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PROCESS OF CONTINUOUSLY GALVANIZING WITH CONTROL OF SPANGLE AND CORROSION

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Our invention relates to the continuous galvanizing of products, particularly those in strand or continuous strip form; and it has for its general object the control of spangle and of corrosion resistance in such processes and in the products thereof, particularly where the processes are carried on at high speeds.

This general object and others which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, we accomplish in that procedure of which we shall now set forth exemplary embodiments.

Processes of continuous galvanizing have in recent years come into widespread use and are tending, both by reason of a superior product produced and lower costs of production, to displace the older procedures in which sheets or articles after having been pickled and washed are sent individually through galvanizing pots. As exemplary of a continuous galvanizing process, reference is made to Patent No. 2,197,622, issued in the name of Tadeusz Sendzimir. In a typical procedure under that patent, the material to be galvanized, in strand form as it comes from cold rolling mills or wire drawing dies, is sent first through an oxidizing furnace wherein oils, greases and other combustible matters are burned from the surfaces of the material, and is thereafter sent through a reducing furnace wherein a thin, controlled oxide layer on the surfaces of the material is completely reduced. The reducing furnace is connected with the galvanizing pot by means of a cooling hood wherein the material is cooled to a temperature slightly above the temperature of the molten zinc in the pot, the material being continuously surrounded by a reducing atmosphere so as to prevent re-oxidation. No entrance flux is employed. The reducing furnace may, if desired, be carried at a temperature such as to produce a distinct annealing and softening effect on the strand-like material, where this is desired. The zinc bath contains a small amount of aluminum.

A process of this nature is not only economical, but also an improved type of product is produced wherein the zinc coating exhibits unusual adherence to the base, such that the galvanized material may be sharply bent, formed, or drawn without peeling or flaking and the loss of the protective effect of its zinc coating.

A spangle or crystalline appearance of the solidified zinc coating on the surfaces of the material being processed is desirable for various reasons and is demanded by the market. In the early days of the use of such continuous processes as the exemplary one above, it was noted that using such zinc as was denominated in the trade "Prime Western" exhibited a tendency to form spangles with depressed boundaries. This is undesirable, and becomes of considerable importance where the product is to be painted or coated with baked enamels, since the relief pattern of the spangles tends to show through the applied coatings. It was further noted that the addition of aluminum to the zinc bath considerably exaggerated spangle relief.

In the previously conventional galvanizing processes of non-continuous character, the tendency of Prime Western zinc or spelter to form depressed spangle boundaries was usually offset by the addition of tin and sometimes antimony to the zinc. In continuous processes, especially where the tendency was exaggerated by reason of the presence of aluminum, it was found undesirable to add tin or antimony, or both, in the quantities necessary to offset spangle relief, because these elements were known to have a detrimental effect on corrosion resistance and coating ductility. As a consequence, it early became a practice in continuous coating processes to employ high purity zinc such as electrolytic zinc to which was added a small quantity of Prime Western zinc to introduce enough impurities to provide nuclei for spangling. This composition, on the equipment in use at the time, gave an adequate spangle without significant depression of the spangle boundaries, and without undue production of dross.

Historically, it is interesting to note that this practice was continued until the supply of electrolytic zinc was cut off by World War II. When this occurred, recourse was had to Prime Western spelter alone and other relatively impure forms of zinc and the disadvantage of depression of spangle boundaries was accepted because there was no available cure for it. It was ultimately found also that the product possessed less corrosion resistance. When electrolytic zinc again became available, after the cessation of hostilities, the formerly used composition was substituted for the interim zinc; but now a new difficulty presented itself. Especially on the lighter gauges (such as 24-gauge and lighter) of continuously galvanized material, the formerly used composition no longer produced an adequate spangle, and in many instances produced no spangle at all.

This, we have now ascertained, is due to developments in manufacturing procedure and in apparatus which, meanwhile, had very considerably increased the speeds at which the materials were treated in the process. Whereas, when the formerly used composition of the zinc bath was employed under the old conditions, the immersion time for medium and lighter gauge materials was a minimum of 6 to 7 seconds at strip speeds below 80 feet per minute, the immersion time of such materials had been decreased to a maximum of 3 to 4 seconds in many operations, and in instances was substantially less, with the strip speed well over 100 feet per minute and even as high as 200 feet per minute.

In order that the invention may be fully understood, it may be pointed out that various factors have an effect on spangle size. The weight of the applied coating is one of these factors, heavier coatings in general producing a smaller spangle size, all other conditions being equal. The roughness of the surface of the strip or other strand-like material, also has an effect, a rougher surface producing smaller spangles.

Yet again, it will be found that the earlier the freezing coating on the strip or wire beyond the coating pot becomes disturbed by such means as air blasts, frequently employed to hasten the freezing, the smaller will be the spangle size. Similarly, the faster the actual cooling rate during freezing, the smaller the spangle size. These last mentioned factors act as indicated on lighter gauge materials, but another factor, acting in the opposite direction, may be encountered with heavier gauges. The reservoir of heat in a heavy galvanized material may be so great that alloying proceeds from the surface of the material entirely through the zinc coating imposed thereon if the freezing is allowed to proceed at its natural rate. Where this happens, there will, of course, be no spangle; yet the spangle can be restored if it is found possible to cool the material so rapidly as to cause freezing before complete alloying takes place.

Our invention takes these factors into account, and to whatever extent they can effectively be employed to control the nature of the spangle in other processes, they may be employed in the process of this invention. In addition to these, we have found that another important factor determining spangle size is the time of immersion of the material being galvanized in the zinc bath. Shorter immersion times produce smaller spangles. For numerous economic and mechanical reasons variation of immersion time is not available as a means of regulating spangle size. This poses a serious problem in attempting to utilize high purity zinc for its improved corrosion resistance and in operating at high speeds to decrease cost, while at the same time attempting to produce an attractively large spangle.

Economical operation of a continuous coating unit

requires that it be operated at as high a speed of the strip being coated as possible, the maximum usually being determined by the capability of the strip preheating furnace. Thus as material of various gauges is coated, the strip speed is normally varied, because the time required to bring the strip to the required temperature depends upon its thickness or gauge. This, it will be seen, results in shorter immersion times for lighter gauge strips.

At the high speeds of the newer strip coating units, we found that it was difficult or impossible to preserve an attractively large spangle on medium or light gauge strips when using high purity zinc. For example, in a particular installation when strip lighter than 24-gauge is being coated, the time of immersion is less than 6 seconds and a satisfactory spangle cannot be produced consistently when coating with high purity zinc.

The difficulty of no spangle or an unsatisfactorily small spangle with high purity zinc arises generally when the immersion time of the strip is less than 6 seconds. In the majority of commercial installations today, speeds are such that the heavier gauges give little trouble, and the difficulties are encountered on the medium and lighter gauges. Nevertheless, the tendency is toward higher speeds which can be attained in various ways, as by the provision of longer furnaces or furnaces with a more rapid rate of heating. Providing a longer strip travel through the bath to increase immersion time would be unduly expensive as a larger pot would have higher heat losses, produce more dross, and would cost more initially. Further, the immersion time would then be too long for the more slowly moving heavier gauges, and would cause excessive alloy formation and loss of spangle. The particular problem to which this invention is addressed, it will be seen from the above, is not necessarily confined to any particular gauge or gauge range, even though at the speeds current in today's operations it manifests itself primarily in 24-gauge and lighter stock. We shall now proceed to a description of our solution for the problem.

The present invention is based on our discovery that the lead content of the spelter or zinc employed has a controlling effect upon spangle formation at high speeds and short immersion times. However, it also strongly affects corrosion resistance. Commercial zinc, such as Prime Western spelter, which is relatively high in lead, gives poor smoothness when aluminum is added; and it is undesirable to correct this by the addition of tin. Further, the corrosion resistance of such coatings is by no means as high as can be obtained. A fundamental teaching of this invention is based upon our discovery that if the lead content of the spelter is held within a critical range, it is possible to produce at high speed a galvanized material having smooth spangle boundaries, attractively large spangles, and exceptionally good corrosion resistance at short immersion times and high speeds; and the provision of such a product is an important object of the invention.

Our investigations have indicated that for maximum corrosion resistance, especially for the type of corrosion resistance indicated by under-water corrosion tests, the lead content must be less than about .30%, and a still smaller lead content is desirable. The high impurity zincs commonly used, therefore, are unsuitable for use as such. On the other hand, we have found that to produce spangle dependably in modern high-speed production, a lead content of at least about .12% is required. Thus, commercially pure zincs known as High Grade Special and High Grade are alone unsuitable for use as such, since their lead contents are invariably well below this figure. We give as a range for commercial operation a lead content of from .12% to .30%, preferring a somewhat narrower range of from .12% to .20%. Within these ranges we have found it possible to gain the object of the invention last set forth above.

In accordance with the teachings of our invention, it is now possible to coat at high speeds and with short immersion times, using commercially pure zinc providing enough lead is added to bring its lead content within the range set forth. This may be done directly, but it may also be done by adding to commercially pure zinc a zinc material which is high in lead, such as Prime Western zinc, providing the range limitations are met. It is not new to add Prime Western zinc to commercially pure zinc in small amounts, as set forth above; but whereas the quantities previously added raised the lead content of the bath to an average of about .06% to .07% and are not known to have raised it at any time above about .10% to .11%, we have found that a range above this is necessary to achieve the objects of this invention.

We shall now describe the conditions of an exemplary operation. The spangling behaviors which we have discussed assume a zinc bath saturated with iron and maintained at temperatures substantially between 830° and 870° F. The iron content at such temperatures at saturation runs around .08%. This is a matter over which the operator has ordinarily no control. The iron content of the bath is picked up rapidly from the immersed article, the galvanizing pot and such apparatus made of ferrous metal as is immersed therein. A pot starting up with fresh, pure zinc will result in an initial absence of spangle; but the iron content is rapidly built up therein and, reaching a maximum at a given temperature, will thereafter vary only with variations in temperature of the molten coating metal.

The aluminum content of the bath may vary from substantially .04% to .35% or even somewhat higher. We prefer to operate at around .15% aluminum which is the amount from which our investigations have indicated the desired advantage of aluminum in producing adherence is realized. Higher values can be used without affecting the coating adversely, if desired. Aluminum appears to have a direct effect on spangle size which is wholly minor in nature, the spangle size being very slightly increased, all other conditions being equal. This is not contrary to the statement made above that where an impure bath tends to produce depressed spangle boundaries, the difficulty is exaggerated by the presence of aluminum.

In operating a continuous galvanizing process in accordance with this invention, it is possible to make up ahead of time a zinc composition which contains the desired ingredients in the desired proportions; and this may be found advantageous particularly where it is possible to purchase zinc to exact specifications. It is equally possible to practice the invention by adding different ingredients individually to the zinc pot. As the coating metal is withdrawn from the bath on the surfaces of the continuous materials being galvanized, it is common practice to add coating metal in the form of bars to the bath or to a preheating reservoir in communication with the bath as required to maintain the desired level of coating metal. In the practice of our invention it is readily possible, as indicated above, to attain the desired composition by adding bars of different material in specified proportions based on their known analyses. For example, we add from 3 to 4 parts of high grade, pure or electrolytic zinc, and one part of Prime Western spelter to maintain the desired composition so far as the ingredients other than aluminum are concerned, adding the aluminum in bars of zinc-aluminum alloy as necessary to maintain the desired aluminum content. As indicated, desired ratios are calculated upon the known analyses of the metallic bars or pieces themselves, and it is quite easy in the light of the teachings herein to determine a ratio of the same or different size bars so that the bars may be added in predetermined groups to maintain both the liquid level and the composition of the bath, as will now be evident to the skilled worker in the art.

Electrolytic and other high-grade zincs contain ordinarily less than .01% lead. Prime Western spelter contains substantially .6% to .9% of lead. These figures are, of course, general, but it is possible to take them as a guide. However, we prefer to base our calculations on ascertained analyses of the materials themselves in making up zinc baths containing lead within the ranges taught herein.

Other substances may be briefly considered. Tin has an adverse effect on corrosion resistance, and we prefer to keep it as low as possible. Our investigations have also indicated that when the tin content rises above .25%, the zinc coating itself becomes more brittle. It is true that a tin content above about .25% increases spangle size and improves appearance; but for reasons which will now be clear, it is undesirable in continuously galvanized products, where ready formability accompanied by high adhesion of the zinc coating is desired, to employ tin as has been done in the older galvanizing procedures. Below about .25%, tin as a bath ingredient has little effect on the appearance of the product. In the preferred practice of our invention, the tin may vary from zero or a trace up to .25% at which its deleterious effects become important. We, therefore, do not add tin. Commercial zinc products contain some of it, the quantity

varying upwardly from a minimum of around .004% in the purest grades of zinc; but we have not found, in the practice of our invention as taught herein, any circumstances in which the tin content of the bath tended to be too high by reason of the employment of commercial zincs.

In our commercial operations our bath generally has a cadmium content of substantially .01% to .04%, due to the presence of this metal as an impurity in the zinc. We prefer not to operate with baths containing over about .06% cadmium as there is some evidence that larger amounts tend to produce brittleness of the zinc coating. The cadmium content of a zinc bath appears to have little or no effect on the spangle size even up to amounts as great as .09%. We may state, therefore, that we prefer that the cadmium in our baths range from a trace up to about .06%. Commercial zincs ordinarily contain some cadmium, about .001% being about the lowest we have encountered in high purity zincs. However, the quantity of cadmium normally found in the less pure zincs is not sufficient to raise the cadmium content of the bath beyond the limits set forth above so that we have encountered no difficulty in using the proportions of such materials as Prime Western spelter set forth above.

Antimony, bismuth and copper are sometimes present in commercial spelter in trace amounts. Antimony and bismuth are believed to act in a manner similar to tin in producing embrittlement of the coating when present in substantial amounts and, therefore, are undesirable in excess. They will not normally be present in deleterious amounts unless added. A small amount of copper is usual, but in the amounts normally present in commercial spelter, such as Prime Western, it apparently has no effect of importance.

It will now be clear that the teachings of our invention can be met by baths made up in part of high purity zinc and in part of less pure grades of metal since such grades normally have a lead content which by dilution can be brought within our critical range. This furnishes a convenient and inexpensive mode of arriving at our bath compositions, whether the composition be made up previously and added in unitary increments to the molten bath, or whether the individual ingredients are added in certain ratios. It will, of course, be evident that our invention is inclusive of the thought of starting with an electrolytic or other high-grade zinc and adding to it aluminum and lead to bring it within the ranges taught herein, although this usually will involve a greater expense.

It will be understood that the practice of the invention involves the use of correct cooling procedures in the light of factors already discussed. With today's apparatus, the importance of the invention is obviously greater with the medium and lighter gauges of metal being galvanized since the heavier gauges still receive an immersion time of substantially six seconds or longer. The use of our invention is not deleterious in any way even with the longer immersion times, and for this reason we employ the baths of the invention irrespective of gauge and through-put rate. As speeds are increased, the importance of the invention in the heavier gauges will obviously also increase. The objects of the invention are attained at the highest speeds which have thus far been employable in continuous galvanizing procedures; and tests have indicated that speed and hence time of immersion does not in itself provide an end point for the effectiveness of the invention.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in certain exemplary embodiments, what we claim as new and desire to secure by Letters Patent is:

1. A process of continuously galvanizing ferrous strip which comprises passing the cleaned ferrous strip through a zinc bath containing substantially .12% to .30% of lead and substantially .04% to .35% of aluminum, the immersion time in the said bath being less than about 6 seconds, the strip speed being greater than about 80 feet per minute.

2. The process claimed in claim 1, wherein the strip is not heavier than about 24-gauge.

3. A process of continuously galvanizing ferrous strip which comprises cleaning the strip, subjecting it under heat to reducing conditions and, while the strip is protected by a reducing atmosphere, passing it beneath the surface of a flux-free galvanizing bath, the said bath containing in addition to zinc substantially .12% to .30% of lead and substantially .04% to .35% of aluminum, the said bath being saturated with iron, the strip having an immersion time in said in bath less than substantially 6 seconds and a speed of travel in excess of substantially 80 feet per minute.

4. The process claimed in claim 3, wherein the strip is not heavier than substantially 24-gauge.

5. The process claimed in claim 4 in which the bath temperature is substantially 830° to 880° F. and in which the ferrous strip is passed into said bath while at a temperature at least substantially equal to the temperature of the bath.

6. The process claimed in claim 5 wherein the galvanizing bath has the following analysis:

Cadmium	Trace to .06%,
Tin	Trace to .25%,
Aluminum	.04% to .35%,
Iron	Substantially .08%,
Lead	Substantially .12% to .30%,

balance zinc, excepting for normal minor impurities therein.

7. A process of continuously galvanizing ferrous strip which comprises passing the cleaned ferrous strip through a zinc bath containing substantially .12% to .20% of lead and substantially .04% to .35% of aluminum, wherein the strip has an immersion time in the zinc bath of less than about 6 seconds and a strip speed greater than about 80 ft. per minute.

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