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 **Method for producing tin-free steel strips having improved lacquer adhesion.**

 Tin-free steel sheets are produced by chromium plating a thin steel sheet through cathodic electrolysis in a chromium-containing bath to deposit a metallic chromium layer, reversely electrolyzing the chromium plated steel sheet by a successive anodizing treatment in the same or another chromium-containing bath, and subjecting the reversely electrolyzed steel sheet to an electrolytic chromate treatment in an aqueous chromate solution. The adhesion of lacquer to the TFS sheet is improved by carrying out the electrolytic chromate treatment in a chromate solution which contains chromic acid, chromates or dichromates as a main ingredient and sulfuric acid, sulfates, thiocyanates, sulfonic acids or sulfonates as an assistant ingredient, in a molar ration of H_2SO_4/CrO_3 between 1/1000 and 1/100 provided that the main and assistant ingredients are converted into CrO_3 and H_2SO_4 , respectively.

Method for Producing Tin-Free Steel Strips
Having Improved Lacquer Adhesion

BACKGROUND OF THE INVENTION

This invention relates to a method for producing tin-free steel strips or sheets having improved lacquer adhesion.

5 Electrolytic chromate treated steel sheets also known as tin-free steel (TFS) of chromium type have improved properties as can-forming material and are regarded as a substitute for tin plates, and the demand for them is increasing in recent years.

10 Since TFS has a two-layer coating of metallic chromium and hydrated chromium oxide layers on the surface, it does not possess sufficient weldability. A can is fabricated from a TFS sheet by coating the sheet with an epoxy-phenol resin and cementing the mating edges of the coated sheet
15 with a polyamide adhesive to form a can barrel.

 Recently, the extent of application of TFS cans has been further spread. That is, TFS cans are not only used for low-temperature packs prepared by packing contents such as carbonated beverage and beer in cans at relatively low
20 temperatures, but also used for the so-called hot packs prepared by packing contents such as fruit juice in cans at relatively high temperatures for sterilization. TFS is also used in those cans requiring a high temperature

retorting treatment for sterilization at the end of packing of coffee, for example. In the latter applications, there often occurred accidents of rupture of can barrels.

5 This can barrel rupture occurs in cemented TFS cans during hot packing and retorting treatment because hot water penetrates through the coating at the barrel junction to deteriorate the interfacial adhesion between the lacquer film and the TFS substrate to eventually separate the lacquer film from the TFS.

10 The inventors previously proposed in Japanese Patent Application Kokai No. SHO 57-177998 a method for producing a tin-free steel sheet having improved lacquer adhesion by chromium plating a steel strip, subjecting the strip to reverse electrolysis with the strip made the anode, and
15 thereafter subjecting the strip to an electrolytic chromate treatment in an aqueous solution containing hexavalent chromium. The reverse electrolysis may be carried out in the chromium plating solution or in another aqueous solution containing chromium ion, with similar results with
20 respect to lacquer adhesion. It was found that the method characterized by inserting the reverse electrolysis step between the chromium plating and electrolytic chromate treatment steps is fully effective in improving lacquer adhesion. Continuing research, we found that reversely
25 electrolyzed steel strips tend to suppress the growth of a chromium oxide layer thereon during the subsequent electrolytic chromate treatment, as long as the chromate

bath contains at least one selected from chromic acid anhydride, chromates and dichromates and concomitant anions such as sulfate (SO_4^{2-}), fluoride (F^-) and chloride (Cl^-) ions. The electrolytic chromate treatment then requires a large quantity of electricity in order to deposit the chromium oxide layer to a sufficient thickness to insure improved lacquer adhesion, resulting in an economic loss in commercial production.

The surface state of steel strips after chromium plating and reverse electrolysis was examined by the electron spectroscopy for chemical analysis (ESCA) to find that as compared with the surface state observed after chromium plating, the quantity of sulfur (probably in the form of sulfate) codeposited in the chromium oxide layer is reduced and the bond energy of O_{1s} is shifted to a lower energy level, that is, from 531.4 eV to 530.1 eV as diagrammatically shown in Fig. 1. This indicates that the proportion of ol linkages (Cr-OH) in the chromium oxide layer is reduced and the proportion of oxo linkages (Cr-O) is increased. This is the reason why the growth of a chromium oxide layer is suppressed on reversely electrolyzed steel strips.

The inventors have studied how to promote the growth of a chromium oxide (Cr^{OX}) layer on reversely electrolyzed steel strips without detracting from subsequent lacquer adhesion. We have found that electrolytic chromate treatment may be advantageously carried out in an aqueous

- 4 -

chromate solution which contains at least one chromium compound selected from chromic acid anhydride, chromates and dichromates as a main ingredient and at least one selected from sulfuric acid, sulfates, thiocyanates, sulfonic acids, and sulfonates as an assistant ingredient.

It is, therefore, an object of the present invention to provide an electrolytic chromate solution which allows chromium oxides (Cr^{OX}) to be effectively deposited on reversely electrolyzed steel strips without detracting from subsequent lacquer adhesion.

SUMMARY OF THE INVENTION

Tin-free steel strips or sheets are advantageously produced by the steps of chromium plating a thin steel strip through cathodic electrolysis in a chromium ion-containing aqueous solution to form a layer consisting essentially of metallic chromium, reversely electrolyzing the chromium plated steel strip by a successive anodizing treatment in said aqueous solution or in another chromium ion-containing aqueous solution, and subjecting the reversely electrolyzed steel strip to an electrolytic chromate treatment in an aqueous solution containing as a main ingredient at least one selected from the group consisting of chromic acid, chromates, and dichromates. In order to improve the adhesion of lacquer to the thus treated steel sheets, the electrolytic chromate treatment should be carried out in the solution which contains as a main ingredient at least one selected from the group

consisting of chromic acid, chromates, and dichromates, and as an assistant ingredient at least one selected from the group consisting of sulfuric acid, sulfates, thiocyanates, sulfonic acids and sulfonates, and has a molar ratio of $\text{H}_2\text{SO}_4/\text{CrO}_3$ in the range between 1/1000 and 1/100 provided that the main and assistant ingredients are converted into CrO_3 and H_2SO_4 , respectively.

BRIEF DESCRIPTION OF THE DRAWING

The above and other objects, features, and advantages of the present invention will be readily understood by reading the following description in conjunction with the accompanying drawings, in which:

Fig. 1 is a diagram showing O_{1s} peaks measured by the ESCA on the surface of chromium plated steel and reversely electrolyzed steel;

Fig. 2 shows the amount of hydrated chromium oxides as a function of the molar ratio of $\text{H}_2\text{SO}_4/\text{CrO}_3$ in the electrolytic chromate solution;

Figs. 3a and 3b illustrate a bonded sample of lacquered pieces and a testing holder having the sample mounted therein for the evaluation of lacquer adhesion.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to TFS strips or sheets having a layer of metallic chromium (Cr^{M}) ranging from 50 to 200 mg per square meter on each sheet surface and a layer of hydrated chromium oxides (Cr^{OX}) ranging from 8 to 30 mg of Cr per square meter on the metallic chromium

-6-

layer. TFS sheets generally have a metallic chromium layer of 50 to 200 mg/m² because thinner layers of less than 50 mg/m² have poor corrosion resistance. Thicker layers exceeding 200 mg/m² do not provide an additional
5 improvement in corrosion resistance.

TFS sheets have a layer of hydrated chromium oxides of 8 to 30 mg/m² (calculated as metallic chromium) because thinner layers of less than 8 mg/m² do not provide the necessary lacquer adhesion. Thicker layers exceeding 30
10 mg/m² have a poor appearance and are prone to cracking during subsequent processing and thus impractical.

The chromate solution in which the electrolytic chromate treatment was carried out contains as a main ingredient at least one chromium compound selected from
15 chromic anhydride, chromates and dichromates. Examples of the chromates and dichromates used herein include potassium chromate K₂CrO₄, sodium chromate Na₂CrO₄, ammonium chromate (NH₄)₂CrO₄, potassium dichromate K₂Cr₂O₇, sodium dichromate Na₂Cr₂O₇, and ammonium dichromate (NH₄)₂Cr₂O₇. The
20 concentration of the chromium compound should be limited to the range of 20 to 200 g of CrO₃ per liter of the solution. At chromate concentrations of less than 20 g/l of CrO₃, the bath voltage must be increased, leading to an electric power loss. Chromate concentrations beyond 200 g/l of CrO₃
25 are costly because the loss of CrO₃ due to entrainment of solution with outgoing steel strips is increased.

The assistant ingredient which is intentionally added to the chromate solution is at least one compound which is selected from the group consisting of sulfuric acid, sulfates, thiocyanates, sulfonic acids, and sulfonates.

5 Examples of the sulfates, thiocyanates, and sulfonic acids and sulfonates used herein include potassium sulfate K_2SO_4 , sodium sulfate Na_2SO_4 , and ammonium sulfate $(NH_4)_2SO_4$; potassium thiocyanate KSCN, sodium thiocyanate NaSCN, and ammonium thiocyanate NH_4SCN ; and phenoldisulfonic acid and
10 catecholdisulfonic acid and the potassium, sodium, and ammonium salts thereof.

The following experiment was carried out to determine the optimum range of the assistant ingredient concentration in the chromate solution. Like the chromate converted into
15 CrO_3 , the assistant ingredient is converted into H_2SO_4 for calculation purpose. The molar ratio of H_2SO_4/CrO_3 was varied over the range between 1/2000 and 3/100. A number of reversely electrolyzed steel pieces were electrolytically chromated. The amount of hydrated
20 chromium oxides (Cr^{OX}) formed thereon was determined and lacquer adhesion was tested.

The results are plotted in Fig. 2 which shows that the assistant ingredient should be present in such concentrations that the molar ratio of H_2SO_4 to CrO_3 is in
25 the range between 1/1000 and 1/100. In region I where the assistant ingredient is present in concentrations to give a molar ratio of H_2SO_4/CrO_3 of lower than 1/1000, the

-8-

assistant ingredient is not effective to assist a chromium oxide layer in growing, failing to achieve the objects of the invention. On the other hand, in region III where the assistant ingredient is present in concentrations to give a molar ratio of H_2SO_4/CrO_3 of higher than 1/100, the chromate film is stained so that the resulting products become commercially unacceptable. For this reason, the assistant ingredient should be added to the chromate solution in an amount (calculated as H_2SO_4) such as to give a molar ratio of H_2SO_4/CrO_3 between 1/1000 and 1/100 as shown by hatched region II in Fig. 2.

It should be noted that the present invention is directed to a method for producing a tin-free steel strip comprising chromium plating, reverse electrolysis, and electrolytic chromate treatment. Unless the reverse electrolysis is interposed between the chromium plating and electrolytic chromate treatment, tin-free steel strips having improved lacquer adhesion cannot be obtained even if the electrolytic chromate bath contains the assistant ingredient in a concentration to give a molar ratio of H_2SO_4/CrO_3 in the range between 1/1000 and 1/100.

Since a controlled amount of SO_4^{2-} is intentionally added to the electrolytic chromate bath according to the method of the invention, a great amount of metallic chromium is deposited during the electrolytic chromate treatment. The amount of metallic chromium (Cr^M) deposited is greater in the presence of reverse electrolysis than in

the absence of reverse electrolysis. The method of the invention thus has the additional advantage of a reduced quantity of electricity required for chromium plating.

The adhesion of lacquer to chromated steel is evaluated by carrying out both U- and T-peel tests in the following manner.

U-peel test

As shown in Fig. 3a, a phenol-epoxy lacquer was applied to one surface of a treated steel sheet 1 to a build-up of 60 mg/m² and baked for 12 minutes at 210°C to form a lacquer film 1A. The same lacquer was applied to one surface of another treated steel sheet 2 to a build-up of 25 mg/m² and baked under the same conditions to form another lacquer film 2A. The sheets were cut into pieces of 70 mm wide by 60 mm long. The longitudinal ends of two different pieces were overlapped each other over a distance of 8 mm with a nylon film 3 of 100 μm thick interposed therebetween as shown in Fig. 3a. Using a hot press, these two pieces were preheated at 200°C for 120 seconds and pressure cemented at 200°C for 30 seconds under a pressure of 3 kg/cm². Ten samples 4 were cemented in this manner for each run. The cemented samples 4 were mounted in a rectangular holder 5 as shown in Fig. 3b and placed in a retort kettle filled with steam at 130°C. Some samples separated at the junction under retorting after 300 minutes. In this U-peel test, lacquer adhesion was evaluated good when zero to one sample separated after 300 minute retorting.

T-peel test

A phenol-epoxy lacquer was applied to a treated steel sheet to a build up of 50 mg/m^2 and baked for 12 minutes at 210°C . The baked sheet was cut into pieces of 5 mm wide.

5 A sandwich of two pieces with a nylon adhesive interposed between the lacquer films was cemented under a hot press at 200°C for 30 seconds. The cemented samples were immersed for 7 days in a 0.4% citric acid aqueous solution at 90°C . Thereafter, T-peel tensile strength was measured to

10 evaluate secondary or wet adhesion of lacquer. In this T-peel test, samples whose T-peel tensile strength was 2.5 kg/5 mm or more after 7-day immersion in 0.4% citric acid solution at 90°C were evaluated good.

Samples which passed both the U- and T-peel tests were

15 evaluated to have excellent secondary or wet adhesion of lacquer.

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

Examples

20 Cold rolled steel sheets (T4CA) having a thickness of 0.22 mm were electrolytically degreased in a 5% homezarine solution at 80°C , rinsed with water, immersed in a 10% H_2SO_4 for 5 seconds for pickling, rinsed again with water, and then subjected to the following treatments in sequence:

- 25
- (1) chromium plating,
 - (2) reverse electrolysis, and
 - (3) electrolytic chromate treatment.

-11-

Steps (1) and (2) were successively carried out in the same electrolytic bath. These steps were carried out in the following conditions.

(1) chromium plating

5 Plating bath composition

Bath A at a temperature of 50°C

CrO₃ 150 g/l

H₂SO₄ 0.8 g/l

Na₂SiF₆ 7 g/l

10 Cr³⁺ 3 g/l

Bath B at a temperature of 60°C

CrO₃ 250 g/l

H₂SO₄ 2.5 g/l

Cr³⁺ 4 g/l

15 Electrolytic conditions

Cathodic treatment

Current density 50 A/dm²

Time 1.2 seconds

(2) Reverse electrolysis

20 The steel sheets were subjected to reverse electrolysis at a current density of 5 A/dm² for 0.2 seconds or at a current density of 15 A/dm² for 0.1 seconds while the sheet was made the anode in the same bath as used for chromium plating. For comparison sake, some steel sheets were not
25 subjected to reverse electrolysis.

(3) Electrolytic chromate treatment

Cathodic treatment was carried out with an electricity quantity of 10 to 20 coulomb/dm² using various chromate baths based on CrO₃ and Na₂Cr₂O₇ and containing varying concentrations of the assistant (H₂SO₄) at a temperature of 40°C. For comparison sake, one chromate bath was free of H₂SO₄.

By carrying out (1) chromium plating, (2) reverse electrolysis, and (3) electrolytic chromate treatment in succession, there were prepared TFS sheets. The amount of chromium oxides (Cr^{OX}) formed on the TFS sheets was determined by X-ray fluorometry and the amount of metallic chromium (Cr^M) was determined by electrolytic analysis. The U- and T-peel tests were carried out to evaluate lacquer adhesion after retorting. The results are shown in Table 1.

Table 1

Example	Chromium plating		Reverse electrolysis			Electrolytic chromate treatment			
	Bath	Current density (A/dm ²)	Electricity quantity (C/dm ²)	Current density (A/dm ²)	Electricity quantity (C/dm ²)	CrO ₃ (mol/l)	H ₂ SO ₄ (mol/l)	H ₂ SO ₄ /CrO ₃ (mol ratio)	Electricity quantity (C/dm ²)
1*	A	50	60	5	1.0	0.6	3 x 10 ⁻⁴	5/10,000	15
2	"	"	40	"	"	"	3 x 10 ⁻³	5/1,000	"
3*	"	"	60	0	0	"	"	"	"
4*	"	"	40	5	1.0	"	3 x 10 ⁻²	2/100	"
5	"	"	"	15	0.1	1.0	9 x 10 ⁻³	9/1,000	10
6	B	"	"	"	"	"	6 x 10 ⁻³	6/1,000	"
7	"	"	"	5	1.0	"	2 x 10 ⁻³	2/1,000	"
8*	A	-	-	"	"	"	9 x 10 ⁻³	9/1,000	60
9*	B	-	-	"	"	"	"	"	"
10	"	50	60	"	"	Na ₂ Cr ₂ O ₇ _{1.6}	6 x 10 ⁻³	6/1,000	15
11	"	"	"	"	"	Na ₂ Cr ₂ O ₇ _{0.6}	3 x 10 ⁻³	5/1,000	"

* comparison

Table 1 (con'd)

Example	Surface properties		Wet lacquer adhesion					Overall evaluation of wet lacquer adhesion	Appearance	
	Cr OX (mg/m ²)	Cr ^M (mg/m ²)	Samples separated after retorting at 130°C/10 samples		T-peel strength (kg/5mm)					
					150 min.	300 min.	Initial			After immersion
1*	7	100	2	8	6.8	2.5	poor	good		
2	15	102	0	0	7.0	4.1	good	"		
3*	18	110	9	10	6.0	0	poor	"		
4*	10	98	0	2	6.9	0	good	poor		
5	11	100	0	0	6.5	4.0	"	good		
6	12	102	0	0	6.3	4.2	"	"		
7	16	105	0	1	6.4	3.9	"	"		
8*	28	103	7	10	6.0	0	poor	"		
9*	28	97	8	10	4.0	0	"	"		
10	15	100	0	0	6.8	4.3	good	"		
11	14	103	0	0	6.9	4.0	"	"		

* comparison

In Example 1 (comparison), chromium plating (1) is followed by reverse electrolysis (2) and then by electrolytic chromate treatment in a bath containing H_2SO_4 in such a lower concentration as to give a molar ratio of H_2SO_4/CrO_3 of 1/2000. A smaller quantity of chromium oxide (Cr^{OX}) was present and the wet (secondary) lacquer adhesion was unsatisfactory.

Unlike Example 1 (comparison), Example 2 used an electrolytic chromate bath having a proper H_2SO_4 concentration to give a molar ratio of H_2SO_4/CrO_3 of 1/200, yielding a sufficient quantity of chromium oxide (Cr^{OX}) which ensures the improved wet lacquer adhesion.

Example 3 (comparison) used an electrolytic chromate bath having the same H_2SO_4/CrO_3 ratio as in Example 2, but omitted reverse electrolysis (2). The elimination of reverse electrolysis (2) resulted in inferior wet lacquer adhesion irrespective of an increased quantity of chromium oxide.

Example 4 (comparison) carried out chromium plating (1) and reverse electrolysis (2) followed by electrolytic chromate treatment in a bath containing H_2SO_4 in such a higher concentration as to give a molar ratio of H_2SO_4/CrO_3 of 2/100. Although wet lacquer adhesion was satisfactory, products were stained to a commercially unacceptable level.

In Examples 5 through 7, chromium plating (1) and reverse electrolysis (2) were followed by electrolytic chromate treatment in a bath having a molar ratio of

-16-

H_2SO_4/CrO_3 in the range of 1/1000 to 1/100, that is, the specific range according to the present invention.

Sufficient quantities of chromium oxide were present and the wet lacquer adhesion was superior.

5 Examples 8 and 9 (comparison) carried out reverse electrolysis (anodic treatment) (2) and electrolytic chromate treatment (cathodic treatment) (3) without chromium plating (cathodic treatment) (1), failing to provide improved lacquer adhesion.

10 These data suggest that improved lacquer adhesion cannot be accomplished unless the series of three essential steps, that is, chromium plating (1), reverse electrolysis (2), and electrolytic chromate treatment (3) are carried out and unless an assistant ingredient capable of
15 generating sulfate ion is intentionally added to the electrolytic chromate bath in such an amount as to give a molar ratio of H_2SO_4/CrO_3 in the range of 1/1000 to 1/100. With these requirements met, TFS sheets having improved
20 lacquer adhesion can be manufactured at a commercially acceptable cost.

-17-

Although in the above-described embodiment, reference is made to electrolytic chromate treatment in a bath containing CrO_3 and $\text{Na}_2\text{Cr}_2\text{O}_7$ as the main ingredient and H_2SO_4 as the assistant ingredient, it should be understood that similar effects are obtained when other compounds are selected as the main and assistant ingredients from the above-described groups as long as the molar ratio of $\text{H}_2\text{SO}_4/\text{CrO}_3$ falls within the optimum range as specified in the present invention.

5

WHAT IS CLAIMED IS:

1. A method for producing a tin-free steel strip having improved lacquer adhesion, comprising

chromium plating a thin steel strip through cathodic electrolysis in a chromium ion-containing aqueous solution to form a layer consisting essentially of metallic chromium,

reversely electrolyzing the chromium plated steel strip by a successive anodizing treatment in said aqueous solution or in another chromium ion-containing aqueous solution, and

subjecting the reversely electrolyzed steel strip to an electrolytic chromate treatment in an aqueous solution containing as a main ingredient at least one selected from the group consisting of chromic acid, chromates, and dichromates, and as an assistant ingredient at least one selected from the group consisting of sulfuric acid, sulfates, thiocyanates, sulfonic acids, and sulfonates,

wherein the solution in which said electrolytic chromate treatment is carried out has a molar ratio of H_2SO_4/CrO_3 in the range between 1/1000 and 1/100 provided that the main and assistant ingredients are converted into CrO_3 and H_2SO_4 , respectively.

-19-

2. The method according to claim 1 wherein the chromium layer is formed to a build-up of 50 to 200 mg per square meter on each surface.

3. The method according to claim 1 wherein the electrolytic chromate treatment is carried out to form a chromium oxide layer to a build-up of 8 to 30 mg of Cr per square meter on each surface.

FIG. 1

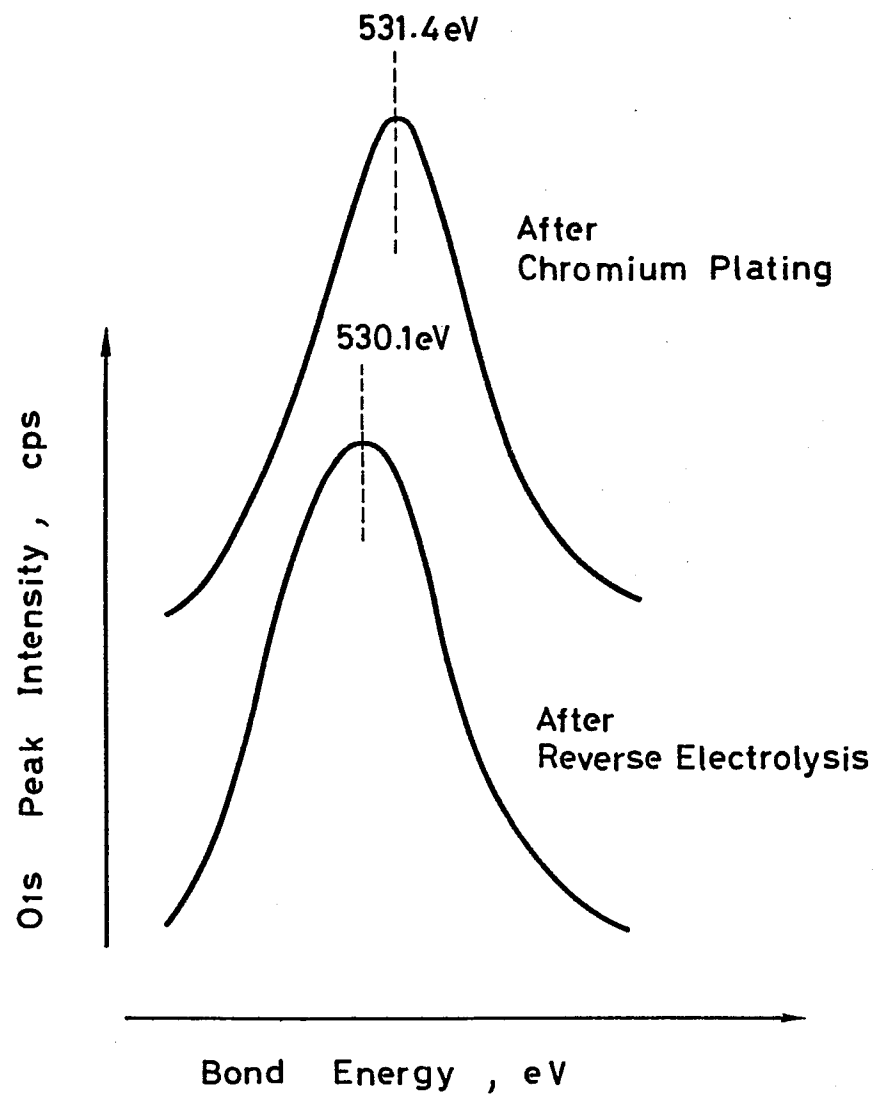


FIG. 2

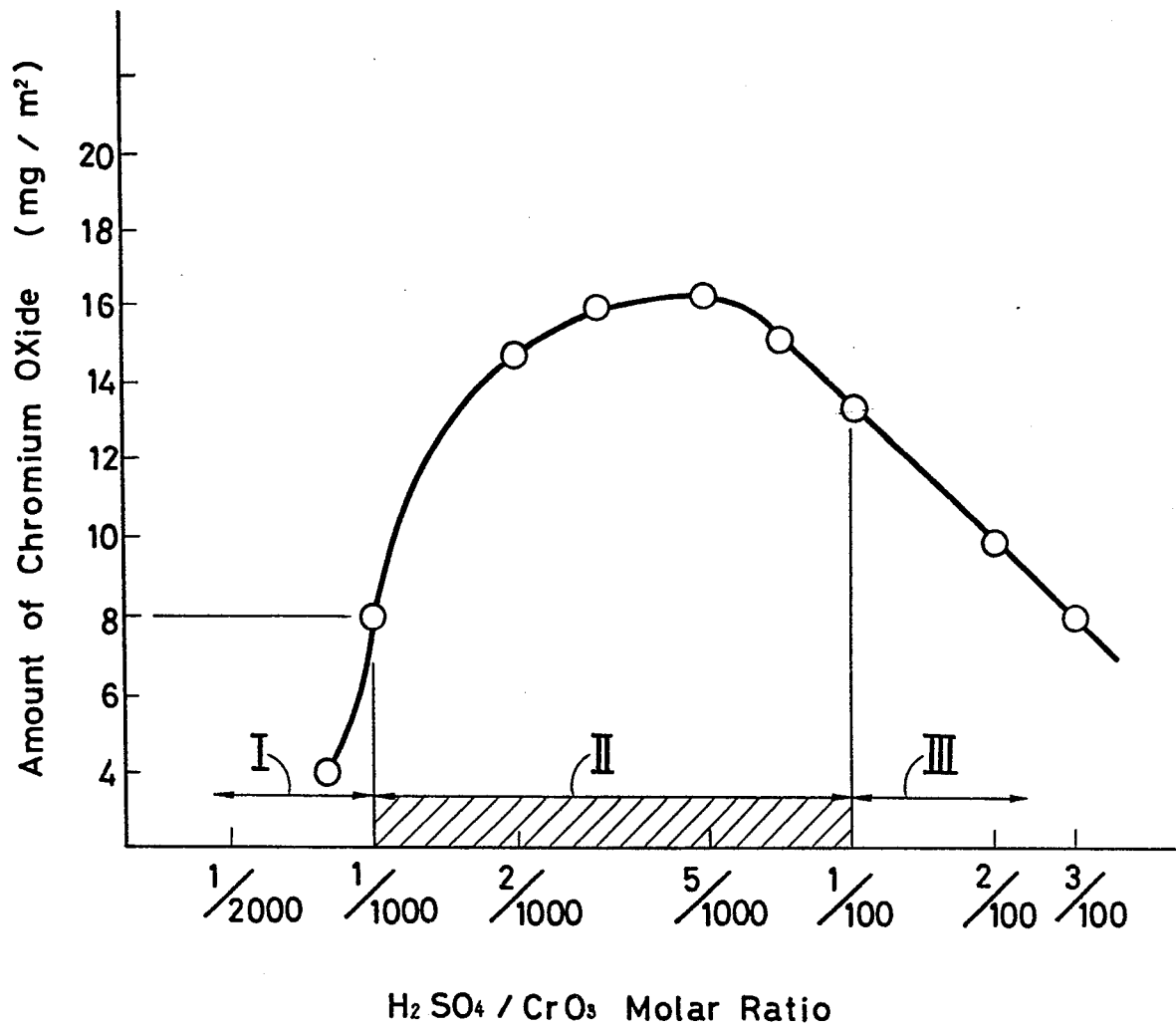


FIG. 3a

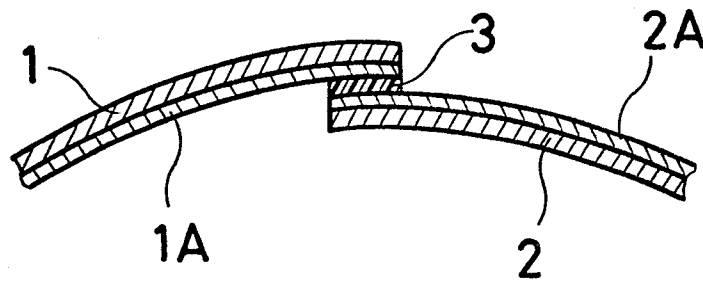
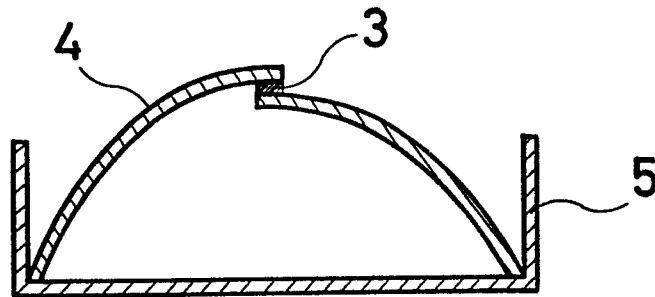


FIG. 3b





European Patent
Office

EUROPEAN SEARCH REPORT

0132722

Application number

EP 84108249.8

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.) 4
X	US - A - 3 986 940 (H. TAKANO et al.) * Abstract; example; claims * --	1,3	C 25 D 11/38 C 25 D 3/04 C 25 D 11/26 C 25 D 7/06
X	US - A - 3 679 554 (H. YAMAGISHI et al.) * Abstract; examples 1,2; claims * --	1-3	
D,X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 7, no. 22, January 28, 1983 THE PATENT OFFICE JAPANESE GOVERNMENT page 55 C 148 * Kokai-no. 57-177 998 (KAWASAKI SEITETSU K.K.) * --	2	TECHNICAL FIELDS SEARCHED (Int. Cl.) 4
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The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 18-09-1984	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



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EUROPEAN SEARCH REPORT

0132722

Application number

EP 84108249.8

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. X) 4
Category	Citation of document with indication where appropriate of relevant passages	Relevant to claim	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 4, no. 98, July 15, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT page 13 C 18 * Kokai-no. 55-58 395 (KAWASAKI SEITETSU K.K.) * -----	1	
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