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3,843,494

## PROCESS FOR PREPARING ZINC COATED FERROUS METAL SUBSTRATES HAVING IMPROVED RESISTANCE SPOT WELDING CHARACTERISTICS

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Continuation-in-part of abandoned application Ser. No. 837,935, June 30, 1969. This application Mar. 13, 1972, Ser. No. 234,010

Claims priority, application Great Britain, July 5, 1968, 32,155/68

Int. Cl. B23k 11/10; C23f 17/00  
U.S. Cl. 204—34

9 Claims

### ABSTRACT OF THE DISCLOSURE

The invention concerns a process for preparing a zinc coated ferrous metal substrate having improved resistance spot welding characteristics consisting of the steps of applying on a ferrous metal substrate separate layers of metallic zinc and of metallic iron, the outermost layer being a metallic iron layer which promotes the ease with which a plurality of said zinc coated ferrous metal substrates may be welded by resistance spot welding, the said outermost metallic iron layer being applied on a metallic zinc layer by electrodeposition from an aqueous iron plating solution or by vacuum deposition.

### RELATED APPLICATION

This application is a continuation-in-part of United States application Ser. No. 837,935, filed June 30, 1969, now abandoned, by David Richard Brown for "A Process for Preparing Zinc Coated Ferrous Metal Substrates Having Improved Resistance Spot Welding Characteristics."

### BACKGROUND OF THE INVENTION

The present invention relates to a process for forming a zinc-iron coating on a steel substrate.

Zinc coated or galvanised steel is widely used throughout industry, for example in the motor car industry. One problem found in the use of zinc coated sheet steel is apparent when such bodies have to be welded. In industry, zinc coated steel steels are normally welded by resistance spot welding where it is necessary to use higher welding currents than when welding uncoated steel. As a result of the use of higher welding current, and the alloying of the zinc with the electrode material, the life of the welding electrodes is consequently much reduced. In an attempt to mitigate this problem iron has been introduced into the zinc coating, for example, see the article by H. A. Jahnle in the British Welding Journal 15 (3) 1968 at 113-119.

In order to produce a zinc-iron coating on sheet steel, it is known to place the steel in a suitable plating solution where a zinc-iron coating is deposited by electrolysis such as described in an article by S. Jepson, S. Meecham and F. W. Salt in the Transactions of the Institute of Metal Finishing, 32 1955 at 160-18P. Although this method of electro deposition is quite satisfactory it is only suitable on a small scale and where industrial users are concerned, this method suffers from the disadvantage that the composition of the coating depends upon too many variables *inter alia* the composition of the plating solution, the temperature of the solution and the rate of agitation of the solution. Moreover, detailed studies by means of X-ray diffraction and analysis have shown that over a range of zinc-iron alloy compositions there are two phases present, see for example the article by H. M. Dalal and D. S. Gill in the Journal of the Institute of Metals, 93 (4) 1964-65 at 130-131. These two phases can be analysed by metal-

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lographic examination to show that these phases are usually formed as alternate layers generally parallel with the steel substrate. One of these phases is inherently brittle and consequently where the alloy coatings contain substantial quantities of iron, these coatings tend to flake off after the mechanical deformation of the basic steel structure and particularly after compression.

### DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED VARIANTS THEREOF

According to one aspect of the present invention, there is provided a process for preparing a zinc coated ferrous metal substrate having improved resistance spot welding characteristics consisting of the steps of applying on a ferrous metal substrate separate layers of metallic zinc and of metallic iron, the outermost layer being a metallic iron layer which promotes the ease with which a plurality of said zinc coated ferrous metal substrates may be welded by resistance spot welding, the said outermost metallic iron layer being applied on a metallic zinc layer by electrodeposition from an aqueous iron plating solution or by vacuum deposition.

According to another aspect of the present invention, there is provided a process of welding comprising the step of welding a plurality of ferrous metal substrates by resistance spot welding, the said ferrous metal substrates having separate layers of metallic zinc and of metallic iron thereon, the outermost layer of the said separate layers of metallic zinc and metallic iron being a metallic iron layer which promotes the ease with which the said plurality of ferrous metal substrates may be welded by resistance spot welding.

The layers of both zinc and iron may be produced by electrodeposition or by vacuum deposition. Alternatively, the layer or layers of zinc may be produced by hot dip galvanising.

The outermost layer of iron, which has substantial corrosion resistance, preferably has a thickness of between 1 and 4 microns, and preferably has a thickness of between 4% and 80% of that of the metallic zinc layer. Thus the zinc layer may be substantially twice as thick as the iron layer.

Thus, if the thickness of the metallic zinc layer is about 2 to 3 microns, that of the metallic iron layer is desirably 1 micron, while if a metallic zinc layer having a thickness of between 20 and 25 microns is applied to the ferrous metal substrate, e.g. by hot dipping, the metallic iron layer may be 3 microns in thickness.

The layers may be constituted by one zinc and one iron layer only, or by a number of (normally alternately arranged) zinc and iron layers, the iron layer being outermost.

The substrate is preferably cathodically polarised relative to a plating solution in which the substrate is immersed during the electrodeposition of each said layer.

Thus use may be made of the sequential steps of washing the substrate, dipping the substrate into a dilute acid, immersing the substrate in an electrolytic tank containing a zinc plating solution with the substrate cathodically polarised relative to said solution, washing the substrate, dipping the substrate into a dilute acid, and immersing the substrate in an electrolytic tank containing an iron plating solution with the substrate cathodically polarised relative to said solution. The said steps may be repeated several times to provide a composite coating which consists of alternate layers of zinc and iron, the iron layer being outermost.

It is desirable that the pH value of the iron plating solution be maintained at a predetermined value to avoid the nodular formation of iron deposits and in general, the pH value should be below 2.

Various other aspects of the present invention will become more apparent from the following description.

As a starting point to the present invention, it should be mentioned that the electrodeposition of zinc onto an iron substrate is a well known process but the converse process whereby iron is deposited electrolytically onto a zinc substrate or a zinc coated substrate presents difficulties. Since zinc is cathodic relative to iron it is necessary to avoid the formation of an immersion coating of iron which tends to be non-uniform and poorly adherent so far as the zinc based substrate is concerned. In order to achieve this, it is necessary for the zinc based substrate to be cathodically polarised during the time that it is in contact with the iron plating solution. However, even if the zinc based substrate is cathodically polarised during plating it is still possible for the electro-plated iron deposit to accumulate into small nodules as mentioned before rather than in uniform layer as desired. It is now proposed that this nodular growth of iron deposit be eliminated by ensuring that the pH value of the iron plating solution is maintained at a predetermined value. Generally speaking it has been found that for an iron plating solution having a pH value above 2 the nodular deposition is very pronounced. However, if the pH value is reduced from 2 to 1.7 the deposited iron becomes increasingly more uniform, but below a pH value of 1.7 the cathode efficiency for iron deposition from ferrous sulphate solution falls off rapidly. However, it has been found that high efficiencies can be obtained at these low pH values by using a ferrous chloride solution.

It is proposed, according to the present invention, to plate a substrate with a zinc-iron coating by alternately placing the substrate in a zinc plating solution and an iron plating solution. Before transferring the substrate between the plating solutions, however, it is generally desirable to wash the substrate with water in order to avoid introducing one plating solution into the other. However, if water is carried by the substrate into the iron plating solution, the pH value of this solution at the interface between the substrate and the solution can rise sufficiently above 2 to cause roughness in the iron deposit. This problem can be overcome by dipping the substrate into dilute acid before immersing it in the plating solutions.

By alternately coating the substrate with zinc and iron, a composite coating can be built up which consists of any desired number of layers of zinc and iron, an iron layer being outermost. The thickness of each layer depends only upon the quantity of electricity passed in producing the layer and hence the composition of the coating is readily controllable. For coating sheet steel or strip, a coating plant of the type used at present for electro-galvanising is easily adapted to carry out this invention. In order to explain the method of the invention in more detail, a number of specific examples will now be described.

#### EXAMPLE I

Two plating tanks constructed from polyvinyl chloride and of similar size were used. One tank constituting a zinc plating bath has pure zinc anodes affixed to the inner surface of its walls and the other tank constituting an iron plating bath had mild steel anodes affixed to the inner surfaces of its walls. The anodes were housed in porous polypropylene bags and each tank contained the appropriate plating solution which was maintained at 50° C. The zinc plating solution consisted of 1 M zinc sulphate and sufficient sulphuric acid to give the solution a pH value of 2. The iron plating solution consisted of 1 M ferrous sulphate, 0.15 M ferrous chloride, 0.4 ml./l. of "Teepol" (registered trademark) and sufficient sulphuric acid to give the solution a pH value of 1.7. A source of electric power was provided to give an electrolytic plating current density in the order of 1000 a./m.<sup>2</sup>.

The steel sheet to be treated was degreased and etched in 20% v./v. sulphuric acid at room temperature, then

rinsed with water and dipped in sulphuric acid of pH value 1. The steel sheet was immersed into the zinc plating tank and cathodically polarised therein. After the entry of the predetermined time to produce a zinc coating of a certain thickness for example 30 seconds, the steel was removed from the zinc plating tank, rinsed with water and dipped into the dilute sulphuric acid with a pH value of 1. The sheet was then placed into the iron plating tank and cathodically polarised therein. The sheet was maintained in the iron plating tank for a duration of time sufficient to produce a desired thickness of iron coating, again for example 30 seconds. The sheet was then removed from the iron plating solution, rinsed with water and dipped into the dilute sulphuric acid. The washed sheet was then cathodically polarised and re-immersed into the zinc plating solution. This process was repeated so that a number of alternate layers of zinc and iron were produced, the outermost layer being a metallic iron layer. Each metallic zinc layer was about 1.4 microns in thickness and each metallic iron layer was about 1 micron in thickness.

Using this zinc-iron coated steel, 19,000 spot welds were performed before there was any deterioration of weld quality or need for dressing of the welding electrode tips. Steel coated with the same thickness of pure zinc gave only 7,200 satisfactory welds under the same conditions.

#### EXAMPLE II

A hot dipped galvanised steel sheet, having a metallic zinc layer about 25 microns in thickness, was etched by dipping, for a period of 5 to 10 seconds, in 20% v./v. sulphuric acid at room temperature. After rinsing in water, the sheet was dipped in a solution of sulphuric acid of pH 1. The zinc coated sheet was next immersed in an iron plating solution which consisted of 1 molar ferrous sulphate, 0.15 molar ferrous chloride, and 0.4 ml./litre of a wetting agent such as "Teepol." The pH of the iron plating solution was 1.7. Plating was continued for 60 seconds at a current density of 1000 a./m.<sup>2</sup>, so as to produce an outermost metallic iron layer having a thickness of about 2.5 microns. After plating, the sheet was washed with water and dried.

Alternatively, the iron could have been deposited from any known iron plating solution, e.g. a ferrous chloride solution.

#### EXAMPLE III

As illustrated in the accompanying drawing, a steel strip 1, having opposite surfaces 2, 3 was passed through an entry seal 4 into a vacuum chamber 5 and withdrawn therefrom through an exit seal 6. The pressure in the vacuum chamber 5 was maintained by the use of vacuum pumps (not shown) at 10<sup>-4</sup> torr.

The strip 1, in passing through the vacuum chamber 5, passed over rolls 7-12 of which the rolls 9-12 were cooled by water or other means. The strip 1, in passing between the rolls 8, 9 travelled over a first horizontal run 13 with its surface 2 lowermost, and in passing between the rolls 10, 11 travelled over a second horizontal run 14 with its surface 3 lowermost.

In travelling over the first horizontal run 13, the surface 2 passed above and adjacent to successively arranged zinc evaporation and iron evaporation crucibles 15, 16 respectively, while in travelling over the second horizontal run 14, the surface 3 passed above and adjacent to successively arranged zinc evaporation and iron evaporation crucibles 15, 16 respectively. Thus each of the opposite sides of the strip 1 was coated successively with zinc and iron layers, the iron layer being outermost. The zinc in the crucibles 15 was heated by means of electrically heated immersion heaters (not shown), whilst the iron in the crucibles 16 was heated by an electron beam gun (not shown).

The thicknesses of the zinc and iron layers, which were for instance 2.5 microns and 1.5 microns respectively,

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could be varied as required by controlling the heat input to the various crucibles 15-18.

If a thick layer of iron, e.g. of 4 microns, was to be deposited, it was necessary to provide for each of the horizontal runs 13, 14, three iron evaporation crucibles 16, the strip 1 being cooled between each said crucible 16 by passing it over water-cooled rolls (not shown). If this was not done, the high temperature of the iron vapour could cause the zinc to melt.

Using the zinc-iron coated steel 20,000 spot welds were performed before there was any deterioration of weld quality or need for dressing of the welding electrode tips.

#### EXAMPLE IV

The process was the same as in Example III above, except that the steel strip 1 already had zinc layers on its surfaces 2, 3 prior to entering the vacuum chamber 5 since it was a hot dipped galvanised steel strip. Accordingly, the zinc evaporation crucibles 15 were omitted.

In order to test the corrosion resistance provided by the outermost layer of iron, a number of samples of hot dipped galvanised steel, each measuring 6" x 4" and each having zinc coatings of 25 microns in thickness, were exposed in a given industrial environment, the weight changes resulting from corrosion being measured at three month intervals. One of the samples had no iron layers (i.e. was a conventional hot dipped galvanised steel article), the other samples having outermost iron layers of varying thickness on the opposite sides of the hot dipped galvanised steel. The results are indicated in the Table I below.

TABLE I

Sample	Weight loss (grams per square meter)		
	6 months	9 months	12 months
Hot dip galvanised steel without iron (HDG).....	3.8	4.5	6.4
HDG plus 0.5 micron iron.....	3.6	4.4	6.0
HDG plus 1 micron iron.....	2.8	3.6	5.2
HDG plus 2 micron iron.....	2.7	3.5	4.8
HDG plus 3 micron iron.....	2.6	3.5	4.6
HDG plus 4 micron iron.....	1.0	0.8	1.6

Clearly with increasing iron thickness the corrosion rate (loss in weight) decreased.

In order to test the spot welding performance, spot welds were performed on a number of samples of hot dipped galvanised steel. One of the samples had no iron layers (i.e. was a conventional hot dipped galvanised steel), the other samples having outermost iron layers of varying thickness. The number of spot welds performed on each sample before there was a need to dressing the welding electrode was counted. The results are indicated in Table II below.

TABLE II

Sample:	No. of spot welds
Hot Dip Galvanised Steel without iron (HDG).....	1700
HDG+1.0 micron iron.....	2300
HDG+1.5 micron iron.....	2800
HDG+2.0 micron iron.....	6700
HDG+2.5 micron iron.....	7200
HDG+3.0 micron iron.....	12000
HDG+3.5 micron iron.....	14000
HDG+4.0 micron iron.....	20000

Clearly with increasing iron thickness the spot welding performance is improved.

I claim:

1. A process for preparing a zinc coated ferrous metal substrate having increased corrosion resistance and im-

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proved resistance spot welding characteristics consisting of the steps of applying on a ferrous metal substrate separate layers of metallic zinc and of metallic iron, the outermost layer being a substantially continuous metallic iron layer which increases the corrosion resistance and promotes the ease with which a plurality of said zinc coated ferrous metal substrates may be welded by resistance spot welding, the said outermost substantially continuous metallic iron layer being applied on a metallic zinc layer by electrodeposition from an aqueous iron plating solution or by vacuum deposition and being unalloyed with the metallic zinc layer, the said outermost metallic iron layer being applied in a thickness between 4% and 80% of that of the metallic zinc layer and having a thickness of at least 0.5 micron, and the metallic zinc layer on which the said outermost metallic iron layer is applied being applied by vacuum deposition or hot dip galvanizing.

2. The process of claim 1 wherein the said outermost metallic iron layer is applied on a metallic zinc layer by electrodeposition from an aqueous iron plating solution.

3. A process as claimed in claim 1 comprising the sequential steps of washing the ferrous metal substrate, dipping the said substrate into a dilute acid, and immersing the said substrate in an electrolytic tank containing an iron plating solution with the said substrate cathodically polarised relative to said second plating solution.

4. A process as claimed in claim 3 in which the pH of the iron plating solution has a maximum value of 2.0.

5. The process of Claim 4 wherein the corrosion resistance of said zinc coated ferrous metal substrate is increased by applying the said outermost metallic iron layer in a thickness of between 1 and 4 microns.

6. A process as claimed in claim 2 in which the said outermost metallic iron layer has a thickness of between 1 and 4 microns.

7. The process of Claim 2 wherein the corrosion resistance of said zinc coated ferrous metal substrate is increased by applying the said outermost metallic iron layer in a thickness of between 1 and 4 microns.

8. A process as claimed in claim 1 in which the said metallic zinc layer is applied by vacuum deposition.

9. A process as claimed in claim 1 in which the metallic zinc layer is produced by hot dip galvanising.

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U.S. Cl. X.R.

117—71 M, 107; 204—38 B, 38 S, 40, 48; 219—91, 117 R, 118