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PROCESS OF IMPROVING GENERAL CORROSION RESISTANCE OF ZINC COATED STRIP

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This invention relates to a process of improving the general corrosion resistance of zinc coated strip. General corrosion implies uniform attack and is measured by weight loss, as compared with localized corrosion such as intergranular attack.

In the coating of ferrous metallic stock by the hot dip method, two basically different processes have been used. In the first, wherein a flux is used, the ferrous sheets or other articles to be coated, are led into the zinc coating bath either through a fused flux such as zinc chloride or zinc ammonium chloride floating on the surface of the bath, or are precoated with an aqueous solution of such a flux and are then led through a coating bath having no flux thereon. The purpose of the flux is to prepare the ferrous metal surface to receive the zinc coating. The coating bath commonly used in the flux process contains a relatively large amount of lead (up to 1.60%) and, where prefluxing is used, a very small amount of aluminum (zero to .01% maximum). Generally, a high lead content is used because lead is an impurity in zinc and the cheaper zinc contains more lead. Thus, for example, a commercial grade of zinc known as Prime Western may contain up to 1.60% lead.

Where a fused flux blanket is used in the flux process, the aluminum must be kept very low because it reacts with the flux material to form aluminum chloride which "kills" the flux so that the flux no longer has a cleaning action. This is particularly intolerable in a sheet process because certain reaction products stick to the various rolls and produce defects in the coating.

When coating strip which has been prefluxed, since the flux coating can be very thin and carefully controlled, more aluminum can be tolerated in the coating bath, even up to .35%.

The coating produced by the so-called flux process has a good general corrosion resistance and also a good resistance to intergranular attack, i.e. an attack which takes place at the grain boundaries. However, the flux process produces a coating which is brittle and has poor ductility and, because it is a slow process, it is a high cost process. The use of magnesium to enhance corrosion resistance has been discussed in a paper by John A. Heath entitled, "A New Frontier in Hop-Dip Galvanizing: a Magnesium Containing Coating," delivered to the American Hot Dip Galvanizers Association, March 24, 1961.

The use of magnesium in die casting alloys has been discussed in an article in Metallurgia, August 1961, by C. W. Roberts. In die casting alloys, the principal problem which it is desired to solve is intergranular attack. Because in a die cast element there is plenty of mass, the problem of general corrosion resistance does not arise. In the Roberts paper it is shown that magnesium in a zinc-aluminum alloy with a minimum of lead produces resistance to intergranular attack.

When it is attempted to apply the teachings from the flux coating art and the die casting art to the continuous zinc coating as for example by the so-called Sendzimir process (Sendzimir patents Nos. 2,110,893, 2,136,957 and 2,197,622), one is faced with an entirely different set of conditions. When a ferrous metal strip is to be coated by the Sendzimir process, the strip is passed through an

oxidizing furnace to provide a very thin layer of oxide on the strip and this oxide layer is subsequently reduced in a reducing portion of a furnace and the strip is then led, in a freshly reduced condition, into the coating bath through a hood containing a protective atmosphere without the use of any flux. The coating produced by the Sendzimir process has the advantage of excellent adherence plus extraordinary ductility so that deep drawing operations and sharp bending operations may be carried out on metal strip which has been coated by the Sendzimir process without causing the coating to crack, chip or peel.

According to the Sendzimir process, the bath will contain aluminum in amounts from .04 to .35% which is effective in minimizing the alloy formation and promotes good adherence. A coating metal containing zinc and aluminum will not have a well developed spangle pattern unless lead is also present. Since industry often demands zinc coated material having an attractive spangle, lead may be added. It should be understood that excellent coatings may be made with no lead at all if spangle is not desired.

In attempting to protect the coating produced by the Sendzimir process from intergranular attack, which occurs under hot moist conditions, i.e., in saturated atmospheres at temperatures above 150° F., an addition of the amount of magnesium suggested by experience in the die casting field produces no improvement from the standpoint of intergranular attack. This type of corrosion in zinc alloys occurs only if the alloy contains aluminum, but it is greatly accelerated by the presence of lead as well. The lead in a Sendzimir bath is generally at least ten times the amount found in a die casting alloy. Since a die cast part does not have to present a spangled surface, the lead may be kept low for the purpose of reducing intergranular attack.

Furthermore, in a die casting alloy, the aluminum content is 1% or more, and in the Sendzimir process an aluminum content above about .35% cannot be used because the aluminum reacts with the iron to form a floating dross. Some aluminum, of course, is required in the Sendzimir process to suppress the alloying action between the base metal and the zinc and to provide ductility, but as pointed out above, the upper limit of the aluminum is about .35%.

The continuous processes differ from the sheet flux process in that the aluminum in the continuous processes is much greater (in the flux process the upper limit is .01%) and the lead content is often much less (in the flux process the lead may be as high as 1.60%).

Workers in the art will realize that the Sendzimir process is not the only continuous galvanizing process. This invention is equally adaptable to the continuous pre-flux process as described in U.S. Patent No. 2,823,641, as well as other gas preparation processes wherein aluminum can be tolerated in amounts up to .35%. The continuous pre-flux process should not be confused with the sheet flux process because they are drastically different. The old sheet flux process utilizes a fused flux blanket which floats on top of the molten coating metal. The pre-flux method of Patent No. 2,823,641 applies a controlled amount of flux in water solution to the strip, dries the flux, and then introduces the strip into the molten coating metal bath. The composition of the coating bath may be similar to that of the Sendzimir process and may be altered as taught by this invention.

With the foregoing considerations in mind, it is an object of the present invention to provide a process of producing in a zinc coating on ferrous strip a greatly enhanced corrosion resistance without in any way deleteriously affecting the other properties of the coating.

Briefly, in the practice of the present invention, there is added to the coating bath magnesium in the amount between about .01% and about .10% and preferably in the range of .01% to about .04%. Thus, it will be seen that the amount of magnesium which is added to the bath is approximately the same as has been added in the die casting art to produce resistance to intergranular attack, and about the same as has been added in the flux coating process to improve general corrosion resistance. As pointed out above, however, in the flux process .02% aluminum has been considered sufficient to ruin the flux blanket (see the Heath paper referred to above, bottom of page 12). In the die casting art, the magnesium is known to have been capable of eliminating intergranular attack because of extremely low lead content. As has been mentioned, the effect of magnesium on general corrosion resistance in a die cast alloy has not been investigated because of nugatory importance.

When magnesium in the amount mentioned above is used in the bath according to the Sendzimir process, there is no improvement in the resistance to intergranular attack but surprisingly there is a great increase in general corrosion resistance.

This surprising result must occur because of a strong synergistic effect of the aluminum and magnesium, although the theory is not clear. It has been found experimentally in the aforementioned Heath article that magnesium has a beneficial effect on general corrosion resistance or weight loss of aluminum free zinc coatings. A comparative study of the effect of magnesium on the coating of this invention on the one hand, and aluminum free coatings on the other hand, shows a substantial unexpected benefit from the aluminum addition. The art has not recognized aluminum as having any effect on corrosion resistance of zinc coatings (except for the detrimental effect of promoting intergranular attack). However, aluminum and magnesium together exhibit a resistance to general corrosion heretofore unknown in the coating art.

Tests have shown that the amount of lead should be kept as low as possible in line with spangle control. The benefit of this invention occurs regardless of the amount of lead present, although the less lead content, the greater the reduction in weight loss appears to be.

The coating bath according to the present invention will therefore contain from about .04% to .35% aluminum, from about .01% to .10% magnesium, and lead from zero to 1.60% (the upper limit for lead in Prime Western grade zinc is 1.60% although it will usually contain an average of .5% to .9% lead). It will be understood that the bath may contain incidental impurities such cadmium and iron in amounts usually less than .20%.

Preferably, the coating bath will contain aluminum between about .10% and about .20%, magnesium from about .01% to about .04%, and lead from zero to .20%. As pointed out above, from the standpoint of corrosion resistance alone, best results will be obtained with a minimum of lead and even in the absence of lead. However, it has been found that an addition of .07% to .20% lead will be effective in producing a spangle which will satisfy the demands of the industry. In other words, the minimum lead is used which will produce the size of spangle desired. The strip, as it enters the coating bath, will be clean, either having a substantially oxide-free surface protected by a hood containing a reducing atmosphere as in the Sendzimir process, or carrying on its surface a thin film of flux as in Patent No. 2,823,641.

The resulting coated strip has all of the desired properties which have now been produced for many years by vantage of the greatly enhanced general corrosion resistance. It has been found that average weight loss due to corrosion in the atmosphere has been reduced by about one-third where the present invention has been used. Although the effect of magnesium on corrosion resistance properties is known in the die casting field and the flux coating field, it was impossible for the skilled worker to predict the benefit realized on continuous galvanized material. Continuous processes, such as the Sendzimir process, operate with bath chemistry different from the other two fields, and the addition of magnesium with aluminum in the ranges set forth gives rise to the abovementioned synergistic effect. Modification may of course be made within the ranges above described and I therefore do not intend to limit myself except as set forth in the claims which follow.

Having now fully described the invention, what I claim as new and desire to protect by Letters Patent is:

1. A process of continuously coating ferrous strip, which comprises passing a clean ferrous strip through a zinc bath containing from about .04% to about .35% aluminum, from about .01% to about .10% magnesium, up to about 1.6% lead, and incidental impurities, each in an amount less than .20% to produce a ferrous strip having a tightly adhering, ductile zinc coating characterized by an enhanced general corrosion resistance.

2. A process according to claim 1, wherein said bath contains up to about .20% lead.

3. A process of continuously coating ferrous strip, which comprises passing a clean ferrous strip through a zinc bath containing from about .10% to about .20% aluminum, from about .01% to about .04% magnesium, up to about 1.6% lead, and incidental impurities, each in an amount less than .20% to produce a ferrous strip having a tightly adhering, ductile zinc coating characterized by an enhanced general corrosion resistance.

4. A process according to claim 3, wherein said bath contains up to about .20% lead.

5. A ferrous strip having a metallic coating comprised of .04% to .35% aluminum, .01% to .10% magnesium and the remainder zinc and incidental impurities, said strip having enhanced general corrosion resistance.

6. A zinc coated ferrous strip according to claim 5, in which the zinc coating contains .10% to .20% aluminum and .01% to .10% magnesium.

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