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CHROMIUM PLATED STEEL SHEET HAVING AN ALMOST COLORLESS AND TRANSPARENT CHROMATE FILM

Osamu Yanabu, Takashi Hada, and Kazuyuki Doi, Himeji-shi, Japan, assignors to Fuji Iron & Steel Co., Ltd., Tokyo, Japan

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ABSTRACT OF THE DISCLOSURE

A process for surface treating chromium plated steel sheet obtained by applying chromium plating directly on a single sheet or strip of carbon steel which comprises: electrolytically contacting said chromium plated steel as the cathode with an aqueous solution of chromic anhydride as the main ingredient and a hydroxide or carbonate of an alkali metal, calcium, magnesium or strontium to form an almost colorless and transparent chromate film on the chromium plating. The film enhances corrosion resistance and does not interfere with any subsequent painting of the plated steel.

This invention relates to a chromium plated steel sheet which is produced by forming directly on the surface of the steel sheet a plated layer of chromium of a thickness of about 0.001–0.1μ and then coating the surface of the chromium layer with an almost colorless and transparent anticorrosive chromate film. This invention also relates to a chromate coating process for a chromium plated steel plate in order to form an almost colorless and transparent chromate film.

The purpose of this invention is to impart to the chromium plated steel sheet improved anticorrosive properties, to retain the fine metallic luster peculiar to chromium, and not inhibiting color effects when painted.

Chromium plated steel sheet wherein the surface is coated with a thin layer of chromium is described in U.S. Patent No. 3,113,845 by the present inventors. Such a coating might be deteriorated by the presence of so-called pinholes. Therefore, a chromate coating on the plated layer is desirable. Investigations by the inventors on chromate coating processes, including dipping and electrolysis processes using various treating solutions, revealed that the anticorrosive property was remarkably improved by electrolysis, but much less by the dipping process. Nevertheless the electrolysis process using the conventional chromate coating liquid which contains chromic anhydride as a major constituent produces a colored opaque film on the plated layer of chromium. Consequently the fine metallic luster peculiar to chromium is lost and the appearance is spoiled. In addition, if the plate is painted, the color effect will be damaged. When paint, for example oily, phenolic, epoxyl, alkyd or vinyl

paint, varnishes or lacquers, is applied, alone or in a mixture, on the colored chromate film produced by electrolysis, the bright color of the paint will be spoiled by interference with the coloration of the chromate film. Repeated applications of paint to avoid the interference of color necessarily decreases the working efficiency and is not recommended from the economical standpoint.

The present inventors, by the detailed investigation of the above difficulties, succeeded in the complete solution of the problem by making the chromate film colorless and transparent.

The present invention relates to a method for obtaining such colorless and transparent chromate film. It particularly relates to a method for surface treating a chromium plated steel sheet which is characterized by cathodically treating in an aqueous solution a chromium plated steel plate which has been obtained by applying a thin chromium coating directly on a single sheet or strip of ordinary carbon steel. The aqueous solution contains chromic anhydride as main component and one or more compounds selected from hydroxides or carbonates of alkali metals, calcium, magnesium or strontium in an amount greater than 20% by weight of the chromic acid.

Alkali metal hydroxides employed in this invention include NaOH, KOH and LiOH. On the other hand alkaline earth metal hydroxides includes $Ca(OH)_2$. In addition to the above hydroxides, similar effects can be obtained by using carbonates which provide these hydroxides when added in the aqueous CrO_3 solution, such as Na_2CO_3, K_2CO_3, Li_2CO_3, Ca_2CO_3, $MgCO_3$ and $SrCO_3$.

The present invention relates to electrolytically treating a chromium plated steel sheet as cathode in an aqueous solution containing chromic anhydride as the main component with the addition of one or more of the above compounds in an amount more than 20% by weight of the chromic acid.

It has been known to cathodically or anodically treat a tin plate in an aqueous solution of sodium dichromate ($Na_2Cr_2O_7$) or potassium dichromate ($K_2Cr_2O_7$). It is considered that $NaCr_2O_7$ or $K_2Cr_2O_7$ will be produced by reaction of chromic anhydride with a chemical equivalent of NaOH or KOH. But various experiments conducted by the inventors shows that there is a large difference in the pH, as shown in Table 1, between an aqueous solution of $Na_2Cr_2O_7$ and an aqueous solution of chromic anhydride with the addition of NaOH in a chemical equivalent amount to the chromic anhydride (40% by weight of the chromic anhydride). The solution of $Na_2Cr_2O_7$ has a pH value between 4.0 and 4.5, while the latter solution has a pH value between about 1.7 and 2.8, depending upon the chromic anhydride concentration.

TABLE 1

$Na_2Cr_2O_7$ Solution		CrO_3+NaOH Solution	
Concentration	pH	Concentration	pH
29.8 g./l.	4.22	CrO_3 20 g./l. plus NaOH 8 g./l.	2.75
74.5 g./l.	4.00	CrO_3 50 g./l. plus NaOH 30 g./l.	1.90
119.2 g./l.	3.95	CrO_3 50 g./l. plus NaOH 32 g./l.	1.76

The present inventors found that there is a large difference in corrosion resistance between a chromium plated steel sheet which has been cathodically treated in an aqueous solution of $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ and a chromium plated steel sheet which has been cathodically treated in an aqueous chromic anhydride solution with the addition of NaOH or KOH. The latter has superior corrosion resistance. The present inventors have also confirmed that this quality shows a similar relation in case of addition of hydroxides etc. of other alkali metals and alkali earth metals.

As for the aqueous solution containing chromic anhydride as main component, it may contain only chromic anhydride. In this case also, trivalent chromium is formed by the reduction of hexavalent chromium ion as the cathodic treatment process. Usually, this trivalent chromium ion is present within a range of 0.2 to 10 g./l.

The cathodic treatment can be accelerated by adding to the aqueous solution of chromic anhydride the following compounds as subsidiary additives which act as catalyst for accelerating the cathodic treatment.

(1) Soluble compounds containing halogen (NaCl, $HClO_3$, Na_2SiF_6, $(NH_4)_2TiF_6$, $CrCl_3$ etc.).

(2) Compounds containing certain anion ($NaNO_3$, Na_2SO_4, $SnSO_4$, $Cr_2(SO_4)_3$ etc.).

(3) Aromatic sulfonic acids ($C_6H_4SO_3H.OH$,

$$C_6H_3(SO_3H)_2.OH$$

etc.).

(4) Soluble salts of metals (sodium stannate, sodium aluminate etc.).

Each of Cl^-, ClO_3^-, SiF_6^{--}, TiF_6^{--} of the additives of the group (1), NO_3^-, SO_4^{--}, of the additives of the group (2), $C_6H_4SO_3H^-$, $C_6H_3(SO_3H)_2^{--}$ of the additives of the groups (3) and $Sn(OH)_6AlO_2^-$ of the additives of the group (4) produces a catalytic effect.

For utilization of these additives in the present invention, care should be taken to prevent precipitates caused by ions of the additives when hydroxides or carbonates of Ca or Sr are used.

It is preferable to avoid formation of such precipitates, although such precipitates are not formed even when hydroxides or carbonates of Ca or Sr are added in a considerable amount since the CrO_3 solution has strong acidity and these additives are added in a small amount, less than 3%. Care should be taken particularly when the sulfate ion is added.

Now, there will be described an optimum content of hydroxides and carbonates of alkali metals, calcium, magnesium and strontium. When the concentration of chromic anhydride is within a range of 20 to 60 g./l., the amount to be added of these hydroxides and carbonates must be more than 20% at least by weight of CrO_3 and an amount less than 20% has no effect to prevent coloring of the chromate film.

As the CrO_3 concentration decreases from 20 g./l., a smaller addition will produce adequate effect and good effect can be obtained if the addition is made in an amount more than 10% by weight of CrO_3. Also as the CrO_3 concentration increases above 60 g./l., the addition of these hydroxides and carbonates in an amount less than 20% by weight will be effective and good effect can be obtained if they are added in an amount more than 10% by weight of CrO_3.

Now considering this matter when these hydroxides and carbonates are added in a larger amount, coloring of the chromate film is effectively prevented through the range in which the precipitate is not formed. And in practice the addition of up to about 100% by weight of chromic anhydride will not adversely affect the corrosion resistance.

In the next place, the electrolytical chromate coating process is carried out under the following condition. The smallest possible concentration of chromic anhydride is about 5 g./l., because the anticorrosive property is decreased at too small a concentration. At very high concentrations, on the contrary, the anticorrosive property can not be substantially improved, therefore the upper limit of the concentration of chromic anhydride is decided from the point of economy.

It has been proved that a CrO_3 concentration within a range of 5 g./l. to 300 g./l. is effective, but in practice a concentration from 50 g./l. to about 100 g./l. is used, and in this case the addition of hydroxides and carbonates of alkali metals, calcium, magnesium or strontium in an amount of 20% to 50% by weight of CrO_3 is adequate.

Current density and the duration of electrolysis correlate to each other. Thus high current density requires only a short time of electrolysis and lower current density requires a longer time of electrolysis. Under the optimum condition, the current density is kept in the range 1 to 45 A./dm.^{2} and the time of electrolysis 0.1 to 15 sec.

The chromate treatment of the present invention is not substantially influenced by temperature. But at higher temperatures where the aqueous solution is gradually concentrated by evaporation difficulties are often encountered in maintaining the constant temperature and composition of the liquid in which the electrolysis takes place. Consequently the range from room temperature up to approximately 90° C. is considered to be adequate.

The composition, structure and the process of formation of the almost colorless and transparent chromate coating film of this invention are not known. Nonetheless the electrolysis of the chromium plated steel sheet as cathode using the chromate coating liquid of this invention can give a colorless and transparent chromate coating film of excellent anticorrosive property, in contrast with the colored chromate films which are formed when conventional chromate coating solutions are used as electrolyte. Thus the almost colorless and transparent product of this invention provides high anticorrosive properties and remarkably enhanced commercial value.

Advantages of the present invention are that the fine metallic luster, peculiar to chromium, of the base is not spoiled and that, when the plate is painted, the bright color of the paint is not deleteriously affected.

This is especially noteworthy with a white coating. Taking a white coating with an alkyd paint for example, single application (15μ) suffices for the effect onto the colorless and transparent chromate film of this invention, while at least two applications are needed onto colored chromate films.

The single operation of painting improves the working efficiency and the thin layer of paint costs less.

The chromate coating of a steel plate covered with a thin layer of plated chromium by the electrolysis process as cathode was comparatively examined relative to the coating by the dipping process. With the anticorrosive property, examined by the saline water spray test, JIS Z2371, the chromate coating of the latter process allowed rust to appear usually in several hours, while with the coating of the former process it took well over ten hours. More particularly rust developed in spots where the pinholes existed in the latter process, while in the former where the chromate coating film was worn out. This fact suggested that the former process produced much stronger and more compact chromate coating films. This is the reason why the thickness of the plated layer of chromium can be reduced, in case of coating by electrolysis, down to 0.001μ as the lower limit. The upper limit of thickness may be about 0.1μ for the ease of working.

The following examples illustrate this invention.

	This invention—Example No.									
	1	2	3	4	5	6	7	8	9	10
Cr^{6+}, g./l.	CrO_3, 80	CrO_3, 50	CrO_3, 60	CrO_3, 50	CrO_3, 20	CrO_3, 20	CrO_3, 100	CrO_3 50	CrO_3, 80	CrO_3, 50
Cr^{3+}, g./l.	(1)	1.5	(1)	(1)	0.11	0.32	8.78	0.58	1.16	1.45
Additives, g./l.	NaOH, 20	NaOH, 20	Na_2SiF_6, 2 NaCl, 5 NaOH, 24	$NaClO_3$, 100 NaOH, 15	$(NH_4)_2TiF_6$, 1 NaOH, 8	$CrCl_3$, 1 NaOH, 4	$NaNO_3$, 5 $C_6H_3(SO_3H)_2OH$, 1 NaOH, 8	NaOH, 20 Na_2SO_4, 5	NaOH, 32 $SnSO_4$, 1	NaOH, 11 $Cr_2(SO_4)_3$, 1
Cathodic current density, A/dm.²	10	18	5	5	30	24	5	5	26	2
Time of electrolysis, sec.	2	1	2	2	0.5	2	5	8	2	5
Temperature, ° C.	40	20	40	50	40	40	40	40	40	40
pH	(1)	2.2	(1)	(1)	2.7	5.4	0.5	3.0	2.0	2.1
Thickness of chromium layer, μ	0.02	0.05	0.008	0.04	0.09	0.1	0.05	0.01	0.01	0.05
Color of coating	(2)	(3)	(3)	(4)	(3)	(3)	(3)	(4)	(3)	(3)
Color effect when painted (white coating with epoxy paint, about 15μ thick)	(5)	(3)	(3)	(5)	(3)	(6)	(3)	(5)	(3)	(3)
Saline water spray test, hr.	>20	>20	>20	>20	>20	>20	>20	>20	>20	>20

	This invention—Example No.								
	11	12	13	14	15	16	17	18	19
Cr^{6+}, g./l.	CrO_3, 40	CrO_3, 80	CrO_3, 80	CrO_3, 20	CrO_3, 50	CrO_3, 20	CrO_3, 50	CrO_3, 50	CrO_3, 10
Cr^{3+}, g./l.	(1)	0.58	(1)	0.20	(1)	0.05	(1)	0.31	0.3
Additives, g./l.	$C_6H_4SO_3H \cdot OH$, 2 NaOH, 16	NaOH, 9.6	NaOH, 15 $NaAlO_2$, 2	KOH, 8	$Ca(OH)_2$, 20	$NaNO_3$, 0.5 NaOH, 8	$NaSiF_6$, 0.5 NaOH, 15	NaCl, 0.5 NaOH, 20	NaOH, 1.2
Cathodic current density, A/dm.²	5	30	5	30	5	5	30	5	5
Time of electrolysis, sec.	2	0.5	2	2	10	2	1	4	2
Temperature, ° C.	40	40	40	40	40	80	80	80	55
pH	(1)	1.0	(1)	2.1	(1)	5.15	(1)	4.6	3.0
Thickness of chromium layer, μ	0.04	0.003	0.05	0.001	0.02	0.06	0.004	0.01	0.05
Color of coating	(3)	(4)	(3)	(3)	(3)	(4)	(3)	(3)	(2)
Color effect when painted (white coating with epoxy paint, about 15μ thick)	(3)	(6)	(3)	(3)	(3)	(6)	(3)	(3)	(3)
Saline water spray test, hr.	>20	>20	>20	>20	>20	>20	15	>20	>20

	Electrolytical colored chromate treatment						Other process	
	1	2	3	4	5	6	1	2
Cr^{6+}, g./l.	CrO_3, 50	CrO_3, 100	CrO_3, 50	CrO_3, 20	CrO_3, 15	CrO_3, 90	CrO_3, 50	$Na_2Cr_2O_7 \cdot 2H_2O$, 119.2
Cr^{3+}, g./l.	1.5	8.78	15.3	0.11	0.2	1.0	0.5	0.8
Additives, g./l.		$C_6H_3(SO_3H)_2OH$, 1		$NaNO_3$, 0.5	NaOH, 0.75	NaOH, 4.5	$Cr_2(SO_4)_3$, 1 NaOH, 5	
Cathodic current density, A/dm.²	18	5	5	5	8	10	5	6
Time of electrolysis, sec.	1	2	2	2	2	2	2	1.5
Temperature, ° C.	20	40	40	80	40	45	50	60
pH	2.2	0.5	0.9	2.8	2.5	0.9	1.9	3.9
Thickness of chromium layer, μ	0.05	0.05	0.03	0.04	0.02	0.03	0.025	0.013
Color of coating	(7)	(8)	(9)	(10)	(13)	(13)	(13)	(4)
Color effect when painted (white coating with epoxy paint, about 15μ thick)	(11)	(12)	(3)	(11)	(11)	(11)	(14)	(15)
Saline water spray test, hr.	>20	>20	>20	>20	>20	>20	>20	Rusting at 8

[1] Not determined.
[2] Almost colorless transparent.
[3] Same as the foregoing.
[4] Colorless transparent.
[5] Good with a single application.
[6] Good.
[7] Pale.
[8] Pale brown.
[9] Dark gray.
[10] Pale gray.
[11] Good with two applications.
[12] Not good even with two applications.
[13] Faint blue.
[14] Not good on two applications.
[15] Good with one application.

As shown in the above example the other process No. 1, is not effective for preventing coloring of the chromate film when NaOH is in an amount of 10% by weight of tion, but almost colorless and transparent chromate film CrO_3 in case of 20 g./l. to 60 g./l. of CrO_3 concentra- is obtained when NaOH is in an amount of 22% by weight of CrO_3, as shown in Example No. 10 of the present invention. Also as shown in the present invention Example No. 19, the chromate film is almost colorless and transparent in case the CrO_3 concentration is less than 20 g./l. even when the amount of NaOH is 12% by weight of CrO_3. But in this case, as shown in Example No. 5 of the electrolytical colored chromate treatment, it is not effective for preventing coloring of the chromate film when the amount of NaOH is 5% by weight of CrO_3.

Further, the chromate film is almost colorless and transparent, as shown in Example No. 12 of the present invention, even when the amount of NaOH is 12% by weight of CrO_3 in case the CrO_3 concentration is more than 60 g./l. In this case also, when the amount of NaOH is less than 5% by weight of CrO_3, coloration takes place, as shown in Example No. 6 of the electrolytical colored chromate treatment.

Meanwhile, as shown in Example No. 2 of the other process, a chromium plated steel sheet which has been cathodically treated in an aqueous solution of $Na_2Cr_2O_7$ has inferior corrosion resistance, whereas in case of Example No. 12 of the present invention where NaOH and CrO_3 are in a chemical equivalent relation, the corrosion resistance is good showing more than 20 hours by the salt spray testing.

The process of this invention forms a colorless and transparent chromate coating film without any loss in the anticorrosive property on a steel plate covered with a thin layer of plated chromium. As is evident in the above examples, the advantages of the colorless and transparent coating film are that the appearance can be remarkably improved by the metallic luster peculiar to chromium, and that, when a white coating is applied with an epoxy paint, a single application can produce a satisfactory color effect, while in contrast a colored chromate coating film requires more than two applications for good color effect. The advantages, of course, considerably enhance the commercial value of the product. In addition, when the product of this invention is painted, the working efficiency can be improved owing to the single application and the consequent thin layer of paint is economical.

What is claimed is:

1. A process for surface treating chromium plated steel sheet which has been obtained by applying chromium plating directly on a single sheet or strip of carbon steel which comprises: electrolytically contacting said chromium plated steel as the cathode with an aqueous solution of chromic anhydride in a concentration of 5 grams per liter to 300 grams per liter of said solution, said solution further containing hydroxides, or carbonates which convert to hydroxides in said solution, of an alkali metal, calcium, magnesium or strontium, and wherein said solution contains (a) greater than 20% of said hydroxide or carbonate, based on the quantity of chromic anhydride, when the concentration of chromic anhydride is in the range of 20 to 60 grams per liter of solution, or (b) at least 10% of said hydroxide or carbonate, based on the quantity of chromic anhydride, when the concentration of chromic anhydride is below 20 grams per liter or above 60 grams per liter of said solution.

2. A process of claim **1** wherein the aqueous solution further contains one or more ions selected from the group consisting of Cl^-, ClO_3^-, SiF_6^{--}, TiF_6^{--}, NO_3^-, SO_4^{--}, $C_6H_4SO_3H^-$, $C_6H_3(SO_3H)_2^{--}$, $Sn(OH)_6^{--}$, and Al_2O^-.

3. A process of claim **1** wherein the concentration of chromic anhydride is from 20 to 60 grams per liter of the aqueous solution and the amount of said hydroxide or carbonate is over 20% by weight of the chromic anhydride.

4. A process of claim **1** wherein the concentration of chromic anhydride is (a) below 20 grams per liter or (b) above 60 grams per liter of said aqueous solution, and said solution contains at least 10% of said hydroxide or carbonate, based on the quantity of chromic anhydride.

5. A process of claim **1** wherein the aqueous solution contains from 0.2 to 10 grams per liter of trivalent chromium ion.

6. A process of claim **1** wherein the electrolytic contact of the chromium plated steel with said solution is effected at a current density of 1 to 45 A per $dm.^2$ for 0.1 to 15 seconds and wherein the temperature of said solution is from room temperature to 90° C.

7. A process for surface treating chromium plated steel sheet which has been obtained by applying chromium plating directly on a single sheet or strip of carbon steel which comprises: electrolytically contacting said chromium plated steel as the cathode with an aqueous solution of chromic anhydride containing (a) chromic anhydride in a concentration of from 20 to 60 grams per liter and (b) a hydroxide or carbonate of an alkali metal or calcium, magnesium or strontium in a concentration of from above 20% to 100% based on the weight of said chromic anhydride and wherein said electrolytic contact is effected at a current density of 1 to 20 A per $dm.^2$ for 0.1 to 7 seconds at a solution temperature of 40 to 65° C.

8. A process of claim **7** wherein said aqueous solution further contains from 0.1 to 5 grams per liter of SiF_6^{--} and the alkali metal is sodium.

9. Chromium plated steel sheet having an almost colorless and transparent corrosion resistant chromate film when prepared by the process of claim **1.**

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

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