

Nov. 15, 1966

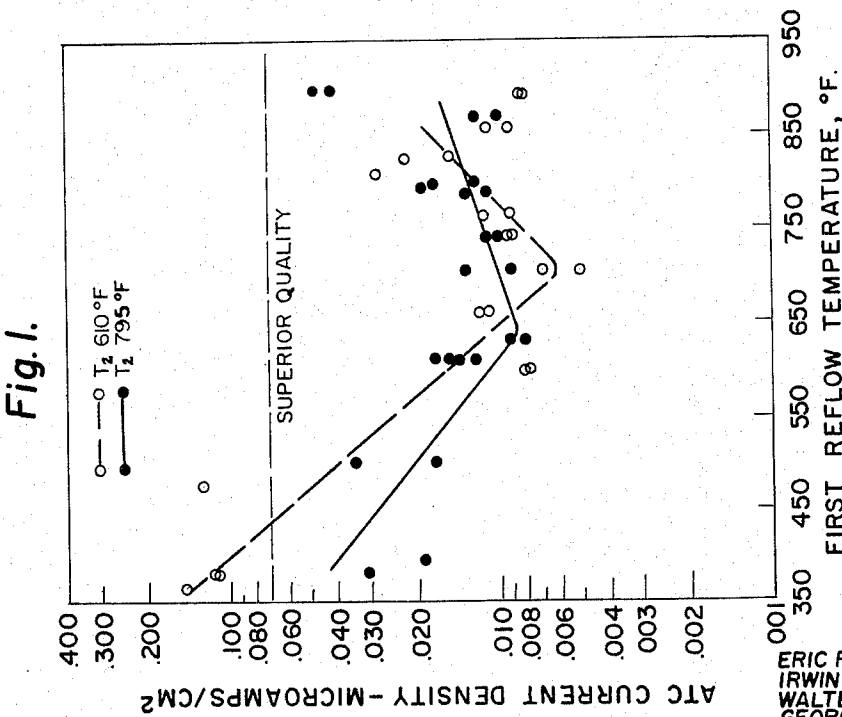
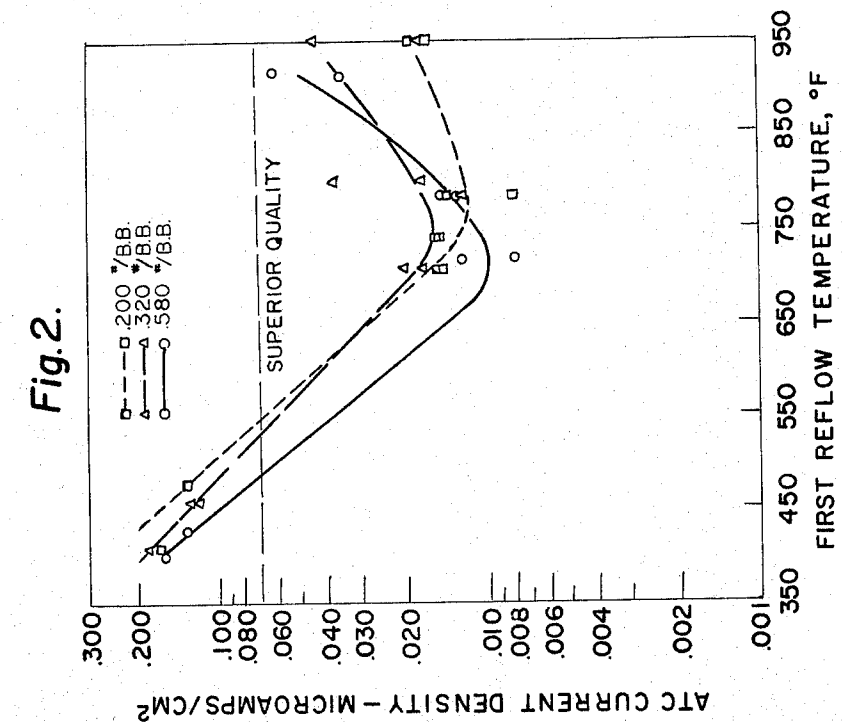
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3,285,838

PRODUCTION OF ELECTROLYTIC TINPLATE

Filed Sept. 17, 1962

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

Fig. 3.

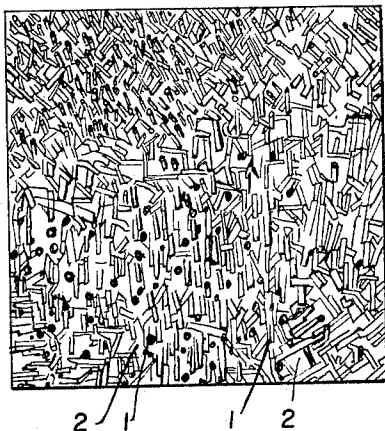


Fig. 4.

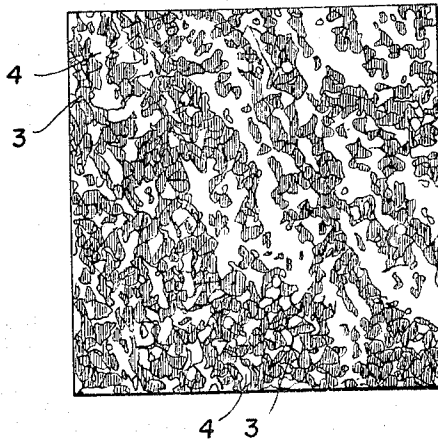
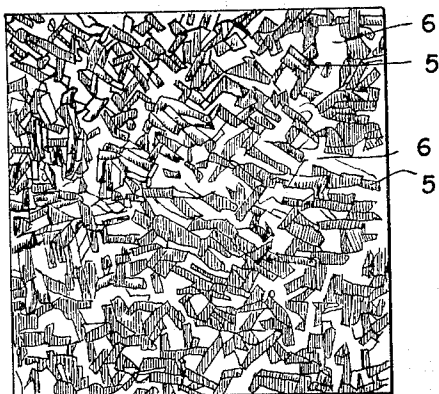
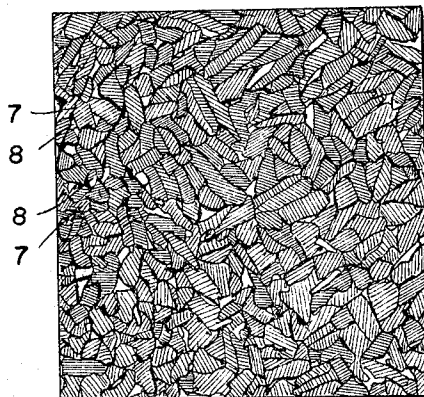


Fig. 5.



490°F

Fig. 6.



535°F

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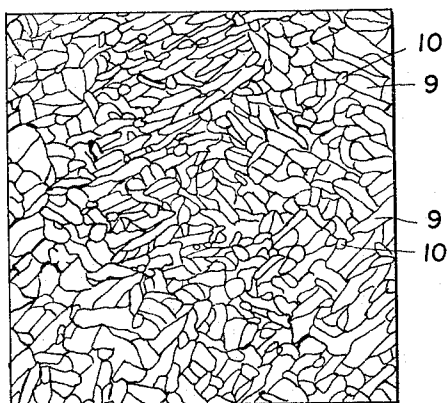
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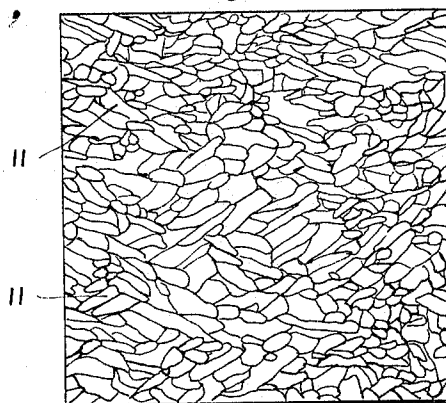
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Fig. 7.



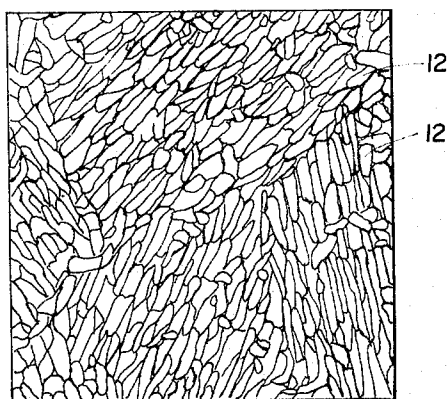
585°F.

Fig. 8.



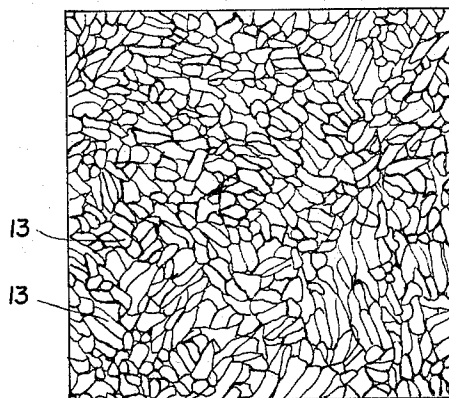
620°F.

Fig. 9.



670°F.

Fig. 10.



705°F.

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3,285,838

PRODUCTION OF ELECTROLYTIC TINPLATE

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3 Claims. (Cl. 204—37)

This invention is concerned with the production of electrolytic tinplate of improved corrosion resistance for use in food packs. It is more particularly concerned with a duplex electrolytic process and the product thereof.

The great bulk of tinplate used today is provided with its tin coating by electrolytic tin processes. 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 1/2 pound of tin per base box of tinplate.

With the thin tin coatings now applied, the electrolytic tinplate used for food packs must be tested carefully to determine its resistance to corrosion by various food products. In the past the determination of corrosion resistance of tin plate has been a rather tedious process, but in recent years it has 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. The 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 79° F. The current density after 20 hours is measured in microamperes per square centimeter, and the figures are referred to as ATC values. Low ATC values indicate good corrosion resistance, whereas high ATC values represent 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 0.01 up to perhaps 0.5. The ATC value of 0.07 has been arbitrarily selected as representing superior quality tinplate, although, as we have mentioned, it is possible to produce tinplate having lower ATC values.

Tin may be electro-deposited upon a steel base using either an alkaline or an acid electrolyte. An alkaline process is disclosed in U.S. Patent 2,424,472, issued to F. A. Lowenheim et al., on July 22, 1947. Alkaline processes have the disadvantage that they are considerably slower than acid processes, and commercial electroplating lines, therefore, usually employ acid electrolytes. One such electrolyte commonly used is that of U.S. Patent 2,407,579, issued to E. W. Schweikher on September 10, 1946. The process of that patent is commonly known as the "halogen process."

It is an object of our invention to provide from an acid bath electroplated strip of superior quality. It is another object to produce such tinplate by two-stage electroplating adapted to provide positive control of the grade of the tinplate. It is another object to provide a process of electroplating which affords positive control of the tin-

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iron alloy layer. Other objects of our invention will appear in the course of the following description thereof.

In an embodiment of our invention presently preferred by us, the steel base in the form of strip is electrolytically cleaned by conventional methods and is then scrubbed with brushes and rinsed with water. The cleaned strip is given a light pickle in 5% sulphuric acid and is again scrubbed and rinsed with water. The clean strip is then passed through an electroplating cell employing a halogen electrolyte and is then given a flash coating of tin. The term "flash coating" is commonly used to describe a very light tin deposit on the order of .02 to .10 pound of tin per base box of tinplate. The flash coated strip is rinsed in water and dried in a warm air blast and is then rapidly heated to a temperature somewhat above the melting point of tin and quickly quenched. We prefer to quench the reflowed flash coating in water. The flash coated strip is again electrolytically cleaned and rinsed in water, and is then introduced a second time into an electroplating cell containing a halogen electrolyte. There it receives an additional tin deposit sufficient to bring the total weight of tin up to the desired value. The strip from the second electroplating bath is rinsed, dried, reflowed and quenched a second time, the second reflowing and quenching being carried out so as to produce a bright tin coating. Our process, to be described more fully in detail, consistently produces tinplate having ATC values well below the limits for superior quality tinplate.

Certain aspects of our invention will be more clearly understood with reference to the attached figures. FIGURE 1 is a graph showing the effect of changes in the first reflow temperature on the ATC values of tinplate of our invention for two values of the second reflow temperature. FIGURE 2 is a second graph showing the effect of various first reflow temperatures on ATC values of tinplate of several coating weights of our invention. FIGURE 3 is an electromicroscope photomicrograph showing the iron-tin alloy structure of conventional halogen tinplate. FIGURE 4 is an electromicroscope photomicrograph showing the nature of the iron-tin alloy produced by our process on tinplate having a flash coating of insufficient weight. FIGURES 5 through 10 are electromicroscope-photomicrographs showing the iron-tin alloy structure of tinplate of our invention which has been subjected to first reflow temperatures ranging from 490° F. to 705° F. as are set out below those figures.

While we do not know the reason or reasons for the gently improved corrosion resistance of tinplate made by our process, we believe that the nature of the tin-iron alloy layer formed between the steel base and the tin coating is significant. Prior investigators have hypothesized that a continuous pore-free alloy layer is required for maximum resistance of tin plate to corrosion. Iron-tin alloy at the interface between the steel and the tin is formed when the electroplated steel is heated to brighten the tin coating. It is necessary to fuse or flow the tin to brighten it, and at temperatures above the melting point of tin, iron-tin alloy is necessarily formed where those metals are in contact. Our investigation shows, however, that a pore-free alloy layer is not easy to obtain by treatment of tinplate provided with tin coatings of conventional weight from acid electroplating baths. The reason for this lies in the way the iron-tin alloy forms. FIGURE 3 is an electromicroscope-photomicrograph at a magnification of 5,750 diameters of the iron-tin alloy formed on a sample of tinplate of conventional coating weight produced in a halogen bath, and reflowed in the conventional manner. The outer layer of tin was stripped from the sample by known techniques. The iron-tin alloy grows in the form of columnar or prismatic crystals 1-1 which are seen to extend in all directions and intersect or overlay

one another. Between the crystals are areas 2-2 which are bare or entirely uncovered by the alloy. This skeletal or jack-straw alloy structure is clearly not well adapted for effective coverage of the base metal, and prolongation of the conditions under which the alloy crystals grow does not correspondingly increase the alloy coverage of the base if each crystal continues to grow principally in the direction of its long axis, as appears to be the case.

On the other hand, we find that if the base is provided with a very thin or flash coating of tin in an acid bath, and that flash coating is reflowed, the crystalline nature of the alloy layer formed is quite different. FIGURES 5 through 10 are electronmicroscope-photomicrographs at a magnification of 5,720 diameters of six samples which were each given a flash coating of tin amounting to .057 pounds per base box in a halogen bath. The samples were then heated to the temperature indicated below each figure to reflow the tin. FIGURE 5 illustrates the crystalline alloy structure which resulted from reflowing the tin at a temperature of 490° F., which is not far above the 442° F. melting point of pure tin. The iron-tin alloy has grown as somewhat elongated crystals 5-5, but those crystals are relatively flat and appear to grow more or less parallel to the tinplate surface. Between the crystals are areas 6-6 which are not covered by the alloy, but these areas are considerably smaller in extent than the corresponding areas in FIGURE 3. In FIGURE 6, which is a photomicrograph of the iron-tin alloy formed by reflowing the tin at a temperature of 535° F., the individual crystals 7-7 are flat or plate-like and the uncovered areas 8-8 are relatively insignificant. In FIGURE 7, which shows the alloy structure obtained by reflowing at 585° F., the individual crystals 9-9 are even more flat and plate-like, and the uncovered base metal 10-10 is insignificant in extent. The microstructures of FIGURES 8, 9 and 10, illustrate the alloy formed at reflowing temperatures of 620° F., 670° F., and 705° F., respectively. These are seen to be very similar to the structure of FIGURE 7. The alloy crystals 11-11, 12-12, and 13-13, respectively, are flat and overlap. When additional tin is electroplated upon the reflowed flash coating, and the tinplate is heated and quenched a second time, there is no appreciable change in the nature of the iron-tin alloy originally formed.

Tinplate produced as above described displays excellent ATC values, which are the result of the flash coating and reflowing. This conclusion is established by the data of Table I which are the results of six series of tests. Each series comprised four samples of steel, each of which was flash coated with tin in a different amount as is indicated.

Corresponding samples of the various series carried the same coating weights. In series 1, these coatings were not reflowed. The ATC values of all the samples in series 1 were quite high. The samples of series 2 were reflowed at a temperature in the neighborhood of 550° F. The ATC values of the samples are much lower than those of series 1, but are still high, on the order of .2 microamps per sq. cm. The samples of series 3 were reflowed at a temperature of about 780° F. Their ATC values are slightly lower than those of series 2.

The samples of series 4 and 5 were given an additional tin coating sufficient to bring their coating weight up to ½ pound per base box. In series 4 this second coating was not reflowed. The ATC values are seen to be considerably worse than those of series 2 and 3. The samples of series 5 were reflowed at temperatures around 550° F. The ATC values are seen to be superior to those of any of the samples of the four previous series. The samples constituting series 6 were flash plated and reflowed in the same way as those of series 2. They were given an additional tin coating sufficient to bring their coating weight to ½ pound per base box, and were reflowed a second time at a temperature about 550° F. The ATC values of those samples are all in the superior quality. It will be observed that the ATC values of the four samples of series 6 are inversely proportional to the weight of the flash coating of the sample. The sample with the flash coating weight of about .05 pound per base box exhibited an ATC value of .022, which is exceptionally good. The weight of the iron-tin alloy formed, however, was not greater than that for the samples of series 5, which displayed appreciably higher ATC values.

The effect of variation in the first reflow temperature on the corrosion resistance of the tinplate is illustrated in FIGURE 1. The broken line curve of that figure represents tinplate produced with a second reflow temperature of 610° F., and the solid line curve represents tinplate given a second reflow temperature 795° F. Both curves reach a minimum ATC value in the same temperature range of about 600° to 700° F., and that ATC value is in the neighborhood of .01 microamps per square inch which is indicative of exceptional corrosion resistance. FIGURE 1 also shows that practically all the samples there plotted were of superior quality.

FIGURE 2 is similar to FIGURE 1, but includes data for tinplate of three different coating weights ranging from .2 to .58 pounds per base box. Again, all three samples reached minimum ATC values at first reflow temperatures around 700° to 750° F.

TABLE I.—DATA RELATING PREPLATE WEIGHT, ALLOY AND ATC UNDER INDICATED CONDITIONS

Series No.	Sample No.	Sample Description	Preplate Weight Lbs./BB	First Reflow Temperature ° F.	Second Reflow Temperature ° F.	Alloy Weight Lbs./BB	Free Tin Weight Lbs./BB	ATC Microamps/CM ²
1	1	Flash Plated	0.057			0.005	0.050	0.843, 0.763
	8	Not Reflowed	0.043			0.010	0.040	0.793, 0.604
	15		0.028			0.005	0.020	0.521, 0.757
2	22		0.014			0.010		0.453, 0.503
	6	Flash Plated	0.057	560		0.056		0.211, 0.182
	13	Reflowed 550° F.	0.043	575		0.049		0.171, 0.194
	20		0.028	565		0.030		0.199
3	27		0.014	535		0.025		0.316
	7	Flash Plated	0.057			0.060		0.142, 0.199
	14	Reflowed 780° F.	0.043	785		0.041		0.110
	21		0.028	785		0.023		0.180
4	28A		0.014	765		0.016		0.360, 0.341
	3	Flash Plated	0.057			0.004	0.609	0.689, 0.709
	10	Not Reflowed	0.043			0.012	0.530	0.642, 0.524
	17	Plate ½#BB	0.028			0.004	0.476	0.714
5	24	Not Reflowed	0.014			0.010	0.510	0.813
	2	Flash Plated	0.057		555	0.082	0.451	0.124, 0.105
	9	Not Reflowed	0.043		570	0.076	0.448	0.130
	16	Plate ½#BB	0.028		540	0.060	0.445	0.192, 0.167
6	23	Reflowed 550° F.	0.014		535	0.049	0.711	0.180
	4	Flash Plated	0.057	560	545	0.066	0.544	0.022
	11	Reflowed 550° F.	0.043	560	555	0.057	0.519	0.031
	18	Plate ½#BB	0.028	575	555	0.056	0.470	0.062
	25	Reflowed 550° F.	0.014	520	550	0.062	0.396	0.069, 0.068

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The data of Table I indicate that for maximum corrosion resistance, the tinplate should be flash coated in an amount of at least .05 pounds per base box. FIGURE 4 illustrates why lower flash coatings are less effective. It is an electronmicroscope-photomicrograph of the iron-tin alloy resulting from the reflow at 785° F., of a sample given a flash coating of .028 pounds per base box. The photomicrograph is at a magnification of 5,750 diameters. The iron-tin alloy 3-3 is in relatively flat plate-like form, but leaves large uncovered areas 4-4 because it is insufficient in amount. This is true even though the total alloy weight of the sample after receiving its second tin coating may be of the same order as the total alloy weight of tin-plate carrying a considerably heavier flash coating. The data with respect to sample series 6 in Table I supports that conclusion.

We claim:

1. The process of producing electro-tinned strip of improved corrosion resistance comprising plating the steel in an acid electro-plating bath with a flash coating of tin to a weight between about .02 and about .10 pound per base box of tinplate, reflowing the flash coating at a temperature sufficient to convert it into a flat plate-like iron-tin alloy, that temperature being between about 490° F. and about 850° F., electro-plating the reflowed electro-

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tinned steel in an acid electro-plating bath with an additional coating of tin and reflowing that additional coating of tin.

2. The process of claim 1 in which the weight of the flash coating is not less than about .05 pounds per base box of tin plate.

3. The process of claim 1 in which the flash coating is reflowed at a temperature of about 700° F.

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