This application is a continuation in part of my co-pending application, Serial No. 176,639, filed November 26, 1937, entitled "Galvanizing sheets of metal."

This invention relates to the art of galvanizing sheets of metal, such as steel, and while serviceable in the production of zinc-coated sheets of different gauges or thicknesses, is especially advantageous in the production of such coated sheets when it is desirable that the zinc coating be of very thin or of minimum weight in meeting the service conditions for which such sheets are intended.

In applying such minimum or light coating of zinc to sheet steel or the like, some difficulty has been encountered in duly immersing the sheet in the molten bath to obtain the intended thin or light-weight coating thereon without having the sheet in its submerged state for so long a period as will frustrate the obtaining of the thinness of coating desired or, in other words, as an incident to complete submergence of the sheet and withdrawal of the same from the bath, causing the sheet to accumulate or take on too much of the zinc with correspondingly added and unnecessary weight of coating.

My invention, therefore, includes in its method of coating the manipulation of the sheet with reference to the molten zinc part of the bath, so that the contact of the sheet with the zinc is of limited duration compared to the travel of the sheet through the bath material, regarded as a whole, said bath material being constituted by a major constituent, such as lead, on which a minor constituent of zinc is superimposed to give an adequate depth of bath to insure appropriate heating of the sheet and subsequent passage thereof through and out of the thin layer of zinc.

However, it has been demonstrated that when subjecting the sheet to such a thin coating of zinc, as has been referred to—as is observable to a less degree in instances of somewhat heavier coatings—the coated sheet as it leaves the bath possesses a highly undesirable characteristic created by black or dark spots marking the facial appearance of the coated sheet and correspondingly preventing a clear and bright appearance of the sheet. The analysis of these dark or black spots shows them to contain lead-oxide, iron, carbon, and zinc; in instances the proportion of lead-oxide being as much as 26.82% of the spot areas. The presence of these dark or black spots in the exposed face of the coating tends also to the irregular or non-uniform formation of spangles, so called, on the coated sheet. This, according to my best understanding is due to the fact that the dark or black spots referred to are composed primarily of lead-oxide, the lead-oxide condition being somewhat aggravated by the thinness or light weight of the zinc coating, and flowing from the passage of said sheet during the submergence of the latter through the adjoining strata of lead and zinc constituents of the molten bath.

As its essential characteristic, my improved method embraces the step of eliminating the presence of the lead-oxide from the coating of a sheet upon the emergence of the coated sheet from the zinc bath material, or as it emerges therefrom, so that the resultant product will be correspondingly devoid of the dark or black spots referred to. More specifically, this step has for its object the reduction or conversion of the lead-oxide to lead, it having been found that such reduction or conversion prevents dark or black spots from forming on the sheet.

Still more specifically, my invention embraces the substitution of the zinc-coated sheet at or immediately after the emergence thereof from the coating bath material to the action or influence of a reducing agent, preferably oxalic acid, desirably mixed with sal ammoniac, the effect of the oxalic acid on the lead-oxide-bearing coating being, as previously observed, to reduce the lead-oxide to lead, and the combined effect of the treatment by the oxalic acid-sal ammoniac mixture being a substantially observable brightness and regularity of exposed coated sheet-facing as compared to the older coated sheet of the prior art possessing the dark or black spots and coincidental dull or less bright appearance.

In carrying my method into practical effect, the same may be assisted by any convenient or suitable apparatus, unnecessary to illustrate herein, as will be obvious.

With all of the foregoing objects and consequent advantages in mind, my improved method will be readily understood, as follows:

Assume that as the first or coating step of my method, a suitable galvanizing bath is provided, through the medium of which the desired thin coating of zinc may be applied to the steel or other sheet to be coated. Said bath preferably consists of layers, so to speak, of supporting-and-heating material, such as lead, constituting the major portion of the bath, provided to give adequate depth to the bath, and a superimposed layer of zinc of relatively shallow depth as compared to the lead constituent layer. The proportions
and combined volume of the bath material are in keeping with those commonly recognized variable requirements determined by the period of immersion, and rapidity of travel of the sheet to be coated through the bath material. The bath is also heated in keeping with such requirements, say from 810° F. to 856° F., depending on the type of coating desired.

The bath, especially the depth of lead, will allow ample room for the sheet being coated to pass through the lead and be appropriately heated by the former, thence through the thin layer of zinc to zinc-coat the heated sheet, whence the zinc-coated sheet will be drawn or fed through feed and/or finishing rolls to regulate the thickness of the coating on the sheet, or directly out of said combined bath, as the case may be.

Now, although I may pre-treat the sheet to be coated at the point of its introduction into the coating bath, as by passing the same through a flux containing a mixture such as about to be defined in connection with the exit or emergence of the coated sheet from the zinc bath, it is at this latter point that my next step of treatment is all-important. As already stated in this specification, it has been found that as the coated sheet leaves the bath, the coating, because of the substantial presence of lead-oxide therein, will cause highly objectionable dark or black spots to appear on the completed or finally coated sheet, marred the appearance of the sheet (in fact, at times rendering the whole useless as a commercial product) and also permitting or causing the formation of spangles of irregular and unsightly appearance on the face or faces of the sheet, so that the product is not of that uniform and nicey of appearance needed in many instances of use in the art; and, as also stated, the actual final step of my process obviates all of the difficulties and disadvantages just outlined. This final step comprises the subjection of the zinc-coated sheet—bearing the objectionable lead-oxide which leads to the formation of the dark or black spots and irregular spangle—referred to—to the action or influence of a so-called reducing agent, a mixture of the oxalic-acid and sal ammoniac in the proportion of one part oxalic acid and four parts sal ammoniac, the mixture being applied to the coated face or faces of the sheet while the coating is still of high temperature, and preferably at the point of emergence of the coated sheet from the bath and/or immediately after such emergence. This may be accomplished by providing a flux-box at said point of emergence, the mixture of the flux-box resting on the upper surface of the top layer of zinc, or by applying the mixture to the coated sheet, in similar fashion above the feeding and/or regulating or finishing rolls at the point of exit of the coated sheet from the bath, or in still other instances it may be feasible to apply the mixture to the faces of the hot coating of the sheet by flowing or spraying the same thereon at a point above said rolls (when employed), if found expedient.

Whatever the manner of the application of the mixture to the hot coating of the sheet after the same has received its treatment in the bath material, the result will be that the mixture, primarily because of its oxalic acid ingredient, will reduce or create conversion of the objectionable lead-oxide to lead and thereby prevent the dark or black spots from forming on the sheet and insuring a clear and bright ultimate appearance of the finished product, with evenly formed or uniform spangles. In this way there is created an article far superior to any product of the general character in question heretofore known.

Although it may be that so far as concerns the theory of action or reaction of the oxalic-acid-sal ammoniac mixture the lead-oxide content of the zinc-coated article, the same may be in error, however, the results as stated herein have been found by ample demonstration to be correct and clearly apparent. With the possibility of error as to theory, just expressed, and with the aim of approximately expressing what takes place upon the application of the oxalic-acid-sal ammoniac mixture to the lead-oxide-bearing hot zinc coating, I offer the following:

$$\text{CuCl}_2 + \text{H}_2 \text{O} \rightarrow \text{CuCl}_2 \cdot \text{H}_2 \text{O}$$

Finally, it is to be understood that in specifying oxalic acid and sal ammoniac as the specific elements entering into the mixture with which I treat the lead-oxide-bearing zinc coating, persons skilled in the art will realize that the invention is not restricted thereto and that the claims in reciting these particular elements are to be construed as covering known or recognized equivalents thereof, if any exist. Also, where special reference has been made to proportions, i.e., one part oxalic acid and four parts sal ammoniac, it will be understood that the same has reference to the proportions found best adapted for the purpose outlined, it being expected that correspondent results, in a measure, though probably less effective, may possibly be obtained through the use of these approximate but not exact proportions.

I claim:

1. A flux characterized by its capability of eliminating lead-oxide spotting from the zinc coating of zinc-coated metallic articles, the same consisting of oxalic acid and sal ammoniac in the proportions of one part of the former to four parts of the latter.

2. In a method of zinc-coating a metallic article, passing the article to be coated through a molten bath comprising a relatively deep supporting layer of lead and a relatively thin layer of zinc, and immediately on emergence of the article from the hot bath subjecting the zinc coating thereof while still hot to the action of a fluxing agent in the presence of oxalic acid.

3. In a method of zinc-coating metallic articles, passing the article to be coated through a molten bath including a supporting layer of lead and a layer of zinc, and immediately on emergence of the zinc-coated article from the bath and while still hot subjecting the same to the action of a mixture of a relatively major proportion of sal ammoniac in the presence of a relatively minor proportion of oxalic acid.

4. The method of coating a metal sheet, comprising the immersion of the same in a lead-zinc coating bath, and on emergence of the coated sheet from said bath subjecting the zinc coating to the action of oxalic acid to prevent the formation of dark or black spots on the surface thereof.

5. The method of coating a metal sheet, comprising the immersion of the same in a lead-zinc coating bath, and on emergence of the coated sheet from said bath subjecting the zinc coating to the action of oxalic acid and sal am-
moniac to prevent the formation of dark or black spots thereon.

6. The method of galvanizing sheet metal, comprising the coating of the same in a molten metal bath the normal effect of which will be to form lead-oxide in the coating, with consequent dark or black spots on the resultant article, and immediately upon the emergence of the lead-oxide-bearing coated article from the bath and while still hot subjecting the same to the action of oxalic acid to reduce the lead-oxide to lead.

7. The method of galvanizing sheet metal, comprising the coating of the same in a molten metal bath the normal effect of which will be to form lead-oxide in the coating, with consequent dark or black spots on the resultant article, and immediately upon the emergence of the lead-oxide-bearing coated article from the bath and while still hot subjecting the same to the action of oxalic acid to reduce the lead-oxide to lead.

8. The method of galvanizing sheet metal, comprising the coating of the same in a molten metal bath the normal effect of which will be to form lead-oxide in the coating, with consequent dark or black spots on the resultant article, and immediately upon the emergence of the lead-oxide-bearing coated article from the bath and while still hot subjecting the same to the action of sal ammoniac and a relatively minor proportion of oxalic acid. 6. The method of galvanizing sheet metal, comprising the coating of the same in a molten metal bath the normal effect of which will be to form lead-oxide in the coating, with consequent dark or black spots on the resultant article, and immediately upon the emergence of the lead-oxide-bearing coated article from the bath and while still hot subjecting the same to the action of sal ammoniac and a relatively minor proportion of oxalic acid.

9. The method of reducing lead-oxide formed on an article coated in a lead-zinc-galvanizing bath, which comprises subjecting the coated article while hot to the action of a mixture of sal ammoniac and oxalic acid.

10. The method of reducing lead-oxide formed on an article coated in a lead-zinc-galvanizing bath, which comprises subjecting the coated article while hot to the action of oxalic acid whereby to eliminate objectionable spotting by any lead-oxide constituent in said coating.

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