Dec. 10, 1963 HIROMU UCHIDA ETAL 3,113,845

CHROMIUM-PLATED STEEL

Filed March 21, 1961

FIG 1

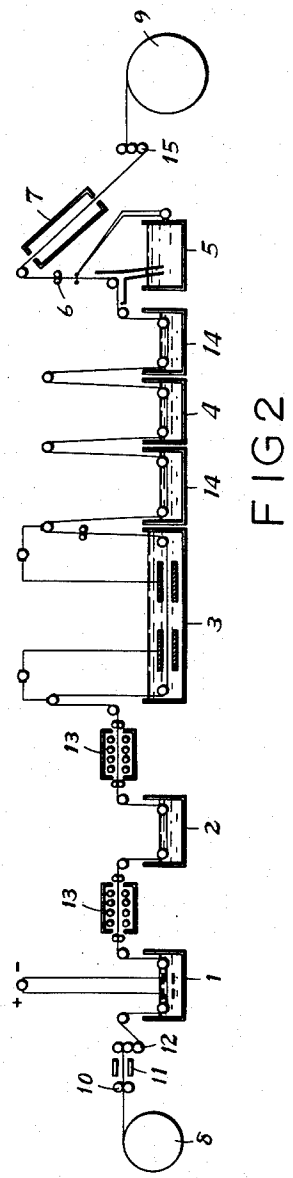
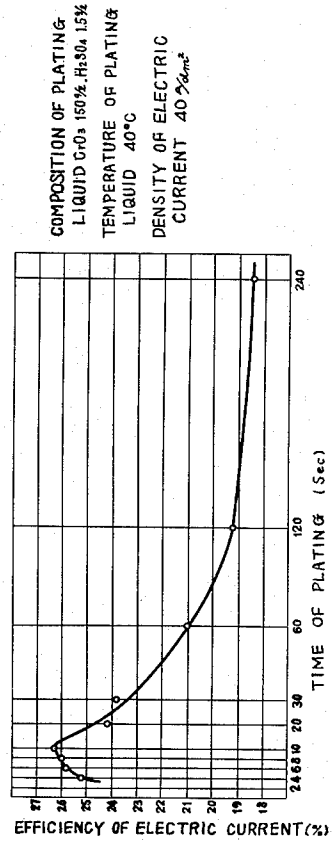


FIG 2



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CHROMIUM-PLATED STEEL

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This invention relates in general to chromium-plated steel adapted to receive surface coatings, and more particularly, to chromium-plated steel sheet adapted to receive surface coatings, such as paint or thin layers of synthetic resin and to a method for making these materials.

The usual chromium plating applied to steel sheets has been applied to shaped steel sheets with the object rendering the steel sheet anti-corrosive or for ornamental purposes. In general, the chromium-plated layer will become hard by the absorption of hydrogen produced thereon. However, pin holes will be caused by the bubbles of hydrogen. In an effort to avoid this in the conventional practice, the chromium of 0.25–1μ has been deposited on copper, nickel or their double plating to be used but mainly for ornamental or anti-corrosive purpose. When the chromium is plated directly on the steel sheet, it has poor anti-corrosive properties unless it is made fairly thick. The thickness of the chromium-plated layer must be made more than 3μ to possess sufficient anti-corrosive power. However, these materials are still troubled with pin holes and are not workable after plating. Moreover, it has sufficient anticorrosive power, so that it has been used without further anti-corrosion coating.

A primary object of the invention is to provide an improved chromium-plated steel.

It is a further object of the present invention to provide a chromium plated steel material which has high adhesive and workability characteristics and which is adapted to readily receive and retain surface coatings so as to give it good anti-corrosion characteristics and at the same time to avoid the difficulties of the prior art.

Other and more specific objects, features and advantages of the invention will appear from the detailed description given below in conjunction with accompanying drawings which form a part of this specification and illustrate by way of examples preferred embodiments of the invention. In the drawings: FIG. 1 is a schematic elevation of an embodiment of the invention, showing a working process thereof. FIG. 2, is a diagram, illustrating the relation between efficiency of electric current and time of plating.

Several methods such as chemical treating, metal plating, etc. have been proposed to give steel sheet desirable properties such as anti-corrosive power, workability, etc. However, the method of the present invention, although involving a plating operation, is entirely different from the metal plating method included in the prior art. Basically, it involves plating a very thin chromium layer (within the limits of specified thickness) directly on the surface of a steel sheet. The surface is preferably precleaned by usual treatment. A surface coating is then applied to the chromium layer. As a result of these steps, a sheet will be made which is provided with such desirable properties as adhesion for paints, anti-corrosive power, workabilities for bending, drawing, etc., heat resistance for baking of coating, etc., and a fine surface which is adapted for support of coatings on polished steel sheet. As compared with other chemically treated steel sheets or steel sheets plated with tin, zinc, etc. in the prior art, the present products are decided improvements.

In the method of chromium plating, according to the present invention, ordinary carbon steel sheet or strip

(band) steel is treated with usual surface cleaning agents. While moving the steel sheet a chromium layer of 0.1μ to 0.005μ thick is continuously plated thereon, the thickness depending on the method employed to effect chromium plating. The chromium plating of this thickness and surface condition is such as to give the optimum surface for steel sheet to be coated with paint.

The chromium plated steel sheet, per se, is excellent in its adhesion to paints, in its resisting power against acid, alkali, weather and salt water, and in its thermostability upon the baking of paints. Moreover, its color and luster are as beautiful as those of tin plate surfaces. In contrast, other chemically treated steel sheets have gray white color or fluorescence, etc. Furthermore, its luster is not lost when a paint layer is coated thereon. When coated with paint as mentioned below, the steel sheet is given further desirable characteristics such as anti-corrosive power and workabilities in addition to the characteristic obtained by chromium plating thereon.

According to this invention, the chromium plating is made in a homogeneous layer by controlling the composition of plating bath, temperature of plating liquid, density of electric current and time of plating, so as to minimize pin holes formation and to avoid the generation of hydrogen.

Moreover, the proper control of these factors avoids the need for a rocker in the plating operation, avoids the generation of stripes due to the movement of non-homogeneous plating liquid etc. and avoids inferiority luster in the product. As the occasion demands, for the purpose of improving the anti-corrosive power to preserve or store the plated steel so that it will maintain its proper characteristics within desired limits, it is effective to employ an auxiliary treatment using 2–3% solution of $Na_2Cr_2O_7$ or about 1% solution of CrO_3.

In the continuous plating of strip steel, it is preferred to use a single bath. However, the numbers of tanks and baths are determined by the particular circumstances. The chromium plated strip steel obtained in accordance with this invention may be preserved for a long time for reception of paint, by daubing it with vegetable oil such as cottonseed oil or wax as anti-corrosive oil, or may be painted as it is.

When the chromium plated surface of this invention is further electrically plated with zinc, a steel sheet for outdoor use, which is particularly excellent in resistance against weather is obtained. Moreover, a surface treated steel sheet, having very good workability adapted for deep drawing is thus also obtained.

The anti-corrosive power of a paint coated chromium plated steel sheet according to the invention will be described below.

It is generally considered that the anticorrosive power of chromium plated steel sheet will be decreased regardless of the thickness of plating when it is subjected to bending or drawing unless it is coated with paint. Even if only spots are coated, the plated layer will be extended, so that it is usually regarded that the thinner the plating, the lower will the anti-corrosive power be decreased during working.

In contrast to this, according to the present invention, both workability and anti-corrosive power of the chromium plated steel sheet will not be decreased in the least when the thickness range of the plating is in the range of about 0.1μ to 0.005μ. It has been found that both workability and anti-corrosive power thereof are superior to that of tin plate which is coated with the same paints in the manner and is drawn in the same method.

In the production of chromium plated steel sheet according to the invention, as shown in FIG. 1 strip (band) steel is moved and oil and fats on its surface are continuously removed in an electrolytical deoiling tank 1. After

washing, it is dipped in a pickling tank 2 to remove rust on its surface. Then it is washed and electric plating is effected with chromium in a chromium plating tank 3. After washing with hot water, it is chemically treated with about 1% chromic acid liquid in a chromic acid treating tank 4, then it is washed with hot water and oiled with emulsion oil by means of oiler 5. It is squeezed by a pair of rolls 6 and dried in a dryer 7, thus the whole working process will be finished.

The chromium plating tank may be either the horizontal type or the vertical type. The negative electrode will be electrically connected to the strip steel through charging rollers and positive electrode will be electrically connected through the lead anodes and the plating liquid is continuously circulated at a constant speed in the tank. In FIG. 1, 8 is an uncoiler, 9 is a recoiler, 10 is a pair of pinch rollers, 11 is a welder, 12 is a tension bridle, 13 are spray washers, 14 are hot water washing tanks and 15 is a drive bridle.

In case the plating tank is increased to two or three units, the strip steel will move from one tank to another. When the strip steel is temporarily exposed in the air, thus interrupting the contact between the surface of strip steel and the plating liquid, discontinuous plating will result with a loss of luster. When a lustrous appearance is desired to be secured on both sides of a strip steel, in vertical and horizontal type plating tanks, it is possible to obtain continuously lustrous plating by dipping both surfaces of the strip steel continuously in the plating liquid.

In order to obtain the thickness of plating between about 0.005μ to 0.1μ, the conditions for plating are as follows:

It has been found that there is a relation between the time of plating and the efficiency of electric current (as shown in FIG. 2), when temperature and density of electric current is held constant in various kinds of chromium plating liquid. According to this relationship, the best efficiency of electric current will be obtained at about 10 seconds of plating time, when the plating is effected under the same conditions. Therefore, in the present invention, the plating will be effected continuously in the range of 1–20 seconds, while the strip steel is moving.

In actual operation, when chromium plating is effected by using a lead anode, if the plating is discontinuously effected by cutting off electric current after a certain time of plating and then further effecting the plating after a certain interval of time, the surface of lead anode will be connected to the lead salt of chromic acid. In such a case, when electricity is conveyed thereto, polarization is caused, thus making the charging difficult. These troubles may be prevented by applying reverse electric current for a few minutes by making the lead anode negative and the strip steel positive, when the plating is finished.

Examples of the test relation to steel plate of 0.27 mm. are shown as follows:

TABLE 1

Degree of drawing	1 m./m.	2 m./m.	3 m./m.	4 m./m.	5 m./m.	6 m./m.
Thickness of plating:						
0.01	A	A	A	A	A	A
0.05	A	A	A	A	A	A
0.10	A	A	A	A	A	A
0.15	A	A	A	A	B	B
0.20	A	A	A	B	B	B
0.25	A	A	A	B	C	B
0.30	A	A	A	B	C	C
0.50	A	A	B	B	C	C
0.90	A	B	C	C	D	D
1.20	A	B	C	C	D	D
1.50	A	B	C	C	D	D

Degree of drawing is shown in Erichsen values. If the value is made more than 7 m./m., the steel sheet, per se, is feared to be broken. The Erichsen value of this steel sheet is 7–8 m./m. In the test, chromium plated steel sheets according to the present invention are coated with phenol resin paint of about 8μ and then they are dipped in ferro-oxyl testing liquid for 30 minutes. In the Table 1, A means that the convex portion is all right, B means that the convex portion has spot corrosions, C means that the convex portion has many spot corrosions and D means that the whole surface has spot corrosions.

The composition of ferro-oxyl testing liquid is: $K_4Fe(CN)_6 \cdot 3H_2O$ . . . 10% g./l., $K_3Fe(CN)_6$ . . . 10 g./l. and NaCl . . . 50 g./l.

TABLE 2

Items of test	Adhesive power of paints	Citric acid proof test (boiling in 1% citric acid solution 5 hr.)	Sulfuric acid proof test (dipping in 5% H_2SO_4 solution for 48 hr. at normal temp.)	Salt water spraying test (for 48 hr. at normal temp.)	Soy-proof test (dipping in soy for 5 days at 75° C.)	Exposure test (exposed on the roof-top for 10 days (including 2 rainy days))
Chromium plated steel plate of the invention: Thickness of plating, M—						
0.05	⊙	A	B	A	A	B
0.04	⊙	A	B	A	A	B
0.03	⊙	B	B	B	A	B
0.02	⊙	B	B	B	A	B
0.01	⊙	B	B	B	A	B
.005	⊙	C	B	B	A	B
.001	⊙	D	C	C	B	C
Polished steel plate	⊙	D	D	D	D	C
Electric tin-plate	○	B	C	B	B	B′

Plating a strip steel within the range of 1–20 seconds to make a finished product has never been shown in the prior art. The speed-up of plating under these conditions brings great advantages to the industrial manufacturing technique.

As accompanying conditions under which the chromium plating is effected, it is preferred that the density of electric current must be taken as 20–60 A./dm.^{2}, that is high density of electric current for high speed plating. The temperature must be preferably between 30–50° C., the concentration must be preferably between 100–250 g./l. as CrO_3, and further the addition agent such as sulfuric acid must be preferably about $\frac{1}{100}$ of CrO_3 in weight.

Above test pieces were painted respectively with phenol resin based paint,[1] oil paint,[2] of 8μ thickness and then drawn in the degree of 5m./m.

Degree of drawing is shown in Erichsen value.

In the Table 2, A means that the convex portion is all right, B means that the convex portion has spot corrosions, ⊙ means no exfoliation, ○ means some exfoliations, C means that all of the convex portions exfoliated,

[1] This is generally used as a paint for food can, and is mixed phenol formaldehyde resin and vinyl-butyral resin with some solvent.

[2] This is generally used as a paint for food can, and is reformed from phenolic resin by addition of tung oil.

D means that all surface corroded and B′ means that the ring part of Erichsen rusted.

The results shown in Table 2 show that the chromium plated steel plates according to the invention are superior to the tin plate painted under the same conditions, and also the sulfuric acid proof power of the former is shown to be better than that of the latter. Therefore, in case of canned food, the chromium plated steel sheets according to the invention will be used without the apprehension of sulfurstain, and in case of canned beer, there is no fear that the beer may become cloudy, so that the steel sheet will be used more advantageously than tin-plate.

As seen from the above description, in the chromium plating, when the thickness thereof becomes more than 0.1μ, the workability of the sheet will decrease as shown in Table 1, so that anti-corrosive power after working thereof will become inferior, and when the thickness thereof becomes less than 0.005μ, both workability and anti-corrosive power of the sheet become decreased as shown in Table 2. Thus, these thicknesses become the base of limiting conditions for chromium plating of the invention.

Further, the comparison between a chromium plated steel sheet of 0.1–0.005μ thick and electrical tin-plate, regarding their adhesive powers for paints, will be shown as follows:

(1) The method for testing.

Drop adhesion test is adopted to investigate the adhesive power of paints. A test piece is placed horizontally, on which 3–5 drops of paint are laid. When the paint spreads in circular shape, it is baked at 210° C. for ten minutes, then cooled to room temperature, and cut by a needle to mark X. The degree of exfoliation is inspected by a cellophane tape and judged by the naked eye from a square root of percentage (%) of exfoliated area of the paint, and it is defined so that no exfoliation is 0 grade and 100% exfoliation is 10 grade, respectively.

Based on the above method, tests were made with chromium plated steel plates and electric tin-plates, which were lain in a tank of constant temperature and humidity (40° C., 97%) for 20 hours, 40 hours, one week and three weeks, respectively. As the paint No. 9635 (Phenol-resin made by Fuller Co.)[3] was used, the values for electric tin-plates are results of the best chemical condition in the operation.

TABLE 3

The time elasped, hours	Electric tin-plates, grade	Chrominium plated steel sheet, grade
20	1	0
40	1	0
70	3	0
116	3	0
183	6	0
280	7	0
377	10	0
504	10	0

From the above table, it will be understood how long the adhesive power of the paint is effective for the products of the invention.

One of the reasons why the surface of chromium plated steel sheet of this invention and the paint have very good adhesive and anti-corrosive powers for long periods of time is thought to be caused by the anti-corrosive power of said surface. The reason thereof is not clear, but it is believed that even if some corrosive substances permeate perpendicularly to the sheet through the paint layer, the corrosion will never spread horizontally, so that any reaction between the steel base and said substance will not be accelerated by such a degree of scratches or pin holes.

As paints to be used for the chromium plated steel sheet according to the invention are, by way of example,

[3] This paint No. 9635 is phenol resin based paint made by Fuller Co. in U.S.A.

phenol based paints, oil based paints, vinyl-resin based paints, epon-series paints, varnish, lacquer, etc., and these paints are used singly or compound. As synthetic resin film, various kinds such as vinyl-series resin, phenolic-series resin, etc. are suitably used with or without binding agent. Particularly, when used for cans to be employed for canned food, it is not necessary to select paints according to the species of canned food as it necessary with tin-plate, yet very good anti-corrosive power will be assured at all times.

Example 1

A polished steel sheet of 0.27 m./m. thick was electrolytically de-oiled in de-oiling liquid containing 5% caustic soda, 3% sodium silicate and 0.2% non-ion inter-surface activator at 80° C., with current density of 6 A./dm.^{2}, for 20 seconds, and washed by cold water. Then the steel sheet was used as a cathode in electrolyte containing 250 g./l. of chromic acid anhydride and 2.5 g./l. of sulfuric acid and was electrolysed at 50° C., with current density of 20 A./dm.^{2} for 10 seconds, forming chromium plating layer of 0.05μ thick on the steel sheet.

Chromium plated steel sheet thus obtained had very good adhesive power to various kinds of paints, and when dipped in 5% sulfuric acid, it displayed an excellent anti-corrosive power and as was unaffected for 168 hours (contrary to other kinds of plated steels which were corroded about 5–48 hours). Its citric acid proof power was found to be about the same as tin-plate. In alkali proof test, it was unaffected for 144 hours. Similarly, in the Hinac test, it showed excellent conditions. In contrast, to this, other kinds of plated sheets lasted only for about 24–48 hours.

In chemical treatment, the chromium plated steel sheet had similar anti-corrosive power to the plate according to the Hinac method, and when anti-corrosive oil was applied to the former, there was found no change for 580 hours.

The color and luster were as beautiful as the tin-plate and adapted for grounding treatment. Various test examples of the chromium plated steel sheets obtained which were coated with phenol-resin based paint layer of 4–8μ thick are shown in the Table 1 and Table 2.

A strip steel of 0.27 m./m. thick was preliminary treated under the same conditions as Example 1, then it was plated with a layer of 0.005μ thick of chromium in an electrolyte containing 150 g./l. of CrO_3 and 1.5 g./l. of H_2SO_4 at 40° C. with current density of 20 A./dm.^{2} for 1 second.

Various test examples of thus obtained chromium plated strip steel which were coated with phenol-resin series paint layer of about 8μ thick are shown in Table 1 and Table 2.

Example 4

A cold rolled steel sheet of 0.9 m./m. thick was preliminary treated under the same conditions as mentioned in Example 1, then it was plated with chromium layer of 0.1μ thick in an electrolyte containing 150 g./l. of CrO_3 and 1.5 g./l. of H_2SO_4 at 40° C., with current density of 20 A./dm.^{2} for 20 seconds, and then the plated surface was applied with vinyl series paints of about 15 thick to make a final product.

Although some preferred embodiments of the invention are herein disclosed for purpose of explanation, various modifications thereof, after study of this specification, will be apparent to those skilled in the art to which the invention pertains. Reference should, accordingly, be had to the appended claims in determining the scope of the invention.

What is claimed is:

1. A method of producing can stock receptive to organic surface coatings, which comprises continuously moving a thin-gauge steel sheet through a chromium plating bath for a period of between about 1 to 20 seconds, thereby to plate said steel sheet with a chromium layer

of a substantially uniform thickness of about between 0.04 to 0.1μ, immersing the chromium plated sheet in a chromate containing bath, washing the sheet with water and finally coating the sheet with a surface layer of an organic coating composition, said organic coating composition being selected from the group consisting of phenol based paints, oil based paints, vinyl-resin based paints, epon based paints, varnishes and lacquers.

2. Can stock essentially consisting of a thin-gauge steel sheet having a chromium layer of a uniform thickness of from about between 0.04 to 0.10μ directly plated thereon, said chromium layer being surface coated with a layer of a coating composition selected from the group consisting of phenol based paints, oil based paints, vinyl-resin based paints, epon based paints, varnishes and lacquers.

3. As an article of manufacture a surface coated thin-gage steel sheet comprising a single sheet of steel having directly plated thereon a chromium layer having a thickness of from 0.005μ to 0.1μ, said chromium layer being surface coated with a coating composition selected from the group consisting of phenol based paints, oil based paints, vinyl-resin based paints, epon based paints, varnishes and lacquers.

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