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(54) **Surface treated steel sheet for welded cans.**

(57) An electrolytically chromated steel sheet which has an outstandingly good high-speed weldability without grinding and presents a lacquered or printed surface having an excellent finish, and which is particularly suitable for use in making a welded can. It carries on one surface thereof a film including a metallic chromium layer having a high proportion of granular metallic chromium having a large particle diameter, while on the other surface thereof, it carries a film including a metallic chromium layer in sheet form, i.e. not containing any granular chromium, or a film including a metallic chromium layer containing only a very low proportion of granular metallic chromium having a large particle diameter. The weight per unit area of the film on each surface, the proportion of granular metallic chromium having a large particle diameter in each film, and the critical particle diameter of such granular chromium are specifically limited from the standpoint of e.g. weldability.

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FIELD OF THE INVENTION:

This invention relates to an electrolytically chromated steel sheet and, more particularly, to a surface treated steel sheet which has a high degree of weldability and presents a surface having an outstanding
 5 good appearance when painted, and is, therefore, suitable for use in making cans by high-speed resistance seam welding.

BACKGROUND OF THE INVENTION:

10 An electrolytically chromated steel sheet, which is obtained by forming on a surface of a steel sheet a film composed of an undercoating layer of metallic chromium and an overcoating hydrated chromium oxide layer consisting mainly of chromium oxide, is widely used for making cans, such as cans for beverage and food, pail cans, 18-liter cans and oil cans, since it is excellent in paintability and corrosion resistance, and is less expensive than a tin plate. The film is usually composed of an undercoating layer of metallic
 15 chromium having a thickness of, say, 0.005 to 0.02 micron and an overcoating hydrated chromium oxide layer having a thickness of, say, 0.01 to 0.02 micron.

There are two methods for forming the film, i.e. the one-step method and the two-step method. The one-step method forms the metallic chromium and hydrated chromium oxide layers simultaneously by the cathode electrolytic treatment of a steel sheet in an electrolyte consisting mainly of chromium trioxide and
 20 containing one or two additives selected from sulfates and fluorine compounds. The two-step method repeats the one-step method to form the metallic chromium and hydrated chromium oxide layers, but further includes dissolving away the hydrated chromium oxide layer and forming a new hydrated chromium oxide layer by cathode electrolytic treatment in an electrolyte consisting mainly of chromic acid.

The electrolytically chromated steel sheet has hitherto been used for making a two-piece can, which is
 25 made by drawing, or a three-piece can, which is made by joining the seams with an adhesive, such as an organic resin or a special cement. It has, however, not often been used for making a seam welded can, since it is very low in weldability.

The recent increase in demand for strong and highly reliable welded cans has, however, been calling for the supply of an electrolytically chromated steel sheet having an improved weldability without grinding.

30 The electrolytically chromated steel sheet known in the art has a low weldability for the reasons which will hereunder be set forth. The overcoating hydrated chromium oxide layer serving as a surface coating is of the nature not conducting electricity or heat. Therefore, the hydrated chromium oxide layer acts as an insulator and produces a very high contact (or static) resistance when electric resistance seam welding is carried out to form a welded seam extending longitudinally of the body of a can.

35 The value of contact resistance can be used as a measure for evaluation as to the possibility of a localized flow of an excessive current in a welding job. If a high value of contact resistance exists, a welding current is allowed to flow only through so narrow a path that a localized flow of an excessive current is likely to occur. The electrolytically chromated steel sheet has a very high value of contact resistance as compared with any other type of surface treated steel sheet used for making welded cans. Therefore, the
 40 welding current flows only in a small quantity during the initial stage of a welding operation and begins to flow in the desired quantity only after the passage of a certain length of time. As a consequence, the localized heating of the steel sheet is likely to occur and result in a splashing, or the formation of a welded joint having blowholes or other defects.

It has, therefore, been necessary to remove by e.g. grinding the chromate film from that portion of the
 45 steel sheet along which a welded seam is going to be formed. This has been a job which requires a great deal of time and labor.

There is known a method proposed to overcome the problems as hereinabove stated. This method is characterized by forming hard granular crystals on the whole surface of the metallic chromium layer, so that, when a welding pressure is applied to the sheet, those crystals may destroy the overlying insulating
 50 hydrated chromium oxide layer and thereby lower the contact resistance of the film to a level enabling welding. The electrolytically chromated steel sheet product of this method including a layer of metallic chromium having granular crystals formed on its whole surface (hereinafter referred to as "granular metallic chromium") can be said to be a material having an improved seam weldability without grinding.

When this type of chromated steel sheet is used to make a welded can, however, it exhibits different
 55 heat-and cooling characteristics between the overlapping inner and outer edge portions thereof to be welded together to form a seam extending longitudinally of the body of a can. More specifically, it is usually the case that, as an inner electrode roll is smaller in diameter than an outer electrode roll, the inner edge portion of the sheet is likely to generate a greater amount of heat, and that the inner edge portion is also

slower in cooling than the outer edge portion. Therefore, the inner edge portion is likely to cause a splash or flash of molten material from its edge, and a nugget is formed closer to the inner surface of the can than to its outer surface.

In view of these problems, the applicants of this application have proposed an improved method of producing an electrolytically chromated steel sheet as disclosed in their Japanese patent application laid open to the public under No. 35797/1988. This method is characterized by subjecting one surface of a steel sheet at least once to anode electrolytic treatment during its cathodic electrolytic chromating treatment to form granular metallic chromium on that surface of the sheet, while hardly any granular metallic chromium is formed on the other surface thereof. This method is based on the concept that, if the formation of granular metallic chromium is restrained on the other surface of the steel sheet, it is possible to attain a low contact resistance on the surface of the sheet defining the inner surface of a can relative to the surface defining the outer surface of the can to thereby equalize the amounts of heat generated in the inner and outer surfaces of the can being manufactured and prevent any splash on its inner surface.

Further consideration by the inventors of this invention has, however, indicated that the electrolytically chromated steel sheet produced by the proposed method cannot necessarily be said to be satisfactory in weldability, for the reasons which will be set forth below:

- (a) As the formation of granular metallic chromium is not satisfactorily restrained on the surface of the sheet defining the outer surface of the can, it is impossible to eliminate the difference between the amounts of heat generated in the inner and outer surfaces of the can being manufactured;
- (b) As the contact resistance between the films on the two surfaces of the sheet is lower than that between each film and the corresponding electrode, the films fail to generate therebetween a sufficiently large amount of heat to ensure the continuous formation of nuggets. Therefore, it is impossible to achieve a sufficiently wide range of a permissible welding current to form a weld having a large nugget pitch.

At any rate, it has been found necessary to reconsider carefully the structures of the films to be formed on the two surfaces of the steel sheet in order to enable it to show an outstandingly improved weldability.

Moreover, it is usual practice to form a beautiful pattern of lacquering or printing on the outer surface of a can for various purposes including rustproofing, protection against scratching, and decoration. The good outlook of the lacquered or printed surface of a can is a factor which has recently come to be considered particularly important, and has created a demand for a steel sheet on which a printed pattern having a bright color tone can be produced, and on which the pigment used for printing is allowed to maintain its own color. There has also arisen a demand for a steel sheet having a metallic white luster on its surface, so that it may retain its metallic luster when coated with a transparent paint. It has, however, been found that the steel sheet which can be produced by the method as hereinabove described is unsatisfactory in that connection, too, since it is likely to present a printed or lacquered surface having a dark and easily changing color tone.

SUMMARY OF THE INVENTION:

In view of the drawbacks of the prior art as hereinabove pointed out, it is an object of this invention to provide an electrolytically chromated steel sheet for a welded can which has an outstandingly good high-speed seam weldability without grinding and also can form a lacquered or printed surface having an outstandingly good outlook.

In connection with the high-speed seam welding of an electrolytically chromated steel sheet without grinding, we, the inventors of this invention, have made a detailed study of the relation which may exist between the contact resistance of the films and the heating and cooling characteristics of the steel sheet, and also of the nature of the nuggets which may be formed. As a result, we have found that, in order to improve the weldability of the sheet, it is important to achieve an optimum balance of resistance heating at the interface between the outer surface of a welded joint to be formed and the electrode, at the interface between the contacting portions of the sheet and at the interface between the inner surface of the joint and the electrode, and also an optimum balance of cooling by the electrodes on the inner and outer surfaces of the joint.

We have studied the film structure which may realize the optimum balances of resistance heating and of cooling, and have found the following:

- (a) It is not sufficient to reduce the amount of granular metallic chromium on one side of the steel sheet which will form the outer surface of a can;
- (b) It is necessary to define strictly the coating weight of the film on each side of the steel sheet;
- (c) Referring to the granular metallic chromium formed on that side of the sheet which will form the inner

surface of the can, it is only the particles of a specified diameter or a larger one that contribute effectively to achieving a lower contact resistance upon application of pressure by the electrodes. It is not sufficient to form granular metallic chromium, but it is necessary to form sufficiently large particles of granular metallic chromium with a strictly defined density; and

(d) The same is true of that side of the sheet which will form the outer surface of the can. It is necessary to define strictly the density of sufficiently large particles of granular metallic chromium formed on that side, too.

The structures of the films formed on both sides of the steel sheet as defined above not only enable the satisfactory passage of a welding current and the prevention of localized heating, as a result of the destruction of hydrated chromium oxide by granular metallic chromium on one side of the sheet, but also make it possible to:

(i) Eliminate substantially any difference between the amounts of heat generated on the inner and outer surfaces of the can being manufactured; and

(ii) Prevent the contact resistance at the interface between the contacting portions of the sheet from becoming too low as compared with that at the interface between each film and the electrode, and achieve an optimum balance therebetween, thereby enabling the sufficient heating of the contacting portions to be welded, and facilitating the continuous formation of nuggets.

We have also made a detailed study of the relation which may exist between the degree of granulation of a metallic chromium layer on an electrolytically chromated steel sheet and the outlook and color tone of a lacquered or painted surface formed on the sheet. As a result, we have found that the surface of the sheet is more likely to scatter or absorb light having a short wavelength, as the density of granular metallic chromium increases, and that the lacquered or painted surface has, therefore, a dark outlook and a color tone which is easily changeable emphasizing a red or like color. It, therefore, follows that the film on that side of the steel sheet which will form the outer surface of a can may not contain any granular metallic chromium, or that, if it contains any granular metallic chromium, it may contain only an extremely small proportion of relatively large particles. Thus, the results of our study confirm that the electrolytically chromated steel sheet as hereinabove defined presents a lacquered or painted surface having an outstandingly good outlook, as well as it has an improved weldability.

This invention is based on our findings as hereinabove described. The object of this invention as hereinabove stated is essentially attained by an electrolytically chromated steel sheet carrying on one of the two principal surfaces thereof an electrolytic chromating film including a metallic chromium layer containing a high proportion of granular metallic chromium having a large particle diameter, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film including either a metallic chromium layer in a continuous sheet form which is free of any granular metallic chromium, or a metallic chromium layer containing only a very low proportion of granular metallic chromium having a large particle diameter. This invention may be reduced to practice in a variety of modes as will hereunder be set forth:

1. A surface treated steel sheet for a welded can which carries on one of the two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to the one surface of the sheet, the granular metallic chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the other surface of the sheet and granular metallic chromium laid on the said metallic chromium in sheet form, the granular metallic chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer.

2. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the one surface of the sheet and granular metallic chromium laid on the said metallic chromium in sheet form, the granular metallic chromium containing at least 50 to 300 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the other surface of the sheet and granular metallic chromium laid on the said metallic chromium in sheet form, the granular

metallic chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer.

3. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to the one surface of the sheet, the granular metallic chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to the other surface of the sheet, the granular metallic chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer.

4. A surface treated steel sheet for a welded can which carries on one of the two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the one surface of the sheet and granular metallic chromium laid on the said metallic chromium in sheet form, the granular metallic chromium containing at least 50 to 300 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to the other surface of the sheet, the granular metallic chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer.

5. A surface treated steel sheet for a welded can which carries on one of the two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to the one surface of the sheet, the granular metallic chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the other surface of the sheet, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer.

6. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the one surface of the sheet and granular metallic chromium laid on the said metallic chromium in sheet form, the granular metallic chromium containing at least 50 to 300 particles having a diameter of at least 0.03 micron per square micron of the layer, and 3 to 15 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the metallic chromium layer, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film comprising 30 to 150 mg, per square meter, of a metallic chromium layer consisting of metallic chromium adhering in sheet form to the other surface of the sheet, and 3 to 30 mg, per square meter, of a hydrated chromium oxide layer (in terms of metallic chromium) formed on the said metallic chromium layer.

DETAILED DESCRIPTION OF THE INVENTION:

The electrolytically chromated steel sheet of this invention is essentially characterized by carrying on one of the two principal surfaces thereof an electrolytic chromating film including a metallic chromium layer containing a high proportion of granular metallic chromium having a large particle diameter, while on the other of the two principal surfaces thereof, it carries an electrolytic chromating film including either a metallic chromium layer in sheet form which is free of any granular metallic chromium, or a metallic chromium layer containing only a very low proportion of granular metallic chromium having a large particle diameter.

A variety of methods can be employed to form a metallic chromium layer containing the desired

granular metallic chromium on the sheet surface to be treated. A few examples of the methods are:

- (a) Anode electrolytic treatment in a plating bath prior to chromium plating;
- (b) Fine anode electrolytic treatment which is carried out during chromium plating; and
- (c) Discontinuous plating which is carried out by providing a dipping time during chromium plating.

5 The anode electrolytic treatment of the steel surface prior to electrolytic chromating is carried out in a bath which is usually employed in the cathode electrolytic treatment for metallic chromium plating or hydrated chromium oxide coating, whereby a very thin hydrated chromium oxide film having a coating weight not exceeding 2 mg/m² is deposited on the electrolytically treated surface. This film has a multiplicity of fine discontinuous portions which enable the subsequent electrolytic chromating treatment to
10 form a metallic chromium layer consisting of granular metallic chromium on the steel surface. This method, therefore, makes it possible to form a film containing granular metallic chromium directly on the steel surface.

The other two methods, i.e. anode electrolytic treatment during chromium plating and discontinuous electrolytic treatment, are also carried out in a bath which is usually employed in the cathode electrolytic
15 treatment for chromium plating or hydrated chromium oxide coating, whereby a hydrated chromium oxide film which facilitates the formation of granular metallic chromium (i.e. which has a low anion content and a very small thickness) is formed on metallic chromium in sheet form adhering to the steel surface. This film has fine discontinuous portions containing anions locally which enable the subsequent electrolytic chromating treatment to form granular metallic chromium on the whole surface of the metallic chromium in sheet
20 form. Thus, it is possible to form by either method a film comprising metallic chromium adhering in sheet form to the steel surface and granular metallic chromium formed thereon.

The metallic chromium layer which is formed on one of the steel surfaces and contains a high proportion of granular metallic chromium having a large particle diameter consists either of a mass of granular metallic chromium adhering to the steel surface, or of a combination of metallic chromium adhering
25 in sheet form to the steel surface and granular metallic chromium formed thereon. The layer having either of these two structures can be formed if an appropriately selected method is employed as hereinabove described.

If the metallic chromium layer consists of a mass of granular metallic chromium, it is required to contain 30 to 150 mg of metallic chromium per square meter. If it contains only less than 30 mg of chromium per
30 square meter, the incomplete growth of granular metallic chromium results in only an incomplete reduction of contact resistance between the sheet surface forming the inner surface of a can and the electrode, and also between the contacting surfaces of the sheet. The incomplete growth of chromium particles means also the incomplete coating of the steel surface and therefore the low corrosion resistance thereof. Any layer containing more than 150 mg of chromium per square meter is uneconomical, though it may satisfactorily
35 achieve the intended result.

The particle diameter and density of granular metallic chromium have a critical bearing on the intended result. It is necessary to ensure that granular metallic chromium having a large particle diameter be formed in a high density, or proportion. More specifically, it is necessary to ensure that at least 30 particles having a diameter of at least 0.03 micron be formed in an area of square micron. The metallic chromium layer
40 consisting of a mass of granular metallic chromium usually contains several hundred particles per square micron of its surface. It is, however, relatively large particles that contribute to achieving a lower contact resistance upon application of pressure by the electrode. Hardly any such result can be expected from particles having a diameter which is smaller than 0.03 micron. Even sufficiently large particles fail to produce any satisfactory result, unless they are uniformly distributed. Therefore, it is necessary for the layer
45 to have a density of at least 30 particles per square micron.

If the metallic chromium layer consists of metallic chromium adhering in sheet form to the steel surface and granular metallic chromium formed thereon, it is required to contain 50 to 150 mg of metallic chromium per square meter. If it contains only less than 50 mg of chromium per square meter, the incomplete growth of granular metallic chromium results in only an incomplete reduction of contact resistance between the
50 sheet surface forming the inner surface of a can and the electrode, and also between the contacting surfaces of the sheet, though it may be satisfactory in corrosion resistance. Any layer containing more than 150 mg of chromium per square meter is uneconomical, though it may satisfactorily achieve the intended result. Therefore 150 mg of chromium per square meter is set as an upper limit.

The metallic chromium layer of this construction is also required to contain a high density or proportion
55 of granular metallic chromium having a large particle diameter. More specifically, it is required to contain 50 to 300 particles having a diameter of at least 0.03 micron per square micron. It is relatively large particles that contribute to achieving a lower contact resistance upon application of pressure by the electrode, and hardly any such result can be expected from particles having a diameter which is smaller than 0.03 micron,

as hereinabove stated.

The deposition of granular metallic chromium on metallic chromium in sheet form tends to be affected to some extent by the crystal orientation of the underlying chromium. In other words, granular metallic chromium is distributed less uniformly than in the metallic chromium layer consisting solely of granular chromium. Therefore, the layer is required to contain at least 50 sufficiently large particles per square micron to ensure that the granular chromium show the expected result. This is a proportion which is higher than the minimum proportion of such particles that the layer consisting solely of granular chromium is required to contain. The maximum proportion of 300 particles per square micron is a limit set to save the amount of chromium, and does not mean that a higher proportion will adversely affect the result expected from granular chromium.

The steel surface which has been coated with granular metallic chromium is electrolytically chromated, whereby a hydrated chromium oxide layer is formed on the metallic chromium layer. The hydrated chromium oxide layer is provided for ensuring the corrosion resistance and paintability of the steel surface. The layer is required to contain 3 to 15 mg of metallic chromium per square meter. If it contains only less than 3 mg of chromium per square meter, the steel surface is undesirably low in corrosion resistance, and if it contains more than 15 mg of chromium per square meter, a satisfactorily low contact resistance is difficult to achieve between the steel surface forming the inner surface of a can and the electrode.

The metallic chromium layer which is formed on the other of the steel surfaces is a layer containing no granular chromium (i.e. consisting solely of chromium in sheet form), or a layer in which granular chromium having a large particle diameter occupies a by far lower proportion than in the layer on the one steel surface. If the proportion of such granular chromium on the other steel surface exceeds a certain limit, the contact resistance at the interface between the contacting portions of the steel sheet becomes too low, as compared with the contact resistance at the interface between the film and the electrode, to generate a sufficiently large amount of heat in those contacting portions.

The metallic chromium layer on the other steel surface in which granular chromium having a large particle diameter occupies a very low proportion, may consist of either a mass of granular chromium adhering to the steel surface, or a combination of chromium adhering in sheet form to the steel surface and granular chromium formed on it, as is the case with the layer on the one steel surface. Either of these two layer structures can be formed by employing an appropriate method as hereinabove described. More specifically, a layer of the former construction is usually formed by the anode electrolytic treatment which is carried out in a plating bath prior to chromium plating, while a layer of the latter construction is usually formed by the fine anode electrolytic treatment which is carried out after chromium plating, or the discontinuous plating which is carried out by allowing a dipping time during chromium plating. If the fine anode electrolytic treatment is carried out on the other steel surface after chromium plating, however, no cathode electrolytic treatment is thereafter carried out, since the cathode electrolytic treatment forms too large an amount of granular chromium having a large particle diameter to be acceptable within the limits as defined by this invention.

The other steel surface is required to contain only a very low proportion of granular chromium having a large particle diameter, as hereinabove stated. More specifically, the granular chromium which is formed on the other steel surface is required to contain only less than 15 particles having a diameter of at least 0.03 micron per square micron of the layer, irrespective of the structure of the layer. It is relatively large particles having a diameter of at least 0.03 micron that contribute to achieving a lower contact resistance upon application of pressure by the electrode. If the layer contains 15 or more such particles per square micron, it begins to show a lower contact resistance, though locally, and disables the steel sheet to exhibit the intended result. Moreover, it will present only a printed or lacquered surface having an outlook which is dark and does not have a good color tone.

The Japanese patent application laid open under No. 35797/1988 discloses a method of producing an electrolytically chromated steel sheet carrying granular metallic chromium on one surface thereof, but hardly any such chromium on the other surface thereof by subjecting the one surface thereof at least once to anode electrolytic treatment during cathode electrolytic chromating treatment. Although this method may hardly form any granular chromium on the other surface of the sheet, the amount of granular chromium which it forms on that surface is considerably greater than the maximum proportion defined for the sheet of this invention. More specifically, the granular chromium which is formed on the other surface of the sheet contains at least about 20 particles having a diameter of at least 0.03 micron per square micron. This is a proportion which is too high to be expected to produce the result of this invention.

We have examined the reason why a certain amount of granular chromium, which is undesirably large from the standpoint of this invention, is formed on the other surface of the sheet when the method of the Japanese patent application as hereinabove referred to is employed, and have found that it is due to the

cathode electrolytic treatment to which not only one, but also the other of the sheet surfaces is subjected after one surface has been given anode electrolytic treatment. It, therefore, follows that, if the steel sheet of this invention is produced by the method including the intermediate anode electrolytic treatment of one surface thereof during cathode electrolytic treatment (i.e. the fine anode electrolytic treatment thereof during chromium plating), it is essential that the subsequent cathode electrolytic treatment be given only to the one surface which has been subjected to the intermediate anode electrolytic treatment.

The metallic chromium layer on the other surface of the sheet is defined as containing 30 to 150 mg of chromium per square meter, irrespective of its structure. If it contains only less than 30 mg of chromium per square meter, it fails to cover the sheet surface sufficiently to render it fully resistant to corrosion. Any layer containing more than 150 mg of chromium per square meter is uneconomical, though it may effectively achieve the intended result. Therefore 150 mg of chromium per square meter is set as an upper limit.

A hydrated chromium oxide layer is formed on the other surface of the sheet, too, when it is electrolytically chromated. This layer ensures the corrosion resistance and paintability of the sheet, as hereinbefore stated. The layer is required to contain 3 to 30 mg of chromium per square meter. If it contains only less than 3 mg of chromium per square meter, it fails to provide any satisfactory corrosion resistance and is also likely to give an undesirably low contact resistance. Any layer containing more than 30 mg of chromium per square meter is somewhat uneconomical, though it may not present any particular problem from a weldability standpoint. Moreover, the presence of too much hydrated chromium oxide is likely to give the sheet a colored surface having an uneven outlook due to the lack in uniformity of oxide distribution. Therefore 30 mg per square meter is set as an upper limit.

EXAMPLES:

The invention will now be described more specifically with reference to a variety of examples.

EXAMPLE 1

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution containing 30 g of sodium hydroxide per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment:

Solution:	The solution used for the pretreatment contained 100 g of chromium trioxide and 1 g of sulfuric acid per liter;
Temperature:	25 ° C;
Method:	Anode electrolytic treatment;
Anode current density:	10 A/dm ² ;
Electrolyzing time:	0.3 sec.

Conditions for the electrolytic chromating:

Solution:	The solution used for the treatment contained 175 g of chromium trioxide, 5 g of Na ₂ SiF ₆ and 0.9 g of Na ₂ SO ₄ per liter;
Temperature:	42 ° C;
Method:	Discontinuous cathode electrolytic treatment (cathodic on and off electrolysis);
Cathode current density:	40 A/dm ² ;
Electrolyzing time:	0.3 sec.;
On and off cycle:	Four cycles were repeated;
Dipping time:	0.3 sec.

EXAMPLE 2

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a

concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed at (a) below in a bath having the composition and temperature shown below, intermediate anodic treatment on one surface alone in the same bath under the conditions listed at (b) below, electrolytic chromating under the conditions listed at (a) below only on the surface given the intermediate anodic treatment, rinsing with water, and drying.

Electrolytic bath:

- 10 Composition: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 40 ° C.
 (a) Cathodic on and off electrolysis:
 Cathode current density: 40 A/dm²;
 15 Electrolyzing time: 0.3 Sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.
 (b) Anodic electrolysis: 2
 Anode current density: 4 A/dm²;
 20 Electrolyzing time: 0.3 sec.

EXAMPLE 3

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed at (A) below, after 10 seconds of dipping, electrolytic chromating on one surface alone under the conditions listed at (B) below, rinsing with water, and drying.

- 30 (A) Conditions for electrolytic chromating:
 Solution: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45 ° C;
 Method: Cathodic on and off electrolysis;
 35 Cathode current density: 40 A/dm²;
 Electrolyzing time: 0.3 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.
 (B) Conditions for electrolytic chromating:
 40 Solution: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45 ° C,
 Method: Cathodic on and off electrolysis;
 Cathode current density: 40 A/dm²;
 45 Electrolyzing time: 0.3 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.

EXAMPLE 4

50 Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment:

Solution: The solution contained 100 g of chromium trioxide and 1 g of sulfuric acid per liter;

Temperature: 25 ° C;

5 Method: Anodic electrolysis;

Anode current density: 10 A/dm²;

Electrolyzing time: 0.3 sec.

Conditions for electrolytic chromating:

10

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 42 ° C;

Method: Cathodic on and off electrolysis;

15 Cathode current density: 80 A/dm²;

Electrolyzing time: 0.3 sec.;

On and off cycle: Two cycles were repeated;

Dipping time: 0.3 sec.

20 EXAMPLE 5

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid
25 having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment:

30

Solution: The solution contained 100 g of chromium trioxide and 1 g of sulfuric acid per liter;

Temperature: 25 ° C;

Method: Anodic electrolysis;

35 Anode current density: 10 A/dm²;

Electrolyzing time: 0.3 sec.

Conditions for electrolytic chromating:

40

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 45 ° C;

Method: Cathodic on and off electrolysis;

Cathode current density: 80 A/dm²;

45 Electrolyzing time: 0.3 sec.;

On and off cycle: Two cycles were repeated;

Dipping time: 0.3 sec.

EXAMPLE 6

50

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by the process which had been employed in EXAMPLE 2, except that cathodic on and off electrolysis was carried out under the conditions shown at (a) below:

(a) Cathodic on and off electrolysis:

55 Cathode current density: 80 A/dm²;

Electrolyzing time: 0.2 sec.;

On and off cycle: Two cycles were repeated;

Dipping time: 0.5 sec.

EXAMPLE 7

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by repeating the process which had been employed in EXAMPLE 2, except that anodic electrolysis was carried out under the conditions shown at (b) below:

(b) Anodic electrolysis:

Anode current density: 0.5 A/dm²;

Electrolyzing time : 0.3 sec.

EXAMPLE 8

EXAMPLE 2 was repeated, except that cathodic on and off electrolysis was carried out at a cathode current density of 30 A/dm².

EXAMPLE 9

EXAMPLE 1 was repeated, except that pretreatment was carried out on both surfaces under the conditions employed in EXAMPLE 1, except for the following:

Anode current density: 10 A/dm² for one surface, and 1 A/dm² for the other surface;

Electrolyzing time : 0.3 sec. for each surface.

EXAMPLE 10

EXAMPLE 9 was repeated, except that electrolytic chromating (cathodic on and off electrolysis) was carried out in a bath having a temperature of 45 ° C.

EXAMPLE 11

EXAMPLE 1 was repeated, except that cathodic on and off electrolysis was carried out by employing a cathode current density of 30 A/dm² and repeating the on and off cycle twice.

EXAMPLE 12

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces in a solution having the composition shown below and under the conditions listed at (a) below, intermediate anodic treatment on the other surface in the same solution under the conditions listed at (b) below, electrolytic chromating on the other surface alone under the conditions listed at (a), rinsing with water, and drying.

Conditions for pretreatment:

Solution: The solution contained 100 g of chromium trioxide and 1 g of sulfuric acid per liter;

Temperature: 25 ° C;

Method: Anodic electrolysis;

Anode current density: 10 A/dm²;

Electrolyzing time: 0.3 sec.

Conditions for electrolytic chromating:

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 50 ° C;

(a) Cathodic on and off electrolysis:

Cathode current density: 40 A/dm²;

Electrolyzing time: 0.3 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.;
 (b) Anodic electrolysis:
 5 Anode current density: 4 A/dm²;
 Electrolyzing time: 0.3 sec.

EXAMPLE 13

10 EXAMPLE 1 was repeated, except that after chromating and before rinsing, posttreatment was carried out on both surfaces under the conditions listed below:

Conditions for posttreatment:

15 Solution: The solution contained 50 g of chromium trioxide per liter;
 Temperature: 45 ° C;
 Method: Cathodic electrolysis;
 Cathode current density: 10 A/dm²;
 Electrolyzing time: 0.3 sec.

EXAMPLE 14

EXAMPLE 2 was repeated, except that after the final chromating and before rinsing, posttreatment was carried out on both surfaces under the conditions employed in EXAMPLE 13.

EXAMPLE 15

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

35 Conditions for pretreatment:

Solution: The solution contained 100 g of chromium trioxide and 1 g of sulfuric acid per liter;
 Temperature: 25 ° C;
 40 Method: Anodic electrolysis;
 Anode current density : 10 A/dm²;
 Electrolyzing time: 0.3 sec.

Conditions for electrolytic chromating:

45 Solution: The solution contained 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;
 Temperature: 40 ° C;
 Method: Continuous cathodic electrolysis;
 50 Cathode current density: 160 A/dm²;
 Electrolyzing time: 0.3 sec.

EXAMPLE 16

55 EXAMPLE 15 was repeated, except that pretreatment was carried out at an anode current density of 5 A/dm² by employing a solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter and having a temperature of 40 ° C, and that electrolytic chromating was carried out by employing a solution having a temperature of 45 ° C.

EXAMPLE 17

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed at (a) below using a solution having the composition and temperature shown below, intermediate anodic treatment on one surface alone in the same solution under the conditions listed at (b) below, electrolytic chromating on the one surface alone given the said intermediate anodic treatment under the conditions listed at (a), rinsing with water, and drying.

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

Temperature: 45 ° C.

(a) Continuous cathodic electrolysis:

Cathode current density: 100 A/dm²;

Electrolyzing time : 0.3 sec.

(b) Anodic electrolysis:

Anode current density : 2 A/dm²;

Electrolyzing time : 0.3 sec.

EXAMPLE 18

EXAMPLE 17 was repeated, except that after the final chromating and before rinsing, posttreatment was carried out under the conditions listed below:

Conditions for posttreatment:

Solution: The solution contained 50 g of chromium trioxide and 0.5 g of NH_4F per liter;

Temperature: 45 ° C;

Method: Cathodic electrolysis;

Cathode current density: 20 A/dm²;

Electrolyzing time: 0.5 sec.

EXAMPLE 19

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed at (A) below, after 10 seconds of dipping, electrolytic chromating on one surface alone under the conditions listed at (B) below, rinsing with water, and drying.

(A) Conditions for electrolytic chromating:

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

Temperature: 35 ° C;

Method: Continuous cathodic electrolysis; 2

Cathode current density: 80 A/dm²;

Electrolyzing time: 0.3 sec.

(B) Conditions for electrolytic chromating:

Solution: The solution contained 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

Temperature: 45 ° C;

Method: Continuous cathodic electrolysis;

Cathode current density: 80 A/dm²;

Electrolyzing time: 0.3 sec.

EXAMPLE 20

EXAMPLE 15 was repeated, except that electrolytic chromating was carried out in a solution having a temperature of 46° C.

EXAMPLE 21

EXAMPLE 17 was repeated, except that anodic electrolysis was carried out at an anode current density of 0.5 A/dm².

EXAMPLE 22

EXAMPLE 15 was repeated, except that pretreatment was carried out by employing a solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter and having a temperature of 40° C, and an anode current density of 5 A/dm², while electrolytic chromating was carried out by using a solution temperature of 45° C and an electrolyzing time of 0.1 sec.

EXAMPLE 23

EXAMPLE 17 was repeated, except that cathodic electrolysis was carried out by employing a cathode current density of 150 A/dm² and an electrolyzing time of 0.1 sec.

EXAMPLE 24

EXAMPLE 16 was repeated, except that after chromating and before rinsing, posttreatment was carried out on both surfaces under the conditions listed below:

Conditions for posttreatment:

Solution:	The solution contained 50 g of chromium trioxide per liter;
Temperature:	45° C;
Method:	Cathodic electrolysis;
Cathode current density:	10 A/dm ² ;
Electrolyzing time:	0.3 sec.

EXAMPLE 25

EXAMPLE 17 was repeated, except that after the final chromating and before rinsing, posttreatment was carried out on both surfaces under the conditions listed below:

Conditions for posttreatment:

Solution:	The solution contained 50 g of chromium trioxide per liter;
Temperature:	45° C;
Method:	Cathodic electrolysis;
Cathode current density:	10 A/dm ² ;
Electrolyzing time:	0.3 sec.

COMPARATIVE EXAMPLE 1

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on both surfaces under the conditions listed at (A) below, electrolytic chromating on both surfaces under the conditions listed at (B) below, rinsing with water, and drying.

(A) Conditions for pretreatment:

Solution:	A solution containing 100 g of chromium trioxide and 1 g of sulfuric acid per liter;
Temperature:	25° C;

Method: Anodic electrolysis;

Anode current density: 10 A/dm²;

Electrolyzing time: 0.3 sec.

(B) Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 40 ° C;

Method: Continuous cathodic electrolysis;

Cathode current density: 160 A/dm²;

Electrolyzing time : 0.3 sec.

COMPARATIVE EXAMPLE 2

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment of both surfaces by dipping under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment (dipping):

Solution: A solution containing 100 g of chromium trioxide and 1 g of sulfuric acid per liter;

Temperature: 25 ° C.

Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 42 ° C;

Method: Cathodic on and off electrolysis;

Cathode current density: 40 A/dm²;

Electrolyzing time: 0.3 sec.;

On and off cycle: Four cycles were repeated;

Dipping time : 0.3 sec.

COMPARATIVE EXAMPLE 3

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;

Temperature: 45 ° C;

Method: Continuous cathodic electrolysis;

Cathode current density: 160 A/dm²;

Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 4

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces in a solution having the composition and temperature shown below under the conditions listed at (a) below, intermediate anodic treatment on both surfaces in the same solution under the conditions listed at (b) below,

electrolytic chromating on both surfaces under the conditions listed at (a), rinsing with water, and drying.

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

Temperature: 40 ° C.

5 (a) Cathodic on and off electrolysis:

Cathode current density: 40 A/dm²;

Electrolyzing time: 0.3 sec.;

On and off cycle: Two cycles were repeated;

Dipping time: 0.3 sec.

10 (b) Anodic electrolysis:

Anode current density: 4 A/dm²;

Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 5

15

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces in a solution having the composition and temperature shown below under the conditions listed below, dipping treatment of both surfaces in the same solution, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying:

20

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

25

Temperature: 45 ° C;

Method: Continuous cathodic electrolysis;

Cathode current density: 100 A/dm²;

Electrolyzing time: 0.3 sec.

30 COMPARATIVE EXAMPLE 6

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed below, posttreatment on both surfaces under the conditions listed below, rinsing with water, and drying.

35

Conditions for electrolytic chromating:

40

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;

Temperature: 45 ° C;

Method: Continuous cathodic electrolysis;

45

Cathode current density: 100 A/dm²;

Electrolyzing time: 0.3 sec.

Conditions for posttreatment:

50

Solution: A solution containing 50 g of chromium trioxide and 0.5 g of NH_4F per liter;

Temperature: 45 ° C;

Method: Cathodic electrolysis;

Cathode current density: 20 A/dm²;

Electrolyzing time: 0.5 sec.

55

COMPARATIVE EXAMPLE 7

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each

treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions listed at (A) below, after 10 seconds of dipping, electrolytic chromating on both surfaces under the conditions listed at (B) below, rinsing with water, and drying.

(A) Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45 ° C;
 Method: Cathodic on and off electrolysis;
 Cathode current density: 40 A/dm²;
 Electrolyzing time: 0.3 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.

(B) Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45 ° C;
 Method: Cathodic on and off electrolysis;
 Cathode current density: 40 A/dm²;
 Electrolyzing time: 0.3 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.

COMPARATIVE EXAMPLE 8

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces under the conditions shown at (A) below, electrolytic chromating on one surface alone under the conditions shown at (B) below, rinsing with water, and drying.

(A) Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 35 ° C;
 Method: Continuous cathodic electrolysis;
 Cathode current density: 80 A/dm²;
 Electrolyzing time: 0.3 sec.

(B) Conditions for electrolytic chromating:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45 ° C;
 Method: Continuous cathodic electrolysis;
 Cathode current density: 80 A/dm²;
 Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 9

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment:

Solution: A solution containing 100 g of chromium trioxide and 1 g of sulfuric acid per liter;
 Temperature: 25 ° C;
 Method: Anodic electrolysis;
 5 Anode current density: 10 A/dm²;
 Electrolyzing time: 0.3 sec.

Conditions for electrolytic chromating:

10 Solution: A solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;
 Temperature: 42 ° C;
 Method: Cathodic on and off electrolysis;
 Cathode current density: 120 A/dm²;
 15 Electrolyzing time: 0.2 sec.;
 On and off cycle: Two cycles were repeated;
 Dipping time: 0.3 sec.

COMPARATIVE EXAMPLE 10

20 COMPARATIVE EXAMPLE 4 was repeated, except that intermediate anodic electrolysis was carried out on one surface alone by employing an anode current density of 0.2 A/dm², and that the subsequent chromating was carried out on that surface alone.

COMPARATIVE EXAMPLE 11

COMPARATIVE EXAMPLE 4 was repeated, except that intermediate anodic electrolysis was carried out on one surface alone by employing an anode current density of 0.5 A/dm².

COMPARATIVE EXAMPLE 12

COMPARATIVE EXAMPLE 4 was repeated, except that a cathode current density of 20 A/dm² was employed instead of 40 A/dm², and that intermediate anodic electrolysis and the subsequent cathodic electrolysis were carried out on one and the same surface alone.

COMPARATIVE EXAMPLE 13

COMPARATIVE EXAMPLE 9 was repeated, except that pretreatment was carried out on both surfaces by employing an anode current density of 10 A/dm² for one surface and 2 A/dm² for the other surface and an electrolyzing time of 0.3 sec. for each surface, and that for the electrolytic chromating cathodic electrolysis was carried out by employing a cathode current density of 40 A/dm² and an electrolyzing time of 0.3 sec., and repeating the on and off cycle four times.

COMPARATIVE EXAMPLE 14

COMPARATIVE EXAMPLE 9 was repeated, except that for the electrolytic chromating cathodic electrolysis was carried out by employing a cathode current density of 40 A/dm² and an electrolyzing time of 0.3 sec., and repeating the on and off cycle four times, and that posttreatment was carried out on both surfaces under the conditions listed below:

Conditions for posttreatment:

Solution: A solution containing 50 g of chromium trioxide per liter;
 Temperature: 45 ° C;
 55 Method: Cathodic electrolysis;
 Cathode current density: 30 A/dm²;
 Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 15

COMPARATIVE EXAMPLE 4 was repeated, except that intermediate anodic electrolysis was carried out on one surface alone, and the subsequent chromating on that surface alone, too, and that posttreatment was carried out on both surfaces under the conditions listed below:

Conditions for posttreatment:

Solution: A solution containing 50 g of chromium trioxide per liter;
 Temperature: 45 ° C;
 Method: Cathodic electrolysis;
 Cathode current density: 30 A/dm²;
 Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 16

COMPARATIVE EXAMPLE 14 was repeated, except that an electrolyzing time of 0.5 sec. was employed for the posttreatment.

COMPARATIVE EXAMPLE 17

COMPARATIVE EXAMPLE 15 was repeated, except that an electrolyzing time of 0.5 sec. was employed for the posttreatment.

COMPARATIVE EXAMPLE 18

COMPARATIVE EXAMPLE 1 was repeated, except that pretreatment was carried out on one surface alone, and that chromating was carried out in a solution having a temperature of 50 ° C.

COMPARATIVE EXAMPLE 19

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, electrolytic chromating on both surfaces in a solution having the composition and temperature shown below under the conditions listed at (a) below, intermediate anodic treatment on one surface alone in the same solution under the conditions listed at (b) below, electrolytic chromating on that surface alone under the conditions listed at (a), rinsing with water, and drying:

Solution: A solution containing 175 g of chromium trioxide, 5 g of Na₂SiF₆ and 0.9 g of Na₂SO₄ per liter;
 Temperature: 45 ° C.
 (a) Continuous cathodic electrolysis:
 Cathode current density: 100 A/dm²;
 Electrolyzing time : 0.3 sec.
 (b) Anodic electrolysis:
 Anode current density : 0.3 A/dm²;
 Electrolyzing time : 0.3 sec.

COMPARATIVE EXAMPLE 20

Two cold rolled steel sheets having thicknesses of 0.22 mm and 0.32 mm, respectively, were each treated by a process comprising electrolytic degreasing in a solution of sodium hydroxide having a concentration of 30 g per liter, rinsing with water, electrolytic pickling in an aqueous solution of sulfuric acid having a concentration of 5 g per liter, rinsing with water, pretreatment on one surface alone under the conditions listed below, electrolytic chromating on both surfaces under the conditions listed below, rinsing with water, and drying.

Conditions for pretreatment:

- 5 Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 40°C ;
 Method: Anodic electrolysis;
 Anode current density: 5 A/dm^2 ;
 Electrolyzing time: 0.3 sec.

10 Conditions for electrolytic chromating:

- Solution: A solution containing 175 g of chromium trioxide, 5 g of Na_2SiF_6 and 0.9 g of Na_2SO_4 per liter;
 Temperature: 45°C ;
 15 Method: Continuous cathodic electrolysis;
 Cathode current density: 100 A/dm^2 ;
 Electrolyzing time: 0.1 sec.

COMPARATIVE EXAMPLE 21

- 20 COMPARATIVE EXAMPLE 20 was repeated, except that electrolytic chromating was carried out by employing a cathode current density of 30 A/dm^2 and an electrolyzing time of 0.3 sec.

COMPARATIVE EXAMPLE 22

- 25 COMPARATIVE EXAMPLE 19 was repeated, except that cathodic electrolysis was carried out by employing an electrolyzing time of 0.1 sec., and anodic electrolysis at an anode current density of 2 A/dm^2 .

COMPARATIVE EXAMPLE 23

- 30 COMPARATIVE EXAMPLE 20 was repeated, except that electrolytic chromating was carried out by employing a cathode current density of 160 A/dm^2 and an electrolyzing time of 0.3 sec., and that posttreatment was thereafter carried out under the conditions shown below:

35 Conditions for posttreatment:

- Solution: A solution containing 50 g of chromium trioxide per liter;
 Temperature: 45°C ;
 Method: Cathodic electrolysis;
 40 Cathode current density: 30 A/dm^2 ;
 Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 24

- 45 COMPARATIVE EXAMPLE 19 was repeated, except that anodic electrolysis was carried out at an anode current density of 2 A/dm^2 , and that after the final chromating and before rinsing, posttreatment was carried out on both surfaces under the conditions shown below:

Conditions for posttreatment:

- 50 Solution: A solution containing 50 g of chromium trioxide per liter;
 Temperature: 45°C ;
 Method: Cathodic electrolysis;
 Cathode current density: 30 A/dm^2 ;
 55 Electrolyzing time: 0.3 sec.

COMPARATIVE EXAMPLE 25

COMPARATIVE EXAMPLE 23 was repeated, except that an electrolyzing time of 0.5 sec. was employed for the posttreatment.

COMPARATIVE EXAMPLE 26

COMPARATIVE EXAMPLE 24 was repeated, except that an electrolyzing time of 0.5 sec. was employed for the posttreatment.

Measurements were made of the densities of metallic chromium and hydrated chromium oxide in the film on each side of each of the electrolytically chromated steel sheets which had been produced in EXAMPLES 1 to 25 and COMPARATIVE EXAMPLES 1 to 26 as hereinabove described. A replica was prepared from the film and the number of chromium particles having a diameter of at least 0.03 micron as observed through an electron microscope was counted as a measure of its granular metallic chromium density. The results are shown in TABLES 1 to 5 below. The results of COMPARATIVE EXAMPLE 11 appearing in TABLE 4 are those obtained from the products of the method disclosed in the Japanese patent application laid open under No. 35797/1988.

The sheets were also evaluated for weldability, outlook after lacquering, and corrosion resistance (filiform corrosion resistance, corrosion resistance after lacquering, and corrosion resistance) by the methods as will hereinafter be described. The results are shown in TABLES 6 to 10. TABLES 6 to 10 confirm the presence of outstanding distinctions between the products of the EXAMPLES embodying this invention and those of the COMPARATIVE EXAMPLES in welding property and outlook after lacquering, and the great advantages of this invention. The results of the evaluation confirm also the good corrosion resistance of all of the products embodying this invention.

The following is a description of the methods which were employed for the evaluation: High Speed Welding:

Each sheet having the thickness of 0.22 mm was slit after printing, and the slit piece thereof was welded to make a size 202 can by a Soudronic wire mushroom welding machine employing a welding current set in a number of ways and in accordance with the conditions set forth below:

Inverter power source frequency	500 Hz
Welding rate	50 m/min.
Electrode pressure	60 kgf
Overlapping width	0.4 mm
Nugget pitch	0.75 mm

The range of a welding current within which a weld strength satisfying a tearing test could be obtained without causing any splashing was found from the graduations marked on a current setting device. The following is a definition of the symbols used in TABLES 6 to 10 to express the results of evaluation:

Symbol	Meaning
⊙	The sheet permitted the use of the range of a welding current as marked at 5 or above, and exhibited very good welding properties;
o	The sheet permitted the use of the range of a welding current as marked at 3 or 4, and exhibited good welding properties;
Δ	The sheet permitted only the use of the range of a welding current as marked at 1 or 2, and was found difficult to use for any practical application, though its welding was not impossible;
x	The sheet did not permit the use of any welding current available on the current setting device, and could not be welded.

5G Welding:

Each sheet having the thickness of 0.32 mm was slit after printing, and an attempt was made to weld the slit piece into a 5-gallon can by a Soudronic wire mushroom welding machine employing a welding current set in a number of ways and in accordance with the conditions set forth below:

Inverter power source frequency	180 Hz
Welding rate	22 m/min.
Electrode pressure	65 kgf
Overlapping width	0.8 mm
Nugget pitch	1.2 mm

The range of a welding current within which a weld strength satisfying a tearing test could be obtained without causing any splashing was found from the graduations marked on a current setting device. The meanings of the symbols are as defined above.

Color Tone of Surface:

The outer surface of each welded can was coated with a layer of a transparent lacquer having a dry coating weight of 60 mg/m², and was visually checked for any change in color tone. The symbols used to express the results have the meanings as defined below:

Symbol	Meaning
o	Good. No change in color tone was found;
x	Bad. A change in color tone was found.

Color Tone of Printed Surface:

The outer surface of each welded can was printed with a wine-colored metallic paint, and the color tone of the printed surface was visually compared with that of the paint itself. The symbols used to express the results have the meanings as defined below:

Symbol	Meaning
o	Good. No difference in color tone was found;
x	Bad. A difference in color tone was found.

Filiform Corrosion Resistance:

The outer surface of each 5G welded can was visually inspected for any product of filiform corrosion that might have been formed in any defective portion of its coating during 12 months of its storage in a warehouse. The symbols used to express the results have the meanings as defined below:

Symbol	Meaning
o	No product of filiform corrosion was found;
x	A product of filiform corrosion was found.

Corrosion Resistance of a Coated Surface:

One side of each sheet, which would be used to form the inner surface of a welded can, was coated with a layer of an epoxy-phenol resin paint having a coating weight of 50 mg/m², and after the paint had been baked, a cruciform cut was made in the coating layer by a sharp cutter knife so as to reach the steel surface, and a force was applied by an Erichsen tester to the other side of the sheet (used to form the outer surface of the can) to prepare an extruded test specimen having an extruded depth of 5 mm from the center of the cruciform cut. The test specimen was dipped in an aqueous solution containing 1.5% of NaCl and 1.5% of citric acid and having a temperature of 38° C, and after 96 hours, measurement was made of the width of the corroded portion of the steel surface in the cruciform cut. The symbols used to express the

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results have the meanings as defined below:

Symbol	Meaning
o	The corroded width was less than 1 mm;
x	The corroded width was 1 mm or more.

Corrosion Resistance:

A stack of 100 sheets to be tested was placed between a pair of plates, and bound together tightly with steel wires passed around them in a cruciform way. After one month of storage in a place having a temperature of 25 ° C and a humidity of 85%, each sheet was examined for corrosion. The symbols used to express the results have the meanings as defined below:

Symbol	Meaning
o	No corrosion was found;
x	Corrosion was found.

TABLE 1

	Density of metallic chromium (One surface of sheet/other surface)*2 mg/m ²	Density of hydrated chromium oxide*1 (One surface of sheet/other surface)*2 mg/m ²	Structure of metallic chromium layer*3 (One surface of sheet/other surface)*2	Density of granular chromium*4 (One surface of sheet/other surface)*2 Particles/μm ²
1	113/108	8/8	a/b	61/4
2	110/56	9/8	b/b	120/2
3	110/53	6/6	b/b	51/8
4	118/121	7/8	a/b	92/13
5	109/109	6/6	a/b	33/5
6	112/60	9/9	b/b	180/14
7	108/60	10/9	b/b	55/2
8	80/36	7/7	b/b	82/2
9	113/109	8/8	a/a	61/13
10	100/98	7/7	a/a	33/6
11	35/35	7/7	a/b	33/2
12	95/48	8/8	b/a	82/13
13	115/110	14/14	a/b	61/4
14	110/60	14/18	b/b	120/2

EXAMPLE

*1 In terms of metallic chromium, *2 One surface of sheet is that which will form the inner surface of a can.

*3 a: A mass of granular metallic chromium:

b: Metallic chromium in sheet form and granular chromium thereon.

*4 Number of particles having a diameter of at least 0.03 μm.

TABLE 2

	Density of metallic chromium (One surface of sheet/other surface)*2 mg/m ²	Density of hydrated chromium oxide*1 (One surface of sheet/other surface)*2 mg/m ²	Structure of metallic chromium layer*3 (One surface of sheet/other surface)*2	Density of granular chromium*4 (One surface of sheet/other surface)*2 Particles/μm ²
15	135/108	7/6	a/c	95/0
16	129/101	5/7	a/c	46/0
17	140/69	10/10	b/c	180/0
18	150/78	14/16	b/c	180/0
19	121/61	10/10	b/c	80/0
20	110/93	7/7	a/c	34/0
21	135/70	10/10	b/c	52/0
22	36/32	5/5	a/c	32/0
23	59/33	9/8	b/c	60/0
24	132/105	14/14	a/c	46/0
25	145/72	14/18	b/c	180/0

*1 In terms of metallic chromium, *2 One surface of sheet is that which will form the inner surface of a can.

*3 a: A mass of granular metallic chromium:

b: Metallic chromium in sheet form and granular chromium thereon.

c: Metallic chromium in sheet form

*4 Number of particles having a diameter of at least 0.03 μm.

TABLE 3

	Density of metallic chromium (One surface of sheet/other surface)*2 mg/m ²	Density of hydrated chromium oxide*1 (One surface of sheet/other surface)*2 mg/m ²	Structure of metallic chromium layer*3 (One surface of sheet/other surface)*2	Density of granular chromium*4 (One surface of sheet/other surface)*2 Particles/μm ²
1	133/135	6/6	a/a	90/101
2	110/112	8/8	b/b	6/4
3	102/101	6/7	c/c	0/0
4	110/110	10/8	b/b	110/110
5	60/56	7/8	c/c	0/0
6	70/66	16/16	c/c	0/0
7	110/112	7/8	b/b	45/40
8	112/65	10/10	b/c	6/0

COMPARATIVE
EXAMPLE

*1 In terms of metallic chromium, *2 One surface of sheet is that which will form the inner surface of a can.

*3 a: A mass of granular metallic chromium:

b: Metallic chromium in sheet form and granular chromium thereon.

c: Metallic chromium in sheet form

*4 Number of particles having a diameter of at least 0.03 μm.

TABLE 4

	Density of metallic chromium (One surface of sheet/other surface)*2 mg/m ²	Density of hydrated chromium oxide*1 (One surface of sheet/other surface)*2 mg/m ²	Structure of metallic chromium layer*3 (One surface of sheet/other surface)*2	Density of granular chromium*4 (One surface of sheet/other surface)*2 Particles/μm ²
9	124/125	10/9	a/b	105/18
10	105/58	8/8	b/b	43/2
11	108/100	9/9	b/b	55/20*5
12	51/27	7/7	b/b	62/2
13	113/110	9/9	a/a	61/20
14	115/112	24/26	a/b	61/4
15	110/58	23/25	b/b	120/2
16	112/112	36/33	a/b	61/4
17	115/60	34/33	b/b	120/2

COMPARATIVE
EXAMPLE

*1 In terms of metallic chromium, *2 One surface of sheet is that which will form the inner surface of a can.

*3 a: A mass of granular metallic chromium:

b: Metallic chromium in sheet form and granular chromium thereon.

c: Metallic chromium in sheet form

*4 Number of particles having a diameter of at least 0.03 μm.

*5 Produced by the method described in the Japanese patent application laid open under No. 35797/1988.

TABLE 5

	Density of metallic chromium (One surface of sheet/other surface)*2 mg/m ²	Density of hydrated chromium oxide*1 (One surface of sheet/other surface)*2 mg/m ²	Structure of metallic chromium layer*3 (One surface of sheet/other surface)*2	Density of granular chromium*4 (One surface of sheet/other surface)*2 Particles/ μ m ²
18	100/81	5/6	a/c	25/0
19	136/69	10/10	b/c	41/0
20	25/22	5/6	a/c	33/0
21	26/23	5/5	a/c	21/0
22	42/23	8/8	b/c	28/0
23	130/105	24/26	a/c	46/0
24	140/70	23/23	b/c	180/0
25	130/110	36/33	a/c	46/0
26	145/75	34/33	b/c	180/0

COMPARATIVE
EXAMPLE

*1 In terms of metallic chromium, *2 One surface of sheet is that which will form the inner surface of a can.

*3 a: A mass of granular metallic chromium:

b: Metallic chromium in sheet form and granular chromium thereon.

c: Metallic chromium in sheet form

*4 Number of particles having a diameter of at least 0.03 μ m.

*5 Produced by the method described in the Japanese patent application laid open under No. 35797/1988.

TABLE 6

		High speed weldability	5G weldability	Color tone of surface	Color tone of printed surface	Filiform corrosion resistance	Corrosion resistance of lacquered surface	Corrosion resistance
EXAMPLE	1	⊙	⊙	○	○	○	○	○
	2	○	⊙	○	○	○	○	○
	3	○	⊙	○	○	○	○	○
	4	⊙	⊙	○	○	○	○	○
	5	○	⊙	○	○	○	○	○
	6	○	○	○	○	○	○	○
	7	○	⊙	○	○	○	○	○
	8	○	⊙	○	○	○	○	○
	9	○	○	○	○	○	○	○
	10	⊙	⊙	○	○	○	○	○
	11	⊙	⊙	○	○	○	○	○
	12	○	⊙	○	○	○	○	○
	13	○	○	○	○	○	○	○
	14	○	○	○	○	○	○	○

TABLE 7

		High speed weldability	5G weldability	Color tone of surface	Color tone of printed surface	Filliform corrosion resistance	Corrosion resistance of lacquered surface	Corrosion resistance
EXAMPLE	15	◎	◎	○	○	○	○	○
	16	◎	◎	○	○	○	○	○
	17	○	◎	○	○	○	○	○
	18	○	○	○	○	○	○	○
	19	○	◎	○	○	○	○	○
	20	○	◎	○	○	○	○	○
	21	○	◎	○	○	○	○	○
	22	○	◎	○	○	○	○	○
	23	○	◎	○	○	○	○	○
	24	○	○	○	○	○	○	○
	25	○	○	○	○	○	○	○

TABLE 8

		High speed weldability	5G weldability	Color tone of surface	Color tone of printed surface	Filiform corrosion resistance	Corrosion resistance of lacquered surface	Corrosion resistance
COMPARATIVE EXAMPLE	1	△	○	x	x	○	○	○
	2	x	x	○	○	○	○	○
	3	x	△	○	○	○	○	○
	4	△	○	x	x	○	○	○
	5	x	△	○	○	○	○	○
	6	x	x	○	○	○	○	○
	7	△	△	x	x	○	○	○
	8	x	x	○	○	○	○	○

TABLE 9

		High speed weldability	5G weldability	Color tone of surface	Color tone of printed surface	Filiform corrosion resistance	Corrosion resistance of lacquered surface	Corrosion resistance
COMPARATIVE EXAMPLE	9	△	△	x	x	○	○	○
	10	△	△	○	○	○	○	○
	11	△	△	x	x	○	○	○
	12	○	○	○	○	x	○	x
	13	△	△	x	x	○	○	○
	14	△	x	○	○	○	○	○
	15	x	x	○	○	○	○	○
	16	x	x	x	x	○	○	○
	17	x	x	x	x	○	○	○

TABLE 10

		High speed weldability	5G weldability	Color tone of surface	Color tone of printed surface	Filiform corrosion resistance	Corrosion resistance of lacquered surface	Corrosion resistance
COMPARATIVE EXAMPLE	18	△	○	○	○	○	○	○
	19	△	○	○	○	○	○	○
	20	○	○	○	○	×	×	×
	21	△	○	○	○	×	×	×
	22	△	△	○	○	×	○	×
	23	×	△	○	○	○	○	○
	24	×	△	○	○	○	○	○
	25	×	×	×	×	○	○	○
	26	×	×	×	×	○	○	○
	27	△	△	×	×	○	○	○

55 Claims

1. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of a

mass of granular metallic chromium adhering to said one surface, said granular metallic chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said other surface and granular metallic chromium laid on said chromium in sheet form, said last-mentioned granular metallic chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of said metallic chromium layer on said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said last-mentioned metallic chromium layer.

2. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said one surface and granular metallic chromium laid on said chromium in sheet form, said granular chromium containing 50 to 300 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said other surface and granular metallic chromium laid on said chromium adhering to said other surface, said last-mentioned granular chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of said metallic chromium layer on said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said last-mentioned metallic chromium layer.

3. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to said one surface, said granular metallic chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to said other surface, said last-mentioned granular chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of said metallic chromium layer on said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said last-mentioned metallic chromium layer.

4. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said one surface and granular metallic chromium laid on said chromium in sheet form, said granular chromium containing 50 to 300 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to said other surface, said last-mentioned granular chromium containing less than 15 particles having a diameter of at least 0.03 micron per square micron of said metallic chromium layer on said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said last-mentioned metallic chromium layer.

5. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of a mass of granular metallic chromium adhering to said one surface, said granular chromium containing at least 30 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated

chromium oxide layer formed on said last-mentioned metallic chromium layer.

6. A surface treated steel sheet for a welded can which carries on one of two principal surfaces thereof an electrolytic chromating film comprising 50 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said one surface and granular metallic chromium laid on said chromium in sheet form, said granular chromium containing 50 to 300 particles having a diameter of at least 0.03 micron per square micron of said layer, and 3 to 15 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said metallic chromium layer, while on the other of said surfaces, said sheet carries an electrolytic chromating film comprising 30 to 150 mg/m² of a metallic chromium layer consisting of metallic chromium adhering in sheet form to said other surface, and 3 to 30 mg/m² (in terms of metallic chromium) of a hydrated chromium oxide layer formed on said last-mentioned metallic chromium layer.