United States Patent Office 3,320,040 Patented May 16, 1967

3,320,040

GALVANIZED FERROUS ARTICLE

William P. Roe, Westfield, and Willard J. Lantz, Milltown, N.J., assignors to American Smelting and Refining Company, New York, N.Y., a corporation of New Jersey

No Drawing. Filed Aug. 1, 1963, Ser. No. 299,164
3 Claims. (Cl. 29—196.5)

This invention relates to a novel galvanized ferrous article.

The present state of the galvanzing art is such that there is a need for a galvanized article possessing an adherent, ductile coating of galvanizing material which presents a paintable surface which is free or substantially free of spangle. One of the principal objects and advantages of the invention is the provision of such an article and a galvanizing bath, alloy and process for producing the same. Other objects and advantages will become apparent from the following detailed description of the invention.

In one aspect, the invention comprehends a novel galvanizing alloy comprising a zinc base alloy containing, by weight, .1–3.5% aluminum, .02–.2% magnesium and less than .1% lead. In another aspect, the invention comprehends a process for galvanzing a ferrous article in which the ferrous article to be galvanized is coated with a coating comprised of said alloy by dipping the ferrous article, preferably in a continuous procedure, in a molten galvanizing bath comprising said alloy, removing the article from the bath and freezing the coating of molten bath metal adhering to ferrous article, preferably before the insoluble ferrous compounds of zinc and aluminum which form as an intermetallic layer at the interface between the ferrous article and the molten bath metal, migrate to the surface of said coating. Thus, in accordance with another aspect of the invention, there is produced a novel galvanized ferrous article having an adherent, ductile coating comprised of said novel galvanizing alloy, which coating presents a paintable surface which is free or substantially free of spangle.

In galvanizing a ferrous article with zinc, the molten zinc in the galvanizing bath relatively rapidly dissolves iron from the surface of the ferrous article at the interface between the article and the bath. The rate at which the zinc dissolves the iron is such that the solubility of the iron in the molten zinc is quickly exceeded. Thereafter, with continuous contact between the article and the bath, the zinc continues to dissolve iron from the article at the interface between article and the bath and the additional iron dissolved by the zinc forms an insoluble iron-zinc compound or compounds in the zinc which builds up in the molten zinc adjacent the interface thereby forming an intermetallic layer of zinc and iron-zinc compound between the article and the bath. The thickness of the thus formed intermetallic layer increases relatively rapidly with continued exposure of the ferrous article in the bath and unless the article is removed from the bath relatively quickly, the coating of bath metal adhering to the article when the latter is removed from the bath will be comprised substantially entirely of said intermetallic layer. Also, if the thickness of the intermetallic layer is less than the thickness of the coating of bath metal adhering to the ferrous article when the latter is withdrawn from the bath, the thickness of the intermetallic layer will continue to increase until the molten coating is frozen. Typically, the total iron content, by weight, of the intermetallic layers is 7–12% but may be as high as 30–35% Fe.

An intermediate layer, for example, the above described intermetallic layer, in the coating adjacent the interface between the coating and the ferrous article is highly desirable, if not essential, in that it causes the solidified coating to adhere to the ferrous article. On the other hand, the ductility of the coating decreases with increasing thickness of the intermetallic layer in the coating in that the coating becomes increasingly brittle and less able to withstand mechanical deformation. Thus, for example, in galvanized steel sheet, the ability of the zinc alloy coating therein to withstand drawing, bending and shaping without peeling or flaking, especially in deep drawing the sheet, decreases with increasing thickness of the intermediate layer in the coating.

In accordance with the present invention, the thickness of the intermetallic layer in the zinc alloy coating on the galvanized article (hereinafter sometimes referred to as the "galvanize coating") is controlled by the presence in the coating of about .1–3.5% aluminum, by weight. This is accomplished by galvanizing the ferrous article in a galvanizing bath containing about .1–3.5%, by weight, of dissolved aluminum. A galvanizing alloy containing about .1–3.5%, by weight, of dissolved aluminum is also provided for establishing, and preferably also maintaining, said aluminum content in said bath. This feature of the invention is based on the fact that such content of such aluminum in the bath and in the galvanized coating results in a thinner intermetallic layer in the coating than would otherwise occur in the latter. An aluminum content less than about said .1% aluminum in said coating and in said bath has no appreciable effect on the thickness of the intermetallic layer in the galvanize coating on the ferrous article. On the other hand, aluminum contents in excess of about said 3.5% aluminum in said coating and in said bath may result in an excessive reduction in the thickness of said intermetallic layer and adherence of the coating to the ferrous article, when commercially acceptable or desirable immersion time and bath temperatures are employed in the galvanized procedure, especially when continuous galvanizing procedures are employed. Also aluminum contents above said 3.5% in said bath result in excessive dross formation in the bath, thereby increasing the possibility of imperfections occurring in the coating due to entrainment of dross therein and requiring more frequent drossing of the bath to reduce to a minimum the possibility of the occurrence of such imperfections. Preferably, in practicing the invention, the aluminum content of the galvanize coating and the dissolved aluminum content of the bath and the instant galvanizing alloy is in the range of .1 to 1%, and most preferably in the range .1–.5%, aluminum, by weight.

In accordance with the invention also, the lead content of the galvanize coating, the bath and the galvanizing alloy is less than .1% lead, by weight, to control the occurrence of spangle in the surface of the coating. This feature of the invention is based on the fact that the presence of amounts of lead in excess of .1% in the galvanize coating causes the formation of spangle in the surface of the coating. Accordingly, in practicing the invention the lead content in the coating, bath and alloy is less than .1% to provide a spangle free or substantially spangle free surface on the coating. Preferably, such lead content is not in excess of .01%, more preferably not in excess of .005% and most preferably not in excess of .003%, by weight, in providing a spangle free surface on the galvanize coating.

It has been found that a ferrous article galvanized with a zinc base alloy having aluminum and lead contents in

the amounts set forth above, possesses a galvanize coating which is smooth due to the absence of spangle. However, the surface of the coating is also bright and shiny and as such is not an acceptable surface for receiving a paint in that paint will not adhere satisfactorily thereto. Thus, where either or both a protective or decorative coating of paint, enamel, lacquer or the like is to be applied to a galvanize coating having such a surface, the latter must be further treated by special procedures to convert it to a surface which is acceptable for purposes of painting.

It has been found, however, that the shiny character of the surface of such galvanized ferrous articles, i.e. those galvanized with a zinc base alloy having aluminum and lead contents in the amounts hereinabove set forth, is eliminated when the galvanize coating contains, by weight, .02–.2% magnesium and that, upon freezing on the ferrous article, the surface of the galvanize coating possesses a smooth dull grey appearance. It has also been found that the adherence of paint or other surface coatings on the galvanize coating is greatly enhanced when the latter possesses the dull grey appearance. Moreover, it has been found that such amounts of magnesium tend to promote the formation of the spangle-free surface on the galvanize coating and do not interfere with the adherence of the coating to the ferrous article. In addition, the galvanize coating possesses a highly desirable degree of ductility, especially in deep drawing the coated ferrous article. However, magnesium in amounts less than .02% do not provide a dull or a satisfactory dull surface. On the other hand, amounts of magnesium in excess of .2%, result in undue embrittlement of the coating and render it undesirable, if not unsatisfactory, in drawing, especially in deep drawing, procedures. In accordance with this feature of the invention, the galvanize coating on the ferrous article contains, by weight, .02–.2% magnesium. This is accomplished by providing in the galvanizing bath, and in the present galvanizing alloy for preparing the bath, a dissolved magnesium content of .02–.2% magnesium, by weight. Preferably, such magnesium in the coating, the galvanizing bath and the alloy is in the range of .02–.08%, and more preferably in the range .03–.06% magnesium, by weight.

In practicing the invention, the galvanizing bath may be prepared in situ in any suitable manner. For example, the bath may be prepared by melting zinc having a sufficiently low lead content, preferably zinc of commercial purity having a lead content below .1%, by weight, and then dissolving therein the requisite amounts of aluminum and magnesium. For best results, however, especially in ease of control of the composition of the bath and the coating on the ferrous article to be galvanized, the bath is prepared from the instant galvanizing alloy, preferably by preparing the latter outside the galvanizing vessel, usually in the form of ingots and then melting the ingots in the galvanizing vessel. The instant galvanizing alloy may also be prepared in any suitable manner for use in the galvanizing bath. Preferably, it is prepared in an alloying vessel by melting therein zinc of commercial purity which has a lead content below .1%, by weight, adding to the molten zinc the requisite amounts of aluminum and magnesium in either the solid or liquid state, stirring the bath until the added aluminum and magnesium are dissolved into the zinc and then casting the resulting molten alloy into ingots for transportation to the site of the galvanizing bath. Preferably, in preparing the present galvanizing alloy or the galvanizing bath when the latter is prepared in situ, the commercial grade of the zinc employed is High Grade zinc. The purity of such zinc metal is such that its minimum zinc content is 99.90%, by weight. The significant impurities which may be contained in High Grade zinc and the maximum amount of each that may be encountered, are, by weight, .07% lead, .02% iron, .03% cadmium, and .03% tin. More preferably, Special High Grade zinc is employed. The purity of such zinc is such that its minimum zinc content is 99.99%, by weight. The significant impurities that may be contained in such zinc and the maximum amount of each that may be encountered are .003% lead, .003% iron, .003% cadmium, and .002% tin, by weight.

It will be understood that, during the galvanizing procedure, the galvanizing bath, especially when a ferrous galvanizing vessel is employed, rapidly become saturated with iron at the temperature of the bath due to the dissolving action of the zinc. Thereafter, with continued galvanizing of ferrous articles in the bath, the zinc continues to dissolve iron and the latter forms an insoluble, zinc-iron dross which sinks to the bottom of the bath. Also in the present galvanizing bath an insoluble zinc-iron-aluminum dross is formed which floats on the bath. For best galvanizing results, such drosses are removed from time to time at appropriate intervals by conventional drossing procedures, in order to reduce to a minimum the possibility of their contaminating the galvanize coating on the ferrous article being galvanized. The bath, with continued use, gradually becomes depleted due to such dross formation and the metal carried out of the bath in the form of the galvanize coating. The bath may be refortified by adding requisite amounts of zinc, aluminum and magnesium, as such. Preferably, however, the bath is refortified by adding the instant galvanizing alloy thereto as required from time to time to maintain a desired bath level in the galvanizing vessel since it has been found that control of the composition of the bath and the galvanize coating on the ferrous article can be more easily obtained by this preferred procedure. It will be appreciated that in determining the dissolved aluminum and magnesium content of the bath, care should be exercised in obtaining a sample for analysis to avoid or minimize contamination of the sample with the above described drosses. Advantageously, for this purpose, samples are taken in the vicinity of the mid-level of the bath. Preferably, such samples are taken after the surface of the bath has been drossed and the bath has been allowed to remain quiescent for upwards of about fifteen minutes.

As stated earlier herein, the presence of the instant amounts of aluminum in the instant galvanizing bath results in the formation of a thinner intermetallic layer in the galvanize coating than would otherwise occur in the latter. However, even when the instant galvanizing bath contains such amounts of aluminum, the thickness of the intermetallic layer will increase with increasing immersion time of the article to be galvanized. In accordance with the process aspect of the invention, the ferrous article to be galvanized is dipped in the present galvanizing bath and is removed therefrom and the galvanize coating adhering thereto is frozen thereon before the intermetallic layer has migrated to the surface of the coating. Preferably, for increased ductility of the galvanize coating, the ferrous article is removed from the bath and the adhering galvanize coating is frozen thereon before migration of the intermetallic layer through more than about half of the thickness of the galvanize coating can occur; more preferably, such migration of intermetallic layer is less than about one quarter, and most preferably not in excess of about one tenth, of the thickness of the galvanize coating adhering to the ferrous article.

The degree of penetration of the intermetallic layer in the galvanize coating may be estimated by observing a cross-section of the coating that has been etched in a conventional manner with an alcoholic solution of nitric acid. Alternatively, the degree of penetration of the intermetallic layer may be determined from the total iron content of the galvanize coating, since the total iron contained in the coating will be proportioned to the thickness of the intermetallic layer. The total iron in the coating may be determined by stripping the coating from a sample of the galvanized ferrous article in a conventional way with an acid solution and then analyzing the resulting solution

for iron. Conventional methods for stripping a galvanize coating from a ferrous article are set worth in the specifications of the American Society for Testing Materials, ASTM designation A90–53. In accordance with this alternative procedure for determining degree of penetration of the intermetallic layer, the total iron content of the coating is preferably below 4% iron, more preferably below 2% iron and most prefereably not in excess of 1.5% iron, by weight.

In practicing the invention, the ferrous article to be galvanized may be treated in any conventional way prior to galvanizing, to clean the surface of the article to remove grease and oxides therefrom. Thus, for example, the article may be degreased by dipping in a suitable solvent or by heating in an oxidizing atmosphere and then subjecting it, in a conventional way, to a conventional flux to remove oxides before the article is galvanized or such oxides may be reduced in a conventional manner in a conventional reducing atmosphere.

The invention may be used to galvanize any ferrous article. It is particularly useful in hot dip galvanizing of ferrous articles and is especially useful in continuously galvanizing steel sheet. In the latter procedure the sheet may be degreased and passed through a conventional flux bath but preferably the oxide on its surface is reduced by passing the sheet through a furnace provided with an appropriate reducing atmosphere. The thus treated sheet, which preferably is at a temperature above the melting point of the galvanizing bath, is then passed through the latter. The molten galvanize coating adhering to the sheet emerging from the bath may be frozen thereon in any desired or conventional manner to provide a sheet which, without any further treatment, possesses the instant smooth dull, grey colored, paintable surface. Preferably, the galvanize coating is frozen by allowing it to cool in the atmosphere. Any conventional galvanizing bath temperature may be employed in the galvanizing step in conducting hot dip or continuous galvanizing procedures. Preferably, especially in continuously galvanizing steel sheet, the temperature of the galvanizing bath is not in excess of about 950° F. and more preferably in the range 800–900° F.; a galvanizing bath temperature of about 850° F. being most preferred. When such bath temperatures are employed and the galvanize coating is allowed to freeze in the atmosphere, the instant coating is obtained with bath immersion times of less than 12 seconds; and in continuous galvanizing of steel sheet, in which the sheet travels through the bath at speeds in excess of 80 feet per minute, the instant coating may be obtained with immersion times of as little as less than six seconds in duration.

The invention is further illustrated in the following examples. It should be understood, however, that these examples are given for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

In this example, the most preferred composition of the instant galvanizing alloy and bath are illustrated. Heated steel sheet after having been cleaned to remove grease and oxides from its surface was dipped in a galvanizing bath which was prepared by melting Special High Grade zinc having a lead content of less than .003% lead, by weight. Sufficient solid aluminum and magnesium were added to the molten zinc to provide therein, by weight, an aluminum content of .2% and a magnesium content of .04%. The bath was stirred until the added aluminum and magnesium were dissolved in the zinc. The steel sheet was dipped in the bath for a period of four seconds while maintaining the bath at a temperature of about 850° F. At the end of the four second period, the sheet was removed from the bath, and the coating of molten bath metal adhering thereto was allowed to freeze on the sheet while the latter was exposed to the atmosphere. The surface of the galvanize coating of the thus galvanized sheet, upon freezing of the coating thereon, was found to be smooth and spangle free and had a dull grey appearance. No flaking or peeling of the galvanize coating occurred upon bending the sheet, thus indicating excellent ductility in the coating and in the bonding of the coating to the sheet. Examination of cross-sections of the coating after the latter was etched with an alcoholic solution of nitric acid indicated that the coating contained an intermetallic layer adjacent the interface of the coating with the sheet and that this layer constituted about one-tenth of the thickness of the coating. Paint, after being applied and dried on the dull grey surface, forms an excellent bond therewith. Upon analysis of the coating for total iron, by stripping in an acid solution as described in the American Society of Testing Materials' specification, ASTM designation A90–53, and analyzing the resulting solution, a total iron content of less than 1.5% by weight, is found in the coating.

Example 2

The procedure of Example 1 was repeated but in this instance, the galvanize bath contained 3%, by weight, of aluminum and the immersion period of the sheet in the bath was 64 seconds. The adherence and ductility of the coating as well as its smooth, spangle free, dull grey surface and the relative thickness of its intermetallic layer were essentially the same as that obtained in the sheet of Example 1.

Example 3

The procedure of Example 1 was again repeated in two tests but in each of these tests no magnesium was added to the galvanizing bath and lead was added to the bath, as required, to provide in the baths of tests one and two, respectively, a lead content, by weight, of .3%, and .002%. The surface of the galvanize coating of the sheets galvanized in the bath containing .3% Pb by weight, was well spangled and shiny. The surface of the galvanize coating of the sheets galvanized in the bath containing .002% lead, were shiny but were substantially free of spangle.

Example 4

Steel sheet was continuously galvanized by passing a heated, cleaned band of the sheet through a galvanizing bath which was established by melting a zinc base alloy containing, by weight, .2% aluminum, .05% magnesium, .006% lead and the balance zinc metal of at least 99.90% purity. The bath metal adhering to the sheet emerging from the bath was allowed to freeze on the sheet by cooling in the surrounding air. The bath was maintained at approximately 850° F. during the galvanizing process. The immersion period of the sheet in the bath was 6–12 seconds and the strip was passed through the bath at appropriate linear speeds in excess of 80 feet per minute to obtain such periods of immersion. The adherence and ductility of the galvanize coating on the sheet as well as its smooth, spangle free, dull grey surface and the relative thickness of the intermetallic layer in the coating were essentially the same as that obtained in the sheet of Example 1.

What we claim is:

1. A galvanized ferrous article having a coating of galvanizing metal adhering thereto which comprises a zinc base alloy containing, by weight, .1–3.5% aluminum, .02–.2% magnesium, and less than .1% lead.

2. A galvanized article according to claim 1 in which said coating comprises a zinc base alloy containing, by weight, .1–1% aluminum, .02–.08% magnesium, and less than .01% lead.

3. A galvanized article according to claim 1 in which said coating comprises a zinc base alloy containing, by weight, .1–.5% aluminum, .03–.06% magnesium, and less than .005% lead.

(References on following page)

7

References Cited by the Examiner

UNITED STATES PATENTS

2,180,291	11/1939	Finkeldey	75—178.6
2,197,622	4/1940	Sendzimir	117—131 X
2,703,766	3/1955	Ellis et al.	117—114
2,986,808	6/1961	Schnedler	117—114 X
3,056,694	10/1962	Mehler et al.	117—114
3,245,765	4/1966	Lawson	117—131 X

8

OTHER REFERENCES

"Iron Age," 187 (23), pp. 100–102, June 8, 1961, Galvanized Panels Improved by Magnesium Additions.

ALFRED L. LEAVITT, *Primary Examiner.*

MURRAY KATZ, *Examiner.*

J. R. BATTEN, JR., *Assistant Examiner.*