MANUFACTURE OF ELECTROLYTIC TINPLATE

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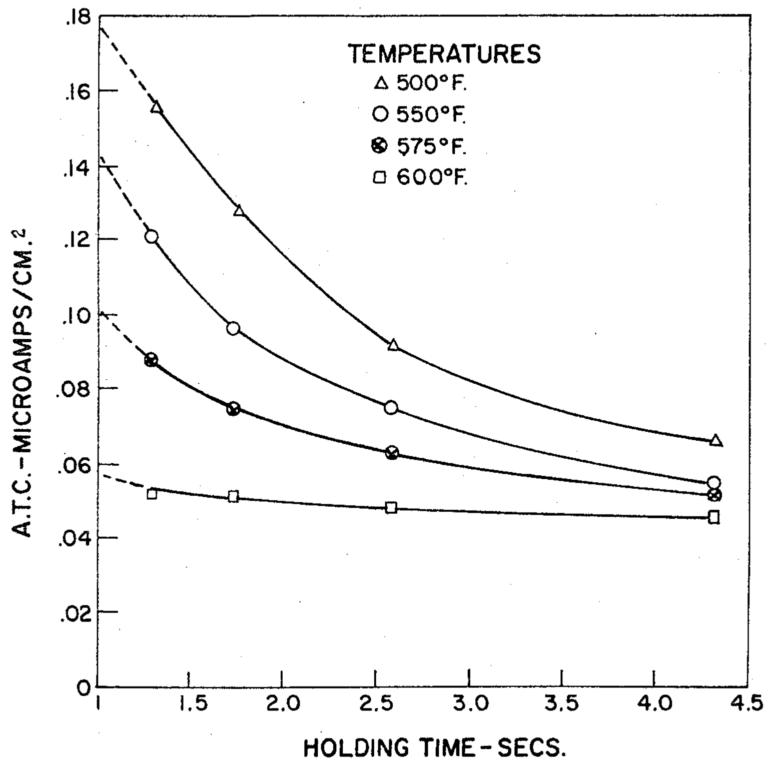

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MANUFACTURE OF ELECTROLYTIC TINPLATE

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ABSTRACT OF THE DISCLOSURE

The brightening temperature of continuously flow-brightened electrolytic tinplate is lowered when the speed of travel of the strip is reduced and increased when the speed of travel of the strip is increased so as to maintain constant the corrosion resistance of the tinplate as indicated by its ATC values.

This invention relates to the manufacture of electrolytic tinplate. It is more particularly concerned with a process of manufacturing continuously flow-brightened electrolytic tinplate having uniform appearance and flatness and uniform corrosion resistance not influenced by changes in the speed of strip travel.

Tinplate is conventionally produced by continuously surface conditioning steel strip, electro-tinning it, heating the tinned strip to a temperature sufficient to flow or melt the tin coating, quenching the heated strip in water, and winding the tinned strip so-formed into coils. The electrolyte may be either acid or alkaline. These processes permit the plating of a relatively thin tin coating which is relatively uniform in thickness. Because the thickness of tin on conventional tinplate is a small fraction of an inch, the amount of tin coating is more conveniently expressed in terms of its weight in pounds for a base box of tinplate. The term "base box" is a measure of area or surface and amounts to 31,360 square inches. Large amounts of electrolytic tinplate are made with coating weights on the order of one-quarter to one pound of tin per base box of tinplate.

Such thin tin coatings must be homogeneous and uniformly distributed, and the tinplate is frequently specially processed before or after tinning to insure that it has adequate resistance to corrosion by various food products. In the past, determination of corrosion resistance of tinplate has been a rather tedious process, but it has recently been found that the corrosion resistance of tinplate used for food packs can be determined by a galvanic test known as the alloy-tin couple test. That test consists of stripping the tin from a sample of tinplate down to the tin-iron alloy surface and measuring the current density developed by a galvanic couple comprising a pure tin electrode and the sample immersed in grapefruit juice containing 100 p.p.m. of soluble stannous tin at a temperature of about 79° F. The current density after 20 hours is measured in micro-amperes per square centimeter and the figures so obtained are referred to as ATC values. Low ATC values indicate good corrosion resistance, and high ATC values indicate poor corrosion resistance. The ATC test is described in the paper "The Alloy-Tin Couple Test—A New Research Tool" by G. G. Kamm, A. R. Willey, R. E. Beese, and J. L. Krickl, published in "Corrosion," Volume 17, February 1961, pages 106–112.

Commercial electrolytic tinplate as produced under varying conditions has ATC values ranging from perhaps 0.50 micro-amperes per square centimeter downward. Conventional tinplate usually displays ATC values in the neighborhood of 0.15 to 0.25, but it is possible to produce

tinplate having considerably lower ATC values. An ATC value of 0.07 has been arbitrarily selected as representing superior quality tinplate for food packing purposes.

Electrolytically deposited tin is dull, and it is conventional to convert the dull or matte finished electro-deposited tin into its bright form by heating the tinned strip to a temperature somewhat above the melting point of tin, which is about 450° F., and then quenching it. However, tinplate is sometimes heated to considerably higher temperatures. U.S. Patent 3,174,917 of Mar. 23, 1965, discloses a process in which the electro-deposited tin is heated to a temperature in excess of 925° F. and it states that the tinplate so produced has considerably improved corrosion resistance. When tinplate is raised to temperatures well above the melting point of tin, the speed at which the tin alloys with the iron base is greatly accelerated and the time at which tinplate having lightweight tin coatings is held at elevated temperature must be very carefully controlled. Furthermore, the coating tends to discolor unless it is surrounded by a protective atmosphere, and strip of tinplate thickness quenched from elevated temperatures tends to buckle or deform. This is particularly troublesome if the heating is not uniform across width of the strip.

Strip is conventionally electro-tinned at a relatively constant speed which depends primarily on the thickness of coating desired. It is quite common to electro-tin strip at a speed of 1000 feet per minute or thereabouts when coatings of one-quarter to one pound per base box of tinplate are deposited. When the end of a coil of strip is reached, it is necessary to slow down the strip and, of course, increase its speed again to its steady value after a new coil is substituted. If the tinplate is being brightened at conventional temperatures not greatly in excess of the melting point of tin, this reduction in speed, which occurs gradually as the trailing end of the coil is processed, does not noticeably affect the color or flatness of the tinplate, even though the time during which the strip is held at the brightening temperature is increased in inverse proportion to its speed of travel. However, if the tinplate is brightened at elevated temperatures, the trailing end of the coil may be quite badly discolored or distorted because of the increased time during which it is subjected to the high temperatures. We have also found that when the tinplate is being brightened at relatively low temperatures, its corrosion resistance is quite sensitive to the length of time it is held at temperature. The corrosion resistance of the trailing end of such strip as measured by ATC values, may be very significantly higher than the corrosion resistance of the strip forming the body of the coil which has been brightened at a constant relatively high speed of travel. As the trailing or outside end of the coil is the only convenient place from which samples of the coiled tinplate can be taken for determination of properties, such samples can be misleading.

It is an object of our invention, therefore, to provide a process for producing relatively high temperature flow-brightened electrolytic tinplate in coils which have no greater discoloration and distortion in their end portions than in their center portions. It is another object of our invention to provide such a process in which the corrosion resistance of the end portions of the coil is not different from that of the center portion. It is still another object of our invention to provide a process of brightening temperature control for an accelerating or decelerating continuous electro-tinning line. Other objects of our invention will become evident from the description thereof which follows.

We have found that the objects above-mentioned are attained by varying the temperature at which the strip is heated for brightening over a limited range in correspondence with the change in strip speed over a limited range. Our process is most conveniently described with respect to the slowdown or deceleration of the line as the trailing end of a coil passes through it, but it is also applicable in reverse order to the speed-up or acceleration of the line when the leading end of a new coil is being introduced.

An embodiment of our process presently preferred by us is described hereinafter as used on a commercial halogen process electro-tinning line with which we are familiar. In respects other than those to be described, the line is conventional. It produces tinplate of conventional gauge, that is, on the order of .010 inch in thickness, and coating weights between one-quarter and one pound per base box. The desired strip speed for tinplate of this weight is about 1000 feet per minute. The distance between the exit end of the induction brightener and the surface of the water in the quench tank is about 21 feet. When the line is changed over from one coil to the following coil, line speed may be reduced to a value below 300 feet per minute, and then increased again to the 1000 feet per minute previously mentioned.

We have found that under these conditions, tinplate brightened at relatively tow temperatures, on the order of 500° F., which may have ATC values on the order of 0.16 micro-ampere per square centimeter throughout the body of the coil, shows ATC values on the order of .07 micro-ampere per square inch at its trailing end. This difference, however, becomes less as the temperature of brightening is increased, and practically disappears when the brightening temperature is raised to 600° F.

In our improved process of manufacture, therefore, we brighten the tin by heating it to a temperature on the order of 600° F. as long as the strip is moving at its normal steady state speed, say 1000 feet per minute, but measure the temperature of the molten tin on the surface of the strip as it leaves the heating means and by suitable adjustment of the heating means decrease this temperature over a relatively narrow range between two predetermined speed values when the strip speed is reduced at the end of the coil. When a new coil is introduced and strip speed is being increased, we repeat the above procedure in the reverse order.

We have found that when the tin is heated to 600° F., neither coating discoloration nor strip distortion appears upon reduction of strip speed immediately below 1000 feet per minute. The speed can, in fact, drop to about 800 feet per minute before correction of temperature is required. At this strip speed we adjust the strip heating means so as to effect a gradual decrease of tin temperature directly proportional to strip speed over a limited range of temperature between two predetermined values and a limited range of speed between two predetermined values. We have found that below a strip speed of about 300 feet per minute changes in the temperature of the molten tin have no significant effect on the corrosion resistance of the tinplate. We therefore confine our temperature control to the strip speed range between about 800 feet per minute and 300 feet per minute, these two values being predetermined as above described. The minimum reduction of tin melting temperature consistent with tolerable discoloration and distortion of the product is, of course, desirable to maintain independence of the tinplate corrosion resistance from changes in strip speed. We find that this minimum is about 40° F., that is, that the brightening temperature need be reduced from 600° F., its first predetermined temperature, only to 560° F., its second predetermined temperature, as the line speed drops from 800 feet per minute to 300 feet per minute.

While we have described our process in terms of strip speed, the significant factor, of course, is the time during which the strip is held at the tin melting temperature. This holding time is inversely proportional to the speed of the strip and directly proportional to the distance between the tin melting means and the level of the quenching medium in the quench tank. In the tinning line above-described, a strip speed of 800 feet per minute corresponds to a holding time of about 1.6 seconds, and a strip speed of 300 feet per minute corresponds to a holding time of about 4.2 seconds.

The attached figure is a plot of ATC values against holding time for four different tin brightening temperatures, 500° F., 550° F., 575° F., and 600° F. It shows that the curves for the various temperatures converge rapidly as holding time is increased, differing insignificantly at a holding time of 4.2 seconds. It also shows that at the highest brightening temperature—600° F.—the holding time has no significant effect on the ATC values of the tinplate, as has been mentioned, Likewise, the figure makes evident that tinplate heated to 600° F. for 1.6 seconds has about the same corrosion resistance as tinplate heated to between 550° F. and 575° F. for 4.2 seconds.

The temperature of the tin on the strip leaving the melting zone is conveniently determined by an optical pyrometer. We have found that the two-color optical pyrometer, so-called, is most suitable for temperature measurements in this range. As the range of temperature change is small with respect to the temperature value, the pyrometer must be capable of precise temperature determination.

We claim:

1. In the process of manufacturing flow-brightened electrolytic tinplate in which steel strip is continuously moved successively through an electro-tinning zone, a tin melting zone, and a quenching zone spaced from the melting zone, at a speed which periodically is reduced from a relatively constant value to a lower value and then raised to a relatively constant value, whereby the time during which the strip is held at tin melting temperature is varied in inverse proportion to the speed of the strip, the improvement comprising measuring the temperature of the tin coating as it leaves the tin melting zone, adjusting that temperature to a first predetermined value, measuring the speed of strip travel, reducing that temperature when the speed of strip travel falls below a first predetermined value and continuing this reduction to a second predetermined value at a rate directly proportional to the speed of strip travel until that speed reaches a second predetermined lower value.

2. The process of claim **1** in which the first predetermined speed is not less than that which at the first predetermined temperature of the tin coating causes discoloration of the tin.

3. The process of claim **1** in which the second predetermined speed is not more than that which at the second predetermined temperature of the tin coating produces brightened tinplate having corrosion resistance equal to that of tinplate brightened at the first predetermined speed and first predetermined temperature of the tin coating.

4. The process of claim **1** in which the first predetermined speed is not less than that corresponding to a time of about 1.6 seconds.

5. The process of claim **1** in which the second predetermined speed is not more than that corresponding to a time of about 4.2 seconds.

6. The process of claim **1** in which the first predetermined temperature is about 600° F.

7. The process of claim **1** in which the second predetermined temperature is about 560° F.

8. The process of claim **1** including the steps of increasing the temperature of the tin coating when the speed of strip travel exceeds the second predetermined value and continuing this increase to the first predetermined temperature at a rate directly proportional to the speed of the strip travel until that speed reaches the first predetermined value.

(References on following page)

References Cited

UNITED STATES PATENTS

2,409,431	10/1946	Hess	204—37.5
2,566,468	9/1951	Taylerson	204—36
2,576,902	11/1951	Duby	204—36
3,285,838	11/1966	Morgan et al.	204—37.5
3,334,030	8/1967	Notman	204—37.5

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