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METHOD OF MANUFACTURING NICKEL-PLATED STEEL PLATE

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This invention relates to a method of producing a nickel-plated steel plate in which the plating is very thin and which is especially high in anticorrosiveness, solderability, lacquerability and workability.

Heretofore, the tin plated articles have been mostly used for food cans and miscellaneous other cans. Tin plates have excellent properties in various points. Steel plates electroplated with any other metal than tin have never been used for materials for making cans, because there has been found nothing superior to tin in respect of anticorrosiveness, solderability, lacquerability, poisonlessness and workability. For example, in nickel-plating and the like, in order to obtain sufficient anticorrosiveness, it is necessary to make the plating more than several microns thick and it is usual to make it more than 10 microns thick. Such thick nickel-plating is not only disadvantageous in economy but is also low in workability. From the view point of workability and economy, the thinner the plating, the more preferable it is. However, if the plating is too thin, its anticorrosiveness will be lower.

An object of the present invention is to provide a method of producing a plated steel plate in which the plate is very thin and which is advantageous in economy and high in workability.

Another object of the present invention is to provide a method of producing a very thinly plated steel plate which is high in not only anticorrosiveness but also heatproofness, solderability, poisonlessness and lacquerability.

For the above mentioned objects, according to the present invention, a steel plate is first very thinly plated with nickel or nickel alloy and then the thus plated steel sheet is further subjected to a surface treatment for coating its whole surface with a passivated film, including not only the nickel or nickel alloy surface, but also such points which are low in anticorrosiveness as pinholes.

A nickel-plating of steel sheet may be carried out, for instance, with nickel or such alloy as of Ni-Fe or Ni-Sn about 0.04 to 0.3 micron thick according to conventional methods. Then, the nickel plated sheet is subjected to an electrochemical treatment as characterized by the present invention.

The surface treatment specified by the present invention shall be detailed in the following. The treating solution to be used in the surface treatment is an aqueous solution of 1 to 5% sodium salt or potassium salt of dichromic acid or chromic acid as alone or mixed, or chromic anhydride. It is effective and economical to keep its concentration within a range of 1 to 5%. That is to say, when the concentration is less than 1%, the solution will be so dilute that it will be difficult to obtain the expected effect. When the concentration is more than 5%, the solution will be uneconomical. The optimum time for the cathode-treatment of the material to be treated in the treating solution is 1 to 10 seconds at a current density of 1.5 to 4.0 A./dm.² from the viewpoint of the effect and industrial economy. Above the upper limit of this range, the treatment will be uneconomical. Below the lower limit, the effect will be very low.

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In the treating method according to the present invention, the cathode-treatment of the plated product is sufficient but, if the anode-treatment of the plated product is additionally carried out following the above mentioned cathode-treatment depending on the plated state, more favorable results may be obtained.

However, the anode-treatment is to be carried out for a treating time of less than 1 second at a current density of 0.1 A./dm.² in the above mentioned treating solution. With a current density and treating time exceeding these values, there will be rather an unfavorable influence on the plated layer. The anticorrosiveness and lacquerability of the thus obtained very thinly nickel-plated or nickel alloy-plated steel plate is as high or higher than that of a tin plate. The solderability thereof is not lower than of the tin plate. The plating according to the present invention is so thin that the workability is high and the cost is low. Even when it is exposed to air at 600° C. for about 100 hours, it will retain sufficient heatproofness. The surface layer of such plate is thought to consist of a dense oxidated film and is well passivated.

The comparison of the anticorrosiveness of the thus nickel-plated steel plate with that of a tin plate is as in the following table. For information, in the table are also given those of a steel plate and a steel plate plated with Ni 0.06 micron thick but not passivated.

RESULTS OF SALT WATER SPRAY TESTS

[Tested for 3 hours. Numerals in the table represent rusted areas in percent]

Samples	Steel plate	Tin plate		0.06 micron nickel-plated steel plate	
		#25	#50	Product of the present invention	Not surface-treated
Rusted areas in percent...	90-100	8	3	0.5	7-10

Not only Ni but also Cr and Sn are considered to be poisonless plating metals for food cans and the like. However, the lustrous plating of Sn is difficult. In order to produce luster, it is necessary to melt the plating after it is made. A thickness of at least about 0.5 micron is required therefor. Thus, a very thin plating is difficult.

On the other hand, when a steel plate plated with Cr or a Cr-Fe alloy about 0.04 to 0.3 micron thick, and thereupon electrochemically treated on the surface was subjected to a salt water spray test, an entirely contrary effect was obtained, showing a reduced anticorrosiveness.

EXAMPLES

(1) Ni-plating

- 55 Nickel-plating solution:
 Nickel sulphate, g./l. ----- 330
 Nickel chloride, g./l. ----- 45
 Boric acid, g./l. ----- 35
 Plating conditions:
 60 Temperature, ° C. ----- 50
 Current density, A./dm.² ----- 6
 Time, seconds ----- 5
 Surface treating solution:
 Aqueous solution of 2.0% sodium dichromate.
 65 Surface treating conditions:
 Cathode-treatment at 2.5 A./dm.² for 3 seconds.

The opposed electrodes were made of very mild steel plate. By the above-mentioned method there have been produced nickel-platings of various thickness which were immediately subjected to the above mentioned surface treatment.

In testing the properties of various samples of the plated steel sheets prepared by the above mentioned method the following results have been achieved.

In the salt water spray test for 3 hours, only 0.5% of the area was averagely rusted and the anticorrosiveness of the products was proved to be higher than of a tin plate.

The Erichsen value and tensile strength of the samples were exactly the same as of the original plate. The mechanical properties were never impaired by plating. In this respect, the thus nickel-plated steel plates were superior to the tin plate.

The expansion and adhesiveness of a lacquer on the samples were investigated. Though it was difficult to quantitatively indicate them, the lacquerability of the products was evidently higher than of the tin plate.

The results of the soldering tests by the normal method with a solder of Sn:Pb=30:70 were as in the following table. An aqueous solution of 10% zinc chloride was used for the flux.

Sample	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Thickness of Ni plating in μ -----	0.01	0.02	0.04	0.06	0.08	0.10	0.20	0.30	0.35
Solder rise in mm-----	14.0	20.5	18.0	21.0	21.2	20.5	21.0	21.0	21.5
Adhesiveness in kg./in-----	7.0	9.0	11.0	15.5	18.0	20.0	22.3	24.2	24.5

Values substantially the same as in the case of the tin plate were obtained.

According to the results of experiments, when the thickness of the nickel plating was less than 0.02 micron, the anticorrosiveness was not sufficient. When the thickness was more than 0.3 micron, not only the plating was disadvantageous in economy but also the workability was somewhat reduced. The most preferable thickness was about 0.06 to 0.15 micron.

(2) Nickel-plating

The steel sheet nickel-plated according to the method of Example 1 was subjected to the following surface treatment.

Surface treating solution:

Aqueous solution of 2 to 3% potassium dichromate.

Temperature of bath, ° C. ----- 40 to 50

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 seconds.

Anode treatment at 0.1 A./dm.² for 1 second.

(3) Nickel-plating

The steel sheet nickel-plated according to the method of Example 1 was subjected to the following surface treatment.

Surface treating solution:

Aqueous solution of 2 to 4% chromic anhydride (CrO₃).

Temperature of bath, ° C. ----- 40 to 60

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 seconds.

(4) Nickel-plating

The steel sheet nickel-plated according to the method of Example 1 was subjected to the following surface treatment.

Surface treating solution:

Aqueous solution of 2 to 4% mixed solution of sodium dichromate and sodium chromate.

Temperature of bath, ° C. ----- 40 to 50

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 to 5 seconds.

Anode treatment at 0.1 A./dm.² for 1 second.

(5) Nickel-plating

The steel nickel-plated according to the method of Example 1 was subjected to the following surface treatment.

Surface treating solution:

Aqueous solution of 2 to 4% mixed solution of potassium dichromate and potassium chromate.

Temperature of bath, ° C. ----- 40 to 50

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 to 5 seconds.

Anode treatment at 0.1 A./dm.² for 1 second.

The tests of the products prepared according to the methods in Examples 2, 3, 4 and 5 showed the substantially same results as in Example 1.

(6) Ni-Sn alloy plating

Composition of the plating bath:

	G./l.
Tin chloride -----	40
Nickel chloride -----	300
Acidic ammonium fluoride -----	55

The bath was adjusted to be of a pH of 2.5 with ammonia water.

Plating conditions:

Bath temperature ----- 60° C.

Current density ----- 3 A./dm.²

Anode ----- Alloy of Sn:Ni=6:4.

Time ----- 10 seconds.

Thickness of plating ----- 0.18 micron.

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 seconds.

Anode treatment at 0.1 A./dm.² for 1 second.

The product of the present invention made by the above method had the following properties:

Anticorrosiveness: In the salt water spray test for 3 hours, only 0.5 to 1.0% of the area was rusted.

Workability: Both Erichsen value and tensile strength of the product were not different from those of the original plate.

Lacquerability: The high temperature baking on the product was possible. The lacquerability of the product was higher than of a tin plate.

Solderability: When an aqueous solution of zinc chloride was used for the flux, the solderability of the product was not different from that of the tin plate.

(7) Ni-Fe alloy plating

Composition of the plating bath:

	G./l.
Nickel sulphate -----	135
Iron sulphate -----	15
Ammonium chloride -----	30
Boric acid -----	30
pH, 4 to 5.	

Plating conditions:

Bath temperature ----- 60° C.

Current density ----- 2 A./dm.²

Anode (A) ----- Alloy of Fe:Ni=64:36

Anode (B) ----- Alloy of Fe:Ni=55:45

Time ----- 20 seconds.

Thickness of plating (A) -- 0.15 micron.

Thickness of plating (B) --- 0.14 micron.

Compositions of anodes and platings in percent:

	Anodes		Electrodeposits of Platings	
	Fe	Ni	Fe	Ni
(A) -----	64	36	81.2	18.8
(B) -----	55	45	20.1	79.9

Surface treating conditions:

Cathode treatment at 3 A./dm.² for 3 seconds.

Anode treatment at 0.1 A./dm.² for 1 second.

Thus, the composition of the electrodeposit of the Fe-Ni alloy plating was difficult to adjust. However, when the electrodeposit was surface-treated according to the present invention, a favorable anticorrosiveness was shown. That is to say, in the salt water spray test for 3 hours, only 10 and 0.5% of the area were rusted in (A) and (B), respectively.

Further, the workability of the product was the same as of the original plate. The lacquerability of the product was higher than of the original plate.

As evidently seen from the above mentioned, the plated steel plate of the present invention consists of a layer of Ni or a layer composed mainly of Ni ranging from 0.02 to 0.3 micron thick on a steel plate and a passivated film of the surface of said layer. This structure seems to render the plated sheet the features of being high in anticorrosiveness, solderability, lacquerability, workability and heatproofness; that is, properties the same as or better than of a tin plate. On the other hand, as it may be much cheaper prepared than the latter, it is a very advantageous material for making cans.

What is claimed is:

1. A method of producing a very thinly nickel-plated steel sheet comprising the steps of plating a steel sheet with a substance selected from a group consisting of nickel and nickel base alloy about 0.04 to 0.3 micron thick, cathode-treating said nickel-plated steel sheet at a current density of 1.5 to 4.0 A./dm.² for from 1 to 10 seconds in an aqueous solution of from 1 to 5% of a compound selected from a group consisting of sodium dichromate and potassium dichromate.

2. A method of producing a very thinly nickel-plated steel sheet comprising the steps of plating a steel sheet with a substance selected from a group consisting of nickel and nickel base alloy about 0.04 to 0.3 micron thick, cathode-treating said nickel-plated steel sheet at a current density of 1.5 to 4.0 A./dm.² for from 1 to 10 seconds in an aqueous solution of from 1 to 5% of a mixture of sodium dichromate and sodium chromate.

3. A method of producing a very thinly nickel-plated steel sheet comprising the steps of plating a steel sheet with a substance selected from a group consisting of nickel and nickel base alloy about 0.04 to 0.3 micron thick, cathode-treating said nickel-plated steel sheet at a current density of from 1.5 to 4.0 A./dm.² for from 1 to 10 seconds in an aqueous solution of from 1 to 5% of a mixture of potassium dichromate and potassium chromate.

4. A method of producing a very thinly nickel-plated steel sheet comprising the steps of plating a steel sheet with a substance selected from a group consisting of nickel and nickel base alloy about 0.04 to 0.3 micron thick, cathode-treating said nickel-plated steel sheet at a current density of from 1.5 to 4.0 A./dm.² for from 1 to 10 seconds in an aqueous solution of from 1 to 5% of chromic anhydride.

5. A method claimed in claim 1, in which a nickel-plated steel sheet is anode-treated at a current density of 0.1 A./dm.² for 1 second after the cathode-treatment.

6. A method claimed in claim 2 in which a nickel-plated steel sheet is anode-treated at a current density of 0.1 A./dm.² for 1 second after the cathode-treatment.

7. A method claimed in claim 3 in which a nickel-plated steel sheet is anode-treated at a current density of 0.1 A./dm.² for 1 second after the cathode-treatment.

8. A surface treating method for nickel alloy-plated steel plates characterized in that a steel plate plated with any of nickel and an alloy composed mostly of nickel is cathode-treated at a current density of 1.5 to 4.0 A./dm.² for 1 to 10 seconds in an aqueous solution of 1 to 5% of any of sodium salt and potassium salt of any of dichromic acid and chromic acid as alone and mixed.

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