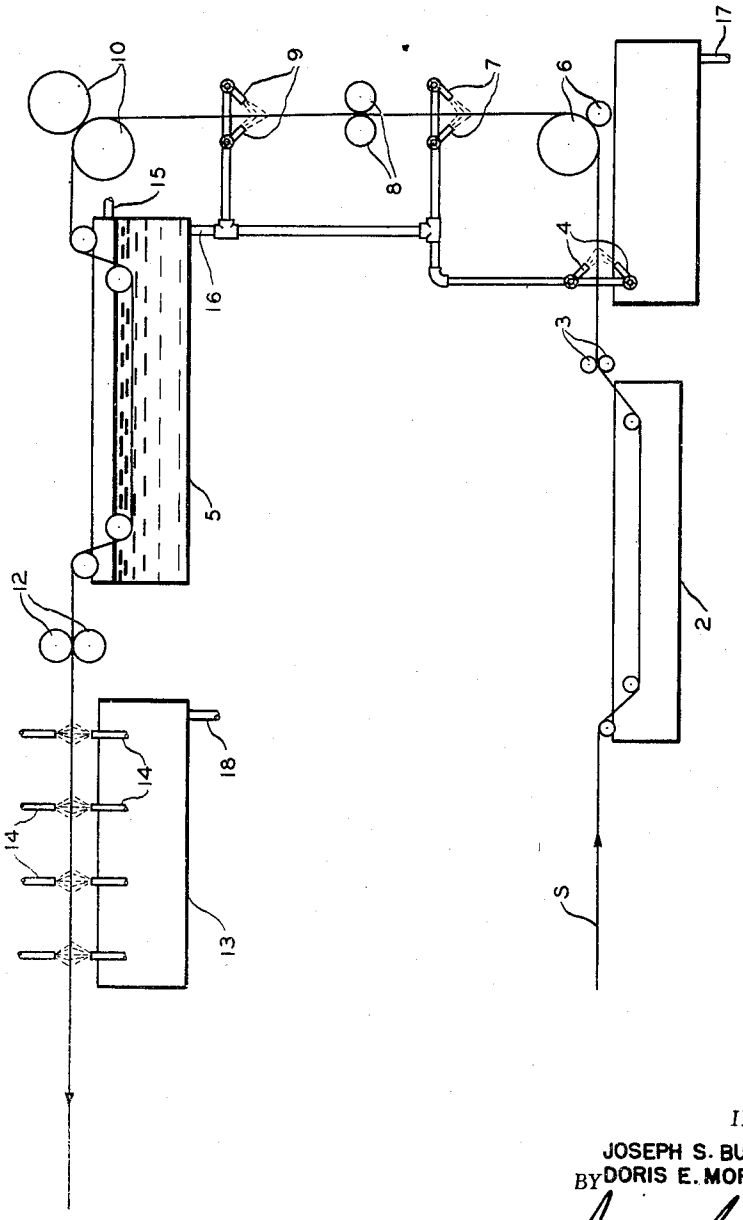
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METHOD OF ELECTROLYTIC COATING

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METHOD OF ELECTROLYTIC COATING

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5 Claims. (Cl. 204—28)

1

The present invention relates to the electrolytic coating of a base metal, and more particularly to the treating of the strip immediately after it has been coated with a suitable metal coating and to the recovery of the electrolyte carried from the plating cells during the coating operation. The invention is particularly applicable to the electrolytic manufacture of tin plate and will be described herein as applied to the manufacture of such a product. However, it will be apparent, as the description of the invention proceeds, that it is not limited to the manufacture of such a product but may be utilized in connection with the coating of various types of base metals with various types of coating metals.

This application is a continuation of application Serial No. 543,318, filed July 3, 1944, by Joseph S. Buser, deceased. Application Serial No. 543,318 is now abandoned.

In the manufacture of electro-coated tin plate, the strip-like metal is preliminarily treated and is then coated by passing it through an electrolytic bath containing a plurality of anode blocks of tin. During its passage through the electrolyte, the strip is the cathode and the tin from the anode blocks is plated on the strip as it passes through the electrolyte. In one such system the strip is successively passed through a plurality of plating cells where the strip is plated on one side and is then passed successively through another group of plating cells where it is coated on the other side. In another system which is in use commercially, the strip is passed vertically downwardly and upwardly through a suitable bath past the anode blocks and is coated on both sides at the same time. The present invention is applicable to either of these systems as it relates to the treating and handling of the strip after it has been coated.

As the strip leaves the final plating cell, it carries with it an appreciable amount of the electrolyte. The electrolyte employed in any of these coating or plating systems is quite expensive and, consequently, it is highly desirable to recover as much of it as is possible and return it to the plating line. However, in the recovery of the electrolyte and the return of it to the plating line several factors of importance must be taken into consideration. In the first place, it is necessary that the rinsing solution be of such character that it will not have a deleterious effect upon the product. And in the second place, the rinsing solution, after it has washed the electrolyte from the coated strip, must be of such character that it can be returned to the plating

2

system without appreciably modifying the electrolyte from the desired composition. The present invention provides a method and apparatus whereby a high proportion of the electrolyte carried from the plating cells by the strip can be recovered and returned to the plating line without adversely affecting the product or the electrolyte in the system. In fact, as will be pointed out hereinafter, the method which this invention provides is decidely advantageous from the standpoint of the quality of the finished product.

Difficulty has heretofore been encountered in obtaining a product having a bright finish thereon. As a consequence, various proposals have been made for eliminating the dull finish of the electro-coated product. It has been proposed to burnish the surface by mechanical brushing apparatus. It has also been proposed to subject the coated strip to temperatures sufficiently high to cause the coating thereon to flow and thereby eliminate the dull mat finish. Flow brighteners of several different types have been proposed, including (1) the passing of the strip through a heated oil bath and (2) the heating of the strip electrically to the temperature required for reflowing the coating. It has been found, however, that the film of electrolyte carried from the plating bath adversely affects the appearance of the resulting product even though it is subjected to a flow brightening operation. It has been found that if the film of electrolyte is not eliminated from the strip it becomes hydrolyzed to stannous or stannic hydroxide and that during the passage of the strip through the flow brightener it is converted to the oxide and that this results in a chalky appearance in the final product. Accordingly, by the present invention one not only recovers the electrolyte which is carried from the plating cells but also provides for the elimination of a substantial proportion of the solution which may later be hydrolyzed to stannic or stannous hydroxide and adversely affect the finished product.

Various types of electrolytes may be utilized in the manufacture of tin plate. For example, tin chloride, tin fluoride, and tin sulphate baths have been utilized heretofore. The electrolyte may contain other salts of the acid constituent employed, such as sodium chloride, sodium fluoride, potassium chloride, potassium fluoride or potassium sulphate. Where a tin chloride or tin fluoride bath is employed, the solution carried from the plating cell includes stannous chloride or fluoride or stannic chloride or fluoride, or both the stannous and stannic chlorides

or fluorides. Where a tin sulphate bath is employed, the solution carried from the plating cells includes stannous sulphate or stannic sulphate, or both.

Where the solution carried from the plating cells includes stannous chloride or stannic chloride, or both, in the absence of proper treatment the stannic chloride will hydrolyze to stannic hydroxide and the stannous chloride will hydrolyze to stannous hydroxide. Similar hydrolysis takes place where tin sulphate is present in the electrolyte; that is, the stannous and stannic sulphates hydrolyze to stannous and stannic hydroxides. The presence of these hydroxides is objectionable in view of the effect on the resulting product. Consequently, it has been found that in recovering the solution which is carried from the plating cells it is desirable to prevent the formation of the objectionable stannous hydroxide or stannic hydroxide on the strip to any substantial extent. Where untreated water is used in the recovery process, an excess of these objectionable compounds is formed and must be removed from the strip before it passes to the reflowing apparatus. It has been found, however, that by utilizing a proper solution for rinsing the strip a substantial proportion of the solution carried from the plating cells can be recovered without the formation of an excessive amount of stannous or stannic hydroxides.

In the operation of a line for the electrocoating of strip, the bath is usually maintained at an elevated temperature, for example, in the neighborhood of 135° F. Considerable evaporation takes place during the operation of the line and, consequently, provision must be made for replacing the evaporated solution. It has been found that this can be accomplished by supplying to the rinsing apparatus an amount of water approximately equal to the evaporation losses and collecting the rinse water and returning it to the plating cells.

In the accompanying drawing there is shown, for purpose of illustration only, apparatus which may be used in carrying out the present invention. However, the invention is not limited to the use of any specific apparatus as it may be otherwise practiced or embodied without departing from the scope thereof. As shown in the drawing, which is diagrammatic only, the strip S passes through the final plating cell 2 and between the contact rolls 3. It is then carried past sprays 4 which spray on the strip a rinsing solution from the recovery tank 5, the nature of which will be described hereinafter. The strip is then passed between squeeze rollers 6. It is then again sprayed by sprays 7 with the rinsing solution from the recovery tank. It then passes between squeeze rollers 8. It again passes between sprays 9 which spray solution from the recovery tank on it, and it is then passed between squeeze rollers 10 adjacent the recovery tank. During the passage of the strip between the alternately arranged sprays and squeeze rollers, it is located above a collecting tank 11 in which the solution sprayed onto the strip by the sprays and squeezed from the strip by the squeeze rolls is collected. The alternate spraying of the rinsing solution and squeezing the solution from the strip results in the elimination of a substantial proportion of the solution carried from the plating cells. The concentration of tin chloride in the electrolyte is approximately 4 ounces per gallon. The first set of sprays 4 dilutes this to approximately 1 ounce per gallon. The succeeding sprays and squeeze rolls further dilute the solution carried by the strip from the plating cells, so that at the time the strip enters the recovery tank the concentration of tin chloride is down to approximately .3 ounce per gallon.

After alternately passing between the sprays and squeeze rolls, the strip is passed into and through the recovery tank 5, which contains the rinse solution, where it is further rinsed. The strip then passes from the tank, between squeeze rolls 12, and then over a tank 13 where it is sprayed with cold water by means of sprays 14. The strip then passes either to the hot rinse described and claimed in the copending application Serial No. 546,091 or to drying apparatus and then to the reflowing apparatus, in the event that the coated strip is to be subjected to a reflowing operation.

The rinsing solution contained in the recovery tank 5 and which is sprayed onto the strip by the sprays 4, 7 and 9 is water which has been treated by the addition of a salt or an acid which will lower the pH value of the water to a point where objectionable hydrolysis of the tin salt carried from the plating cell is eliminated. Where an acid is added to the rinse water, the pH value of the rinsing solution should be maintained at approximately 1.90 or under. However, where salts are employed, it has been found that the pH value may be somewhat higher, for example, approximately 2.5, without substantial hydrolysis taking place and without adversely affecting the electrolyte solution when the rinsing solution is returned to the system.

Where the solution carried from the plating cells includes stannous chloride or stannic chloride, it has been found that excellent results can be obtained by utilizing a rinse water which has been treated with sodium fluoride, sodium bifluoride or hydrofluoric acid. Hydrochloric acid also may be used, but it has a definite tendency to etch the tin coating, and hence it has been found preferable to utilize hydrofluoric acid instead. Various other salts of hydrofluoric and hydrochloric acids may be used so long as the pH value of the rinse water is lowered to a suitable extent and so long as they will not have a deleterious effect upon the final product.

Where the solution carried from the plating cells contains stannous or stannic sulphates, sulphuric acid, phenol disulphonic acid and various salts of these acids may be used to bring the pH value of the rinse water down to the required value.

Where the electrolyte contains tin chloride, the pH of the bath is ordinarily maintained between approximately 2.5 and 3.5. Therefore, the use of large quantities of hydrofluoric acid in the rinse water would deleteriously affect the pH of the electroplating bath since the rinse water is returned to the electroplating bath. For this reason, it is preferable to use a salt such as sodium fluoride or sodium bifluoride in the rinse water instead of the acid since a higher pH value in the rinse water can be maintained without hydrolysis taking place where the salt instead of the acid is used.

The water for the rinsing spray may be fed to the recovery tank through an inlet 15. The treating agent may be added to the water before it enters the recovery tank or it may be added

directly to the tank. Fresh water is supplied to the recovery tank at the rate necessary to replace the rinsing solution fed to the sprays. Since the rinsing solution is returned to the plating system in the manner described below, the rate at which fresh water is supplied to the recovery tank is maintained at the amount required to replace the loss due to evaporation of the plating bath and strip carry-out. The rinsing solution is fed to the sprays 4, 7 and 9 from the outlet 16. The rinsing solution which is sprayed onto the strip and a high percentage of the solution carried from the plating cells are collected in the collecting tank 11, which is located below the sprays and the squeeze rolls. This collecting tank 11 has an outlet 17 which is connected by suitable piping to one of the cells in the plating line. Instead of being connected directly to the plating cells, the outlet 17 may be connected to the supply tank for the cells. The rinsing solution returned to the plating system is fed to the system at a sufficient rate to take care of the loss of the plating solution occasioned by evaporation and by the strip passing therethrough.

As stated above, after the strip passes through the recovery tank, it is sprayed with cold water by the sprays 14. This rinse water is not fed into the electrolytic circulatory system but is discharged to the sewer through an outlet 18.

The final rinsing of the strip with cold water hydrolyzes any stannous or stannic chlorides or sulphates remaining on the strip, but, due to the fact that the major portion of the stannic or stannous chlorides or sulphates has been eliminated from the strip, the adverse effects of the hydrolyzing of the small remaining amount of stannous or stannic salts can be eliminated by subjecting the strip to a suitable hot rinsing spray, such as is described and claimed in the copending application referred to above, prior to the time that the strip passes to the flow brightener.

From the above description, it will be apparent that the invention has provided a method and apparatus whereby the solution carried from the plating line by the strip can, in large measure, be recovered and that this can be accomplished without deleterious results to the final product and without deleteriously affecting the electroplating bath by lowering the pH value of the rinsing bath to the point where very little or no hydrolysis of the tin salts takes place during the recovery operation. The recovery of the solution carried from the plating line by the strip effects a substantial saving in operating costs and, as stated, this can be accomplished without adversely affecting the final product.

While the invention is described as applied to the manufacture of tin plate and while having referred only to electrolytic baths of the chloride or sulphate types, it will be understood that the invention may be utilized with other electrolytic baths and in the manufacture of other coated products.

What is claimed is:

1. The method of continuously and progressively manufacturing electro-tinplated strip comprising the steps of passing strip through an electrolytic cell containing an acid plating bath of aqueous electrolyte solution including tin salt and fluorine ions, a source of the fluorine ions being a tin-free acidic fluorine compound present as a component of the electrolyte solution, electrodepositing a layer of tin on the strip while the strip is in contact with the electrolyte solution, thereafter passing the strip from the plating bath with tin salt-containing electrolyte solution carried from the plating bath on the strip, rinsing the strip with an aqueous rinse solution to remove electrolyte solution including tin salts from the strip by alternately spraying the aqueous rinse solution onto the strip and squeezing the resulting solution from the strip, the first spraying and squeezing operation diluting the concentration of tin salts in the solution remaining on the strip and each subsequent spraying and squeezing operation further diluting the concentration of tin salts in the residual solution remaining on the strip, thereafter rinsing the strip with an aqueous rinse to remove residual electrolyte solution including tin salt remaining on the strip after being alternately sprayed and squeezed, said last-mentioned aqueous rinse being obtained by admixing water and a tin-free acidic fluorine compound, said tin-free acidic fluorine compound being in an amount sufficient to reduce the pH value of the aqueous rinse to a point where hydrolysis of tin salt carried from the plating bath on the strip and not removed by the alternate spraying and squeezing is substantially prevented, and utilizing aqueous rinse solution from said last-mentioned rinse step as the aqueous rinse solution for said spraying steps.

2. The method of continuously and progressively manufacturing electro-tinplated strip as set forth in claim 1 wherein said tin-free acidic fluorine compound in the aqueous rinse is a sodium salt of hydrofluoric acid.

3. The method of continuously and progressively manufacturing electro-tinplated strip as set forth in claim 1 wherein said tin-free acidic fluorine compound in the aqueous rinse is sodium fluoride.

4. The method of continuously and progressively manufacturing electro-tinplated strip as set forth in claim 1 wherein said tin-free acidic fluorine compound in the aqueous rinse is sodium bifluoride.

5. The method of continuously and progressively manufacturing electro-tinplated strip as set forth in claim 1 wherein said tin-free acidic fluorine compound in the aqueous rinse is hydrofluoric acid.

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Formerly Doris E. Buser, administratrix of the estate of Joseph S. Buser, deceased.

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