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[54] PROCESS OF FORMING COLORLESS CHROMATE FILM ON AL, AL-ALLOY OR AL-COATED STEEL

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[58] **Field of Search**......... 148/6.2, 6.27; 117/132 R, 117/49; 134/2

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[57] **ABSTRACT**

Colorless chromate film having good corrosion resistance and adhesive property on Aluminium, Aluminium alloy or Aluminium-coated steel when these materials are subjected to a pre-treatment stage wherein the material is rinsed with hot water after de-oiling and dried while the water film still lying on the surface is wiped by drawing rolls, a treatment stage wherein the material is processed with an aqueous solution of about 2 to 10g/l of CrO_3, 0.05 to 1g/l Cr^{+3}, 0.2 to 5g/l F^-, 0.01 to 5g/l of Ferricyanide and/or Ferrocyanide, 0.01 to 1g/l Al^{+3} and a post treatment stage wherein the material is processed with an aqueous solution containing water soluble copolymer of itaconic acid and acrylonitrile.

3 Claims, No Drawings

PROCESS OF FORMING COLORLESS CHROMATE FILM ON AL, AL-ALLOY OR AL-COATED STEEL

BACKGROUND OF THE INVENTION

The present invention relates to forming a corrosion resistant film on aluminium, aluminium alloys or aluminium coated steel, and, more in particularly, to the formation of a colorless chromate film having excellent corrosion resistance and adhesive properties.

BRIEF REVIEW OF THE PRIOR ART

Various attempts have been made heretofore to form a film on the surface of aluminium, aluminium alloys and aluminium coated steel. Particularly known among them are the anodic oxidation treating method and the film forming method through chemical substitution.

The former method forms an oxide film having good corrosion resistance and paint adhesive properties thereon by the anodic oxidation treatment. It is, however, difficult to shorten the treating time at the present level of art. For instance, it requires at least 1 minute to form an oxide film having the minimum thickness of 2 μ in the continuous anodic oxidation treating line, so that when a workpiece is passed through as a strip a problem is presented in meeting today's demand for high speed productivity. On the other hand, the latter film forming method through chemical substitution may roughly be classified into one of using a treating solution mainly comprising phosphoric acid and hexavalent chromium and the other of using an acid treating solution mainly comprising hexavalent chromium and fluoride. The aluminium surface formed by the method using a treating solution containing mainly phosphoric acid and hexavalent chromium is covered with a thin green film and although it is effective as a ground coat and has improved paint adhesive property, the appearance is not very desirable. The aluminium surface obtained by the method using the acid treating solution mainly containing hexavalent chromium and flouride ranges widely from colorless to golden color. However, it is difficult to obtain corrosion resistance and paint adhesiveness expected when a material available in the market which may be able to form a colorless film is employed.

A material such as disclosed in the specification of U.S. Pat. No. 2796371 or in the Japanese Patent Publication No. Showa 45–32922 (No. 32922/**70**) will improve the corrosion resistance and the material thus obtained is effective as a ground coat. However, it is known that its surface is covered with lusterous golden film, which is undesirable. At the same time, it, generally, requires more than 30 seconds for treating in order to give an excellent film with a solution of this kind. When the above treating time is shortened, it is unavoidable that the surface will become dull yellow color and show varied patches of color.

The increased demand for aluminium as a construction material in recent years requires a finishing of the pear-skin type rather than a glazed finish. Consequently, such a finishing causes increased activity of the surface and promotes the formation of a colored film on a rougher surface. Thus, the situation prevailing today in the art is that a treating process for obtaining uniform and stable colorless chromate film without patch-like discolorations or patches is not available.

The present invention has been developed to obviate such difficulties in the art and is characterized in that ferricyanide or ferrocyanide has been further added to the aqueous solution comprising CrO_3, trivalent chromium, fluorine ion and aluminium ion. In order to enhance the uniform and stable properties of the chromate film thus obtained, the invention contemplates pre-treatment steps of de-oiling, rinsing with hot water and drying, with the water film remaining on the surface and, a post treatment step after a chemical treatment in which an aqueous solution containing water soluble copolymer of itaconic acid and acrylonitrile is used.

OBJECTS OF THE INVENTION

The object of this invention is to provide a uniform and stable chromate film on aluminium, aluminium alloy or aluminium coated steel.

Another object of the present invention is to form colorless chromate film having excellent corrosion resistance and paint adhesive properties.

Other objects and advantages of the present invention will become apparent from the following detailed description.

DETAILED DESCRIPTION

According to the chemical treating process for aluminium, aluminium alloy or aluminium coated steel contemplated herein, position of the treating solution is:

Component of CrO_3: 2 to 10g/l
Trivalent chromium: 0.05 to 1g/l
Fluorine ion: 0.2 to 5g/l
Aluminium ion: 0.01 to 1g/l
Ferricyanide and/or ferrocyanide: 0.01 to 5g/l

According to the pre-treating process contemplated, the workpiece is de-oiled and rinsed with hot water. And then with the water film still on the surface the workpiece is wiped by drawing rolls and dried.

The post-treating is carried out on the workpiece on which the above-mentioned chromate film is formed. The workpiece is processed in an aqueous solution containing a water soluble copolymer of itaconic acid and acrylonitrile of 10 to 50g/l.

In elaboration of the chemical treatment described first, the treating solution used in the present invention is an aqueous acid solution which contains hexavalent chromium required for forming a desirable film on the surface of the workpiece. The amount thereof is 2 to 10g/l in the form of CrO_3. If it is below 2g/l, sufficient corrosion resistance is not obtainable and if it exceeds 10g/l, an undesirable yellowish film tends to be formed on the surface.

Next, said treating solution contains trivalent chromium which is effective for forming a colorless film. That is to say, the film formed on the surface of the material does not become yellowish, although the amount of chromium increase on the surface, because of the existence of the trivalent chromium. It is desirable that the amount of the trivalent chromium should be 5 to 20% of the total amount of chromium in the solution, i.e. 0.05 to 1g/l as Cr^{+3}. If it is below 5%, the effect is negligible while if it exceeds 20%, reactivity of the solution is lowered.

Further, fluorine ion in an amount sufficient to dissolve the aluminium surface and form a good, sound and uniform film should be contained. The fluorine ion is added to the solution as at least one or more of those selected from the group consisting of HF, H_2SiF_6,

H_2BF_4 and the salts thereof and should be 0.2 to 5g/l. The most preferable range of the same is 0.2 to 4g/l, since an amount less than 0.2g/l will not form a good film and more than 5g/l will not form the film at all or cause an undesired dissolution of the surface.

Moreover, 0.01 to 5g/l of a ferricyanide such as potassium ferricyanide is added to the solution. This ferricyanide not only promotes the reaction of forming a film but also, even when the treatment time is shortened considerably, brings a great improvement on the formation of a colorless chromate film showing excellent corrosion resistance. This is similar to the effect of adding trivalent chromium in the treating solution and it is presumably the source of supplying Cr^{+3} in the proximity of the surface where the treating reaction occurs. Accordingly, the amount of potassium ferricyanide of less than 0.01g/l will decrease excessively the effect desired and conversely an amount exceeding 5g/l will not show any increase in effectiveness. If more is added, a good film cannot be obtained. It is possible to add potassium ferrocyanide in place of such potassium ferricyanide. This ferrocyanide is not limited to the salts of potassium, but any water soluble salt may be used. The amount to be added is the same as that of above mentioned ferricyanide and the two may be mixed and used together. However, the most important factor lies in the relation of concentration of the ferricyanide and the fluorine ion. For instance, it is desirable that when the solution contains more than 0.5g/l of ferricyanide, there should be a fluorine ion concentration of less than 2.4g/l.

In the present invention, the forming of colorless and uniform film is stepped up by adding aluminium ion to the above mentioned solution. The amount thereof should be within the range of 0.01 to 1g/l. If the amount is less than the above mentioned range, expected effects are not obtained while that exceeding above range will impair stability of the treating solution.

When aluminium, aluminium alloys or aluminium coated steel is treated with an aqueous solution of the above mentioned composition, it is easy to form a colorless chromate film having excellent corrosion resistant and paint adhesive property. However, it was recognized that various patch-like discolorations occur in actual operation. It is particularly noted that such patches occur more readily when the film surface shows luster. Upon closer examination of such phenomenon, it is noted that a big difference existed in the amount of chromium on the surface depending on the places where measurement was taken and that the corrosion resistant and paint adhesive properties was different at these places. On the other hand, the recent demand for colorful aluminium and the importance attached to the luster after painting suggests that a lusterous surface is desirable as a ground for colored aluminium. Defects tend to increase with the treatment speed as the moving workpiece line is increased, for instance to less than 30 seconds, and the situation can no longer be disregarded. In the present invention, a new pretreating was contrived as a continuous process wherein no patch-like discolorations on the surface appear with high speed. Such a pre-treating process is as hereinbefore described.

A process for pre-treating in accordance with the present invention method is based on confirmation of the facts that the patches are mainly caused by the imperfect pre-treating. In the use of the treating solution where the treatment is performed on the workpiece. These patches do not always occur owing only to the incompleteness of the pre-treating. However, an investigation of the phenomenon revealed that many of these patches depend upon a thick and uneven water film on the surface of the workpiece which had been caused by the pretreating just before it is introduced into the chemical treating solution. That is to say, the difference thickness of the water film still lying on the surface causes a difference in the dissolution speed of the surface aluminium at the first stage of the chemical reaction and it was recognized that the shorter treating time was, the greater the difference in water thickness. For this reason, the present invention aimed at improving the pretreating process conventionally used heretofore which comprises the steps of de-oiling, rinsing with water and chemical treating. That is, the water film still lying on the material surface after the washing with water is completely removed and the surface is dried.

As one step of improvement, the materials was dried by the hot air at 80°C and then passed through said treating solution. The above mentioned patches completely disappeared in this step. Further, investigations were made as to the use of rubber drawing rolls, for causing the water film lying on the surface to become extremely thin and uniform instead of said drying step prior to the chemical treating. The result obtained was the same. Then, it was found and confirmed that the simultaneous use of these two steps obtain still better results. Although it may be difficult to cause the water film on the strip surface to become extremely thin and uniform in the actual production line by the use of the drawing roll alone, the desirable results were obtained when a combined step coupled with the drying step were employed. It was further recognized that rinsing with hot water instead of usual cold water further enhanced the above mentioned effects. Thus, in accordance with the above mentioned pre-treating process, it becomes easy to accomodate the higher line speed of several seconds for chemical treating and at the same time eliminate the various patch-like discolorations seen in the conventional workpieces.

When the chemical treatment of forming a chromate film is performed using a solution consisting of the above-mentioned composition following the pretreatment, it is possible to obtain a colorless chromate film having sufficient corrosion resistance and paint adhesive property. However, it is still found in actual operation that some differences were noted in the painting property depending upon the combination of the components even though they may be within the range of the composition. The present invention then further proposed to perform the post-treating as aforementioned for stabilizing the painting property. The post-treating step is to use a neutral aqueous solution containing a water soluble copolymer of itaconic acid and acrylonitrile just after the chemical treating. It is preferable to use at least 1% or more of said resin in order to sufficiently improve the paint adhesiveness, since an amount of less than the above will not provide effective results. The upper limit thereof is 5%, as an amount exceeding 5% will damage the appearance after treating. It is also permissible to contain hexavalent chromium of 0 to 4g/l in the post-treating solution. The treated material may be wetted with this post treating solution by spraying or immersion, the excess solution being removed by rubber drawing rolls and then the material may be dried by the hot air at 80° to 100°C. Coating may be done with rolls as the case may be.

The pre-treating and the post-treating mentioned hereinabove naturally show their effectiveness when applied and used before and after the conventional method of chemical treatment. However, when they are employed with a chemical treating solution of the aforementioned composition, it becomes possible to prevent various defects often noted in the prior art and to form a uniform and stable colorless chromate film showing maximum corrosion resistance and paint adhesive property.

The following is the comparison of the chemical treating process in accordance with the present invention and that of the conventional art.

EXAMPLE 1

CrO_3:	4 g/l	Cr^{+3}:	0.3 g/l
$NaHF_2$:	0.42 g/l	$K_3Fe(CN)$:	0.01 g/l
Al^{+3}:	0.05 g/l		

The aqueous solution having the above mentioned composition was prepared and the four following test pieces were used;

1. Aluminium coated steel sheet
   Thickness of coated layer: 20 μ
   Surface roughness: H max = 0.3 μ
2. Aluminium coated steel sheet
   Thickness of coated layer: 20 μ
   Surface roughness: H max = 8 μ
3. Aluminium plate (JIS - ALPS - ½ H)
   Surface roughness H max = 8 μ
4. Aluminium plate (JIS - ALPS - ½ H)
   Surface roughness H max = 8 μ

These test pieces were de-oiled, rinsed with cold water, subjected to spraying for 5 minutes at 45°C and under the spraying pressure of 0.6 Kg/cm², and dried with hot air of 80°C.

The test pieces thus obtained had a colorless film uniformly formed.

EXAMPLE 2

CrO_3:	8 g/l	Cr^{+3}:	0.4 g/l
$NaHF_2$:	0.3 g/l	$K_3Fe(CN)_6$:	0.01 g/l
Al^{+3}:	0.2 g/l		

The solution having the above composition was prepared and the treatment was given to the same test pieces as in Example 1 and under the same conditions therein. The resulting film was uniform and colorless as in the case of Example 1.

EXAMPLE 3

CrO_3:	4 g/l	Cr^{+3}:	0.1 g/l
$NaHF_2$:	2.0 g/l	$K_3Fe(CN)_6$:	3 g/l
Al^{+3}:	0.2 g/l		

The aqueous solution having the above mentioned composition was prepared and used in the treatment of the test pieces (2) and (4) in Example 1 under the same conditions as mentioned in Example 1. In spite of the approximately same amount of surface chromium as in the golden colored film, colorless and uniform film was formed.

EXAMPLE 4

CrO_3:	8 g/l	Cr^{+3}:	0.8 g/l
$NaHF_2$:	5 g/l	$K_4Fe(CN)_6.2H_2O$:	5.2 g/l
Al^{+3}:	0.3 g/l		

The aqueous solution having the above mentioned composition was prepared and the test pieces as in the above Example 3 were treated under the same treatment conditions as in the Example 1. The same result was obtained as in Example 3.

EXAMPLE 5

The sheets treated in the Example 3 were immersed in the aqueous solution containing 1% of a solid resin of a water soluble copolymer of itaconic acid and acrylonitrile, then wiped by drawing rolls and dried by blowing hot air of 100°C for 3 seconds. The product obtained had colorless transparent film on the surface.

EXAMPLE 6

CrO_3:	5 g/l	$K_3Fe(CN)_6$:	1 g/l
$BaNO_3$:	1.9 g/l	Na_2SiF_4:	1.35 g/l
pH:	1.5		

In accordance with the specification of U.S. Pat. No. **2,796,371, 2,796,371,** a treating solution having the above composition at a temperature of 25°C, spray pressure 1 Kg/cm² for 1 minute were employed for test piece (2) mentioned in Example 1. The yellow film formed on the piece tested.

EXAMPLE 7

Colorless type chromate treating solution available in the market containing hexavalent chromium of about 1g/l when calculated as chromic acid and borofluoric acid ion at a degree not to color the formed film was used in treating the test piece (2) of the Example 1 under the same condition as in the Example 1. The appearance of the resulting product was no different from that before the treatment.

As has been mentioned hereinbefore, the Examples 1 to 5 are in accordance with the present invention while the Examples 6 and 7 are in accordance with the conventional art. The resulting products of respective examples were subjected to salt spray test in accordance with JIS-Z-2371 and the humidity cabinet test in accordance with JIS-Z-0228 for corrosion resistance of the film and they were coated with a baking paint of melamine resin to test the paint adhesive property. The following tables 1 and 2 show the results thereof.

In this case the amount of chromium adhering to the surface and the color thereof were as noted in Table 1 and the basis for evaluation was as follows.

Basis for evaluation
○:hardly changed
◎:area of rust generation 1–10%
▲:area of rust generation 11–25%
X:area of rust generation 26–50%
XX:area of rust generation more than 50%

Table I

	Corrosion resistance									
	Humidity cabinet test 1000 hr.				Salt spray test 1000 hr.				Chromium amount on surface mg/m^2	Surface color
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)		
Example 1	○	○	○	○	○	○		○	14 to 17	colorless
Example 2	Δ	○	Δ	○	Δ	○	X	○	10 to 15	″
Example 3	—	◎	—	◎	—	○	—	○	25 to 30	″
Example 4	—	◎	—	◎	—	○	—	○	35 to 40	″
Example 5	—	◎	—	—	—	○	—	—	—	″
Example 6	—	◎	—	—	—	○	—	—	35	golden
Example 7	—	XX	—	—	—	XX	—	—	5	colorless

Note: " — " indicates no test pieces or no measurements taken.

Examples 1 to 5 are in accordance with the present invention method and Examples 6 and 7 are in accordance with the conventional method.

Table 2

	Paint adhesive							
	Cross-cut test				Cross-cut erichsen test			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Example 1	◎	◎	○	◎	○	○	○	○
Example 2	○	◎	○	◎	Δ	○	Δ	○
Example 3	—	Δ	—	—	—	XX	—	—
Example 4	—	Δ	—	—	—	XX	—	—
Example 5	—	◎	—	—	—	○	—	—
Example 6	—	Δ	—	—	—	XX	—	—
Example 7	—	Δ	—	—	—	X	—	—

The method of painting used for test pieces in Table 2 was such that melamine resin was coated with a bar coater and baked for 20 minutes at 140°C with the thickness of painted layer being 20–31 μ and hardness of the same at H–2H. The test method employed was as follows:

Cross-cut test: 100 squares were marked at an internal of 1 mm on the coated surface. A strip of cellophane tape was adhered on the surface and then wax peeled.

Cross-cut erichsen test: Squares were marked as above and the test pieces were stretched for 5mm by Erichsen tester. A strip of cellophane tape was adhered on the surface and then peeled.

EXAMPLE 8

In addition to the above tests, the influence of pretreating process was examined. The testing requirements and results was as follows.

1. Pre-treating process in accordance with the present invention:

Material: aluminum-coated steel having aluminium-layer of 20 μ thickness and aluminum-plate.

Pre-treating in accordance with this invention: deoiling by spraying aqueous solution at 45°C containing 3% of the sodium silicate for 5 min, rinsing with hot water, wiping by drawing rolls and drying by hot air at 80°C.

Chemical-treating depending on the prior art: conventional treating solution 45°C consisting of CrO_3 of about 4.5g/l. ferricyanide of about 0.5g/l. fluoride of about 1g/l and others are sprayed for 5 sec. under pressure of 1.0 Kg/cm^2.

Results: uniform yellowish film was obtained on the surface of the both and no patch was seen.

2. Pre-treating process depending on the prior art: [Material and chemical treating were the same as shown in the above Example 1.]

Pre-treating depending on the prior art: de-oiling and rinsing with cold water.

Results: either film on the test pieces showed considerable treating patches.

Thus, it will be well understood that the process in accordance with the present invention is far superior to that of the prior art.

What is claimed is:

1. In the chemical process for treating a workpiece of aluminum, aluminum alloy or aluminum coated steel to form a colorless chromate film thereon, the improvement therein wherein the workpiece is subjected to a pre-treatment comprising deoiling, rinsing with hot water, drying with hot air and, then wiping the water film still lying on the surface using drawing rolls and drying to obtain a uniform water thickness on the workpiece, the treating solution consisting of the following composition:

CrO_3 : 2 to 10g/l
Trivalent chromium: 0.05 to 1.00 g/l
Fluorine ion : 0.2 to 5g/l
Aluminum ion : 0.01 to 1.00g/l
Ferricyanide and/or ferrocyanide : 0.01 to 5.00g/l.

2. A process according to claim **1** wherein a post treating following the chemical treating is performed using an aqueous solution of water soluble copolymer of 10 to 50 g/l containing itaconic acid and acrylonitrile.

3. A process according to claim **1** wherein the concentration of fluorine ion is selected within the range of 0.2 to 2.4 g/l, when the concentration of ferrocyanide and/or ferricyanide is within the range of 0.5 to 5.0 g/l.

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