

[54] CAN PRODUCED FROM
CHROMIUM-COATED STEEL PLATE

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[57] ABSTRACT

A can made of a steel sheet the surface of which is coated with a three-layered chromium coating, consisting of a metallic chromium coating, a crystalline chromium oxide coating and a non-crystalline hydrated chromium oxide coating in this order. A layer of an organic enamel or fused film may be provided further on top of the non-crystalline hydrated chromium oxide coating.

9 Claims, 2 Drawing Figures

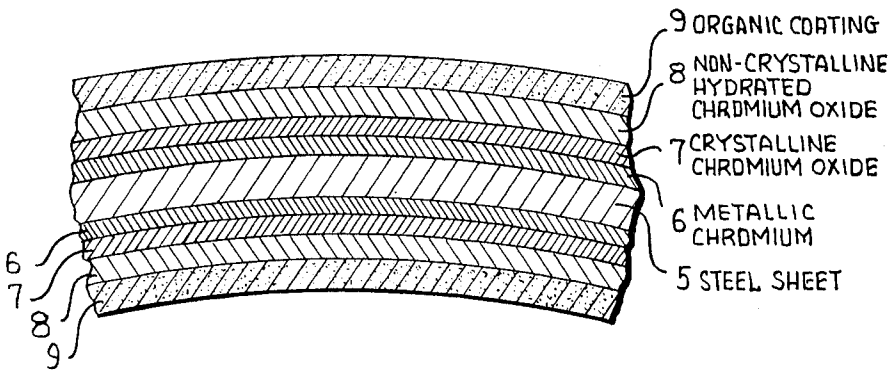


FIG. 1

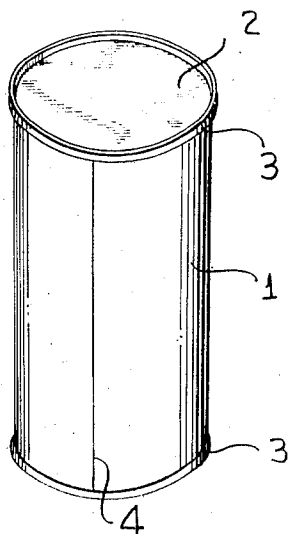
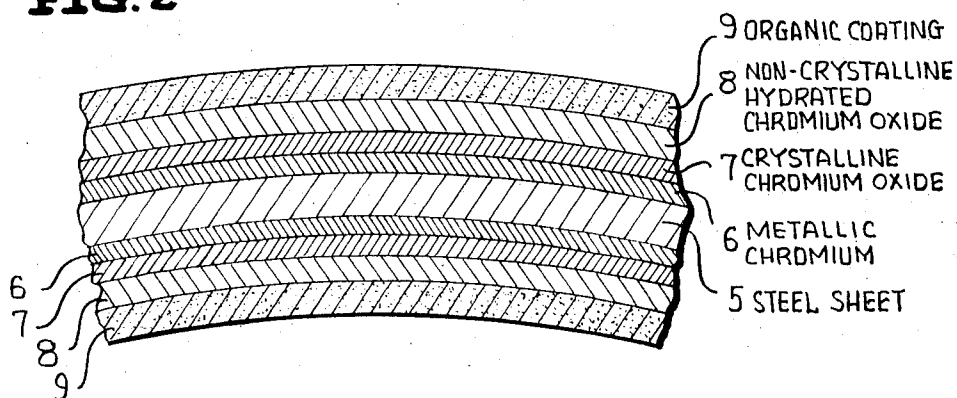


FIG. 2



CAN PRODUCED FROM CHROMIUM-COATED STEEL PLATE

This invention relates to a can produced from a steel plate having a chromium-coated layer on its surface. More specifically, the invention relates to a can produced from a steel plate having a three-layered anti-corrosive chromium coating or one further having an organic coating on the chromium coating.

Enameled or lacquered cans made of steel plate have come into use as cans for foods, drinks and other products that require corrosion resistance.

Chromium plated steel sheets are useful for producing coated cans because of good adhesion of the plated layer with organic coating, and are also suitable for coating with a transparent lacquer because of their good appearance. However, the provision of a metallic chromium layer only can not lead to the prevention of cracks or pin holes.

With a view to overcoming this difficulty, Japanese Pat. No. 6323/71, for example, proposed steel sheets coated with a thin layer of metallic chromium plating and a top coating of hydrated chromium oxide. The steel sheet coated with the two layers has the defect that the adhesion between the metallic chromium layer and the hydrated chromium oxide layer is not satisfactory, and the fabricability of the steel sheet, such as deep drawing or the bending of the seam portion of the can body, is insufficient, and cracks tend to occur.

It is an object of this invention to provide a crack-free or pin hole-free can, especially a can suitable for coating, and a coated can, wherein a layer of hydrated chromium oxide and a layer of metallic chromium adhered to each other with good bonding strength.

Another object of this invention is to provide a can and a coated can both having superior corrosion resistance.

These objects of this invention can be achieved by adhering a layer of metallic chromium intimately to a layer of hydrated chromium oxide through a layer of crystalline chromium oxide. According to this invention, there is provided a can at least a part of which is made of a steel plate having on its surface a layer of metallic chromium coating, a layer of crystalline chromium oxide coating and a layer of non-crystalline hydrated chromium oxide coating in this order beginning with the surface of the steel sheet, or a steel plate having on its surface these three layers and further a fourth topcoat layer of organic coating.

The invention will be described below by reference to the accompanying drawings in which:

FIG. 1 is a perspective view showing one example of a can in accordance with this invention; and

FIG. 2 is a schematic view of the section of the coated layers in this invention.

The can of this invention consists of a main body 1, a can lid 2 and double seams 3 formed between the flange of the main can body and the end portion of the can. The main body 1 includes a side seam portion 4 formed by bonding both side edges of a rectangular metal blank or welding them in a superposed state, or by means of a hook seam. Instead of forming the upper and lower double seam portion 3 on the main body 1, one of the main body 1 and the lid 2 may be formed continuously in the case of, for example, deep drawn can or deep drawn and ironed can. In this case, the main body part 1 generally does not have a side seam.

A lid made of an aluminum sheet having a known opener and a score cut enable to open the can easily at the time of drinking or taking out of the contents may be formed at one or both of the can lids.

In the can of this invention, as shown in FIG. 2, the main body portion 1 is composed of a steel sheet having a metallic chromium layer 6, a crystalline chromium oxide layer 7 and a non-crystalline hydrated chromium oxide layer 8 formed on the surface of the steel sheet in this order starting from the surface. If desired, this three-layered coating may be coated only on one surface of the base steel plate.

In another aspect of this invention, an organic coating layer 9 is further formed on the above three-layered coating.

The three-layered or four-layered coating may be formed on a blank steel sheet either before or after making the blank into a can body.

The chromium coated steel sheet that constitutes the can of this invention can be produced by various methods, and some of them will be illustrated below. Of course, the invention is not limited to these examples.

1. The chromium coated steel sheet is obtained cathodically in an electrolyte consisting of chromic acid (CrO_3) as a main component, and SO_4^{--} and HS^- as catalyst, whereby three layers can be deposited simultaneously with good efficiency. A conventional electrolyte containing 5 g/l to 300 g/l of chromic acid and 0.05 g/l to 5 g/l of sulfuric acid for electrolytic chromic acid treatment may be used by adding 0.1 g/l to 10 g/l, calculated as HS^- , of a compound capable of generating HS^- such as NaHS or KHS.

2. The chromium coated steel sheet is obtained cathodically under the same electrolysis conditions for conventional electrolytic chromic acid treatment except that the pH of the electrolyte at a point about 1 mm apart from the steel sheet as the cathode is adjusted to at least 5.5. The pH adjustment can be performed by controlling the stirring condition of the electrolyte in the case of batch treatment. In this method, the electrolytic solution containing HS^- mentioned in (1) above may be used.

3. The three-layered chromium coated steel sheet is obtained in the following manner: Non-crystalline hydrated chromium oxide layer of a chromium coated steel sheet having a non-crystalline hydrated chromium oxide layer on a metallic chromium layer is converted to crystalline chromium oxide by aging. Then, a coating of non-crystalline hydrated chromium oxide is formed on the crystalline chromium oxide layer by a conventional chromate treatment.

4. A crystalline chromium oxide coating is formed on a chromium plated steel sheet by oxidation in the vapor phase, and then by a conventional chromate treatment, a non-crystalline coating is formed.

Another can of this invention can be produced by using the chromium coated steel sheet coated with a thermocurable resin enamel such as a phenolic resin, urea resin, epoxy resin or a mixture of these, a thermoplastic resin enamel such as a vinyl chloride resin, acrylic resin, or a vinyl chloride/vinyl acetate copolymer, or a thermoplastic resin such as polyethylene, polypropylene or linear polyester on the desired part of the three-layered coating. These organic coatings may be applied by roller coating, spray coating, powder coating, fusing, etc. Or the above organic coatings may

be applied to the desired part of a can made from a steel sheet having the above three-layered coating.

The amount per unit area of each of the layers on the steel plate that constitutes the can of this invention is not particularly restricted. Preferably, however, the amount of the metallic chromium layer is 0.1 to 3 mg/dm², the amount of the crystalline chromium oxide layer is 0.01 to 0.2 mg/dm², and that amount of the non-crystalline hydrated chromium oxide layer is 0.05 to 0.5 mg/dm², all calculated as chromium. Optimum results can be obtained when the amount of the metallic chromium layer, the crystalline chromium oxide layer, and the non-crystalline hydrated chromium oxide layer are 0.3 to 1.8 mg/dm², 0.03 to 0.15 mg/dm², and 0.1 to 0.3 mg/dm², respectively, calculated as chromium.

The composition of each of the coating layers of the can of this invention can be identified by various methods. For example, the outermost surface of the coated steel sheet can be identified clearly as a non-crystalline coating by a reflection electron diffraction. This non-crystalline hydrated chromium oxide coating is removed by dissolving it in accordance with a well known method of immersing in concentrated hot alkali. The surface of the coated steel sheet after removal of the non-crystalline hydrated chromium oxide coating is fixed with a carbon film, and the steel sheet and the metallic chromium on the opposite side are then dissolved completely in a solution of bromine in anhydrous methyl alcohol. An electron diffraction of the remaining layer shows that this layer consists of crystalline chromium oxide present uniformly, and only oxygen and chromium were detected for this layer by electron probe X-ray microanalysis.

Then, from another test piece, the base steel is removed by dissolving with nitric acid, and the surface of the coated layer on the side of the removed steel sheet is tested by reflection electron diffraction, and it is ascertained that the layer adjacent to the steel sheet is a metallic chromium layer.

The amount per unit area of the coated layer of the can of this invention is measured by the following method.

1. The X-ray intensity *I_a* of chromium is measured with respect to the entire sample by an X-ray fluorescence analysis. The non-crystalline hydrated chromium oxide layer is removed by the same method as mentioned above, and the X-ray intensity *I_b* of the remaining part is measured by an X-ray fluorescence analysis. The amount per unit area of the non-crystalline hydrated chromium oxide layer can be calculated from the difference between the X-ray intensity *I_a* and the X-ray intensity *I_b*.

2. The remaining part after removal of the non-crystalline hydrated chromium oxide in (1) above is anodically dissolved in an alkaline solution galvanostatically leaving only the base steel. The X-ray intensity *I_c* of chromium is measured by an X-ray fluorescence analysis on the remaining base steel. The combined amount per unit area of the crystalline chromium oxide layer and the metallic chromium layer can be obtained by calculation from the difference between the X-ray intensity *I_b* and the X-ray intensity *I_c* of the base steel.

3. The non-crystalline hydrated chromium oxide is removed from the sample using concentrated hot alkali and further the steel sheet and the metallic chromium layer are removed in a solution of bromine in anhy-

drous methyl alcohol. The X-ray intensity of chromium is measured by an electron probe X-ray microanalyzer with respect to the remaining crystalline chromium oxide layer. The amount per unit area of the crystalline chromium oxide can be obtained by calculation from the measured X-ray intensity.

4. The amount per unit area of the metallic chromium layer can be determined from the difference between the combined amount per unit area of the crystalline chromium oxide layer and the metallic chromium layer determined in (2) above and that of the crystalline chromium oxide layer.

The amounts per unit area of the coated layers that can be measured by the above-described procedure are obtained as chromium.

The can of this invention is free from pin holes, and the adhesion between the coated layer and the base steel sheet and between the adjacent coated layers is extremely good. In the production of cans, the coated layers have good resistance to cracks. Also, the cans of this invention have far superior resistance to corrosion to cans obtained from conventional chromium-coated steel sheets.

The can of this invention can be used without organic coating, but is especially suitable for use with organic coating, that is another aspect of this invention.

The following examples illustrate the advantages of this invention specifically.

In the following examples, storage test was conducted for 10 cans (with contents) for each sample after 1 year storage and the following items were evaluated as indicated

Dissolved iron:

Dissolved iron (mg)/contents (1,000 gr.)

Perforation:

Number of perforated cans during storage for 1 year

Failure of can body:

Failure at the side seam portion

Flavor:

Results of flavor test conducted by 10 panels.

Evaluation on a scale of 1 to 5 as shown below.

5: Excellent, 4: Good, 3: Fair, 2: Poor, 1: Very poor

Discoloration:

Change of the color of the contents (fading, discoloration, or browning, etc.)

State of the inside surface of the can:

Evaluation of visual observation of the inner surface of the can after opening the can (rusting, change of the organic film, etc.)

Examples 1 to 22 and Comparative Examples 1 to 4

An example of producing a chromium coated steel sheet material for producing the can of this invention, an example of producing a can using this coated steel sheet material, and comparative examples are shown below.

Example of Preparing Chromium Coated Steel Sheet Material For Cans

The chromium coated steel sheets used in Examples 1 to 22 were produced cathodically in an aqueous solution containing 50 g/l of chromic acid and 0.25 g/l of sulfuric acid, by adding sodium hydrogen sulfide in the concentration shown in Table 1 at 50°C, using a lead-tin (5%) alloy as an anode. The current density and the electrolysis time are indicated in Table 1. The pH of the electrolyte was adjusted by controlling the stirring con-

dition of it. The excess amount of the non-crystalline hydrated chromium oxide that deposited under the conditions shown in Table 1 was removed by dipping the coated steel in the bath without electrolysis. The chromium amount of each of the coated layers is also shown in Table 1.

In Examples 23 to 26, the cans were deep drawn and ironed 211 dia. cans with a capacity of 350 ml, wherein an epoxy-urea resin enamel layer on the inner surface of the can and a vinyl chloride/vinyl acetate copolymer layer was provided on top of the coated layer.
In Examples 27 to 31, the cans were 301 dia. deep

Table 1

Example	Chromium amounts (mg/dm ²)			Electrolysis Conditions				
	Metallic chromium layer	Crystalline chromium oxide layer	Non-crystalline hydrated chromium oxide layer	Concentration of NaHS (g/l)	Current density (A/dm ²)	Electrolysis time (sec)	Dipping time (sec)	pH*
1	0.8	0.08	0.2	2.5	30	1.2	2	5.5
2	do.	0.09	do.	do.	do.	do.	do.	7.0
3	do.	0.11	do.	do.	do.	do.	do.	7.0
4	do.	0.14	do.	do.	do.	do.	do.	9.5
5	1.2	0.06	0.12	2.5	30	1.8	3	6.5
6	do.	0.10	do.	do.	do.	do.	do.	8.0
7	do.	0.12	do.	do.	do.	do.	do.	8.5
8	do.	0.15	do.	do.	do.	do.	do.	10.0
9	0.1	0.10	0.15	0.5	20	0.5	0.8	6.5
10	0.5	do.	do.	do.	do.	2.0	1.0	7.0
11	1.0	do.	do.	2.5	do.	2.2	0.5	8.5
12	1.5	do.	do.	5.0	do.	2.7	0.3	8.5
13	2.5	do.	do.	do.	do.	4.5	do.	6.5
14	1.0	0.08	0.05	1.5	25	2.2	7	7.5
15	do.	do.	0.10	do.	do.	do.	4	8.0
16	do.	do.	0.20	do.	do.	do.	2	8.0
17	do.	do.	0.30	do.	do.	do.	1	7.0
18	do.	do.	0.50	do.	do.	do.	0.2	8.5
19	1.3	0.06	0.22	0	40	2.0	8	5.5
20	0.7	0.09	0.16	do.	do.	1.0	6	8.5
21	0.3	0.12	0.20	do.	do.	0.4	0	9.0
22	1.5	0.15	0.14	do.	do.	2.3	10	12.0
Comparative Examples								
1	0	0	0.18					
2	0.8	do.	0					
3	0.8	do.	0.2					
4	0	0	0					

*pH of the electrolyte at a point about 1 mm apart from the base steel plate.

Example of Producing Cans

Cans were produced by the following procedure using the materials obtained above.

An epoxy-phenol enamel was coated on both surfaces of a chromium-coated steel sheet blank having a size of 125 mm × 210 mm, and baked for 10 minutes at 210°C. Both edge parts of this blank along the 125 mm long side were heated to about 240°C., and a nylon type adhesive tape was melt-adhered to one surface of one edge portion. To the other surface of the other edge portion the above adhesive tape was melt-adhered, and at that time the cut edge of the blank was protected by covering with the adhesive.

The blank was formed into a cylindrical shape having a height of 125 mm using a can body maker, and both edge portions to which the adhesive had been applied were heated to about 240°C. and superimposed so that the edge portion whose cut edge is protected by the adhesive forms part of the inside surface of the can. The adhesives were bonded to each other to produce a 211-dia. side lap seam can body. Width of the lap seam of the can body was 5 mm. Then, by an ordinary method, a flange was provided, and the lid was double-seamed. A lacquer consisting of a modified copolymer of vinyl chloride and vinyl acetate was applied to the inside of the can and baked.

Examples 23 to 37

Examples of cans of various structures produced from the chromium coated steel sheets are shown below.

drawn cans having a capacity of 150 ml. In Examples 27 to 30, an epoxy-phenol resin enamel was provided on the inner surface of the can body and, in Example 31, a melt-adhered coating layer of a linear polyester resin was provided on the inner surface of the can body. In Examples 32 and 33, the cans were 211 dia. welded cans having a capacity of 350 ml. in which an epoxy layer was provided on the welded part of the can body and furthermore, an epoxy-urea resin enamel was applied on the inner surface of the can, and further, a vinyl chloride resin enamel layer was provided. In Examples 34 to 36, the resulting cans were hook seam cans in which the hook seam portions were bonded by a heat curable adhesive. In Examples 34 and 35, the cans obtained were cans in which an epoxy phenol resin coating layer was provided on the inner surface of the cans. The can obtained in Example 36 was a can to which an organic coating was not applied to its inner surface. The can obtained in Example 37 was a 5-gallon rectangular can in which the hook seam portion and the can end seam portion were bonded by a thermoplastic adhesive and a phenol-epoxy resin enamel layer was provided on the inner surface of the can.

Storage Test

Various contents were filled in the cans obtained in Examples 1 to 37 and Comparative Examples 1 to 4, and the can lids were double-seamed. These cans were offered for an actual storage test. The results are shown in Tables 2 and 3.

Table 2

Example No.	Results of Storage Test									
	1	2	3	4	5	6	7	8		
Drinks	Beer					Tomato Juice				
Dissolved iron amount (ppm)	0.08	0.06	0.06	0.07	1.1	0.91	1.0	1.7		
Perforation (Number of can)	0	0	0	0	0	0	0	0		
Flavor	5	5	5	5	5	5	5	5		
Discoloration	No	No	No	No	No	No	No	No		
State of the inside surface of the can	change	change	change	change	change	change	change	change		
Drinks	Cola					Peach nectar				
Dissolved iron amount (ppm)	0.59	0.49	0.80	1.0	0.98	0.86	0.90	1.5		
Perforation (Number of can)	0	0	0	0	0	0	0	0		
Flavor	5	5	5	5	5	5	5	5		
Discoloration	No	No	No	No	No	No	No	No		
State of the inside surface of the can	change	change	change	change	change	change	change	change		
Drinks	Carbonated beverage with dye					Carbonated beverage with lactobacilli.				
Dissolved iron amount (ppm)	0.57	0.45	0.78	0.98	1.1	0.87	0.93	1.8		
Perforation (Number of can)	0	0	0	0	0	0	0	0		
Flavor	5	5	5	5	5	5	5	5		
Discoloration	No	No	No	No	No	No	No	No		
State of the inside surface of the can	change	change	change	change	change	change	change	change		
Example No.	9	10	11	12	13	14	15	16	17	18
Drinks	Colorless carbonated beverage						Orange nectar			
Dissolved iron amount (ppm)	2.0	0.67	0.63	0.64	0.98	2.7	0.96	0.85	1.3	2.9
Perforation (Number of can)	0	0	0	0	0	0	0	0	0	0
Flavor	4	5	5	5	5	4	5	5	5	4
Discoloration	No	No	No	No	No	No	No	No	No	No
State of the inside surface of the can	change	change	change	change	change	change	change	change	change	change
Drinks	Orange juice						Apple juice			
Dissolved iron amount (ppm)	2.1	0.96	0.85	0.88	1.5	2.9	1.0	0.90	1.4	2.7
Perforation (Number of can)	0	0	0	0	0	0	0	0	0	0
Flavor	4	5	5	5	5	4	5	5	5	4
Discoloration	No	No	No	No	No	No	No	No	No	No
State of the inside surface of the can	change	change	change	change	change	change	change	change	change	change
Drinks	Vegetable juice						Carbonated beverage with dye			
Dissolved iron amount (ppm)	2.8	1.0	0.95	1.1	2.1	2.5	0.53	0.47	1.7	2.8
Perforation (Number of can)	0	0	0	0	0	0	0	0	0	0
Flavor	4	5	5	5	5	4	5	5	5	4
Discoloration	No	No	No	No	No	No	No	No	No	No
State of the inside surface of the can	change	change	change	change	change	change	change	change	change	change
Example No.										
Comparative Example No.										
Drinks	19	20	21	22	1	2	3	4		
Drinks	Beer				Beer					
Dissolved iron amount (ppm)	0.07	0.05	0.09	0.08	4.0	2.3	1.0	—		
Perforation (Number of can)	0	0	0	0	3	2	0	Failure at side-seam		
Flavor	5	5	5	5	1	1	3	—		
Discoloration	No	No	No	No	turbid	turbid	slightly turbid	—		
State of the inside surface of the can	change	change	change	change	rusting	spotty stain	No change	rusting		
Drinks	Cola				Cola					
Dissolved iron amount (ppm)	0.51	0.45	0.70	0.62	9.7	6.0	3.3	—		
Perforation (Number of can)	0	0	0	0	8	5	0	failure at side-seam		
Flavor	5	5	5	5	1	1	3	—		
Discoloration	No	No	No	No	turbid	turbid	No	—		
State of the inside surface of the can	change	change	change	change	many spotty stains	a little failure at side-seam	change spotty stain	rusting		
Drinks	Carbonated beverage with dye				Carbonated beverage with dye					
Dissolved iron amount (ppm)	0.47	0.40	0.68	0.66	9.5	6.8	3.1	—		
Perforation (Number of can)	0	0	0	0	5	2	0	failure at side-seam		
Flavor	5	5	5	5	1	1	3	—		
Discoloration	No	No	No	No	fading: 5 cans	fading: 3 cans	slightly fading: 2 cans	—		
State of the inside surface of the can	No change	No change	No change	No change	many spotty stains	many spotty stains & a little failure at side-seam	spotty strain	rusting		

Table 3

Ex No.	Structure of can	Chromium amount (mg/dm ²)			Results of storage test					Contents
		Metallic chromium layer	Crystalline chromium oxide layer	Non-crystalline chromium oxide layer	Dissolved iron amount (ppm)	Perforation (Number of can)	Flavor	Discoloration or vacuum of the can	Visual observation	
23	Deep drawn and ironed can	1.0	0.10	0.20	0.05	0	5	no change	no change	Beer
24	do.	1.2	0.08	0.15	0.41	0	5	do.	do.	Cola
25	do.	0.8	0.11	0.21	0.40	0	5	do.	do.	Carbonated beverage with dye
26	do.	1.0	0.09	0.18	0.21	0	—	do.	do.	Hair spray
27	Deep drawn can	1.0	0.10	0.20	0.62	0	5	Vacuum of the can: 20 cmHg	do.	Saurel seasoned with tomato sauce
28	do.	1.2	0.08	0.15	0.48	0	5	18 cmHg	do.	beef cooked in Japanese style
29	do.	0.8	0.11	0.21	0.35	0	5	20 cmHg	do.	Pudding
30	do.	1.0	0.09	0.18	0.42	0	5	21 cmHg	do.	Bean jelly
31	do.	0.7	0.05	0.15	0.70	0	5	21 cmHg	do.	tuna brine
32	Welded can	0.9	0.10	0.20	0.06	0	5	No change	No change	Beer
33	do.	1.1	0.12	0.21	0.61	0	5	do.	do.	Colorless carbonated beverage
34	Hook seam can	1.0	0.10	0.19	1.50	0	—	do.	do.	detergent
35	do.	0.9	0.09	0.20	0.61	0	5	Vacuum of the can: 21 cmHg	do.	boiled salmon
36	do.	0.8	0.08	0.22	0.05	0	5	No change	do.	salad oil
37	5-gallon can	1.2	0.10	0.20	0.88	0	5	do.	do.	Tomato puree

Examples 1 to 4 cover examples in which the amounts of the metallic chromium layer and the non-crystalline hydrated chromium oxide layer of the chromium-coated steel sheets constituting the can were maintained constant, but the amount of the crystalline chromium oxide layer was varied. Examples 5 to 8 are similar to Examples 1 to 4 but the amount of the metallic chromium layer was increased over those in Examples 1 to 4 and the amount of the non-crystalline hydrated chromium oxide layer was made smaller. Examples 9 to 13 cover examples in which the amounts of the crystalline chromium oxide layer and the non-crystalline hydrated chromium oxide layer were maintained constant, but the amount of the metallic chromium layer was varied.

Examples 14 to 18 cover examples in which the amounts of the metallic chromium layer and the crystalline chromium oxide layer were maintained constant, but the amount of the non-crystalline hydrated chromium oxide layer was varied. Examples 19 to 22 cover examples in which the amounts of all of the layers were varied.

Comparative Example 1 covers an example in which only a non-crystalline hydrated chromium oxide layer was formed on the surface of the steel sheet. In Comparative Example 2, only a metallic chromium layer was formed on the steel sheet. In Comparative Example 3, only a metallic chromium layer and a non-crystalline

hydrated chromium oxide layer were formed on the surface of the steel sheet. In Comparative Example 4, neither of these layers was provided.

It is apparent from Examples 1 to 22 in comparison with the Comparative Examples that the cans of the present invention exhibited very superior advantages in 15 comparative tests. It is seen from the results obtained in Examples 23 to 37 that the cans of the present invention exhibit very superior effects on any contents of the cans irrespective of their structures.

What we claim is:

1. A can at least a part of which is made of a steel sheet at least one surface of which is provided with a three-layered chromium coating consisting of a metallic chromium coating, a crystalline chromium oxide coating and a non-crystalline hydrated chromium oxide coating in this order beginning with the surface of the steel sheet.

2. The can of claim 1 wherein the chromium coated layer is provided on both surfaces of the base steel sheet.

3. The can of claim 1 wherein the amounts per unit area of the metallic chromium layer, the crystalline chromium oxide layer, and the non-crystalline hydrated chromium oxide layer, calculated as chromium, are 0.1 to 3 mg/dm², 0.01 to 0.2 mg/dm², and 0.05 to 0.5 mg/dm², respectively.

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4. The can of claim 1 wherein the amounts per unit area of the metallic chromium layer, the crystalline chromium oxide layer, and the non-crystalline hydrated chromium oxide layer, calculated as chromium, are 0.3 to 1.8 mg/dm², 0.03 to 0.15 mg/dm², and 0.1 to 0.3 mg/dm², respectively.

5. The can of claim 1 wherein an organic coating is formed at least a part of the outer surface of the chromium coated layer.

6. The can of claim 5 wherein said organic coating is composed of a thermocuring resin enamel selected from the group consisting of a phenol resin, a urea resin, an epoxy resin and mixtures of two or more of these with each other.

7. The can of claim 5 wherein said organic coating is composed of a thermoplastic resin enamel selected

from the group consisting of a vinyl chloride resin, acrylic resin and vinyl chloride/vinyl acetate copolymer.

8. The can of claim 5 wherein said organic coating is composed of a fused coating of a polyethylene resin, polypropylene resin or linear polyester resin.

9. The can of claim 5 wherein said organic coating consists of a primer of a thermo-curable enamel selected from the group consisting of a phenol resin, urea resin, epoxy resin and mixtures of two or more of these with each other and formed thereon a thermoplastic resin enamel layer selected from the group consisting of a vinyl chloride resin, acrylic resin and vinyl chloride/vinyl acetate copolymer.

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