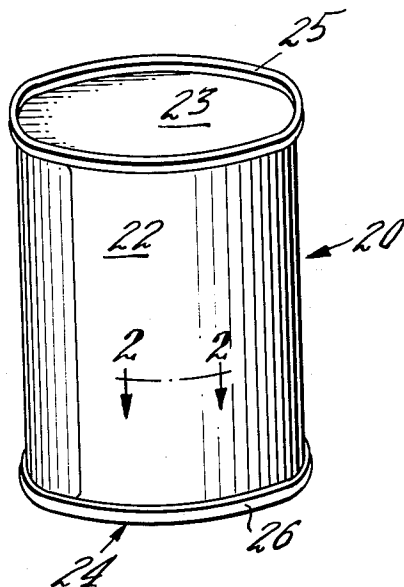


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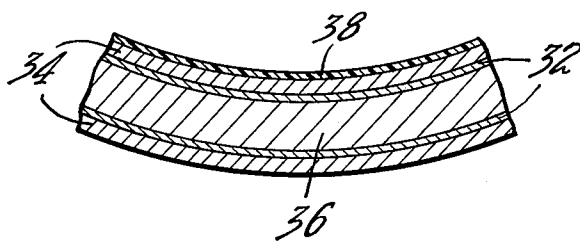
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TIN PLATE HAVING A TIN-NICKEL-IRON ALLOY LAYER  
AND METHOD OF MAKING THE SAME  
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*Fig. 1*



*Fig. 2*



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## TIN PLATE HAVING A TIN-NICKEL-IRON ALLOY LAYER AND METHOD OF MAKING THE SAME

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This invention relates to coated ferrous metal sheet and the method of making the same. More particularly, the invention pertains to ferrous metal sheet covered with a composite coating comprising an outer layer of tin and an intermediate layer of a tin-nickel-iron alloy between the ferrous metal sheet and the tin outer coating, and to the method of making the same.

Although the conventional "tin can," which is essentially made of sheet steel covered with a thin layer of metallic tin, has proved very effective as a container for corrosive products, there have been continuing efforts over the years to improve the corrosion resistance of the cans in order to increase the length of time that corrosive products may be sealed within the containers without spoilage of the product.

With the advent of the electroplating process for coating steel sheet, rather than the hot dip method, the thickness of the tin deposit has decreased significantly. This in turn has increased the susceptibility of the material to corrosion by the products within cans made from the sheet.

Based upon various tests, tin plate having superior corrosion resistance is designated grade A plate, whereas tin plate having average corrosion resistance is designated grade B plate. 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 simpler production of plate which consistently has corrosion resistance equal to or better than commercial grade A plate.

It is therefore an object of this invention to provide a coated steel that will have superior corrosion resistance and a method for making such a material.

Another object is to provide a composite coated ferrous metal sheet for use in the manufacture of metal containers.

An additional object is to provide a ferrous metal sheet having thereon uniformly thin coating layers which increase the corrosion resistance of the sheet.

A further object of this invention is to provide tin plate having corrosion resistance equal to or better than present-day commercial grade A plate even though the tin is deposited from an acid tin plating bath.

A still further object is to provide a corrosion-resistant tin plate which gives cans made therefrom a longer storage or shelf life when packed with products which corrode the can.

Yet another object is to provide a relatively simple and less expensive method of making tin plate having improved corrosion resistance which may be readily incorporated into present-day, commercial tin plate production.

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, disclose a preferred embodiment thereof.

The above and other objects of the present invention are obtained by providing a ferrous basis metal sheet having thereon an outer coating of flow-brightened tin and a tin-nickel-iron alloy layer between the tin outer

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coating and the ferrous basis metal. This ternary alloy is obtained by the co-deposition of tin and nickel over the basis metal and thereafter depositing a layer of tin over the intermediate tin-nickel layer. Subsequently the coated sheet is heated to a temperature sufficient to melt the deposited tin coating and alloy a portion of the basis ferrous metal and tin with the deposited binary alloy coating, thus forming a composite sheet having a bright tin outer coating and a ternary Sn-Ni-Fe alloy intermediate alloy.

Referring to the drawings:

FIG. 1 is a perspective view of a container made from the material of this invention.

FIG. 2 is an enlarged fragmentary sectional view taken substantially along line 2—2 of FIG. 1.

As a preferred or exemplary embodiment of the present invention, FIG. 1 illustrates a metal container, generally designated 20, having a body 22, and upper and lower ends thereon 23, 24 respectively, made integral with the body 22 by any suitable means such as upper and lower double seams 25, 26 respectively.

The material, from which the container is made, is a composite coated metal sheet having a tin-nickel-iron ternary alloy 32, lying between an outer bright tin coating 34 and a low carbon ferrous basis metal 36 (FIG. 2).

It may sometimes be desirable to coat the inner surface of the container 20 with a synthetic resin 38. This would, of course, depend upon the product to be packaged. Among many resins that may be utilized for this purpose are phenolics, epoxies, organosols, vinyls, etc.

The tin-nickel-iron ternary alloy 32 is a thin, substantially continuous layer formed by diffusing a tin-nickel intermediate layer with the basis metal 36 and an as-deposited or matte tin coating, by a method which will be described more fully hereinafter.

Thickness of the ternary alloy 32 will range from  $0.25 \times 10^{-6}$  to  $8 \times 10^{-6}$  inch, with a thickness of  $1 \times 10^{-6}$  to  $6 \times 10^{-6}$  inch preferred. Although the thickness of the alloy is very small, it is thought that its uniformity and excellent coverage of the basis metal 36, together with its metallurgical composition, results in increased corrosion resistance of the composite sheet when compared to conventional tin plate.

Tin plate made according to conventional procedures generally shows that neither the bright outer tin layer nor the tin-iron alloy layer lying between the tin and the steel basis metal are completely continuous. In other words, voids or discontinuities exist in each of these layers. Some of the voids in each layer are in alignment, so that through them basis 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 basis steel exposed. These exposed areas of base steel are, in some products, vulnerable to direct corrosive attack, while in others they accelerate corrosion of tin from the plate surface.

In the present invention the Sn-Ni-Fe alloy layer is substantially continuous over the ferrous metal surface, thus obviating the discontinuity usually encountered with the Sn-Fe alloy layer in conventional tin plate. It is thought that this continuity is primarily due to the presence of nickel in the alloy, which acts to promote uniform nucleation during flow brightening of the as-deposited tin coating, which process will be described in more detail hereinafter.

The composite metal of this invention is produced by providing low carbon ferrous metal sheet, preferably in coil form, which is electrolytically cleaned in a hot alkaline cleaning solution, by means well known to those skilled in the art. Thereafter the strip is pickled in a 5%

sulfuric acid solution to remove any oxides present on the metal surface.

Once the surface contamination has been removed by cleaning and pickling, the strip is rinsed and then immersed in a tin-nickel plating bath having the following nominal composition:

	Oz. per gal.
Stannous chloride anhydrous -----	6.5
Nickel chloride -----	40.0
Ammonium bifluoride -----	7.5
Ammonium hydroxide to pH 2.5.	

Using the above tin-nickel alloy plating solution, a steel sheet, cleaned and pickled according to the method hereinbefore described, was immersed in the electrolyte, whose temperature was maintained at 150° F. A direct current at a density of 25 amperes per square foot was then passed through the electrolyte for 2 seconds, while agitation of the solution was kept at a minimum. A total current of 50 ampere-seconds per square foot was thus passed, resulting in a tin-nickel alloy deposit having a thickness of approximately  $1.1 \times 10^{-6}$  inch.

Alloy anodes may be used in the plating operation. However, the usual procedure, which is what was used in the example, is to employ separate anodes of tin and nickel, using one tin anode for each two nickel anodes. An alternate method is to use only nickel anodes and to maintain the tin concentration in the bath through the periodic addition of anhydrous stannous chloride. Deposition carried out at a current density of from 25 amperes per square foot (a.s.f.) to 600 a.s.f., depending upon the degree of solution agitation, at a temperature of approximately 150° F.

During the coplating operation, the current is passed for a time of 0.025 to 10 seconds, with an optimum plating time of 1 to 4 seconds and 2 seconds preferred. It is readily apparent that the plating time will vary according to the current density employed. This will give a deposit having a nominal composition of 65% tin and 35% nickel. This composition has the nominal atomic percentage of Sn-Ni, with the deposited composition remaining substantially constant over a wide range of operating conditions and solution variables.

The Sn-Ni thickness will range from  $0.275 \times 10^{-6}$  inch to  $5.5 \times 10^{-6}$  inch, with a preferred deposit thickness of  $1.1 \times 10^{-6}$  inch. The thickness range may be produced by passing from 6.25 to 250 ampere-seconds of current per sq. ft.

Although electroplating of the alloy coating is preferred, primarily for economic reasons, other techniques such as vacuum deposition or gaseous deposition may be used.

Subsequent to the deposition of Sn-Ni the strip is rinsed and then immersed in a tin plating bath. Either an alkaline or acid tin plating bath may be used, but the acid type is considered more desirable due to the higher current densities that may be used, and consequently the shorter plating cycles that may be attained.

One of numerous acid tin plating baths that may be used has a composition as follows:

	Oz. per gal.
Stannous sulfate -----	13
Sulfuric acid -----	4
Tartaric acid -----	4
Animal glue -----	0.4-0.8
Cresol or -----	0.8
B-naphthol -----	0.13

The bath is operated at room temperature and pure tin anodes are used in order to minimize the formation of sludge during plating.

Using a current density of from 10 to 400 a.s.f., dependent upon the degree of agitation in the bath, a coating of tin from  $10 \times 10^{-6}$  to  $90 \times 10^{-6}$  inch in thickness is depos-

ited upon the intermediate Sn-Ni layer. Preferably the tin deposit will have a thickness from  $30 \times 10^{-6}$  to  $60 \times 10^{-6}$  inch.

It is possible to deposit the tin coating by such techniques as vacuum or gaseous deposition, although the hereinbefore mentioned electrolytic method is preferred.

Once the composite coating has been deposited upon the ferrous metal strip, the next operation in the process is to flow brighten the coating and thereby produce a bright tin surface, in addition to transforming the intermediate Sn-Ni alloy coating to a Sn-Ni-Fe ternary alloy.

Either resistance or induction heating may be used to heat the coated strip. By means of either heating method the coated metal is heated to a temperature ranging from 450° F., the melting point of tin, to approximately 550° F. The temperature is maintained above 450° F. for a period of 0.01 to 1 second, and preferably 0.25 second.

The flow brightening step causes the tin to flow out into a smooth, bright film and to become firmly anchored to the alloy layer. In addition, the heating during flow brightening results in the formation of the tin-nickel-iron ternary alloy which lies between the bright tin outer coating and the ferrous basis metal.

Although not wishing to be bound by any particular theory as to the reaction in forming the ternary alloy layer during flow brightening, it is thought that some of the melted tin diffuses into the tin-nickel alloy and then some surface iron in contact with the tin-nickel alloy combines with the binary alloy in a second diffusion reaction. The diffusion reactions may proceed simultaneously. During the diffusion process the nickel, in the now ternary alloy, functions as centers for nucleation, thus resulting in uniform nucleation and a uniform alloy layer.

Although satisfactory results are obtainable by flow brightening the 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 tin. It is preferred that the tin remain at the temperature above its melting point for as short a time as possible. 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.

One test which is used in determining the quality of tin plate is the alloy-tin-couple test or, as it is most commonly called, the ATC test. Attention is given to the electrochemical factors important to tin plate corrosion in this test in which steel is protected from corrosion by coupling with tin. The rate of detinning or corrosion is determined by the galvanic couple current and is measured in microamperes per square centimeter. ATC measurements for typical electrolytic tin plate will generally range from 0.02 to 0.30 microamperes per square centimeter, with the grade A plate having the lower values and grade B plate, usually resulting from commercial acid tin plating procedures, having the higher values. When tin plate made according to the present invention, even plate on which the tin was deposited from an acid plating bath, was subjected to the ATC test, the values ranged from only 0.015 to 0.050 microampere per square centimeter. Thus, with plate made according to this invention, it is possible to obtain ATC values even lower than for conventional grade A tin 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 form, construction and arrangement of the parts and that changes may be made in the steps of the method described and the order of accomplishment without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the form hereinbefore described being merely a preferred embodiment thereof.

We claim:

1. A coated ferrous metal sheet, comprising: a ferrous basis metal; an inner coating over and in contact with said basis metal consisting essentially of a ternary alloy of tin, nickel, and iron; and an outer coating of tin over and in contact with said ternary alloy, said ternary alloy being produced by the diffusion of an intermediate deposit of a binary tin-nickel alloy with said ferrous basis metal and said outer tin coating while said tin coating is molten.
2. The sheet of claim 1 wherein said ternary alloy coating has a thickness from  $0.25 \times 10^{-6}$  to  $8 \times 10^{-6}$  inch.
3. The sheet of claim 2 wherein said ternary alloy coating has a thickness from  $1 \times 10^{-6}$  to  $6 \times 10^{-6}$  inch.
4. The sheet of claim 2 wherein said outer tin coating has a thickness from  $10 \times 10^{-6}$  to  $90 \times 10^{-6}$  inch.
5. A method of manufacturing a composite coated ferrous metal sheet, comprising the steps of: depositing a layer of a tin-nickel binary alloy on a ferrous basis metal sheet; maintaining said binary alloy substantially in its as deposited condition while depositing a layer of tin over said binary alloy, said tin deposit having a thickness greater than said deposit of tin-nickel alloy; heating said coated ferrous sheet to a temperature above  $450^\circ \text{F.}$ , for a time sufficient to melt said tin coating and to diffuse iron from said basis metal into throughout said binary alloy while said basis metal and said binary alloy are solid to form a tin-nickel-iron ternary alloy over and in contact with said basis metal; and thereafter cooling said coated sheet to a temperature below the melting point of tin to solidify said tin as a surface coating over and in contact with said ternary alloy.

6. The method of claim 5 wherein said tin-nickel alloy is electrodeposited.

7. The method of claim 5 wherein said tin-nickel alloy is deposited to a thickness from  $0.275 \times 10^{-6}$  to  $5.5 \times 10^{-6}$  inch.

8. The method of claim 5 wherein said tin is electrodeposited.

9. The method of claim 5 wherein said tin is deposited to a thickness from  $10 \times 10^{-6}$  to  $90 \times 10^{-6}$  inch.

10. The method of claim 5 wherein said ternary alloy has a thickness from  $0.25 \times 10^{-6}$  to  $8 \times 10^{-6}$  inch.

11. The method of claim 5 wherein said bright tin has a thickness from  $10 \times 10^{-6}$  to  $90 \times 10^{-6}$  inch.

12. The method set forth in claim 5 wherein said coated ferrous sheet is maintained at said temperature above  $450^\circ \text{F.}$  for a period of from 0.01 to 1 second.

13. The method set forth in claim 12 wherein said coated ferrous sheet is maintained at a temperature between  $450^\circ \text{F.}$  and  $550^\circ \text{F.}$

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