April 30, 1963 G. G. KAMM 3,087,871

METHOD FOR IMPROVING ACID TIN PLATE QUALITY

Filed Sept. 14, 1960 4 Sheets-Sheet 1

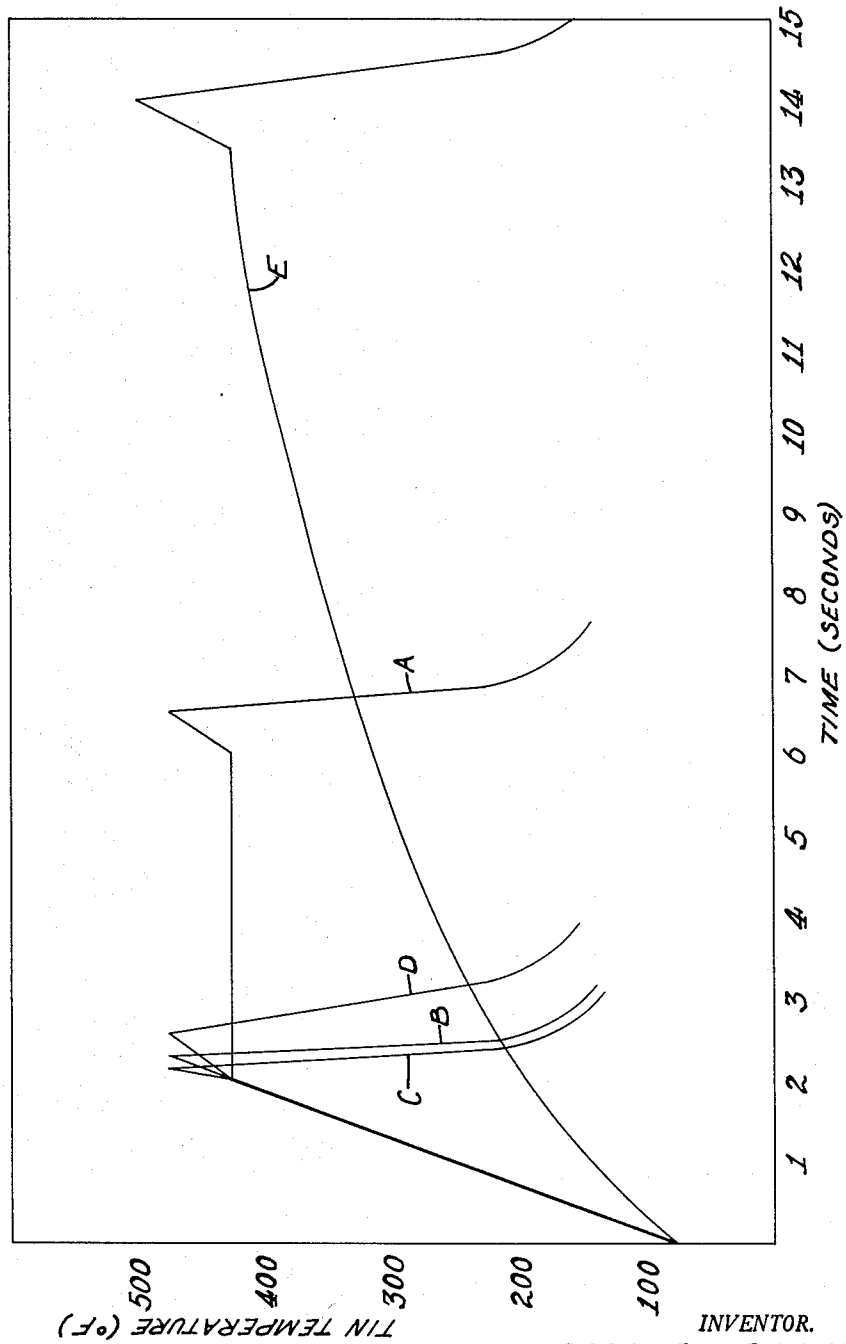


Fig. 1.

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Filed Sept. 14, 1960 4 Sheets-Sheet 2

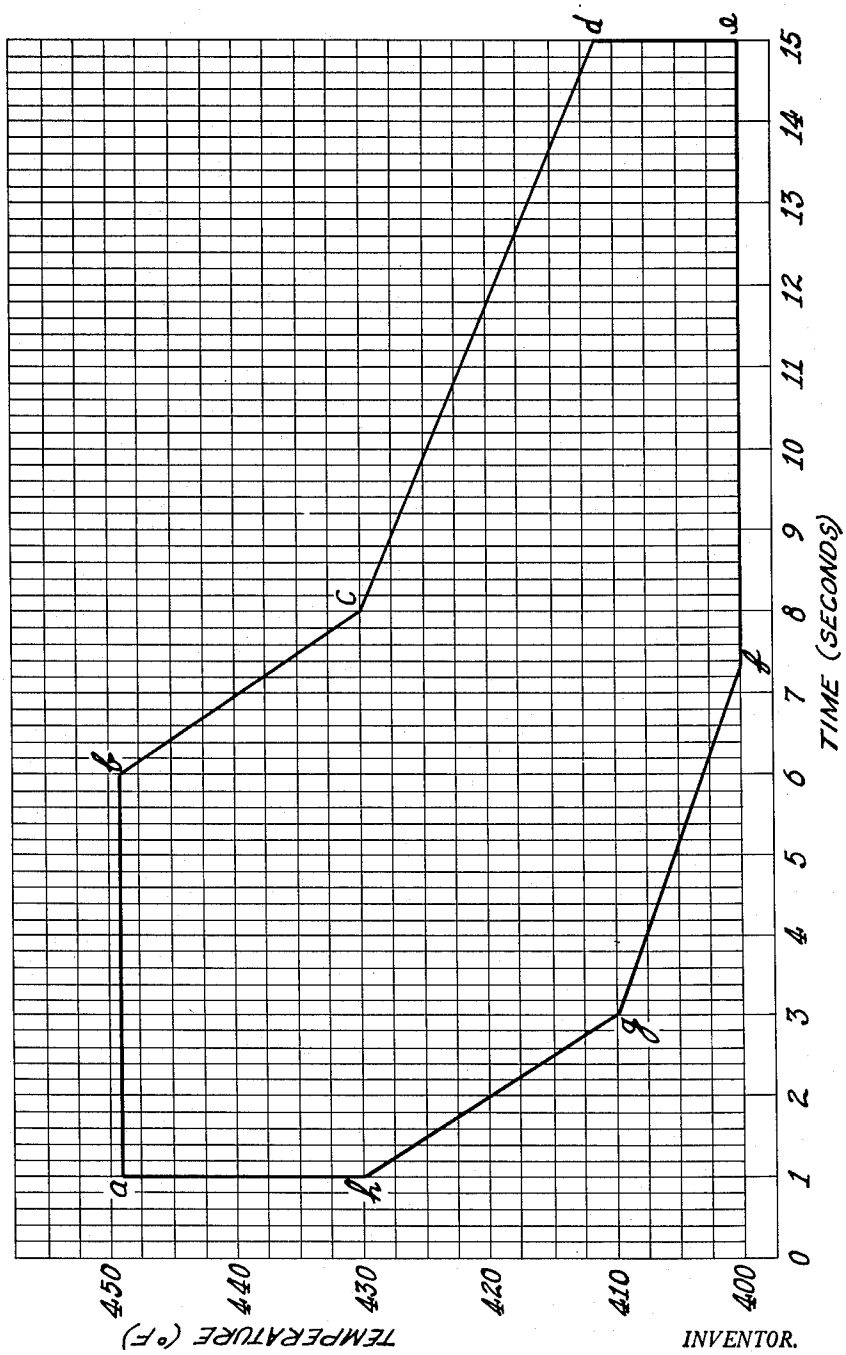


Fig. 2.

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METHOD FOR IMPROVING ACID TIN PLATE QUALITY

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Fig. 4

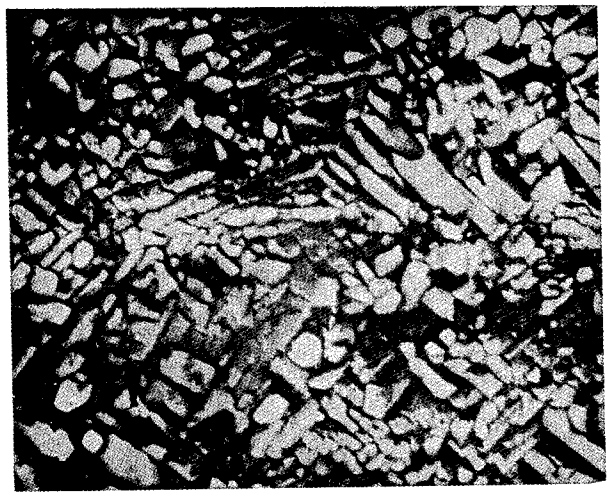
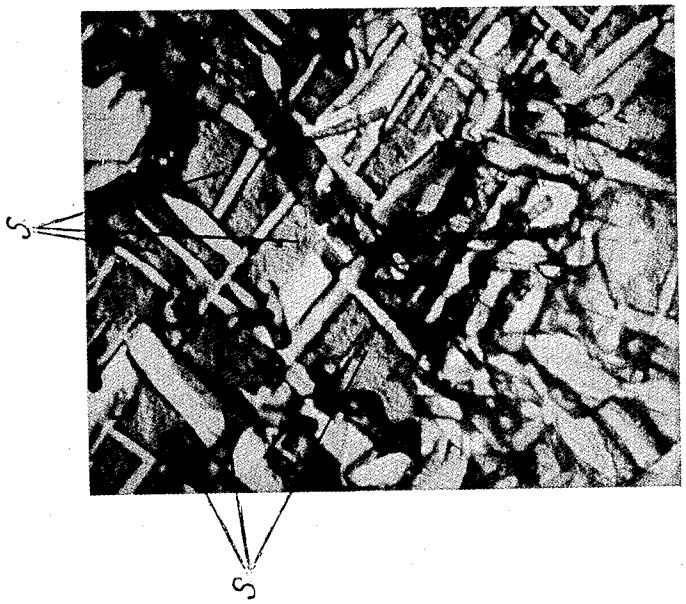


Fig. 3



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METHOD FOR IMPROVING ACID TIN PLATE QUALITY

Filed Sept. 14, 1960 4 Sheets-Sheet 4

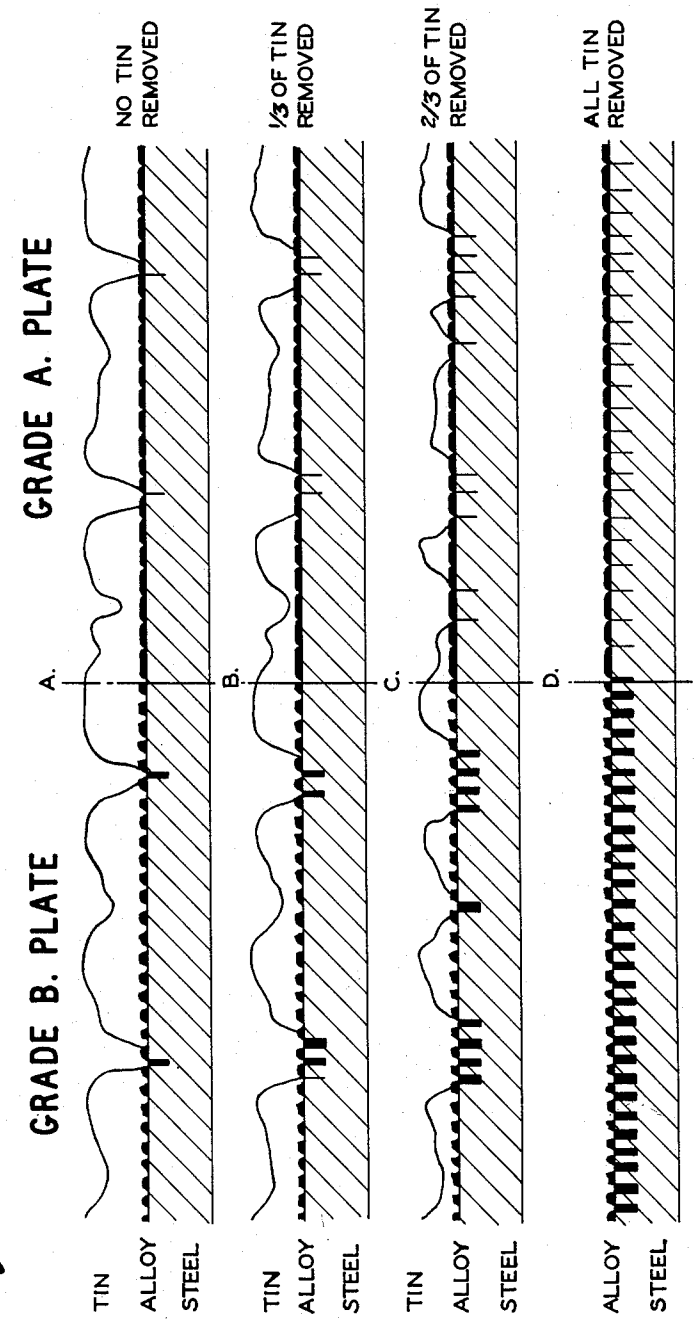


Fig. 5.

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3,087,871

METHOD FOR IMPROVING ACID TIN PLATE QUALITY

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Filed Sept. 14, 1960, Ser. No. 56,039
8 Claims. (Cl. 204—36)

The present invention pertains to a method for increasing the corrosion resistance of acid plated electrolytic tin plate. More specifically, it pertains to a method of heat treating matte finish tin electrolytically deposited from an acid plating solution whereby tin plate having increased corrosion resistance is obtained. The instant application is a continuation-in-part of my copending application Serial No. 821,622, filed June 22, 1959 now abandoned, which in turn is a continuation-in-part of my application Serial No. 807,282 filed April 20, 1959, now abandoned.

Most tin plate used in the metal container industry is electrolytic tin plate produced either from an acid plating solution or an alkaline solution. The acid electrolytic plating system is considered by many to be a faster and simpler technique. Therefore, a greater proportion of tin plate is produced by the acid plating system than by the alkaline plating system. However, alkaline tin plate having satisfactory special property test values, i.e. pickle lag, iron solution values, and tin crystals size, consistently demonstrates superior corrosion resistance; whereas acid tin plate having similarly satisfactory special property test values characteristically demonstrates only average corrosion resistance. Based on these differences, tin plate having superior corrosion resistance is designated grade A plate; whereas tin plate having average corrosion resistance is designated grade B plate; and acid tin is usually rated grade B. It follows that a large number of products packed in cans made from grade A plate have a longer shelf or storage life than in cans made from grade B plate. The present invention is especially concerned with the production of acid tin plate which is consistently grade A, a result not achieved heretofore.

The tin deposited from both the acid and alkaline electrolytic plating solution is known in the art as matte finish or matte tin, because of its relatively dull appearance. In present day commercial practice wherein the sheet steel is carefully prepared prior to the plating operation, the matte tin is substantially continuous and void free over the base steel. However, no tin-iron alloy is present between the layer of matte tin and base steel as a result of the electrolytic deposition of the tin from an acid plating bath. In commercial practice, the tin-iron alloy is formed by heating the matte tin to a temperature above its melting point, whereupon tin-iron alloy forms rapidly wherever the molten tin contacts the base steel. This procedure, known in the art as flow brightening, produces, upon quenching the tin to solidify it, tin plate having a bright, shiny appearance. However, this treatment impairs the continuity of the tin layer. Photomicrographs of prior art flow brightened acid tin plate show that neither the outer tin layer nor the tin-iron alloy layer is completely continuous over the steel base. In other words, voids or discontinuities exist in each of these layers. Many of the voids in each layer are not in alignment, i.e. a void in the alloy is covered by tin and a void in the tin is bottomed by alloy. However, some of these voids are more or less in alignment so that through them base steel is exposed to the environment in contact with the tin plate. Obviously the more discontinuous either layer is, the greater the incidence of alignment and consequently the greater the amount of base steel exposed. These exposed areas of

base steel are in some products vulnerable to direct corrosive attack, while in others they acclerate corrosion of tin from the plate surface.

Tin plate cans are considered failures when vacuum is lost because of hydrogen generated by corrosion within the can, or when the can wall is perforated by internal corrosion. Experimental evidence indicates that the mechanism of corrosion in a tin can by the product packed therein usually falls into one of two main categories.

In a substantial number of the foods with pH in the range of 3.0 to 4.5, of which grapefruit juice is typical, tin is anodic to steel and forms a galvanic cell in which tin is anode and steel is cathode. The tin is not attacked directly but is driven into solution by the galvanic couple current; an equivalent amount of hydrogen is formed at the steel surface which receives cathodic protection from corrosion as a result of the couple current. The tin-iron alloy, which is relatively inert to corrosion in this class of products, is anodic to steel and slightly cathodic to tin; it offers little electrochemical protection to steel but is easily protected by coupling to tin and causes little galvanic corrosion of the tin. The galvanic detinning caused by coupling tin to tin-iron alloy is only about 1/50 as great as that caused by an equal area of steel coupled to tin. The rate of detinning, and hence the rate of hydrogen formation within a can, is governed mainly by the area of steel exposed through voids in the combined layers of free tin and tin-iron alloy. The continuity of the alloy layer plays an important part by limiting the amount of steel exposed, minimizing the effect of high tin porosity and preventing rapid acceleration of corrosion as detinning progresses to the point where some areas are detinned to the alloy layer.

In a number of other products, representing the entire range of pH found in canned foods, steel is anodic to tin and receives no electrochemical protection from the coupling to tin. Corrosion of the steel occurs as a result of direct attack and to some extent is accelerated by the galvanic current caused by coupling with the cathodic tin. Hydrogen is formed equivalent to the steel corroded. The tin and iron-tin alloy are not attacked and serve as mechanical barriers which reduce corrosion by limiting the area of steel exposed to the product.

It has been discovered that the corrosion performance of tin plate for the majority of foods packed in cans is improved by having a substantially continuous tin-iron alloy layer. In the products similar to grapefruit juice, where the rates of detinning and hydrogen formation are determined by the area of steel exposed, good coverage of the steel by the alloy reduces the amount of steel exposed to the product. At the start of corrosion the degree of continuity of alloy layer is important as it determines the area of steel exposed at the base of pores in the tin coating. As detinning progresses to the point where additional alloy is exposed, the coverage afforded the steel by the alloy becomes even more important. To the extent that the alloy is discontinuous or contains voids, more and more base steel becomes exposed as the tin is removed. Each new area of steel enters into the electrochemical reaction, whereby the resulting detinning accelerates or proceeds at an ever increasing rate. When the alloy layer contains many voids, detinning accelerates rapidly, causing rapid evolution of hydrogen and consequent dissipation of can vacuum. The galvanic detinning continues until insufficient tin remains to provide cathodic protection for the steel, at which time the corroding medium attacks the base steel, generating hydrogen at an even faster rate. On the other hand, if the alloy layer is substantially continuous, removal of tin exposes mainly tin-iron alloy through which only a very small amount of base steel is exposed; the accelerating effect on galvanic

detinning is relatively minor. Thus, hydrogen is produced at a slower rate and a longer time is required for complete detinning, delaying markedly the time when insufficient tin remains to protect the steel. Even then the more nearly continuous alloy coverage gives greater protection, mechanically and electrochemically, to the steel and defers for a longer period the accumulation of hydrogen to the point of failure.

In the products where the tin does not protect steel electrochemically, the rates of steel corrosion and the resulting evolution of hydrogen are a function of the area of steel exposed. The tin and iron-tin alloy layers serve as relatively inert mechanical barriers limiting the area of steel exposed, thereby reducing the rate of hydrogen evolution and increasing the service life of the container. A continuous alloy layer is essential to keep exposed steel to a minimum.

There are some products containing oxidants which attack tin directly and to which the corrosion mechanisms just described do not apply. However, most products fall into either of the two categories described, and therefore attaining a substantially continuous layer of tin-iron alloy in acid plate results in superior corrosion resistance with most canned products. This substantially continuous alloy layer serves to limit the area of exposed steel which can drive tin into solution galvanically or which can be corroded by direct attack, depending upon the corrosion mechanism obtaining in the product under consideration.

The prior art has attempted to solve this problem by affecting the nature of the steel base so as to obtain large tin crystals and incidentally make the tin layer more continuous. However, even with the best prior art procedures, voids still exist in both the tin layer and in the tin-iron alloy layer after flow brightening. Because of its generally lower corrosion resistance and from certain experimental evidence, it is reasonably assumed that the acid tin plate contains more voids either in its tin layer or alloy layer or both than alkaline plate.

The present invention solves the problem of corrosion of the base steel in acid tin plate in a completely different and novel manner than has been tried before. This novel solution to the problem is to make the alloy layer substantially continuous and void-free. In other words, I have discovered that a continuous alloy layer in acid tin plate is essential to good corrosion resistance, and that the beneficial effect is a function of continuity of the tin-iron layer and not its thickness. A continuous layer of alloy improves corrosion resistance regardless of the degree of continuity of the tin layer.

It is therefore an object of the instant invention to provide a method of consistently producing acid tin plate of improved quality.

Another object is to provide a method of producing acid tin plate having little or no bare steel exposed to the environment in contact with the tin plate.

It is also an object to provide a method whereby grade A acid electrolytic tin plate may be produced consistently.

Another object is to provide a method of consistently producing high-grade acid tin plate which involves a minimum of change to conventional flow brightening operations.

Yet another object is to provide a method which may be readily and accurately controlled to produce acid tin plate having a substantially continuous and relatively flexible tin-iron alloy resulting in greater corrosion resistance than prior art acid tin plate.

A further object is to provide a corrosion-resistant acid tin plate which gives cans made therefrom a longer storage or shelf life when packed with products which corrode the can either by galvanic detinning of the tin plate or by direct attack of the steel without initial detinning than has heretofore been possible with cans made from acid tin plate.

Numerous other objects and advantages of the invention will be apparent as it is better understood from the following description which, taken in connection with the accompanying drawings, discloses a preferred embodiment thereof.

I have discovered the above objectives may be accomplished by heating electrolytic tin plate produced from a conventional acid plating procedure to a temperature within the range of from 400° F. and 449° F., changing the rate of temperature increase of the acid matte tin plate so as to maintain it within this range for a brief time interval, and then melting the matte tin to flow brighten it. The higher the temperature at which the matte tin is maintained, the shorter the holding time necessary to produce the desired tin-iron alloy.

Referring to the drawings:

FIGURE 1 illustrates time-temperature curves showing different heating procedures discussed herein for matte tin plate;

FIG. 2 is a chart showing the time-temperature relations operable in the method of the instant invention;

FIGS. 3 and 4 are reproductions of electron photomicrographs of tin-iron alloy layers; and

FIG. 5 is a schematic sectional view comparing detinning of grade A and grade B acid tin plate.

The terms acid tin and acid tin plate, as used herein, are meant to describe tin plate, either matte or flow brightened, wherein the tin is electrolytically deposited onto a steel base from an aqueous acid solution. This procedure is old and well known in the art; and in general involves immersing thin gage steel, prepared in the manner described hereinafter, into a low pH aqueous solution of stannous ions, making the steel a cathode, a tin bar immersed in the solution an anode, and passing a current between the two electrodes through the solution. The stannous ions being positively charged migrate to the cathodic steel and plate-out thereon as a matte deposit of metallic tin. This product is then washed, fluxed, and dried and ready for the flow brightening operation. Acid matte tin plate is acid tin plate prior to flow brightening. Also, as used herein, the term sheet is meant to include continuous strip as well as individual sheets.

Although, by means of the present invention, even poor acid tin plate can be improved in corrosion resistance, only steel produced by the best and latest commercial procedures will yield grade A acid tin plate when treated according to the invention. In general, the production of the steel strip includes the following steps. Steel slabs are hot rolled into relatively heavy gage strip which is then quenched to 1150° to 1250° F. as it is coiled. This quenching operation produces a uniform and fine dispersion of the carbides in the steel to provide maximum corrosion protection for the steel itself when used in the manufacture of acid tin plate. The strip is then pickled, cold reduced, electrolytically cleaned, annealed, either box or continuously, and temper rolled. To produce the base steel preferred for use in the present invention, steel sheet made as described above is electrolytically cleaned, pickled in dilute sulfuric acid, and then acid tin-plated.

The most prevalent commercial practice for flow brightening is to heat the matte tin plate rapidly at a substantially constant rate of temperature increase to a temperature above the melting point of the tin and thereafter quenching the tin at substantially the same rate. Such a method produces the cone-shaped curve B shown in FIG. 1. The heavy line in FIG. 1 represents the temperature increase or come-up rate of the tin plate and is the same for each of the curves A, B, C, and D in FIG. 1. The heating performed in this procedure is usually electric resistance heating and is accomplished in a matter of seconds. Substantially all of the tin-iron alloy formed by this procedure is formed during the brief time interval the tin plate is above the melting point of tin. Two other flow brightening procedures described in the prior art involve increasing the temperature of the matte

tin plate at a rapid constant rate to a temperature between 400° F. and the melting point of tin and thereafter either raising its temperature at a faster rate to a temperature above the melting point of tin, curve C, FIG. 1; or increasing its temperature at about one half the come-up rate, curve D, FIG. 1.

With the first of these latter two procedures, substantially all of the alloy is formed above the melting point of tin, as with the first mentioned procedure. With the second of the latter two procedures, although some alloy may be initiated or formed during the slower second portion of the heating operation, here again most, if not all, of the alloy is formed above the melting point of tin, since the matte tin and base steel spend insufficient time at the elevated temperatures close to but below the melting point of the steel.

Still another flow brightening procedure is described in the prior art wherein the temperature of the matte tin plate is raised at an ever decreasing rate to a temperature near but below the melting point of tin and thereafter raised at a more rapid rate to a temperature above the melting point of tin, curve E, FIG. 1. This last mentioned method is of no commercial importance today, since, if the rate is to approach the melting point of tin asymptotically, i.e. reach a point where the slope of the curve is substantially zero, too long a come-up time is necessary. If on the other hand, an economically feasible come-up time is used, the temperature increase becomes substantially constant, so that the curve is very similar in appearance to that of B or C in FIG. 1. For some unknown reason, acid electrolytic tin plate flow brightened by any of these prior art procedures sufferers from the deficiency mentioned previously; that is, the alloy layer is discontinuous, having a multiplicity of voids therethrough. As mentioned previously, such acid tin plate is not considered grade A, having only a moderate or average corrosion resistance.

In distinction from any of these prior art flow brightening processes, the instant invention depends upon and makes effective use of alloy growth below the melting point of tin, i.e. 449.4. This procedure involves heating the acid matte tin plate having a steel base of the type described hereinbefore, to a temperature of at least 400° F. but not more than 449° F., and preferably to a temperature of from 425° to 445° F. For the purpose of the present invention, the initial temperature increase or come-up to a temperature of at least 400° F. must be at a substantially constant rate within a time of not more than 8 seconds and preferably 1 to 4 seconds. Thereafter the heated acid matte tin plate is maintained within the 400 to 449° F. temperature range for a period of time by reducing the rate of temperature increase sufficiently to meet the requirement below as to time of dwell below 449° F. This operation induces uniform nucleation of the tin-iron alloy between the steel base and the acid matte tin coating while each is in the solid phase. At temperatures approaching 449° F., a time as short as 1 second induces sufficient alloy nucleation to produce the new and improved alloy layer of the present invention; whereas at 400° F. as long as 15 seconds may be required to produce the desired result. Between these extremes of time and temperature, different time-temperature relationships, as shown in FIG. 2, are used. In the preferred temperature range, i.e. 425 to 445° F., a time of about from 4 to 8 seconds is preferred.

To insure the desired alloy nucleation, the temperature come-up rate to at least 400° F. must be reduced an amount sufficient to maintain the acid matte tin plate within the 400–449° F. temperature range for the necessary 1–15 second time interval. Because it is much more readily controllable, it is preferred that the rate of temperature increase of the plate after come-up be reduced to substantially zero, so that the acid matte tin plate is maintained at a substantially fixed temperature during alloy nucleation. However, it is within the purview of the present invention that the rate of temperature increase of the acid tin plate after come-up may be reduced somewhat more or less than 100% whereby the temperature of the acid matte tin plate is either slightly raised or lowered during the nucleation operation but still remains within 400–449° F. range.

Heating for times less than one second does not produce the desired upgrading of the tin plate, apparently due to insufficient uniform alloy nucleation. It is probable that certain sites between the contiguous matte tin and steel surfaces are very reactive, so that some alloy nuclei, and even some alloy grains, would be formed at these sites below the melting point of tin merely by heating the matte plate rapidly and directly to a temperature above its melting point, such as curve B, FIG. 1. However, such alloy nuclei and possible alloy grains would be relatively few and widely separated. The instant invention requires that a multitude of closely spaced nuclei be formed; and to achieve this result requires adherence to the prescribed time-temperature schedule, so that the less reactive as well as the more reactive sites are activated. No appreciable increase in plate quality results by heat treating longer than 15 seconds. From this it would appear that it is the uniformity and absence of voids that are the critical factors in the alloy layer rather than the thickness thereof.

I have found that acid tin plate heat treated in accordance with the present invention and before flow brightening has an amount of tin-iron alloy of about 0.005 to 0.050 pound per base box of base steel, with 0.010 to 0.030 pound per base box formed at optimum conditions. As explained more fully hereinafter, the amount of alloy formed will depend upon the time and temperature conditions of the nucleation heat treatment. This amount of alloy will be within the ranges designated above and may be less than or substantially equal to the amount of alloy finally present after flowing brightening. The amounts of alloy specified represent total alloy on both sides of the plate. Also, these amounts are not actual alloy weights; but are the weight of tin present in the alloy. This method of specifying alloy weights is standard practice in the tin plating art.

After the nucleation operation, rate of temperature change of the acid matte tin is substantially increased, preferably to the come-up rate, so as to rapidly raise the tin to a temperature above tis melting point but below 500° F. in order to flow brighten the acid tin. This flow brightening step causes the tin to flow out into a smooth film and to become firmly anchored to the alloy layer. Upon its solidification, the acid tin no longer has a matte finish but has a relatively bright, reflective surface. Although satisfactory results have been obtained by flowing the acid matte finish tin at temperatures substantially above its melting point, for best results, both as to appearance and corrosion resistance, the tin should be flowed at temperatures above, but as close as possible to, the melting point of the tin. It is preferred that the tin remain at the temperature above its melting point for as short a time as possible. In other words, no dwell time is provided for the acid tin plate at the temperature above 450° F. To this end, the molten tin is solidified as rapidly as possible, such as by a cool air bath or a water quench or both. This sequence of steps for flow brightening acid matte tin in accordance with the preferred operation of the present invention is represented by curve A in FIG. 1.

Example

A sheet of low carbon steel, produced in a manner described hereinbefore, and having on its surface a solid coating of matte finish tin electrolytically deposited in a conventional manner from a conventional acid plating bath, was divided into two samples.

Sample 1 was attached to electrodes of a resistance heater having controls thereon for varying the voltage

input and thereby temperature of the sample. Sample 1 was heated from room temperature to about 475° F. at a uniform rate in about 4 seconds, thereby melting the tin coating. Immediately thereafter, it was immersed in water maintained at approximately room temperature to rapidly quench the sample and solidify the tin coating thereon.

Sample 2 was then attached to the electrodes of the resistance heater and its temperature increased at a constant rate to a temperature of about 430° F. in about 4 seconds. Thereafter the rate of temperature rise was reduced to zero so as to maintain the acid matte tin plate at this temperature for 4 seconds. Test data from experimentation with similar acid matte tin indicate that sample 2 at this point had an amount of tin-iron alloy of between 0.01 and 0.03 and most probably about 0.02 lb. per base box. The heating rate was then increased by increasing the voltage input so that the temperature of the sample was rapidly raised to about 475° F. in less than ½ second, whereupon the tin coating melted. Immediately thereafter, the sample was immersed in a water bath maintained at approximately room temperature, thereby quenching the sheet and solidifying the tin.

FIGS. 3 and 4 are photomicrographs representing the alloy layer of samples 1 and 2 respectively. For each micrograph the tin layer was electrolytically stripped from the flow brightened acid tin plate. Each micrograph was taken through an electron microscope at a magnification of 5600 times, using a chromium shadowed carbon replica technique. These micrographs were then magnified optically to 20,000 times. By the procedure used on sample 1, which is similar to conventional prior art practice, most, if not all, of the alloy is formed above the melting point of tin. FIG. 3, representing the alloy layer of sample 1, shows the relatively large areas of exposed steel, S, and the upstanding position of many of the alloy grains. This alloy is present in an amount of 0.090 lb. per base box. Apparent in FIG. 4, representing the sample 2 alloy layer, are the absence of exposed base steel and the continuous and substantially uniplanar or level nature of the alloy layer. This alloy is present in an amount of 0.054 lb. per base box.

It is essential and critical that the acid matte tin be given sufficient heat treatment in the solid phase at least to produce a multitude of closely spaced alloy nuclei, the amount of which can be determined and expressed as lb. of alloy per base box of steel. As disclosed hereinbefore, this minimum amount of alloy is about 0.005 lb. per base box. For any given temperature in the 400 to 449° F. range, the minimum time specified for the practice of the present invention will produce this minimum condition. For times greater than this minimum time, up to the maximum specified time at a given temperature within the specified range, some of the initially formed alloy nuclei will grow into alloy grains and probably additional alloy nuclei will form. Further heat treatment beyond this maximum time causes the alloy nuclei or formed alloy grains to grow in size toward each other in a direction substantially parallel to the contiguous tin and steel surfaces. Continuing this further heat treatment causes the alloy grains to meet one another and to fill in the spaces between themselves to form a substantially continuous and substantially uniplanar layer of alloy between the tin and steel.

The preferred further heat treatment of the multitude of alloy nuclei is to heat the plate immediately after the nucleation operation to a temperature above the melting point of tin to flow brighten the tin. Upon melting of the acid matte tin, the alloy nuclei grow extremely rapidly, almost instantaneously, to form the substantially continuous, uniplanar alloy described above.

The alloy nuclei and grains can also be further heat treated to form the above described substantially continuous and uniplanar alloy layer by continuing the heat treatment of the acid matte tin at a temperature within the 400 to 449° F. range for a sufficient length of time beyond the maximum time limit of the present invention at that temperature. Under this condition, the formed nuclei and any grains grow in the manner described above but at a rate slower than the rate obtaining during flow brightening and probably with the formation of new nuclei. The grains of the substantially continuous alloy layer formed by this procedure are usually smaller than those produced by the preferred procedure. It is believed that this is due to the formation of the new nuclei, which, by forming in spaces between earlier formed nuclei and grains, restricts the area of growth for all.

This latter procedure of further heat treating although operable, is not preferred, since no commensurate increase in plate quality results, justifying the longer times required. Further, to produce commercial tin plate, the acid matte tin will always be flow brightened to give it the necessary bright, shiny appearance. Since flow brightening immediately after the alloy nucleation operation will produce an alloy layer of desired continuity, and consequently acid tin plate of desired quality, additional heat treatment at a temperature of from 400–449° F. but beyond the maximum time limits of the instant invention is somewhat superfluous. However, it is to be understood that additional heat treatment at a temperature of from 400 to 449° F., beyond the specified maximum time limits is also within the scope of the instant invention.

If the nucleation operation is not prolonged for a time sufficient to produce the substantially continuous alloy layer, i.e. the amount of alloy formed below the melting point of tin is at least 0.005 but less than 0.05 lb. per base box, flow brightening, as it forms the substantially continuous alloy layer in the manner described above, will also cause an increase in the amount of alloy. For the purpose of the instant invention, the amount of alloy present after flow brightening will be from 0.02 to 0.15 and preferably from 0.05 to 0.07 lb. per base box depending upon the amount of alloy present before the flow brightening operation and upon the time and temperature conditions of flow brightening, i.e. the higher the temperature above the melting point of tin and/or the longer the time the tin is maintained in the molten state, the heavier or thicker will be the substantially continuous alloy layer.

On the other hand, if a substantially continuous alloy, i.e. about 0.05 lb. per base box, is formed during a nucleation operation, continued treatment at the same or a different nucleation temperature, or even flow brightening, does not appreciably increase the amount of alloy. While not wishing to be bound by any particular theory, it is believed that this is due to the already continuous nature of the alloy layer, whereby either the base steel is effectively sealed off from contact with the tin or the abutting grains of alloy have no room for further growth in their initial planar direction, or both.

As mentioned previously and repeated here for emphasis, it is the substantially continuous alloy layer in the flow brightened acid tin plate that is primarily responsible for the new and unexpected results of the instant invention; and the prescribed heat treatment of the acid matte tin to form from 0.005 to 0.05 lb. per base box of alloy before flow brightening is a prerequisite to obtaining the substantially continuous alloy after flow brightening. Without the nucleation operation described above, the tin-iron alloy forms in a loosely-knit open patchwork with relatively large areas of bare steel exposed between the alloy grains. Experimental evidence has also shown that the alloy grains formed in such case tend to grow upward from the steel surfaces rather than parallel to the tin and steel surfaces as in the instant invention. Obviously, these upstanding alloy grains do

not have the covering ability of the alloy grains produced by the nucleation operation.

FIG. 5 illustrates, schematically, my explanation of detinning, as described hereinbefore, of prior art acid tin plate, which is grade B plate, and acid tin plate produced in accordance with the present invention, which is grade A plate, when each is in contact with an acid medium such as grapefruit juice. The discontinuous alloy layer of the grade B plate fails to cover relatively large areas of the base steel, some of which uncovered steel is exposed through voids in the tin plate directly to the acid environment in contact with the plate. The degree of this exposure is indicated by the width of the vertical, heavy, black lines. The substantially continuous alloy layer of the grade A plate permits very little base steel to be exposed. As detinning progresses, the grade B plate exposes more and more base steel to its environment and detinning rapidly accelerates; whereas with the grade A plate, detinning is initially slow, due to little or no base steel exposure; and accelerates little, if at all, as detinning progresses, because the alloy layer covers substantially all of the base steel even after tin is removed. It is known that the stannous ions in solution tend to inhibit detinning, i.e. solution of the metallic tin. However, so much bare steel is exposed in the grade B plate that the electrochemical force driving the tin into solution overcomes this inhibiting effect. Since grade A plate exposes little or no base steel, this inhibiting effect can function to prevent acceleration of detinning, and in some cases, to actually slow the detinning process.

It is to be understood that FIG. 5 is schematic and no attempt was made to accurately depict the relative sizes or position of the alloy grains or the number and size of the voids in the alloy layer. It does, however, illustrate the fact that the grade B alloy layer is much more discontinuous than the grade A alloy layer. Also, FIG. 5 does not compare the rates of detinning of the grade A and grade B plates, merely the procedure. In actuality, many months longer would be required to reach each stage of detinning, i.e. ⅓, ⅔ and complete, for the grade A than for the grade B plate. For example, flow brightened acid tin plate having an alloy layer as shown in FIG. 4 (grade A plate) would require a time 30–50% longer to reach the completely detinned stage than would flow brightened acid tin plate having an alloy layer as shown in FIG. 3 (grade B plate).

It is thought that the invention and many of its attendant advantages will be understood from the foregoing description and it will be apparent that various changes may be made in the steps of the method described and their order of accomplishment without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the method hereinbefore described being merely a preferred embodiment thereof.

I claim:

1. In a method of flow brightening matte finish tin electrolytically deposited from an acid plating solution onto a steel base, the three steps comprising (1) heating said tin at a predetermined rate to a temperature of from 400° F. to 449° F. in a time interval of 1 to 8 seconds, (2) heating said tin at a temperature and for a time represented in the area enclosed by the points *a, b, c, d, e, f, g, h, a* of FIG. 2 at a rate different from the rate of step (1) to produce at least a multitude of tin-iron alloy nuclei between said tin and base, and (3) heating said tin at a rate different from the rate of step (2) to a temperature above the melting point of said tin to produce flow brightened tin plate having a substantially continuous and level layer of tin-iron alloy between said tin and base.

2. In a method of flow brightening matte finish tin electrolytically deposited on a steel base from an acid plating solution the steps comprising: (1) increasing the temperature of the tin from ambient temperature to from 400° F. to 449° F. in a time interval of 1 to 8 seconds at a substantially constant rate, (2) heat treating said tin at a temperature and for a time represented in the area enclosed by the points *a, b, c, d, e, f, g, h, a* of FIG. 2 at a rate of temperature change different from the rate of step (1) to produce at least a multitude of tin-iron alloy nuclei between said tin and base, and (3) thereafter rapidly increasing the temperature of said tin above the melting point of tin at a substantially constant rate different from the rate of step (2) to produce flow brightened tin plate having a substantially continuous and level layer of tin-iron alloy between said tin and base.

3. The method set forth in claim 2 wherein the rate of temperature change of step (2) is positive and substantially constant.

4. The method set forth in claim 2 wherein said rate of temperature change of step (2) is substantially zero.

5. The method set forth in claim 2 wherein said tin is heated to and maintained at a temperature of from 425 to 445° F. for a time of from 4 to 8 seconds.

6. The method set forth in claim 2 wherein said first mentioned constant rate is between 100 and 400° F. per second.

7. In a method of flow brightening matte finish tin electrolytically deposited from an acid plating solution onto a steel base, the three steps comprising (1) heating said tin at a predetermined rate to a temperature of from 400° F. to 449° F. in a time interval of 1 to 8 seconds, (2) heating said tin at a temperature and for a time represented in the area enclosed by the points *a, b, c, d, e, f, g, h, a* of FIG. 2 at a rate different from the rate of step (1) to produce from 0.005 to 0.05 lb. of tin-iron alloy per base box of said base between said tin and said base, and (3) heating said tin at a rate different from the rate of step (2) to a temperature above the melting point of said tin to produce flow brightened tin plate having a substantially continuous and level layer of tin-iron alloy between said tin and base.

8. The method set forth in claim 7 wherein said heating of step (2) produces from 0.01 to 0.03 lb. of tin iron alloy per base box of said base between said tin and said base.

References Cited in the file of this patent

UNITED STATES PATENTS

2,357,126	Nachtman	Aug. 29, 1944
2,418,088	Nachtman	Mar. 25, 1947
2,420,377	Jones	May 13, 1947

FOREIGN PATENTS

729,914	Great Britain	May 11, 1955