zinc and thereafter applying a coating of aluminum to the zinc-coated steel surface by depositing aluminum vapor thereon in sufficient amount to provide an aluminum coating of at least about 5×10^{-6} inch in thickness.

6. A method according to claim **5** wherein said zinc coating has a thickness of at least about 20×10^{-6} inch.

7. A method according to claim **5**, wherein said aluminum coating is between about 15×10^{-6} inch and about 100×10^{-6} inch in thickness.

8. A method of producing a zinc-coated steel article with a vapor deposited aluminum overlay, comprising applying to a steel surface an adherent coating of zinc to a thickness of at least about 20×10^{-6} inch, and thereafter applying a coating of aluminum to the zinc-coated steel surface by depositing aluminum vapor thereon in vacuum in sufficient amount to produce an aluminum coating of between about 5×10^{-6} inch and about 100×10^{-6} inch in thickness.

9. A zinc-coated steel article with a vapor deposited aluminum overlay, consisting essentially of a steel base having a surface carrying a layer of zinc in adherence to said steel surface, said zinc layer having integrity as a zinc coating upon said steel surface, and an adherent coating of aluminum applied over said zinc coating by vapor deposition.

10. A zinc-coated steel article with a vapor deposited aluminum overlay, consisting essentially of a steel base having a surface carrying a layer of zinc, having a thickness of at least about 20×10^{-6} inch, in adherence to said steel surface, said zinc layer having integrity as a zinc coating upon said steel surface, and an adherent coating of aluminum applied over said zinc coating by vapor deposition.

11. A zinc-coated steel article with a vapor deposited aluminum overlay, as defined in claim **10**, in which the aluminum coating has a thickness of at least about 5×10^{-6} inch.

12. A zinc-coated steel article with a vapor deposited aluminum overlay, as defined in claim **10**, in which the aluminum coating has a thickness in the range of about 15×10^{-6} inch to about 100×10^{-6} inch.

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