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(54) **Coated stainless steel strips and process for making.**

(57) Coated stainless steel is produced by forming a chromate layer on a stainless steel strip and coating the strip with a transparent color resin composition. The chromate layer has a total chromium content of 0.5 to 50 mg/m^2, with trivalent chromium occupying at least 60% by weight of the total chromium content and amounting up to 40 mg/m^2.

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This invention relates to coated stainless steel strips and a process for preparing the same.

BACKGROUND OF THE INVENTION

Stainless steel characterized by high corrosion resistance has been widely used in a variety of fields including chemical industry. In the recent years, there is an increasing demand for etched, polished, colored or otherwise surface treated stainless steel as interior materials of large buildings. Especially, etched or polished and colored stainless steel having decorative features now finds widespread use as entrance materials in hotels and apartments.

Most colored stainless steel strips rely on chemical color development which utilizes surface oxide layers formed by concentrated chromic acid solution or the like. The chemically colored stainless steel is versatile in that a color tone is available in accordance with the finish of the underlying steel because color development is based on optical interference within a very thin oxide layer. On the other hand, coated stainless steel often used as roof covers are few in this field because the stainless steel surface is completely covered with color coatings based on color pigments which do not reflect the polished or etched finish of the underlying steel.

Nevertheless, the coating technique has several advantages over the chemical coloring method in that the coating method is easy to carry out and the coated stainless steel is resistant against fingerprint and easy in storage and maintenance when used as interior material. Therefore, attempts have been made in the coating technique in order to develop transparent color coatings capable of reflecting the surface of the underlying substrate, but none of them have succeeded in producing transparent color coated stainless steel meeting all the requirements of coating's durability, workability, and weather resistance.

Often, coated stainless steel is subject to a number of complex working steps. Since the paint coating can be stripped where substantial work is done, the use of coated stainless steel is limited in such applications requiring noticeable working.

Stainless steel is well resistant against corrosion due to a passive film on its surface, but unsusceptible to surface treatment such as coating because of the same surface inertness. The passive film must be removed electrochemically before electroplating can be carried out. In the case of paint coating, it is impossible in practice to carry out such complete pretreatment. Particularly for worked articles of stainless steel, a pretreatment for coating should be as easy as possible.

Most stainless steel strips are bent as by rolling and pressing when used as building materials. As the radius of curvature at the bend is reduced, the degree of working is drastically increased. Therefore, for coated stainless steel, the adhesion of the coating against working and the durable adhesion of the coating at worked sites are critical.

One known pretreatment for coating is chromate treatment as disclosed in Japanese Patent Application Kokai No. 161069/1982. Transparent color coated stainless steel is generally required to have a faintly colored coating (having a reduced amount of coloring pigment) so that the finish of the underlying steel may be seen through the coating. In this respect, it is undesirable that the pretreatment for improving coating receptivity leaves the steel surface colored or spotted. Most chromate treatment results in a more or less colored steel surface. There is a need for chromate treatment capable of minimizing surface coloring.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a coated stainless steel strip based on a steel substrate having improved coating receptivity and provided with a transparent resin coating through which the finish of the steel substrate is seen. Another object of the present invention is to provide a process for producing such a coated stainless steel strip.

According to the present invention, there is provided a coated stainless steel strip comprising a stainless steel strip having a chromate layer on a surface thereof with a total chromium content of 0.5 to 50 mg/m^2. Trivalent chromium occupies at least 60% by weight of the total chromium content and amounts up to 40 mg/m^2. A transparent resin coating is on the chromate layer.

Such a coated stainless steel strip is produced by a process comprising the steps of chromating a stainless steel strip on a surface thereof to form a chromate layer as defined above and applying a transparent resin composition to the chromated strip.

The term "transparent" used with the resin coating means that the texture of the underlying steel strip can be substantially seen through the coating.

DETAILED DESCRIPTION OF THE INVENTION

The subject stainless steel strip which is to be processed and coated according to the present invention is a group of cold rolled stainless steel plates, sheets, coils and similar products. Such starting strips are obtained by cold rolling hot rolled stainless steel slabs to a desired thickness, followed by annealing and pickling or bright annealing for relieving internal stresses introduced by the cold rolling and imparting appropriate mechanical properties, and optional shot blasting, dull skin pass, polishing or similar post-treatment for regulating the surface finish.

The type of stainless steel is not critical. Any desired type of stainless steel may be used although high corrosion resistant stainless steel of a grade equal to or higher than SUS 304 is recommended for service as exterior materials.

According to the present invention, stainless steel strips are subject to chromate treatment prior to coating.

Chromate treatment prior to coating as such is common to ordinary steels and has also been recently practiced on stainless steel in accordance with the widespread use of coated stainless steel. However, most of conventional coated steel strips including stainless steel strips used coating compositions containing pigments in high contents for coloring purpose so that the resulting coats were opaque. As a result, no difference was observable in outer appearance to know whether the underlying strips were of ordinary steel, stainless steel or aluminum. Then any type of pretreatment was acceptable prior to coating as long as it can impart coating receptivity.

With the recent advance of transparent color coatings through which attractive lustrous or versatile surface finishes of stainless steel can be seen, the conventional pretreatments for coating were found ineffective for transparent color coating because they resulted in undesirable color development or luster change.

The present invention employs chromate treatment for the purposes of imparting enhanced adhesion to subsequent overlying coatings and forming a light transmitting chromate film. A chromate layer capable of meeting both the requirements of coating adhesion and transparency can be formed by controlling such that the layer may have a total chromium content of 0.5 to 50 mg/m^2, preferably 5 to 50 mg/m^2, more preferably 5 to 30 mg/m^2 and trivalent chromium occupy at least 60% by weight of the total chromium content and amount up to 40 mg/m^2, preferably 5 to 30 mg/m^2.

A total chromium content of less than 0.5 mg/m^2 fails to achieve any improvement in coating adhesion whereas chromate layers containing more than 50 mg/m^2 of chromium become white or green and opaque even when the trivalent chromium content is at least 60% thereof. If the content of trivalent chromium is less than 60% by weight of the total chromium content, differently stated, if the proportion of hexavalent chromium increases, the chromate layer would lose transparency and exhibit brown colored spots. A trivalent chromium content in excess of 40 mg/m^2 undesirably causes the entire chromate layer to turn green.

The chromate layer may contain colloidal silica or a particulate organic resin such as acrylic resin.

The chromate layer may be formed on a surface of a stainless steel strip by thoroughly degreasing and cleaning the strip surface, and applying a chromate treating solution thereto, followed by drying. The chromate solution used herein is an aqueous solution containing anhydrous chromic acid, phosphoric acid, silica, and optionally, acrylic resin, epoxy resin, silane coupling agent or the like. In the case of transparent coatings through which ultraviolet light can reach the chromate layer, it is desirable, particularly in building exterior applications, to avoid the addition of resinous components to the chromate solution for the purpose of retaining weather resistance.

Also contained in the chromate solution is a reducing agent for reducing hexavalent chromium of chromic acid into trivalent chromium, the reducing agent including glycols (e.g., glycerin and ethylene glycol), hydrogen peroxide, saccharides (e.g., sucrose and starch), alcohols (e.g., methanol), and hydrazine. Phosphoric acid or phosphorous acid is added to the chromate solution for the purpose of adjusting pH and inhibiting precipitation of chromium ions. Silica is added for the purpose of retaining coating adhesion on bending and useful examples are colloidal silica and silica synthesized by gas phase method.

The chromate solution may be applied to the strip surface to a predetermined build-up by means of a roll coater for transfer coating or by spray or shower coating followed by squeezing by means of a Ringer roll. Subsequent heating at a temperature of about 70 to 120 ° C yields a chromate layer.

A specific total chromium content and specific trivalent chromium content and proportion of the chromate layer within the above-defined ranges may be achieved by regulating the coverage of the chromate solution and the proportion of trivalent chromium relative to the total chromium in the chromate solution which in turn, is regulated by controlling the degree of reduction.

The thus pretreated stainless steel strip is adapted to receive a transparent resin coating thereon. The resin coating composition which can be coated herein include a resin component which may be selected from fluoro resins, acrylic resins, acrylic-silicone resins, epoxy resins, polyester resins, vinyl chloride resins, and urethane resins.

Since the coating is transparent enough to allow ultraviolet light to pass through the coating interior to the stainless steel surface where light reflects and reenters the coating, the coating undergoes severer deterioration than conventional opaque coatings. In this regard, the use of fluoro resins characterized by weather resistance is recommended particularly for use as building exteriors.

Pigments or dyes are added to the resin coating composition for coloring purpose insofar as the composition is maintained transparent. UV absorbers such as oxalic anilide are desirably blended for preventing pigments from being degraded by ultraviolet light. Examples of the pigment or dye include inorganic pigments such as red iron oxide, carbon black, and titanium oxide; and organic pigments or dyes such as Phthalocyanine Blue, Phthalocyanine Green, Quinacridone Red, and Indanthrene Orange. These coloring agents such as pigments and dyes are added in such amounts that their content in the dry coating is up to 3% by weight whereby a transparent color coating is obtained.

In applying a transparent resin coating to the chromate treated stainless steel strip, any desired well-known coating techniques, for example, brush coating, roll coating, flow coating, and spray coating may be used. Flow coating is desirable for coating a number of large flat plates. Roll coating is often used for steel coils. After the resin coating composition is applied, it is cured into a transparent coating through an appropriate measure for a particular type of resin, for example, heating and UV exposure or simply by allowing to stand at room temperature. The resin coating is usually 5 to 30 μm thick.

As opposed to the conventional coated stainless steel strips, the coated stainless steel strips according to the present invention have the feature that the steel surface can be directly seen from the outside through the coating, thus offering products capable of taking advantage of the inherent surface texture of stainless steel. By applying the present process to the stainless steel surface which has undergone a certain surface finish, for example, by hair line polishing, ordinary polishing, dull finishing, and various types of etching, there are obtained good looking coated steel strips which are particularly useful as building exteriors. The coated steel strips are worked by panel forming and roll forming into a variety of configured members which will find a variety of applications including interior and exterior wall members, roof covers, floor members, and ceiling members.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples 1-5 & Comparative Examples 1-8

Hair line polished 1.5-mm thick strips of stainless steel SUS 304 were cleaned by alkali degreasing. Three chromate solutions having a percentage reduction of hexavalent chromium to trivalent chromium of 30%, 60% and 90% were applied to the strips by means of a roll coater and dried at 70°C, obtaining chromated strips having a total chromium content as reported in Table 1. A highly transparent fluoro resin coating composition commercially available under the trade name of New Gamet #9300 Clear from Toa Paint Co., Ltd. was applied to the chromated strips by means of a roll coater and dried at 190°C for 5 minutes, yielding a coating of 20 μm thick.

The coated strips were visually observed for a change of the steel surface through the clear coating. Additionally, the coated strips were examined for coating adhesion by a cross cut tape test using a pressure sensitive adhesive Cellophane tape (Scribed peeling test) and a cross cut tape test using a pressure sensitive adhesive Cellophane tape following scribed Erichsen working (6 mm cupping) (Scribed Erichsen test) according to the standard coating adhesion test prescribed under JIS K5400, item 8.5.2.

The results are shown in Table 1.

Table 1

		CE1	E1	E2	CE2	E3	E4	CE3	E5	CE4	CE5	CE6	CE7	CE8
Chromate layer	Total Cr (mg/m^2)	5	5	5	21	21	22	48	48	47	76	75	77	degreasing only
	Trivalent Cr proportion(%)	30	60	90	30	60	90	30	60	90	30	60	90	
	Trivalent Cr (mg/m^2)	1.5	3	4.5	6.3	12.6	19.8	14.4	28.8	42.3	22.8	45	69.3	
Surface color appearance through coating		brown (spots)	clear	clear	brown (spots)	clear	clear	brown (spots)	clear	greenish white	brown (spots)	greenish white	greenish white	clear
Coating adhesion*	Scribed peeling test	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	100/100	72/100
	Scribed Erichsen test	100/100	100/100	100/100	100/100	100/100	100/100	100 100	100/100	100/100	100/100	100/100	100/100	0/100

* the number of sound or retained coating sections after/before Cellophane tape peeling

As seen from Table 1, the chromated strips all showed improved coating adhesion over the only degreased sample. With respect to the surface appearance under the coating, however, Comparative Examples 1, 2, 3 and 5 having a lower trivalent chromium proportion developed a brown spot pattern associated with hexavalent chromium and Comparative Examples 4, 6 and 7 having a higher trivalent chromium proportion developed greenish white color. In contrast, Examples 1 to 5 having a total chromium

content, trivalent chromium proportion and trivalent chromium content within the scope of the present invention not only offered a surface appearance under the coating comparable to the only degreased sample, but also retained the coating tightly.

Examples 6-7 & Comparative Examples 9-10

Using a continuous coating apparatus, transparent color coated stainless steel coils were manufactured from 2B-finished 0.7-mm thick coils of stainless steel SUS 304. After the coils were cleaned by alkali degreasing, a chromate solution having a percentage reduction of hexavalent chromium to trivalent chromium of 90% was applied to the coils by means of a roll coater and dried at 110 °C, obtaining chromated coils having a total chromium content of 20 mg/m^2. Then fluoro resin coating compositions were applied to the chromated coils by means of a roll coater and baked at 200 °C, yielding a coating of 20 μm thick. The coating compositions used were commercially available under the trade name of New Gamet #9300 Bronze (Example 6) and Gold (Example 7) from Toa Paint Co., Ltd.

For comparison purposes, a sample was manufactured by the same procedure as above except that chromate treatment was omitted over a portion of the coil. The non-chromated and coated sample and the chromated and coated sample were compared by a visual observation. Both the samples had a bronze or gold colored coating which was enough transparent to see the underlying stainless steel therethrough. The chromated and coated sample exhibited no spots or color, with no recognizable difference from the non-chromated and coated sample.

The samples were subject to a scribed Cellophane tape peeling test and a scribed Erichsen peeling test as in Examples 1-5. The chromated and coated sample retained the coating tightly as seen from Table 2.

Table 2

	E6	CE9	E7	CE10
Coating color	Bronze	Bronze	Gold	Gold
Chromate layer	present	absent	present	absent
Coating adhesion*				
Scribed peeling test	100/100	20/100	100/100	15/100
Scribed Erichsen test	100/100	0/100	100/100	0/100

* the number of sound or retained coating sections after/before Cellophane tape peeling

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

1. A coated stainless steel strip comprising
   a stainless steel strip having a chromate layer on a surface thereof with a total chromium content of 0.5 to 50 mg/m^2, trivalent chromium occupying at least 60% by weight of the total chromium content and amounting up to 40 mg/m^2, and
   a transparent resin coating on the chromate layer.

2. The coated stainless steel strip of claim 1 wherein said chromate layer has a total chromium content of 5 to 50 mg/m^2.

3. The coated stainless steel strip of claim 1 wherein trivalent chromium is present in said chromate layer in an amount of 5 to 30 mg/m^2.

4. The coated stainless steel strip of claim 1 wherein said chromate layer has a total chromium content of 5 to 50 mg/m^2, trivalent chromium occupying at least 60% by weight of the total chromium content and amounting from 5 to 30 mg/m^2.

5. The coated stainless steel strip of claim 1 wherein said transparent resin coating is 5 to 30 μm thick.

6. A process for producing a coated stainless steel strip, comprising the steps of:

chromating a stainless steel strip on a surface thereof to form a chromate layer with a total chromium content of 0.5 to 50 mg/m^2, trivalent chromium occupying at least 60% by weight of the total chromium content and amounting up to 40 mg/m^2, and

applying a transparent resin composition to the chromated strip.

7. The process of claim 6 wherein the chromating step includes applying a chromate solution to the strip surface followed by drying.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 5852

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	CHEMICAL ABSTRACTS, vol. 82, no. 4, 27 January 1975, Columbus, Ohio, US; abstract no. 20470Z, TAKAMURA, HISAO: 'coloring stainless steel' page 250 ;column 2 ; * abstract * ---	1-4,6,7	C23C22/30 C23C22/33
Y	CHEMICAL ABSTRACTS, vol. 110, no. 7, 3 April 1989, Columbus, Ohio, US; abstract no. 119119A, SAITO, KATSUSHI: 'chromating of galvanized or aluminized steel strip' page 277 ; * abstract * ---	1-4,6,7	
A	FR-A-2 117 842 (SOCIETE CONTINENTALE PARKER) * page 2, line 6 - page 3, line 7; claim 1; example 3 * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 138 (C-231)(1575) 27 June 1984 & JP-A-59 047 387 (NITSUSHIN SEIKOU KK) 17 March 1984 * abstract * ---		TECHNICAL FIELDS SEARCHED (Int. Cl.5) C23C
A	GB-A-1 122 173 (INTERNATIONAL NICKEL LIMITED) ---		
P,X	PATENT ABSTRACTS OF JAPAN & JP-A-3 271 379 (KAWASAKI STEEK KK) 3 December 1991 * abstract *	1-7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 MAY 1992	LANDAIS A.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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