April 17, 1962 J. N. CROMBIE ETAL 3,030,240

MANUFACTURE OF ELECTROLYTIC TIN PLATE

Filed Aug. 11, 1959

FIG. 1

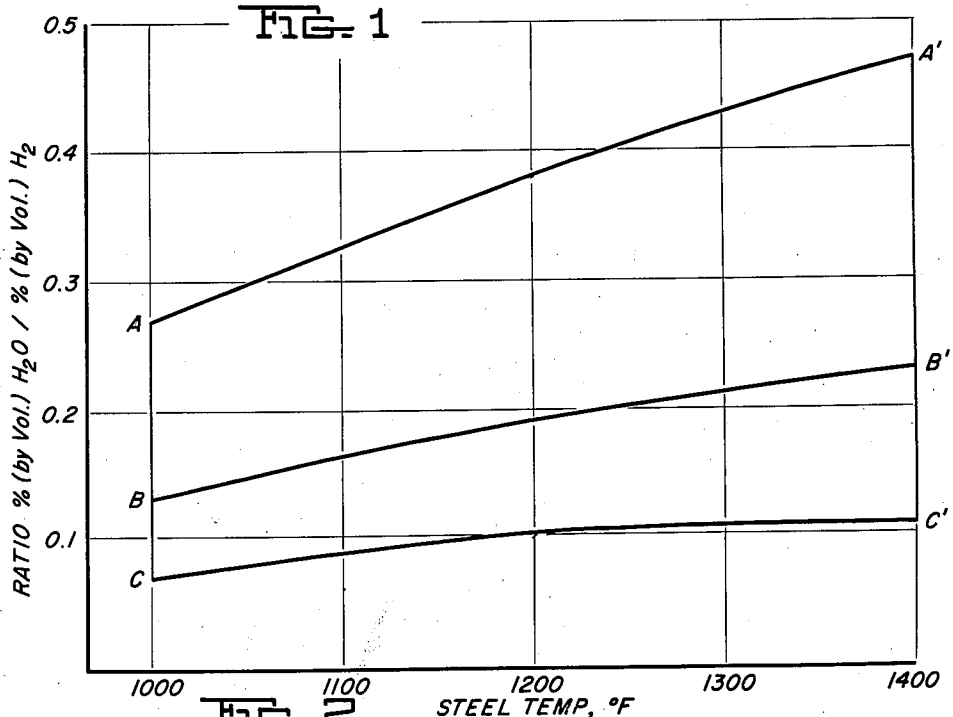
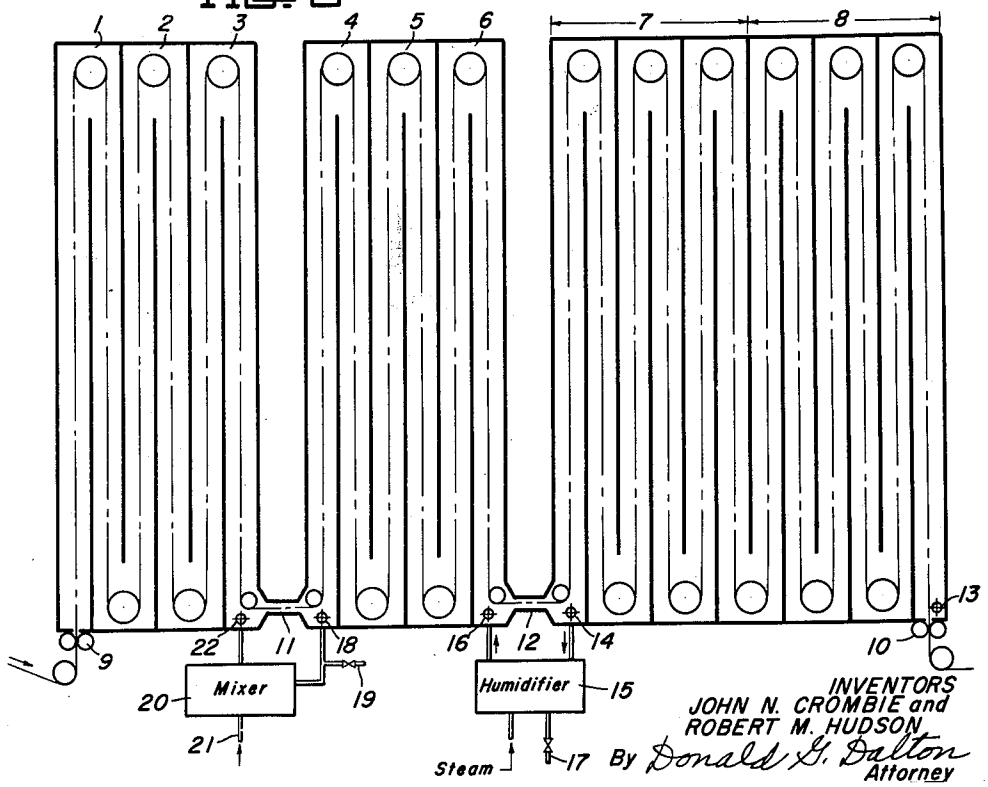


FIG. 2



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MANUFACTURE OF ELECTROLYTIC TIN PLATE

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This invention relates to improvements in the manufacture of electrolytic tin plate.

Tin plate for container stock is now commonly made by the continuous electrolytic process. Briefly, a suitable low carbon, low metalloid steel is not rolled to about 16 gage; the resulting strip is then continuously pickled to remove the hot mill scale and cold reduced to final gage; after which it is alkaline cleaned to remove the cold mill lubricants, annealed, temper rolled and delivered to the plating lines where the strip is unwound and passed as a strand through cleaning, tin-plating and various finishing operations. It has been found that the corrosion resistance of the resulting electrodeposited tin plate coating is markedly influenced by certain of the aforementioned manufacturing steps, particularly by the annealing step. Two types of annealing are commonly practiced. The older method, termed box annealing, requires a heat treatment of 50 to 70 hours and comprises slowly heating coils of the cleaned cold reduced steel in a closed chamber, soaking the coils at annealing temperature for a period of 2 to 6 hours and then very slowly cooling the coils to about room temperature. The other method, termed continuous annealing, may be completed in a period of 3 to 4 minutes and comprises passing the cleaned, cold-reduced metal as a strand through a furnace in which the moving strand is raised to annealing temperature in a matter of seconds, held for a few seconds at temperature and then rapidly cooled. The continuous method produces a ductile but considerably stiffer material than box annealing. Both methods however are bright annealing methods, i.e., the heating and cooling steps are conducted in a protective atmosphere designed to minimize oxidation and preserve the smooth, bright surface produced by the prior cold reduction. In the latter regard, it has long been taught that the protective atmosphere must be maintained as dry as possible. More recently it was reported by Donelson et al. (U.S. Patent No. 2,587,605) that if, in addition to maintaining the annealing gas dry ,water vapor content $\frac{1}{10}\%$), the carbon dioxide is held less than $\frac{1}{10}\%$, the hydrogen content at between 2 and 7% and the carbon monoxide at a maximum of 3½%, the corrosion resistance of the tin plate produced from the steel was unexpectedly increased.

We have found the costly restrictions imposed by foregoing teachings can be avoided and tin plate of better and more uniform corrosion resistance produced by the practices of our invention.

Accordingly, it is an object of the present invention to provide an improved, less costly method for improving the corrosion resistance of electrolytic tin plate.

These and other objects will be apparent from the following specification when read in conjunction with the attached drawings in which:

FIGURE 1 is a graph showing the effect of temperature as respects limiting values of the ratio of the percent (by vol.) H_2O: percent (by vol.) H_2 present in the atmospheres used in the invention and,

FIGURE 2 is a schematic view of a continuous furnace adapted to the practices thereof.

Tin plate stock adapted to the practices of our invention may contain between .025 to .14 carbon, .20 to .70 manganese, .02 max. phosphorus, .01 max. sulphur, .01 max. silicon, .20 max. copper; the remainder is essentially iron. The stock is hot rolled, pickled, cold-reduced to gage and cleaned in the usual manner. The resulting strip is then annealed by either the box annealing or the continuous method. The annealing temperatures, heating and cooling rates, are those usually practiced, i.e., the steel is brought to a temperature between 1000 and 1400° F., preferably to about 1200° F., held at temperature for a period sufficient to effect desired structural changes in the metal and then cooled to below 300° F. before discharge into the air.

For the purposes of our invention, the annealing cycle is divided into heat-up, holding and cooling portions defined as follows:

(1) The heat-up portion; the time required to bring the steel to a temperature of about 1000° F. If continuous annealing is practiced, this portion of the cycle may comprise as little as 10 or as much as 25 seconds depending upon the gage and width of material being processed and the heating capacity of the equipment. If box annealing is practiced, heat-up will require 18 to 24 hours depending mainly on furnace capacity and features of furnace design affecting heating rates.

(2) The holding portion; the time the metal is above 1000° F. For continuous annealing this will comprise a period of 15 to 60 seconds, while for box annealing, 2 to 6 hours will be required. The time in either method depends upon the maximum temperature to which the steel is heated, as well as the factors previously mentioned.

(3) The cooling portion; the time required to cool the metal from 1000 to below 300° F., about 60 to 80 seconds in a continuous annealing, 30 to 40 hours in a box annealing operation.

During the aforedefined periods of the annealing cycle, it is essential to the purposes of our invention to maintain protective atmospheres of the following compositions in intimate contact with the surfaces of the steel:

	H_2	CO	CO_2	H_2O	N_2
	Percent by volume				
During:					
heat-up	2-16	less than 1.0.	less than 0.1.	see note 1	bal.
holding	2-16	less than 1.0.	less than 0.1.	see note 2	bal.
cooling	2-16	less than 1.0.	less than 0.1.	see note 3	bal.

NOTE 1.—Water vapor in an amount not exceeding 3.2% and regulated with respect the hydrogen content of the gas so that the ratio of the percent (by vol.) H_2O to the percent (by vol.) H_2 present in the atmosphere will not exceed 0.2.

NOTE 2.—Water vapor in an amount sufficient to maintain a ratio of the percent (by vol.) H_2O to the percent (by vol.) H_2 present in the atmosphere at a value between about .10 and .38, preferably between .23 and .27.

NOTE 3.—Water vapor in an amount insufficient to exceed a value of about .04 for the ratio of percent (by vol.) H_2O to percent (by vol.) H_2 present in the atmosphere.

Free access of the atmospheres to the surface of the steel must be maintained. Ideal conditions in this regard are inherently present in continuous annealing. In box annealing however, access of the atmospheres to the surface is considerably hindered due to the fact that the steel is in coil form and, although the longer times of treatment used in this operation have an off-setting effect, it is necessary to loose-coil strip to be box annealed to provide a space equal to at least half the thickness of the strip between adjacent wraps of the coil if the full benefits of our practices are to be achieved.

Upon completion of the annealing, the steel may be temper-rolled to flatten and regulate its stiffness, after which it is cleaned, pickled, rinsed, continuously electroplated with a desired weight of tin, rinsed, dried, and the coating melted in accordance with normal practices.

The practices outlined above produce tin plate which is 25% or more more resistant to the corrosive action of acid food products than conventional tin plate. The reasons for this improvement in pack-life are not too well understood. However, the practices appear to modify the steel surface in some manner which promotes conditions favorable to a beneficial change in the iron-tin alloy layer produced upon melting of the electrodeposited tin. This is indicated by an appreciably lower current density in the Alloy-Tin Couple Test. In the latter, a tin plate sample of known area is carefully de-tinned to expose its alloy layer; the sample is then immersed in deaerated grapefruit juice containing 100 p.p.m. of stannous ion and coupled to a pure tin electrode also disposed in the solution; and the current flowing in the resulting cell is measured. The amount of this current bears a definite relationship to the service life of the plate and the test is used as a rapid means for determining suitability of various lots of tin plate for the packing of citrus fruits and juices. In general the lower the current, the greater is the resistance of the plate to corrosion by the juices. Typical alloy-tin couple test results for tin plate produced by our practices, material A, and by conventional practices, material B, are tabulated below:

Material	Alloy-Tin Couple Test Results
A	0.12 μamp./cm.² avg.; 39% under 0.10.
B	0.16 μamp./cm.² avg.; 8% under 0.10.

It will be noted that the average improvement effected by our practices is about 25% and that 39% of our product will give test readings below .10 μamp./sq. cm. whereas only 8% of conventional material will exhibit currents under this amount.

Atmospheres for use in the present invention may be prepared in any known way. While the method of preparation forms no part of our invention, attention is called to the following:

(1) CO and CO_2 are not essential components of the atmospheres but rather can be tolerated up to the tabulated maximums.

(2) Water vapor, an essential part of the atmosphere during the holding portion of the cycle, is an undesirable component in the cooling portion and the cooling atmosphere is preferably prepared as dry as practical.

(3) The amount of water vapor which must be maintained during the holding portion of the cycle is a function of the annealing temperature used as well as the H_2 content of the gas. The relationship of temperature and the ratio of percent (by vol.) H_2O to percent (by vol.) H_2 in the holding portion of the cycle is shown in FIGURE 1. Line AA' defines maximum values of the ratio over the range 1000 to 1400° F. While the graphed data indicate that at 1400° F. the ratio of H_2O/H_2 can be as high as .47, practical considerations prevent the utilization of such value, i.e., when using a 1400° F. annealing temperature the steel will be at temperatures above 1000 and below 1400 requiring lower ratios of H_2O/H_2 for appreciable periods. Accordingly, the practical maximum is about .38 and the ratio is preferably maintained below .27 (indicated by point A of the graph). Line CC' defines the minimum values of the H_2O/H_2 ratio over the range 1000–1400° F. at which any benefits of our invention are obtained; line BB', the minimum limits at which full benefits are achieved. While the graphed data indicate a ratio as low as .07 can be used if the steel is not heated above 1000° F., again practical considerations fix the minimum at about .10 and it is preferable to maintain the ratio above .23 (indicated by B' of the graph). Use of ratios between .23 to .27 permits the operator to regulate the annealing temperature at any value between 1000 and 1400° F. as may be required to achieve specific mechanical properties in the steel without adjusting the water vapor content of the atmosphere.

(4) Water vapor up to the previously tabulated maximum is a desirable rather than an essential component of the atmosphere in "heat-up". Accordingly, the dry atmosphere produced for cooling may be used in this portion of the cycle if desired. When box annealing, the use of a dry atmosphere (H_2O to H_2 ratio less than 0.04) is preferable since the heat-up portion of this operation extends over a period several hours greatly increasing the possibility of oxidizing the surface of the steel to an undesirable degree. Since the possibility of oxidation during "heat-up" in continuous annealing is negligible, atmospheres having H_2O to H_2 ratios between 0.1 and 0.2 are preferred.

The following examples further explain our invention and illustrate preferred modes of practice thereof:

Example 1

A strip of steel of analysis within the previously specified range adapted to a specified end use is electrolytically cleaned to remove mill lubricants and other foreign matter, and is then passed as a strand through a furnace shown schematically in FIGURE 2. The furnace includes several zones **1**, **2** and **3** adapted to heat a given weight of steel to about 1000° F.; zones **4** and **5** adapted to raise the steel to a temperature between 1000 and 1400° F. and maintain it at a selected temperature in this range, preferably at about 1200° F., for a minimal interval of about 15 seconds; a first cooling zone **6** adapted to cool the steel to about 1000° F. and several zones **7** and **8** adapted to further cool the strip to below 300° F. The strip enters the furnace through seal rolls **9** and leaves through a similar set of rolls **10**. For the purposes of our invention, zones **1**, **2** and **3** comprise a "heat-up" section; zones **4**, **5** and **6** in which the strip is above 1000° F., a "holding" section; zones **7** and **8**, a "cooling section." These sections are separated by strip passageways **11** and **12** adapted to restrict in a controllable manner the flow of gas between sections. Each section is provided with an inlet and outlet gas port. According to preferred practices of our invention, an atmosphere of N_2 containing 9% H_2, 20% CO, .05% CO_2 and having a dew point of 10° F. or about 0.18% H_2O (ratio percent H_2O:percent H_2=.02) is introduced at inlet port **13** located in zone **8** adjacent exit rolls **10** to flow through the cooling section to outlet port **14** located in zone **7** adjacent the passageway **12**. The gas from port **14** is passed through a humidifying unit **15** where sufficient live steam is intermixed to raise its water vapor content to about 2.25% (ratio percent H_2O:percent H_2=.25) and is then introduced into the holding section through inlet port **16** located in zone **6** adjacent the passageway **12**. A small variable portion of the dry gas from the cooling section flows directly through passage **12** into the holding section; this is offset by additional humidification as experience indicates. Loss of gas through leaks in the cooling section are offset by supplying fresh gas to the humidifier through supply pipe **17**. The flow of humidified gas leaves the holding section through outlet port **18** located in zone **4** adjacent gas restricting passage **11**. A portion of this gas is now bled off into the atmosphere through exhaust line **19** and the balance passed through mixing unit **20** wherein sufficient fresh, dry gas is introduced through supply line **21** to lower the water vapor content to about 1.4% and provide ratio percent H_2O:percent H_2=.155. The resulting gas is then introduced through inlet port **22** located near the end of zone **3** to flow through the heating section and be discharged at the entry rolls **9** of the furnace. The flow of the atmospheres in each section is counter to the direction of strip movement and is regulated to maintain a positive pressure of between ½ and 1 inch of water in the furnace. The furnace includes a conventional uncoiler, welder for joining strips end to end, slack accumulators, tension regulated devices, drive bridle and

recoilers, not shown. The furnace is preferably designed to process a fixed maximum weight of steel per unit time. The speed of travel is therefore regulated as a function of the gage and width of strip being processed. Each zone of the furnace is provided with a separate temperature controller to facilitate control. Following annealing in the described manner, the strip is temper rolled, cleaned, electroplated with a desired weight of tin, rinsed, dried, heated to slightly above the melting point of tin and immediately quenched to brighten the coating and alloy a portion thereof with the steel surface, dried and further finished as required by the trade.

Example 2

After electrolytic cleaning the steel of Example 1 is loose-coiled, e.g., by the practices described in Industrial Heating, vol. XXV, May 1958, pages 950–952, under Coil Expanding.

The loosely wound coil is loaded into a conventional box annealing furnace, the furnace purged and nitrogen containing 9% H_2; .20% CO; .05% CO_2 and .18% H_2O (dew point of 10° F.; ratio percent H_2O:percent H_2=.02) is introduced under the inner cover thereof to circulate upwardly, around and through the loosely wound wraps of the coil. After a brief purge period the furnace is fired to heat the charge to 1200° F. at a rate of about 50° per hour. When the charge reaches 1000° F., the water vapor content of the gas being introduced into contact with the steel is increased to 2.25% (ratio percent H_2O:percent H_2=.25) by modifying operations at the gas house or by introducing a controlled amount of live steam into the gas as it enters the furnace. The charge is soaked at 1200° F. for about 4 hours at the end of which time fuel to the furnace is discontinued and the charge permitted to cool. The flow of humidified gas is maintained during the whole of this period and until the charge has cooled to 1100° F. At this point the water vapor content of the gas is decreased to 0.18% or less and a flow of gas of this analysis continued until the charge reaches a temperature of at least 300° F., preferably to 250° F., at which point the charge is uncovered and allowed to cool to room temperature in air. After annealing in the above manner, the steel is temper rolled and coated as described in Example 1.

While we have shown and described certain specific embodiments of our invention, it will be apparent that modifications and adaptations may be made without departing from the scope of the following claims.

We claim:

1. In the manufacture of electrolytic tin plate wherein a steel basis metal suitable for such plate is annealed by heating to a temperature of between 1000° and 1400° F., holding at a temperature within said range and then cooling to at least 300° F. before exposure to air prior to the coating thereof with tin, the improvement comprising conducting said annealing in an atmosphere of N_2 containing by volume between 2 and 16% H_2, not more than 1.0% CO, not more than 0.1% CO_2 and water vapor, and regulating the water vapor content of said atmosphere to maintain:

(1) a volume ratio of H_2O to H_2 of not more than 0.2 in the atmosphere contacting said steel during the interval of said annealing required to bring the steel to 1000° F.,

(2) a volume ratio H_2O to H_2 of between 0.10 and 0.38 in the atmosphere contacting said steel during the interval of annealing in which the steel is above 1000° F., and

(3) a volume ratio H_2O to H_2 of not more than 0.04 in the atmosphere contacting said steel during the interval of annealing required to cool the steel from 1000 to at least 300° F.

whereby electrolytic tin plate characterized by improved resistance to citrus corrosion by fruit juices is produced.

2. In the manufacture of electrolytic tin plate, the improvement according to claim 1 wherein the volumetric ratio of H_2O to H_2 in the atmosphere contacting the steel during the interval of the annealing in which the steel is above 1000° F. is maintained between 0.23 and 0.27.

3. In the manufacture of electrolytic tin plate wherein a suitable steel basis metal, prior to the tin coating thereof, is annealed by heating a continuously moving strand of said steel to a temperature of between 1000 and 1400° F., holding at a temperature within said range and then cooling to at least 300° F. before exposure to air, the improvement comprising conducting said annealing in an atmosphere of N_2 containing by volume between 2 and 16% H_2, not more than 1.0% CO, not more than 0.1% CO_2 and water vapor, and regulating the water vapor content of said atmosphere to maintain:

(1) a volume ratio of H_2O to H_2 of between 0.1 and 0.2 in the atmosphere contacting said steel during the interval of said annealing required to bring the steel to 1000° F.,

(2) a volume ratio H_2O to H_2 of between 0.23 and 0.27 in the atmosphere contacting said steel during the interval of annealing in which the steel is above 1000° F., and

(3) a volume ratio H_2O to H_2 of not more than 0.04 in the atmosphere contacting said steel during the interval of annealing required to cool the steel from 1000 to at least 300° F.,

whereby electrolytic tin plate characterized by improved resistance to citrus corrosion by fruit juices is produced.

4. In the manufacture of electrolytic tin plate wherein a suitable steel basis metal, prior to the tin coating thereof, is annealed by heating a coiled strand of said steel to a temperature of between 1000 and 1400° F., holding at a temperature within said range and then cooling to at least 300° F. before exposure to air, the improvement comprising conducting said annealing in an atmosphere of N_2 containing by volume between 2 and 16% H_2, not more than 1.0% CO, not more than 0.1% CO_2 and water vapor, and regulating the water vapor content of said atmosphere to maintain:

(1) a volume ratio of H_2O to H_2 of not more than 0.04 in the atmosphere contacting said steel during the interval of said annealing required to bring the steel to 1000° F.,

(2) a volume ratio H_2O to H_2 of between 0.23 and 0.27 in the atmosphere contacting said steel during the interval of annealing in which the steel is above 1000° F., and

(3) a volume ratio H_2O to H_2 of not more than 0.04 in the atmosphere contacting said steel during the interval of annealing required to cool the steel from 1000 to at least 300° F.,

whereby electroltyic tin plate characterized by improved resistance to citrus corrosion by fruit juices is produced.

5. In the manufacture of electrolytic tin plate, the improvement according to claim 4, characterized by loose-coiling the ferrous metal strip to provide a space between convolutions of at least half the thickness of said strip.

References Cited in the file of this patent

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Jenkins: Controlled Atmospheres for the Heat Treatment of Metals, 1946, pages 196–207.

1948 Metals Handbook by ASM, pages 294–298 and 709.

The Making, Shaping and Treating of Steel, pages 632, 633.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,030,240 April 17, 1962

John N. Crombie et al.

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 1, line 13, for "not" read -- hot --; line 47, for "dry ,water" read -- dry (water --; column 4, line 43, for "20%" read -- .20% --.

Signed and sealed this 14th day of August 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents