

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) LEAD ZINC WET-FLUX GALVANIZING PROCESS

(71) We, JOHN LYSAGHT (AUSTRALIA) LIMITED, a Company incorporated under the laws of the State of New South Wales, Commonwealth of Australia, of 50 Young Street, Sydney, in the State of New South Wales, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the galvanizing of ferrous articles, that is to say the coating of the articles with a zinc or zinc alloy layer.

For descriptive convenience the term "coating metal" is used hereinafter and is intended to refer not only to zinc but also to the zinc alloys commonly used in conventional galvanizing practice.

Also the term "galvanizing bath" is used hereinafter and is intended to refer to a bath or pool of molten coating metal.

The usual way of galvanising steel articles, is to immerse them in or direct them through a galvanizing bath. In that process a certain amount of alloying of the two metals occurs, and this is manifested as an iron-zinc alloy layer sandwiched between the steel base and the coating metal layer.

The presence of the alloy layer is detrimental, as it is relatively brittle and hence is not readily amenable to cold working. Ability to withstand cold working is particularly desirable where the galvanized articles are in the form of sheets or strip which, or parts of which, are required to be worked by roll-forming, crimping, lock-seaming, or in other ways necessitating sharp-cornering or small-radius bending.

If the alloy layer is sufficiently thin it is better able to deform in a pliant manner; but upon cold working, even a thin alloy layer frequently fails under the loads so imposed upon it thus to cause flaking, cracking or peeling of the coating metal layer.

It is already well known that addition of a small proportion of aluminium to a galvanizing bath will suppress formation of a brittle iron-zinc alloy layer sufficiently to avoid, or satisfactorily reduce, subsequent failure of that layer under cold-working. A suitable proportion of aluminium is about 0.15% the balance being zinc in excess of 90% and other metals (all percentages stated herein are by weight). If the proportion of aluminium is allowed to fall below about 0.08% the effectiveness of the aluminium addition, for all practical purposes, ceases.

It will thus be seen that mere addition of aluminium to the galvanizing bath is not sufficient. It must be maintained at an effective concentration.

In most of the modern large-scale processes for the continuous galvanizing of steel strip, maintaining an effective concentration of aluminium in the galvanizing bath is not difficult because such processes do not use a wet flux with which the aluminium can adversely react. This is achieved by cleaning the steel strip in known manner and then directing it into the bath through a trunk or snout containing a protective inert atmosphere. This permits the molten coating metal to be laced with aluminium in the necessary proportion, and kept that way, without the aluminium undergoing unwanted reaction with matters alien to the actual coating step of the full process.

However, in the large-scale process referred to just above, extensive and expensive equipment is necessarily involved, and the process is quite unsuited for the galvanizing of single sheets of steel or in similar relatively small-scale galvanizing operations.

Three other galvanizing processes, each of which involves the use of a flux are commonly used. These are: the traditional wet fluxing process; the Cook-Norteman process; and the lead-zinc process.

In the wet fluxing process, the cleaned sheet is passed into a galvanizing bath through a

5 fenced-in layer of molten, or wet, flux, the common fluxes being chlorides. It is not possible to add aluminium to these baths in sufficient quantities to suppress the growth of undesirable iron-zinc alloy layers, because of rapid-reactions between the aluminium and the flux.

10 In the Cook-Norteman process, a chloride-based flux is dried onto the cleaned steel strip before passing into the galvanizing bath. In this process it is possible to add aluminium, but in amounts less than desired due to the rapid reaction of the aluminium with the fluxing medium. The pre-galvanizing processes of pickling, cleaning, washing, flux application and drying require more expensive equipment, and are far more difficult to control than the pre-galvanizing treatment required for wet fluxing. Furthermore, the process cannot be used for the manufacture of single sheets, and is confined to the galvanizing of strip.

15 The lead-zinc method consists in directing an article to be galvanized downwardly through a suitable fenced-in pool of, commonly, liquid chloride-bearing flux which floats on a bath of molten lead; then through the lead bath, and then upwardly through a fenced-in pool of molten coating metal which also floats on the molten lead. The lead, which does not readily form a coating on steel, acts as a separating medium between the flux and galvanizing bath, and the actual galvanizing (or most of it) is effected in the galvanizing bath. In this last connection it is found that the galvanizing process starts in the lead bath due to migration thereinto of a small proportion of the zinc with which the lead bath is in contact. This migration is usually such that the zinc dissolves into the lead to about 1.0—2.0% concentration, but this is sufficient to initiate galvanizing and is one of the factors resulting in an undesirably thick iron-zinc alloy layer in the finished article when the process goes forward in the manner conventional heretofore.

20 It has not previously been proposed in the galvanizing art to include aluminium in the lead-zinc wet-flux process in quantities and distribution sufficient to substantially suppress undesirable alloy growth at any stage in that process. However, in experiments leading to the present invention such additions were tried. Because of the abovementioned dissolved zinc in the lead bath, aluminium additions to the galvanizing bath alone are not sufficient to produce an alloy free product with a ductile coating. By adding aluminium to the lead bath, it was discovered that by keeping the aluminium content of the lead bath at somewhat more than the level it normally reaches by dissolution by some of the aluminium from the galvanizing bath and concurrently keeping the aluminium content of the coating metal at an appropriate level, the effectiveness of the flux is not significantly reduced notwithstanding its

contact with the aluminium-lead solution; and, the suppression of iron-zinc alloy growth in both the lead bath and the galvanizing bath is sufficient to ensure a thinness of iron-zinc alloy layer on the coated articles as will endow them with the required cold working properties.

It has been also found that as the galvanizing bath is not in direct contact with the wet fluxing agent additions of aluminium can be made to the molten metal without danger of rapid reaction between aluminium and the wet fluxing agent and that the concentration of aluminium in the lead bath required to inhibit alloy growth in that bath is sufficiently low as to avoid any rapid reaction with the wet fluxing agent.

Therefore, the invention consists in a process of galvanizing ferrous articles comprising the step of directing the articles into a molten lead bath containing aluminium and from the lead bath upwards through a galvanizing bath floating on the lead bath.

Preferably, the method of the invention includes the further steps of pretreating and fluxing the article before it enters the lead bath, and the step of stripping molten coating metal from the article after it leaves the galvanizing bath to control the thickness of the finished coating. Conveniently the fluxing may be effected by directing the article into the lead bath through a pool of flux floating thereon.

Further, for preference, the galvanizing bath also contains aluminium.

The operation of the invention will become more clear by the following illustrative description of preferred embodiments, made with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of a preferred apparatus for effecting the method of the invention;

Figure 2 is a schematic diagram of an alternative apparatus for effecting the method of the invention, and

Figure 3 shows drawings of photomicrographs of cross sections of galvanized coatings.

In the examples below the term "sheet" or "sheets" refers to flat rolled products in which the rolled thickness of the product is substantially less than either its length or width. The term "strip" refers to a similar product to "sheets", but where the length is such that the product must usually be coiled up for convenience in storage, for instance lengths measured in thousands of feet.

Referring to Figure 1, uncoated sheets of a ferrous base material may be pretreated by well known means, for example, by pickling in acid followed by water rinsing, and then passed individually along pass line 4 into a molten lead bath 5 contained in a kettle 6 via a flux cover 7 which, as is known, pre-

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pares the strip for coating. The flux cover 7 is contained by weirs 8. The sheets are guided through the lead bath 5 by means of guide rolls 9 and 10 and other means not shown.

5 The sheets, following pass line 4, are guided upwards into a galvanizing bath 11 from which the sheets emerge between coating weight controlling rolls 12. Thereafter the sheets may be cooled by natural or forced convection, chemically treated to prevent corrosion of the coating and stacked.

10 Small amounts of aluminium are provided within the lead bath 5. It has been found that, for normal coating metal compositions, containing less than 0.5% aluminium, the aluminium diffusing from the galvanizing bath 11 into the lead bath 5 is insufficient for alloy suppression and that other means are necessary. Still referring to Figure 1, a molten aluminium-zinc alloy pool 13 is maintained in direct contact with the lead bath 5 by containment by weirs 14 similar to those containing the flux cover 7. The weirs 14 include any excess zinc from the alloy pool 13.

25 The aluminium concentration in the alloy pool 13 may be varied up to about 20%, depending on requirements and the ratio of the interfacial surface area to the volume of lead present. The selection of the concentration of aluminium in the alloy pool 13 is effected by the desired level of aluminium in the lead bath 5 since an equilibrium will eventuate between these two molten phases, and control of the composition of the lead bath 5 is achieved by varying the composition of the alloy pool 13 according to the results of regular analyses of the lead bath 5. The melting point of alloys with greater aluminium concentrations than 20% is likely to be higher than the operating temperature of the bath.

30 The preferred proportion of aluminium in the lead bath 5 is somewhat more than the level normally reached by dissolution of the aluminium from the galvanizing bath and not greater than that needed to provide a saturated solution (about 0.06%). That is, the preferred aluminium concentration in the lead bath is between 0.0005% and 0.06%. It has been found that, under normal operation conditions, aluminium concentrations between 0.001% and 0.008% are usually satisfactory.

35 Figure 2 displays a lead bath 15 in a kettle 16 supporting a galvanizing bath 17 and a flux cover 18 contained by weirs 19 all much the same as the corresponding components displayed by Figure 1. For clarity the means for feeding a strip or other article through the cover 18 and baths 15 and 17 have been omitted.

60 Figure 2 illustrates alternative means for controlling the aluminium percentage in the lead bath. Those means comprise a first molten metal pump 20, operated by a drive rod 21 and immersed in the lead bath 15, which delivers lead bath material into an alloying

kettle 22 which contains a lead pool 23 with a molten aluminium-zinc alloy or aluminium cover layer 24 floating on it.

The temperature of the metals 23 and 24 in the alloying kettle 22 may be increased considerably above that of the lead bath 15 to increase the rate of dissolution of aluminium into the lead pool 23. This dissolution rate may be further assisted by any of several conventional means of agitating the lead pool 23 and cover layer 24. The lead enriched in aluminium is then pumped by a second pump 25, driven by rod 26 via conduit 27 back into lead bath 15. The composition of the cover layer 24 may be varied depending on those factors mentioned in the first described example of the invention, although in this case, with increased temperatures possible, the cover 24 may contain up to 100% aluminium depending on the actual temperature.

The pumping operations, from the kettle 16 to the alloying kettle 22, and return, may be either continuous or intermittent. Control of the aluminium concentration in the lead bath 15 is achieved by adjusting the pumping rate and the factors mentioned above viz: temperature of the lead pool 23, composition of the alloy layer 24 and agitation, these adjustments depending on regular analysis of the lead bath 15.

Aluminium additions to the galvanizing bath are made in well known manner to control its composition. The preferred concentration of aluminium in the galvanizing bath is from 0.14—0.30% by weight, as is usually used in the large-scale and expensive processes referred to above. Higher aluminium levels are not normally employed since, in these large scale processes, they are not necessary to prevent undesirable alloy growth, and further, they interfere with certain properties of the finished coating, such as solderability. However, if such properties are not required in the final product, or in other circumstances, higher aluminium concentrations if desired may be used in the galvanizing bath up to about 20% by weight at normal galvanizing temperatures and higher than 20% if the process is carried out at higher temperatures. Aluminium contents below 0.14% have been found to produce the desired effect of suppression of the alloy layer, provided a suitable aluminium level is maintained in the lead bath 5.

The galvanizing bath may contain other alloying elements which are added for special purposes well known to those skilled in the art.

Figure 3 demonstrates the effectiveness of the aluminium in the lead bath in suppressing the growth of the iron-zinc alloy 30 between the ferrous base 31 and the galvanized coating 32.

The Table 1 below shows compositions of the galvanizing bath and the lead bath under the conditions corresponding to the three

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photomicrographs of representative cross sections of galvanized coatings shown in Figure

3, together with the results of adherence tests carried out on each of the coatings illustrated.

Reference to Figure Number	Galvanizing Bath Analysis		Lead Bath Analysis		Adherence Rating
	Al%	Pb%	Al%	Zn%	
3A	<0.01	1.37	Nil	1.30	3T
3B	0.17	1.50	<0.001	1.81	2T
3C	0.18	1.14	0.0035	1.42	0T

Examination of Figures 3A, 3B and 3C clearly demonstrate the alloy suppression properties of the aluminium in the lead bath and that an aluminium concentration in the galvanizing bath is only slightly effective in this regard.

The adherence rating of the coatings associated with the structures shown in Figures 3A, 3B and 3C is shown in Table 1. The adherence test used is one commonly employed, whereby a sample of the galvanized sheet is bent through 180° over a number of other, flat, pieces of the same sheet. The galvanized coating on the outside of the bend is then examined to see if it remains adherent. The test is repeated as many times as necessary, each time increasing by one the number of pieces of sheet, and hence the radius over which the test sample is bent, until the galvanized coating no longer flakes off. The adherence is then expressed as a "T" rating; the number being the smallest number of pieces of sheet inside the bent sample when no failure of the galvanized coating occurs. For example, "0T" means that the coating is adherent when the sample is bent 180° on itself; this represents the severest bend possible with this test; "1T" that the coating is adherent when the sheet is bent over one thickness of its own gauge, and so on.

The above described examples serve to illustrate preferred embodiments of the invention and in no way limit its applications. For example, still other means of lacing the lead bath with aluminium may be employed such as by holding aluminium or aluminium alloy (for example, containing less than 10% zinc) ingots or sheets under the surface of the lead bath or, for instance, by making direct additions to the lead bath of ingot or pigs of lead enriched in aluminium in a completely separate alloying process; indeed maintaining an ingot or plate of pure aluminium in contact with the lead bath is a simple and highly effective way of providing aluminium in the bath.

In addition, the invention is not restricted to the galvanizing of sheet and the ferrous base may be passed through the bath in the form of other types of articles, such as steel strip or a plurality of strips joined to form a continuous web (although, of course, in such case terminal equipment—decoilers and recoilers instead of sheet stacks—is different to that described above, as is guide means for strip passage and other factors, but all these are well known to those skilled in the art). Further the means of controlling coating weight is not restricted to the rolls mentioned above, but any of the other well known methods, for example, gas jet stripping nozzles, may be employed.

Conventional gas jet stripping is effected by using superheated steam as a stripping medium and, if desired, superheated steam may be used in methods according to the invention. However, it has been found that the use of superheated steam causes some oxidation of coating produced by the method of invention and according to another aspect of the invention the excess coating is stripped by means of a blast of air which may be either hot or cold. For reasons which are not presently fully understood the use of air, as aforesaid, on the coating produced by the method of the invention produces a bright unoxidised coating of exceptional attractiveness.

WHAT WE CLAIM IS:—

1. A method of galvanizing ferrous articles comprising the step of directing the articles into a molten lead bath containing aluminium and, thence, upwardly through a galvanizing bath floating on the lead bath.

2. A method according to Claim 1 including the further steps of pretreating and fluxing the article before it enters the lead bath.

3. A method according to either Claim 1 or Claim 2 including the further step of stripping molten coating metal from the article after it leaves the galvanizing bath to control the thickness of the final coating.



photomicrographs of representative cross sections of galvanized coatings shown in Figure

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Conventional gas jet stripping is effected by using superheated steam as a stripping medium and, if desired, superheated steam may be used in methods according to the invention. However, it has been found that the use of superheated steam causes some oxidation of coating produced by the method of invention and according to another aspect of the invention the excess coating is stripped by means of a blast of air which may be either hot or cold. For reasons which are not presently fully understood the use of air, as aforesaid, on the coating produced by the method of the invention produces a bright unoxidised coating of exceptional attractiveness.

WHAT WE CLAIM IS:—

1. A method of galvanizing ferrous articles comprising the step of directing the articles into a molten lead bath containing aluminium and, thence, upwardly through a galvanizing bath floating on the lead bath.

2. A method according to Claim 1 including the further steps of pretreating and fluxing the article before it enters the lead bath.

3. A method according to either Claim 1 or Claim 2 including the further step of stripping molten coating metal from the article after it leaves the galvanizing bath to control the thickness of the final coating.

4. A method according to Claim 3 wherein said stripping is effected by directing a blast of air against the article as or shortly after it emerges from the galvanizing bath.
- 5 5. A method according to Claim 4 wherein said air is unheated.
6. A method according to any one of the preceding claims wherein the ferrous articles are steel sheets.
- 10 7. A method according to any one of Claims 1 to 5 wherein ferrous articles are lengths of steel strip.
8. A method according to Claim 7 wherein the lengths of steel strip are joined together
- 15 to form a continuous web.
9. A method according to any one of the preceding claims wherein the aluminium concentration of the lead bath lies in the range of from 0.0005% to .06% by weight.
- 20 10. A method according to Claim 9 wherein the aluminium concentration of the lead bath lies in the range of from 0.001% to .008% by weight.
11. A method according to any one of the preceding Claims wherein the aluminium content of the lead bath is maintained and controlled by floating a molten aluminium-zinc alloy pool on the lead bath.
- 25 12. A method according to any one of Claims 1 to 10 wherein the aluminium content of the lead bath is maintained and controlled by circulating the lead in the lead bath through an alloying kettle containing a molten lead pool upon which floats a molten aluminium-zinc alloy or aluminium cover layer.
- 30 13. A method according to Claim 12 wherein the contents of the alloying kettle are kept at a temperature greater than that of the lead bath.
- 35 14. A method according to either Claim 12 or Claim 13 wherein the contents of the alloying kettle are agitated.
- 40 15. A method according to Claim 11 wherein the concentration of aluminium in the lead bath is controlled by varying the composition of the molten aluminium-zinc alloy pool.
- 45 16. A method according to Claim 15 wherein the molten aluminium-zinc alloy pool comprises from 0.5% to 20% aluminium by weight; the remainder, excluding impurities, being zinc.
17. A method according to any one of Claims 12 to 14 wherein the aluminium concentration in the lead bath is controlled by
- 55 varying the composition of the molten cover layer.
18. A method according to Claim 17 wherein the molten cover layer comprises from 0.5% to 100% aluminium by weight; the
- 60 remaining if any, excluding impurities, being zinc.
19. A method according to any one of Claims 1 to 11 wherein the aluminium content in the lead bath is maintained by holding
- 65 a solid aluminium or aluminium alloy body immersed in the lead bath.
20. A method according to Claim 19 wherein said body is of an alloy of aluminium and zinc.
- 70 21. A method according to Claim 20 wherein the composition of the body alloy includes no more than 10% zinc by weight.
22. A method according to any one of Claims 1 to 11 wherein the aluminium content in the lead bath is maintained by adding
- 75 pigs or ingots of aluminium enriched lead to the lead bath.
23. A method according to any one of the previous claims wherein the galvanizing bath contains 0.30% aluminium or less by weight.
- 80 24. A method according to Claim 23 wherein the galvanizing bath contains from 0.14—0.30% aluminium by weight.
25. A method according to any one of Claims 1 to 10 wherein the aluminium content in the lead bath is maintained by providing an aluminium concentration in the galvanizing bath of greater than 0.3% by weight.
- 85 26. A method according to Claim 25 wherein the aluminium concentration in the galvanizing bath is between 0.3% and 20% by weight.
- 90 27. A galvanized ferrous article when produced by a method according to any one of the preceding claims.
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