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3,075,897

METHOD OF MAKING TIN PLATE

Richard F. Higgs, Wilkensburg, Pa., assignor to United States Steel Corporation, a corporation of New Jersey
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1 Claim. (Cl. 204-42)

This invention relates to a method of making tin plate and, in particular, to the manufacture of electrolytic tin plate having improved corrosion resistance.
It is known that a controlled oxidation of cleaned, pickled sheet steel, prior to electrolytic tinning, will enhance the quality of the product. It is one of the objects of my invention to provide an improved method of performing such oxidation. A further object is to provide a method including such pre-oxidation of the steel followed by a light electroplating thereof from an alkaline bath, then completion of the desired deposit of tin from an acid bath. This latter procedure results in a product having markedly superior properties, particularly in respect to corrosion resistance.

Generally speaking, my method comprises the formation of a film of hydrated iron oxide on cleaned pickled steel sheet, immediately before electroplating it, by subjecting it to anodic electrolysis in a strong solution of an alkali-metal hydroxide or carbonate. The film of oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) should be from 100 to 500 A. thick so it will not be completely removed by the acid electrolyte used for electroplating the steel base. The latter requires no other treatment except water rinsing, before electroplating, but I have found that a surprisingly improved product is obtained by tinning the base first lightly from an alkaline bath and then depositing additional tin to the desired total amount from an acid electrolyte.

In a preferred practice of my invention, I take black plate, i.e., low-carbon sheet steel, conveniently in the form of strip which has been cleaned and lightly pickled, and pass it through a water solution of sodium hydroxide containing from 400 to 700 grams per liter of NaOH. Other alkali-metal hydroxides or alkali-metal carbonates may be used instead of NaOH. While the strip is in the solution, I make it anode in a circuit including a source of direct current and cause a current to flow therein at a density of from 100 to 300 amperes per square foot. The anodic treatment should continue until at least 200 coulombs per square foot have been delivered. For the desired speed of travel of the strip, the solution should be at a temperature of from 225 to 275° F. Within that range, the desired thickness of film, 100 to 500 A., is formed in from 1.5 to 4 seconds.

Further details of the invention will be apparent from the following description of typical examples of the practice thereof.

Example 1

Black plate of tin-plate gage was cleaned of grease and dirt in an electrolytic alkaline cleaner of known type. The strip was water-rinsed and then electrolytically pickled in a solution of 5% (weight) sulfuric acid at ambient temperature, using cathodic-anodic polarity at a current density of 100 a.s.f. for 1.5 seconds at each polarity. The strip was then water-rinsed and treated electrolytically as anode, as shown by the following data:

Aqueous solution	g./l.	NaOH	600
Temperature	° F.		250
Current density	a.s.f.		100
Time	seconds		4

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Following the above treatment, the strip was water-rinsed and then tin plated in an aqueous solution consisting of
Sn⁺⁺ (as SnSO_4) g./l. 30
Phenosulfonic acid (calculated as sulfuric acid) g./l. 15
Dihydroxy diphenyl sulfone g./l. 6

under the following plating conditions:

Temperature	° F.	100
Current density	a.s.f.	200

The resulting tin coating was 0.000060 inch thick. Following the plating, the strip was rinsed, dried and the coating melted by resistance heating. The finished tin plate was bright and smooth and exhibited the following improvement in quality as compared with tin plate produced in an identical manner except that the oxidation step was omitted:

	Iron solution value ¹	Solder bond strength ² (lb./in.)	Prune pack life (wks.)
Treated	27	48	28
Untreated	52	43	23

¹ Lower values are better.
² Higher values are better.

Example 2

The same procedure as described in Example 1 was used except that oxidation-treatment current density was increased to 184 a.s.f. The following results were obtained:

	Iron solution value	Solder bond strength (lb./in.)	Prune pack life (wks.)
Treated	21	51	27
Untreated	52	43	23

In other trials the improvement in iron solution value has averaged 50% and the improvement in solder bond strength has averaged 15%. The available pack-life data are not extensive but indicate that a 25 to 30% improvement may be expected.

I have found that the results obtained simply by oxidation of the black plate before tinning, may be greatly exceeded by effecting the tin coating in two stages, viz., first applying a light coating by the known alkaline electroplating process and then plating the balance of the desired total amount of tin by the known acid process.

In practicing this phase of my invention, black plate is cleaned, rinsed, pickled and again rinsed in accordance with conventional electroplating practice. It is then subjected to oxidation of the surface in any convenient manner, e.g., that described above, viz., in a hot, concentrated caustic solution wherein the steel strip is made the anodic pole. This oxidation step, as aforesaid, results in the formation of a hydrated iron oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) on the surface of the strip having a thickness of from 100 to 500 A. Following oxidation, the strip is rinsed and then plated with a flash coating of tin (0.05 lb./bb. or less) from a solution consisting of an alkali-metal stannate, either sodium or potassium, and an alkali-metal hydroxide, such as sodium or potassium. The strip is then rinsed and plated with tin from an acid bath as set forth in Example

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1, in conventional manner, to the desired final coating weight, usually 1.0 lb./bb. tin.

The second stage of this phase of my invention, considered more explicitly, consists of depositing a thin coating of tin from an alkaline tin-plating solution over the oxidized surface of the steel strip without prior removal of the oxide film. For this purpose, I prefer to use a conventional alkaline-tin electrolyte consisting of about 70 g./l. Sn^{++++} and 11 g./l. NaOH, at a temperature of 170° F. and a current density of about 30 a.s.f. The plating solution is not limited to sodium stannate-sodium hydroxide, since a bath of potassium stannate-potassium hydroxide or combinations of sodium and potassium salts could also be used. For my purpose, the amount of tin deposited from an alkaline bath need be no greater than 0.05 lb./bb. and can range from about 0.005 to 0.05 lb./bb. I prefer that the coating be about 0.03 lb./bb. alkaline tin.

Following the alkaline plating step by conventional tin plating from an acid bath, the weight of the coating is increased to the desired final value.

Typical examples of the practice outlined above are as follows:

Example 3

Black plate was cleaned of grease, dirt, oil, etc. in an electrolytic alkaline cleaner. The strip was water rinsed and then electrolytically pickled in a solution of 5% (weight) sulfuric acid at ambient temperature using cathodic-anodic polarity at a current density of 200 a.s.f. for 1.5 seconds at each polarity. The strip was then water rinsed and treated electrolytically as anode under the following conditions:

Aqueous solution	g./l. NaOH	500
Temperature	° F.	255
Current density	a.s.f.	200
Time	seconds	2.5

Following the above treatment the strip was water rinsed and plated from an alkaline electroplating bath to a coating weight of 0.05 lb./bb. tin under the following conditions:

Aqueous solution	g./l. Sn^{++++}	70
	g./l. NaOH	11
Temperature	° F.	170
Current density	a.s.f.	30

The strip was then water rinsed and plated to a total in coating weight of 1.0 lb./bb. tin in an acid aqueous solution as follows:

Sn^{++}	g./l.	32
Phenolsulfonic acid (calculated as H_2SO_4)	g./l.	18
Dihydroxy diphenyl sulfone	g./l.	5
Temperature	° F.	100
Current density	a.s.f.	200

The strip was then rinsed, and the tin coating was reflowed by melting by conventional resistance heating.

Since acid tin plate of improved corrosion resistance is ordinarily needed only for citrus products, a special test has been developed to indicate, without actually packing the food in cans, the corrosion performance of tin plate in contact with citrus products. This test is the alloy tin couple (ATC) test, which involves removing the free (unalloyed) tin from the specimen to an iron-tin alloy (FeSn_2) layer, coupling the specimen with a piece of tin foil, immersing the specimen and foil in grapefruit juice for 20 hours, and measuring the current between the alloy and the tin in microamperes per square centimeter of exposed alloy. The current so obtained indicates the pack-life performance that could be expected if the in plate were fabricated into cans, packed with citrus products, and stored until the cans failed. In this particular test, the lower the current, the greater the corrosion resistance of the tin plate.

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The results of ATC tests made on tin plate treated as last described above and conventional tin plate (produced without the steps comprising my invention) are shown below:

	ATC, $\mu\text{a./cm.}^2$	Grapefruit-Juice Pack Life Pre- dicted from ATC Current, weeks
Untreated	0.25	36
Treated	0.07	84

These results indicate that my invention improves the predicted grapefruit-juice pack life of conventional acid tin plate by about 130%. The alkaline-tin undercoat treatment alone improves the predicted grapefruit-juice pack life by about 70%, but the preoxidation treatment alone does not materially improve the predicted pack life. It would thus be reasonable to expect about a 70% improvement in predicted pack life for a combination of the two treatments. However, I have discovered that the treatments cooperate synergistically in a manner not yet understood, to improve the predicted pack life nearly twice as much as expected.

Example 4

Black plate was cleaned and pickled as in Example 3, except that the time for cleaning was reduced to 2 seconds. The oxidation treatment was carried out in a solution containing 600 g./l. NaOH at 250° F. 3 seconds, at a current density of 100 a.s.f. The alkaline tin coating was deposited under the conditions described in Example 3 except that the amount of tin deposited was only 0.005 lb./bb. This was followed by overplating in acid electrolyte (using a solution as in Example 3) to a total coating weight of 1.0 lb./bb. tin. The performance of plate so produced as measured by the ATC test is shown below:

	ATC, $\mu\text{a./cm.}^2$	Grapefruit-Juice Pack Life Pre- dicted from ATC Current, weeks
Untreated	0.32	28
Treated	0.17	50

Thus even with a reduction in the intensity of the oxidation treatment and a reduction in weight of the alkaline undercoating, the improvement in predicted pack life was about 80%. This demonstrates that an improvement greater than the 70% ordinarily to be expected from using the combination of treatments can be achieved, even under conditions less favorable than the optimum.

It will be evident from the foregoing that the invention provides a cheap yet effective method of forming an oxide film of predetermined thickness and composition which materially improves the quality of the finished product made by electrolytically tinning the oxide-filmed black plate. An even higher quality product, from the standpoint of corrosion resistance, is obtained when the oxide-filmed black plate is subjected first to a light tin coating from an alkaline bath and the balance of the coating from an acid bath.

Although I have disclosed herein the preferred practice of my invention, I intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

I claim:

A method of making tin plate which comprises treating electrolytically as anode, sheet steel of tin-plate gage, in a water solution at from 225 to 275° F. containing from 400 to 700 grams per liter of an alkali-metal compound selected from the group consisting of hydroxides and carbonates, at a current density of from 100 to 300 amps.

per sq. ft. for from 1.5 to 4 seconds, thereby forming on the steel a film of hydrated iron oxide from 100 to 500 A. thick, then electrodepositing over said film a first tin coating from an alkaline bath and then depositing over the first tin coating a second tin coating from an acid bath. 5

References Cited in the file of this patent**UNITED STATES PATENTS**

2,078,868	Oplinger -----	Apr. 27, 1937
2,274,963	Hopper -----	Mar. 3, 1942
2,303,035	Fink -----	Nov. 24, 1942

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,075,897

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Richard F. Higgs

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 20, for "plaing" read -- plating --;
line 49, for "in", first occurrence, read -- tin --; line 72,
for "in" read -- tin --; column 4, line 30, before "3 seconds"
insert -- for --.

Signed and sealed this 20th day of August 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents