

[54] SURFACE TREATMENT OF TINPLATE FOR
IMPROVING SULFUR RESISTANCE

[75] Inventors: Shunichi Harada; Takahisa
Yoshihara, Chiba, both of Japan

[73] Assignee: Kawasaki Steel Corporation, Kobe,
Japan

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Primary Examiner—Ralph S. Kendall

Assistant Examiner—Charles R. Wolfe, Jr.

[57] ABSTRACT

Surface treatment of tin-plated steel for food can and the like for improving sulfur resistance, by applying chromate treatment on the plated tin, immediately after electroplating thereof, in an aqueous solution containing 6-valent chromium ions, and then heating at a temperature above 100°C.

5 Claims, No Drawings

SURFACE TREATMENT OF TINPLATE FOR IMPROVING SULFUR RESISTANCE

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to surface treatment of tinplate for improving sulfur resistance, and more particularly to surface treatment of tin-plated steel for food can and the like for improving sulfur resistance thereof.

2. Description of the Prior Art

Tin-plated steel for food can has been produced by electroplating tin on steel sheet, applying reflow treatment to the thus plated sheet, and then applying a suitable chemical treatment thereto.

More particularly, cold-rolled low-carbon steel sheet basis sheet (to be referred to simply as "basis sheet", hereinafter) is pretreated by cleaning in an alkaline solution, pickling with an inorganic acid solution, and rinsing with cold or hot water. Tin is electroplated on the pretreated basis sheet by using the basis sheet as a cathode in an electroplating bath. In most cases, reflow treatment is applied by resistance heating by feeding electric current therethrough, for improving brightness. Thereafter, the so-called "chemical treatment" is applied by electrolysis in an aqueous solution containing 6-valent chromium ions.

The conventional tin-plated steel has a shortcoming in that, when being used as food can, it is susceptible to blackening due to sulfurization, which tends to degrade the appearance and the commercial value of the can and canned goods. Such blackening is caused by sulfur-containing foods, such as fish, meat, powdered milk, other protein rich foods, green peas, asparagus, and the like. Accordingly, there is a pressing need for improving the sulfur resistance of tinplate for food can.

Therefore, an object of the present invention is to provide tinplate with a high sulfur resistance, by applying an improved treatment thereto. The inventors noticed that the conventional chemical treatment after the reflow is not effective in providing a desired level of sulfur resistance, and carried out years of studies and experiments to overcome the shortcoming. As a result, the inventors have succeeded in developing a new treatment which overcome the shortcoming.

In addition to the aforesaid foodstuff, fruits and juices (to be referred to as juices, hereinafter) containing organic acids are also canned by using tin-plated steel. Such juices tend to dissolve tin therein. To prevent food poisoning, the concentration of tin in the juices is restricted by law to be below a certain level; for instance, below 150 ppm in Japan, below 250 ppm in England, and below 300 ppm in the U.S.A. On the other hand, the presence of tin in the juice acts to preserve vitamin C therein, to prevent the juice from discoloring, and to enhance the refreshing taste of the juice. Thus, it is generally believed that about 80 ppm of tin in the juice is desirable, although the actual desirable tin concentration varies depending on the kind of juices.

The conventional tinplate tends to excessively dissolve in the juice, so that a suitable coating has been applied to the inside of food can for suppressing the dissolution of tin. Such coating means an additional cost, and it also appears to be detrimental to the taste of the food.

Therefore, another object of the present invention is to provide tin-plated steel whose tin is difficultly dis-

solvable in juices, so as to avoid food poisoning while ensuring excellent taste of solid or juicy foodstuff to be canned thereby.

The surface treatment according to the present invention also provides a tinplate having excellent physical and chemical properties: namely, low porosity, high brightness (in the case of reflowed tinplate), good lacquer adhesion, appropriate solderability, and excellent stability as determined by thiocyanate test and iron dissolving test.

SUMMARY OF THE INVENTION

The present invention provides a surface treatment of tinplate for improving sulfur resistance, which tinplate is particularly suitable for food can, by applying chromate treatment on tin film, immediately after the tin is electroplated on a basis sheet, in an aqueous solution containing 6-valent chromium ions, and then heating at a temperature above 100°C.

With the present invention, the so-called chemical treatment may be further applied to the tinplate after the last mentioned heating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In practising the treatment of the present invention, a basis sheet, i.e., cold-rolled low-carbon steel sheet, is electrolytically cleaned, rinsed with water, pickled with acid, and again rinsed with water in the same manner as in the case of conventional pretreatment for tin electroplating. It is conventional to reflow tin film immediately after the electroplating thereof. On the other hand, according to the present invention, chromate film is formed on the tin layer immediately after the electroplating of the latter, by means of chromate treatment.

The chromate treatment of the present invention may be carried out, for example, under the following conditions.

Bath composition	aqueous solution of sodium dichromate at 10 to 50 g/l
pH	3.0 to 5.0
Temperature	room temperature to 70°C
Current density	0.1 to 10 A/dm ²
Treating time	0.1 to 3 seconds
Polarity	Cathodic electrolysis by using tinplate as cathode

The chromate treatment may also be effected by dipping the tinplate in a solution of chromic acid.

After the chromate film is formed, the tinplate is heated at 100°C to 400°C, preferably at 280°C to 350°C, for instance by resistance heating with an electric current fed therethrough. Upon completion of the heating, the tinplate is cooled. The heating at below 100°C does not produce any noticeable improvement of sulfur resistance of the tinplate, while the heating at a temperature above 400°C results in an unacceptably poor formability thereof. The heating temperature of higher than 280°C enhances the sulfur resistance, but the heating at above 350°C tends to deteriorate the formability of the tinplate.

Instead of using the tinplate as a cathode, it may also be used as an anode or alternately as a cathode and anode in the chromate treatment of the invention. In this case, the sulfur resistance is enhanced, but in the

case of reflowed tinplate, the brightness is poor due to the formation of oxide layer thereon prior to the reflow treatment. Accordingly, if high brightness is required, the last mentioned chromate treatment is not suitable.

The reason why the sulfur resistance can be improved by the treatment of the present invention is not fully understood yet. However, the inventors have found out through tests that the treatment of the invention provides a better sulfur resistance than that which is obtained by anodic treatment of tinplate in a solution of sodium carbonate, sodium dichromate. The anodic treatment with sodium carbonate will produce an oxide film, but such an oxide film will not be converted into a strongly sulfur resistant film upon heating. It may be assumed that the presence of a small amount of chromium oxide on the electroplated tin film acts to form a surface layer which has a high sulfur resistance.

With the present invention, it is also possible to apply the so-called chemical treatment to the tinplate after the aforesaid heating, which tinplate has a kind of tin-chromium double layer. The chemical treatment will further enhance the sulfur resistance and suppress excessive dissolution of tin. This chemical treatment means the conventional cathodic treatment in an aqueous dichromate solution which is applied immediately after the reflow treatment.

The mechanism for the improvement of the tin dissolution by the aforesaid chemical treatment is not clearly understood yet. Test result indicates that the chemical treatment provides a much higher sulfur resistance than that which is obtained by the aforesaid oxide

film formed by the anodic treatment in sodium carbonate solution. Accordingly, the deposit of a small amount of chromium oxide before and after the heating seems to produce a surface layer which has ability of suppressing any excess dissolution of tin.

Comparative tests were made on various properties of tinplates processed by the treatment of the present invention and those of conventional tinplates. The tests covered sulfur resistance, tin dissolution, porosity (pinholes), thiocyanate tests, iron dissolution, oxide film, solderability in terms of capillary rise, lacquer adhesion, and surface brightness. The result is shown in Table 1. The following eight kinds of test specimens, i.e., 1, 2, 2', 2'', 3, 4, 5, and 6, were used in the tests.

1. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb, or pound/base box) were chromate treated by cathodic electrolysis in a solution of sodium dichromate, and then reflow treatment was applied by resistance heating at 290°C by directly applying electric current thereto.

2. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were chromate treated by cathodic electrolysis in a solution of sodium dichromate, and reflow treatment was applied by resistance heating at 290°C by directly feeding electric current thereto, and then cathodic chemical treatment was applied in a sodium dichromate solution of 30 g/l concentration at 45°C for 1 second while keeping current density at 5 A/dm².

2'. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were chromate treated by cathodic electrolysis in a solution of sodium dichromate, and

Table 1

Specimen treatment		Chromate treatment before reflow					Sulfur resistance	Thiocyanate test (mg/dm ²)	Porosity (pinholes/cm ²)	ISU in iron dissolving test (μg/cm ²)
		Concentration (g/l)	pH	Temperature (°C)	Current density (A/dm ²)	Treating time (sec)				
Tinplate processed by the treatment of the invention	(1)	10	4.5	45	5.0	1	SB	4.73	100-150	—
		30	"	"	"	"	DB	4.63	"	—
		50	"	"	"	"	DB	4.01	50-100	—
		70	"	"	"	"	DB	4.25	"	—
		30	3.0	"	"	"	DB	4.25	30-50	—
		"	4.0	"	"	"	DB	4.57	50-100	—
		"	5.0	"	"	"	DB	4.73	"	—
		"	6.0	"	"	"	DB	4.57	"	—
		"	4.5	25	"	"	DB	4.17	"	—
		"	"	35	"	"	DB	4.09	"	0.30
	(2)	"	"	45	"	"	DB	4.82	"	0.51
		"	"	55	"	"	DB	4.72	"	0.48
		"	"	65	"	"	DB	5.46	30-50	—
		"	"	75	"	"	DB	5.54	"	—
		"	"	45	1.0	"	DB	4.20	"	—
		"	"	"	2.5	"	DB	4.01	"	—
		"	"	"	5.0	"	DB	4.09	"	—
		"	"	"	10.0	"	DB	4.57	"	—
		30	"	30	5.0	"	NB	2.31	0-5	0.58
		"	"	45	"	"	NB	2.31	"	0.51
		50	"	30	"	"	NB	0.94	"	0.51
Tinplate processed by the treatment of the invention	(2)'	"	"	45	"	"	NB	1.91	"	0.29
		30	"	"	0.25	0.2	DB	3.60	"	—
		"	"	"	0.5	"	NB	3.46	5-10	—
		"	"	"	1.0	"	NB	3.13	0-5	—
		"	"	"	2.5	"	NB	2.85	"	—
		"	"	"	5.0	"	NB	2.50	"	—
		30	0.7	80	Dipped	"	DB	4.32	20-30	—
		Tinplate → Cathode-Anode electrolytic chromate → reflow					(3)	NB	4.98	10-20
		Tinplate → Anode electrolytic chromate → reflow					(4)	NB	5.38	150 or more
										—

Table 1 - Continued

Specimen treatment	Chromate treatment before reflow					* Sulfur resistance	Thio-cyanate test (mg/dm ²)	Porosity (pinholes/cm ²)	ISU in iron dissolving test (μg/cm ²)
	Concentration (g/l)	pH	Temperature (°C)	Current density (A/dm ²)	Treating time (sec)				
Reference	Conventional tinplate (without chemical treatment)				(5)	HB	6.60	150	0.55
	Conventional tinplate (with chemical treatment)				(6)	EB	4.01	or more	0.55
	Conventional tinplate (with chemical treatment)				(6)	HB	4.21	20-30	0.55

*
 NB: No blackening at all
 DB: Hardly detectable spotty blackening
 SB: Slight spotty blackening
 EB: Slight blackening over entire surface
 HB: Heavy blackening

Table 1A

Specimen treatment	Sulfur* resistance	Tin dissolution			Oxide film (mc/ cm ²)	Solder capil- lary rise (mm)	Lacquer adhe- sion	Bright- ness (%)	Overall evalua- tion						
		(Condi- tion)	mg	ppm											
Tinplate processed by the treatment of the invention	Tin plating ↓ Cathodic electrolytic chromate treating ↓ Reflow	SB	A	14.6	146	0.96	12	Very good	99	Fairly good					
		DB		13.0	130	0.89	12	"	97	Good					
		DB		13.3	133	0.85	13	"	98	Good					
		DB		13.2	132	0.92	10	"	93	Not good					
		DB	A	13.8	138	0.96	12	"	102	Good					
		DB		14.0	140	1.06	12	"	101	Good					
		DB		14.1	141	0.99	12	"	102	Good					
		DB		14.3	143	0.85	10	"	100	Good					
		DB	A	13.7	137	0.99	12	"	98	Good					
		DB		15.6	156	0.96	13	"	100	Good					
		DB		12.5	125	0.92	12	"	99	Good					
		DB		14.6	146	0.92	12	"	96	Good					
		DB		14.4	144	0.89	11	"	92	Fairly good					
		DB		14.1	141	0.81	11	"	93	Fairly good					
		DB	A	15.0	150	0.98	12	"	100	Good					
		DB		14.4	144	0.99	12	"	98	Good					
		DB		10.9	109	0.81	12	"	99	Good					
		DB		14.3	143	0.71	13	"	98	Good					
		NB	A	9.0	90	0.39	14	"	96	Good					
		NB		8.6	86	0.39	15	"	99	Good					
		NB		8.8	88	0.35	10	"	96	Good					
		NB		8.4	84	0.32	8	"	93	Fairly good					
		DB	B	2.5	25	1.27	13	"	101	Good					
		NB		1.8	18	0.97	12	"	99	Good					
		NB		1.5	15	0.54	"	"	99	Good					
		NB		0.8	8	0.64	"	"	97	Good					
		NB		1.0	10	0.48	"	Fairly bad	91	Fairly bad					
		(2)''	DB	B	2.3	23	1.03	12	Fairly bad	100	Fairly good				
Tinplate → Cathode-Anode electrolytic					(3)	NB	B	—	—	1.60	16	ood	62	Bad	
chromate → reflow															
Tinplate → Anode electrolytic chromate → reflow					(4)	NB		—	—	1.73	14	ood	52	Bad	
Reference	Conventional tinplate (without chemical treatment)					(5)	HB	A	15.3	153	1.66	14	ood	100	Bad
	Conventional tinplate (with chemical treatment)					(6)	EB		14.1	141	1.88	15	ood	100	Bad
	Conventional tinplate (with chemical treatment)					(6)	HB	B	5.5	55	1.00	12	ood	100	Bad

*
 NB: No blackening at all
 DB: Hardly detectable spotty blackening
 SB: Slight spotty blackening
 EB: Slight blackening over entire surface
 HB: Heavy blackening

reflowing treatment was applied by resistance heating at 290°C by directly feeding electric current thereto, and then cathodic chemical treatment was applied in a sodium dichromate solution with a concentration of 30 g/l at 45°C for 1 second while keeping current density at 1 A/dm².

2". Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were chromate treated by dipping them in a solution of chromic acid (30 g/l) at 80°C, and reflow treatment was applied by resistance heating at 290°C by directly feeding electric current thereto, and then cathodic chemical treatment was applied in a sodium dichromate solution with a concentration of 30 g/l at 45°C for 1 second while keeping current density at 1 A/dm².

3. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were chromate treated by anodic-cathodic electrolysis (cathodic treatment at 5 A/dm² for 1 second and anodic treatment at 1 A/dm² for 0.25 second) in a sodium dichromate solution (30 g/l), and then reflow treatment was applied by resistance heating at 290°C by directly feeding electric current thereto.

4. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were chromate treated by anodic electrolysis (1 A/dm², 1 second) in a sodium dichromate solution (30 g/l) at 45°C, and then reflow treatment was applied by resistance heating at 290°C by directly feeding electric current thereto.

5. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were reflow treated by resistance heating at 290°C by directly feeding electric current thereto.

6. Tin-deposited steel sheets (with tin deposit of 0.50 lb/bb) were reflow treated by resistance heating at 290°C by directly feeding electric current to them, and then chemical treatment was applied by cathodic electrolysis (5 A/dm², 1 second) in a sodium dichromate solution (30 g/l) at 45°C.

The process for each test was as follows.

Sulfur resistance test

Specimens were dipped in a test solution at 95°C for 20 seconds, and blackening due to sulfurization was checked with bare eyes. The test solution contained 8 g/l of potassium polysulfide and 2 g/l of sodium hydroxide. The result was classified into the following 5 grades.

NB: No blackening at all

DB: Hardly detectable spotting blackening

SB: Slight spotty blackening

EB: Slight blackening over entire surface

HB: Heavy blackening

Thiocyanate test

This test is to quantitatively determine the amount of iron ions which are dissolved in a corroding solution from exposed steel surface through the pinholes of the tin layer, by converting the iron ions into red thiocyanate for analysis by a colorimeter. The corroding solution contained the following.

ammonium thiocyanate	20 g/l
acetic acid	10 g/l
hydrogen peroxide solution (20 vol. %)	10 g/l

Rectangular test specimens of 6 cm by 8 cm were prepared and cleaned by organic solvent, such as trichloroethylene and carbon tetrachloride. Cut edges of

the test specimens were tightly sealed by wax, and then dipped in the above corroding solution (250 cc) at 20°C to 25°C for 15 minutes. The color of the solution after the dipping was determined by a colorimeter. The concentration of iron ions, in terms of mg/dm², was determined on the basis of a separately prepared calibration curve.

Porosity (pinhole) test

Specimens were dipped in a 10% chromic acid solution at 90°C for 5 minutes. After thoroughly washed with water, the specimens were dipped in a distilled water with a pH 4.5 at 95°C for 40 minutes. Thereafter, the number of rust points was counted with bare eyes.

Iron solution test (iron solution value ISV)

This test determines the amount of iron dissolved in a corroding solution under the conditions in which tin is slightly more anodic than iron. The corroding solution contained the following.

sulfuric acid	2.18 N	23 cc
ammonium rhodanate	40 g/l	25 cc
hydrogen peroxide solution	3%	2 cc
Total		50 cc

Circular test specimens with an effective surface area of 2,581 mm² were punched out, anodically treated in a 0.5% aqueous solution of sodium carbonate at 1.5A for 30 seconds, washed with water, and dried by using acetone.

The test specimen was placed in a 150 cc glass vessel containing the aforesaid corroding solution, and a threaded plastics lid was so turned as to press the test specimen. An iron-free gasket was used to prevent any leakage.

At the time of colorimeter measurement, 2 cc of hydrogen peroxide solution was added. The aforesaid corroding solution was forced to come in contact with 2,581 mm² surface area of the test specimen at 26.7°C for 2 hours. Then, the amount of iron dissolved, in terms of µg/cm², was determined by the colorimeter.

As the amount of iron thus determined increases (large ISV), the tin-plated steel sheet becomes more susceptible to corrosion.

Tin dissolving test

Specimens were vertically dipped in 100 cc of a corroding solution at 25°C for a given time period. The difference of the weight of the test specimen before and after the dipping was measured, and the dissolution of tin into solution was calculated in terms of ppm.

Condition A

degassing of the solution; heat degassing treatment in an argon gas atmosphere

corroding solution; citric acid 0.4% (pH 2.8)

NO₂-N (see Table 5) 100 ppm (0.61 g/l KNO₂)

test specimen dimension; 2.5 cm by 10 cm (total surface area of 50 cm²)

edge sealing of test specimen; none

dipping time; 120 minutes

Condition B

degassing of the solution; none (oxygen is dissolved in equilibrium with air)

corroding solution; citric acid 0.4% (pH 3) NO₂-N (see Table 5) 20 ppm

test specimen dimension; 3.0 cm by 10 cm (total surface area of 60 cm²)

edge sealing of test specimen; sealed with wax dipping time; 60 minutes.

Oxide film

The thickness of the oxide film was expressed in terms of the amount of electricity which was necessary for reducing the oxide film on the unit surface area. To this end, the electrolytic reducing process was used with an electrolyte of 0.1 N potassium chloride solution. A test specimen with a given surface area was used as a cathode while carrying it by a holder, and a constant current was fed across the cathode and a carbon rod anode. Whereby, potential-time characteristics curves were obtained, which were used as the basis for determining the thickness of the oxide film.

Solderability test (capillary rise)

This test is to check whether solder can permeate into the side seam of a tinplate can. Rectangular test specimens were made, each being 75 mm by 25 mm. The longitudinal direction of the rectangular test specimen coincided with the moving direction of steel during tinplating. Each test specimen was so folded as to form a capillary portion which was surrounded by the tin-plated surface of the specimen. The specimen was dipped in a palm oil at a depth of about 5 mm, which palm oil acted as a flux. Then, the test specimen was dipped into a solder bath at a given temperature by a depth of 30 mm for 1 minute. Upon removal from the solder bath, the specimen was quickly cooled with water.

The solder consisted of 70% of lead and 30% of tin, and the solder bath temperature was 277°C. The folded portion was opened after the quick cooling, and the height of capillary rise above the top surface of the solder bath was determined.

The large value of the capillary rise means that the tinplate has a good solderability.

Lacquer adhesion

An epoxy phenol varnish was applied to each specimen and baked at 200°C for 10 minutes. The varnished surface was scratched in lattice form. The scratched specimen was spherically stretch-formed by a depth of 5 mm by using an Erichsen cupping test machine with a spherical punch (diameter: 20 mm). Trials were made to peel off the varnish layer by a piece of Scotch tape (Trademark of The Minnesota Mining and Machine Co.). Those specimens which did not allow any peeling were graded as "very good".

Brightness

The brightness of the specimens of the tinplate as treated by the method of the present invention was measured and expressed in terms of percentage on the basis of the brightness of Reference specimen of conventional tinplates.

As apparent from Table 1, the tin-plated steel sheet which is processed by the treatment of the present invention, i.e., the chromate treatment immediately after tin-plating and reflow treatment thereafter, has a much higher sulfur resistance, as compared with that of a conventional tin-plated steel sheet without any chemical treatment. Besides, the number of pinholes, as determined by the hot water test, can be reduced to one half to one third by the treatment of the present invention. The test value of the thiocyanate test can also be reduced to about two thirds by the treatment of the present invention.

On the other hand, the tin dissolution, solderability (capillary rise), lacquer adhesion, and the brightness of the tin-plated steel sheet are not affected by the treatment of the present invention.

If the chemical treatment, e.g., the cathodic electrolytic treatment with a sodium dichromate solution, is applied after the reflow treatment in the method of the present invention, the sulfur resistance can be greatly improved over that of similarly treated conventional tinplate, as can be seen from Table 1. The chemical treatment after the reflow is also effective in reducing the number of pinholes and cutting down the thiocyanate test value to less than one half. Furthermore, a remarkable improvement in the tin dissolution can be achieved by the chemical treatment after the reflow, so that the undesirable excessive dissolution of tin can be completely eliminated thereby.

The chemical treatment after the reflow does not affect other properties of the tin-plated steel sheet: namely, it does not deteriorate the iron dissolution, solderability in terms of capillary rise, lacquer adhesion, and brightness.

It should be noted that, if the chromate treatment is effected by the anodic-cathodic electrolysis or by anodic electrolysis, the sulfur resistance itself can be improved over that which can be obtained by the cathodic electrolytic chromate treatment. However, the anodic-cathodic electrolytic and anodic electrolytic chromate treatments result in an increased thickness of the oxide film, and the succeeding reflow treatment cannot produce the desired brightness of the tin-plated steel sheet.

Immediately after the tin electroplating, a chromate coating is formed on the electroplated tin without reflowing the latter. Thereafter, the tinplates were heated at 50°C to 300°C by electric resistance heating by directly feeding electric current thereto. The relation between the heating temperature and the sulfur resistance of the tinplates thus treated was measured. The test included the plates which were not heated at all after the chromate treatment and plates with electroplated tin alone. The result is shown in Table 2.

Table 2

Test* specimen	Duration** of sulfur resistance test (sec)	Sulfur resistance of specimens heat at***								
		without heating	50°C	100°C	150°C	170°C	200°C	240°C	280°C	320°C
A	20	DB	DB	NB	NB	NB	NB	NB	NB	NB
	40	SB	SB	DB	DB	DB	DB	DB	NB	NB
B	20									
	40					HB				

*Test specimen A:

Immediately after tin electroplating (1.50 lb/bb), cathodic electrolytic chromate treatment was applied in a solution of sodium dichromate.

Test specimen B:

Plates with tin electroplating alone (0.50 lb/bb).

**Sulfur resistance test was the same as that of Table 1.

***Grading notations of the sulfur resistance are the same as those of Table 1.

As apparent from Table 2, in the case of tinplates which are chromate treated immediately after the tin electroplating, the heating at a temperature above 100°C is effective in improving the sulfur resistance even when the heating temperature is below the melting point of tin.

The reason for the improvement of the sulfur resistance is not clearly understood yet. Judging from the fact that the heating of tinplate with tin coating alone did not produce any improvement of the sulfur resistance, the oxides of chromium deposited on the tin layer by the chromium treatment produce a highly sulfur-resistant layer upon heating.

The invention will now be described in further detail, by referring to examples.

EXAMPLE 1

Basis sheets of cold-rolled low-carbon steel was pre-treated by electrolytic cleaning, rinsing with water, pickling with acid, and rinsing with water, and they were tin-plated (5.6 g/m²) and rinsed again with water. Chromate treatment was applied to the thus tin-plated steel by cathodic electrolysis in a solution containing 30 g/l of sodium dichromate at 45°C with a current

30 g/l at 45°C with a current density of 5 A/dm² for 0.5 second. The sulfur resistance of the thus treated tinplate was measured. The result is shown in Table 3, together with the corresponding properties of conventionally treated tinplate.

EXAMPLE 2

Basis sheets of cold-rolled low-carbon steel was pre-treated by electrolytic cleaning, rinsing with water, pickling with acid, and rinsing with water, and they were tin-plated (5.6 g/m²) and rinsed again with water. Chromate treatment was applied to the thus tin-plated steel by cathodic electrolysis in a solution containing 30 g/l of sodium dichromate at 45°C with a current density of 0.5 A/dm² for 0.2 second. Then, reflow treatment was applied by electric resistance heating at 290°C by directly feeding electric current thereto, which was followed by chemical treatment of cathodic electrolysis in a sodium dichromate solution of 30 g/l at 45°C with a current density of 1 A/dm² for 1 second. Food cans of inside volume 152.5 cc, diameter 65.4 mm, and height 52.7 mm were made from the tinplates thus prepared, and reference food cans of the same size

Table 4

Treatment	Tests in 2 g/l cysteine chloride solution							
	Tin dissolution (ppm)				Can inside corrosion by sulfur			
	Immediately after heat sterilization	After storing at 38°C for			Immediately after heat sterilization	After storing at 38°C for		
		1 week	2 weeks	3 weeks		1 week	2 weeks	3 weeks
The invention	9	55	61	80	Normal	Normal	Normal	Slightly colored
Conventional	21	103	128	155	Considerable blackening was noticed			

40

density of 5 A/dm² for 0.5 second. Then, reflow treatment was applied to them by electric resistance heating at 290°C by directly feeding electric current thereto, which was followed by a chemical treatment of cathodic electrolysis in a sodium dichromate solution of

were made from conventional tinplates which were processed by conventional chemical treatment.

Accelerated tin dissolution tests were made on those cans by using cysteine chloride solution and citric acid solution. The result is shown in Tables 4 and 5.

Table 3

Treatment	Sulfur resistance, as determined by		
	Cysteine chloride process	Sodium thiosulfate process	Potassium polysulfide process
The invention Tin-plating → chromate by cathodic electrolysis → reflow → chemical treatment	Normal	Normal	Normal
Conventional tinplate (0.50 lb/bb), with chemical treatment	Considerable blackening noticed	Considerable blackening noticed	Considerable blackening noticed

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Table 5

Treatment	Corroding solution	Tests in citric acid solution	
		Tin dissolution (ppm)	
		Immediately after heat sterilization	After keeping at 38°C for 24 hours
The	Citric acid pH 3.0 do. , +NO ₂ -N 5	42 76	79 105

Table 5 Continued

Tests in citric acid solution				
Treatment	Corroding solution		Tin dissolution (ppm)	
			Immediately after heat sterilization	After keeping at 38°C for 24 hours
invention	do.	, ppm* , +NO ₂ -N 10	121	184
	do.	, ppm , +NO ₂ -N 20	126	200
Conven- tional	Citric acid pH 3.0	, ppm	79	116
	do.	, +NO ₂ -N 5	116	131
	do.	, ppm , +NO ₂ -N 10	184	231
	do.	, ppm , +NO ₂ -N 20	210	263

*NO₂-N stands for the amount of nitrogen which was added in the form of potassium nitrite.

What is claimed is:

1. Surface treatment of tin-plated steel for a food can and the like for improving sulfur resistance and producing a bright finish, comprising plating tin on the surface of steel, applying cathodic electrolytic chromate treatment to the tin thus plated by using an aqueous acid solution containing 6-valent chromium ions and whose pH value is 3 to 6 prior to reflowing and treating the chromate treated tin-plated steel at a temperature from 280° to 350°C.

2. Surface treatment for tin-plated steel for a food can and the like for improving sulfur resistance and producing a bright finish, comprising plating tin on the surface of steel, subjecting the thus plated tin to a dip chromate treatment with chromic acid prior to reflow-

ing and heating the chromate treated tin-plated steel at a temperature from 280° to 350°C.

3. Surface treatment of tin-plated steel according to claim 1, wherein said heating of the chromate treated tin-plated steel is effected at temperatures from the melting point of tin to 350°C.

4. Surface treatment of tin-plated steel according to claim 1 further comprising applying an aqueous acid solution containing 6-valent chromium ions after the heating step.

5. Surface treatment of tin-plated steel according to claim 2 further comprising applying an aqueous acid solution containing 6-valent chromium ions to the tin after the heating step.

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