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(54) Method for producing tin-free steel sheets having improved lacquer adhesion.

(57) 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 hexavalent chromium in an amount of 0.2 to 1.4 mols per liter of CrO_3 and a fluoride in a molar ratio of F^- to Cr^{6+} of 1/1000 to 1/20.

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

BACKGROUND OF THE INVENTION

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

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.

Since TFS has 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 a blank with an epoxy-phenol lacquer and cementing the mating edges of the coated blank 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 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.

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 coating and the TFS substrate to eventually separate the lacquer coating from the TFS.

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 sheet, subjecting the sheet to reverse electrolysis with the sheet made the anode, and thereafter subjecting the sheet 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 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 the reversely electrolyzed steel sheet tends 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 sheets after chromium plating and reverse electrolysis was examined by the electron spectroscopy for chemical analysis (ESCA) or X-ray electron spectroscopy to find that as compared with the surface state observed after chromium plating, the quantity of anions 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 diagramatically 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 sheets.

The inventors have studied how to promote the growth of a chromium oxide layer on reversely electrolyzed steel sheets without detracting from subsequent lacquer adhesion.

More specifically, electrolytic chromate treatment was carried out in a variety of aqueous chromate solutions which contained at least one chromium compound selected from chromic acid anhydride, chromates and dichromates as a main agent and at least one fluoride selected from H_2SiF_6, HBF_4, HF and salts thereof and $KAlF_4$ as an additive. We have found that efficient electrolytic chromate treatment is carried out by carefully controlling the proportion of the chromium compound and the fluoride to a specific range.

It is, therefore, an object of the present invention to provide an electrolytic chromate solution which allows chromium oxides to be effectively deposited on reversely electrolyzed steel sheets without detracting from subsequent lacquer adhesion.

SUMMARY OF THE INVENTION

Tin-free steel sheets are advantageously produced by the steps of chromium plating a thin steel sheet 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 sheet by a successive anodizing treatment in said aqueous solution or in another chromium ion-containing aqueous solution, and subjecting the reversely electrolyzed steel sheet to an electrolytic chromate treatment in an aqueous solution of at least one selected from the group consisting of chromic acid, chromates, and dichromates. In order to improve the adhesion of a lacquer to the thus treated steel sheets, the electrolytic chromate treatment should be carried out in the solution which contains hexavalent chromium in an amount of 0.2 to 1.4 mols of CrO_3 per liter of the solution and a fluoride in an amount to give a molar ratio of F^- to Cr^{6+} in the range of 1/1000 to 1/20.

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 a chromium plated sheet and a reversely electrolyzed sheet;

Fig. 2 shows the amount of hydrated chromium oxides as a function of the molar ratio of F^-/Cr^{6+} in the electrolytic chromate solution;

Fig. 3 shows the retorting resistance of cemented samples as a function of the molar ratio of F^-/Cr^{6+} in the electrolytic chromate solution; and

Figs. 4a and 4b illustrate a bonded sample of lacquer coated 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 sheets having a layer of metallic chromium ranging from 50 to 200 mg per square meter on each sheet surface and a layer of hydrated chromium oxides ranging from 8 to 30 mg of Cr per square meter on the metallic chromium layer. TFS sheets generally have a metallic chromium layer of 50 to 200 mg/m^2 because thinner layers of less than 50 mg/m^2 have poor corrosion resistance. Thicker layers exceeding 200 mg/m^2 do not provide an additional improvement in corrosion resistance.

TFS sheets have a layer of hydrated chromium oxides of 8 to 30 mg/m^2 (calculated as metallic chromium) because thinner layers of less than 8 mg/m^2 do not provide the necessary lacquer adhesion. Thicker layers exceeding 30 mg/m^2 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 agent at least one chromium compound selected from chromic acid anhydride, chromates and dichromates. The concentration of the chromium compound should be limited to the range of 0.2 to 1.4 mols of CrO_3 per liter of the solution. At chromate concentrations of less than 0.2 mol/l, the growth of a chromium oxide layer is suppressed, failing to achieve the object of the invention. Chromate concentrations beyond 1.4 mol/l do not further increase the rate of formation of chromium oxides and are thus costly.

The additive which is intentionally added to the chromate solution is at least one fluoride which may be selected from H_2SiF_6, HBF_4, HF and salts thereof, and $KAlF_4$. The following experiment was carried out to determine the optimum range of the fluoride ion (F^-) concentration in the chromate solution. The molar ratio of fluoride ion to hexavalent chromium ion (F^-/Cr^{6+}) was varied over the range between 1/5000 and 1/5. The electrolytic conditions for cathodic treatment were fixed to a current density of 15 A/dm^2 (amperes per square decimeter) and a time of 1 second. A number of reversely electrolyzed steel pieces were electrolytically chromated under these conditions. The amount of hydrated chromium oxides formed thereon was determined and lacquer adhesion was tested.

It was found that the concentration of the fluoride should be kept at a relatively lower level, that is, a molar ratio of F^-/Cr^{6+} in the range of 1/1000 to 1/20. In general, industrial grade chromate (CrO_3) reagent contains a concomitant fluoride impurity in an amount to give a molar ratio of F^-/Cr^{6+} of the order of 1/5000. In order that the fluoride be sufficiently effective to promote the formation of chromium oxides, it must be present in an amount to give a molar ratio of F^-/Cr^{6+} of at least 1/1000 as seen from Fig. 2. When the molar ratio of F^-/Cr^{6+} exceeds 1/20, a further improvement in the formation of chromium oxides is not observed and the lacquer adhesion diminishes as seen from Figs. 2 and 3. For this reason, the concentration of the fluoride is limited to the above-defined range.

The lacquer adhesion was evaluated in the following manner by preparing a test sample as shown in Fig. 4. A phenol-epoxy lacquer was applied to one surface of a treated steel sheet 1 to a build-up of 50 mg/dm² and baked for 10 minutes at 200°C to form a lacquer film 1A. The same lacquer was applied to the opposite surface of the sheet 1 to a build-up of 50 mg/dm² and baked for 10 minutes at 200°C to form another lacquer film 1B. The double-coated sheet was cut into pieces of 70 mm wide by 60 mm long. The longitudinal ends of two pieces were overlapped each other over a distance of 8 mm with a nylon film of 100 um thick interposed therebetween as shown in Fig. 4a. 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 3 were cemented in this manner for each run. The cemented samples 3 were mounted in a rectangular holder 4 as shown in Fig. 4b and placed in a retort kettle at 130°C. Some samples separated at the junction under retorting after 150 minutes and 300 minutes. In the following example, lacquer adhesion was evaluated good when zero to one sample separated after 150 minute retorting and zero to five samples separated after 300 minute retorting.

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

Example

Cold rolled steel sheets having 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, rinsed again with water, and then subjected to the following treatments in sequence:

(1) chromium plating,

(2) reverse electrolysis, and

(3) electrolytic chromate treatment.

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

(1) Chromium plating

<u>Plating bath composition</u>

Bath A at a temperature of 50°C

CrO_3	1.5 mol/ℓ
H_2SO_4	0.008 mol/ℓ
Na_2SiF_6	0.037 mol/ℓ
Cr^{3+}	3 g/ℓ

Bath B at a temperature of 55°C

CrO_3	0.8 mol/ℓ
NaF	0.1 mol/ℓ
H_2SO_4	0.00001 mol/ℓ
Cr^{3+}	1 g/ℓ

<u>Electrolytic conditions</u>

Cathodic treatment

Current density	50 A/dm^2
Time	1.2 seconds

(2) Reverse electrolysis

The steel sheets were subjected to reverse electrolysis at a current density of 5 A/dm^2 for 0.2 seconds or at a current density of 10 A/dm^2 for 0.2 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 subjected to reverse electrolysis.

(3) Electrolytic chromate treatment

Cathodic treatment was carried out with an electricity quantity of 15 to 20 coulomb/dm^2 using different chromate baths based on CrO_3 and containing a variety of fluorides at a temperature of 40°C.

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 formed on the TFS sheets was determined by X-ray fluorometry and a retorting test was carried out to evaluate lacquer adhesion in the same manner as described previously. The results are shown in Table 1.

As evident from the data in Table 1, by carrying out reverse electrolysis after chromium plating and further carrying out electrolytic chromate treatment in a chromate solution having the optimum composition as specified above, the necessary and sufficient amount of chromium oxides is formed with a quantity of electricity as generally required and the resultant TFS sheets exhibit excellent adhesion to lacquer.

TABLE 1

			Chromate solution				Samples separated in retorting at 130°C after	
	Chromium plating	Reverse electrolysis	CrO_3 (M/ℓ)	Fluoride	F^-/Cr^{6+} (molar ratio)	CrOx (mg/m^2)	150 min.	300 min.
Example 1	Bath A	10 A/dm^2 0.2 s	0.6	HF 1/30 M/ℓ	1/60	28	0	0
Example 2	"	5 A/dm^2 0.2 s	1.0	Na_2SiF_6 1/600 M/ℓ	1/100	15	0	0
Comparative Example 1	"	omitted	"	"	"	30	10	10
Comparative Example 2	"	5 A/dm^2 0.2 s	0.1	Na_2SiF_6 1/6000	"	8	5	10
Comparative Example 3	"	"	1.0	HBF_4 1/40 M/ℓ	1/10	25	4	10
Comparative Example 4	"	"	"	NaF 1/5000 M/ℓ	1/5000	5	6	10
Example 3	Bath B	10 A/dm^2 0.2 s	0.4	H_2SiF_6 1/120 M/ℓ	1/8	23	0	1
Example 4	"	"	1.2	$NaBF_4$ 1/4000 M/ℓ	1/120	12	0	0
Example 5	"	5 A/dm^2 0.2 s	0.8	$KAlF_4$ 1/200 M/ℓ	1/40	19	0	0
Comparative Example 5	"	omitted	"	"	"	28	10	10
Comparative Example 6	"	5 A/dm^2 0.2 s	0.6	NaF 3/50 M/ℓ	1/10	30	5	10
Comparative Example 7	"	"	"	Na_2SiF_6 1/12000 M/ℓ	1/1200	9	3	8

WHAT IS CLAIMED IS:

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

chromium plating a thin steel sheet 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 sheet by a successive anodizing treatment in said aqueous solution or in another chromium ion-containing aqueous solution, and

subjecting the reversely electrolyzed steel sheet to an electrolytic chromate treatment in an aqueous solution of at least one selected from the group consisting of chromic acid, chromates, and dichromates,

the improvement wherein the solution in which said electrolytic chromate treatment is carried out contains hexavalent chromium in an amount of 0.2 to 1.4 mols of CrO_3 per liter of the solution and a fluoride in an amount to give a molar ratio of F^- to Cr^{6+} in the range of 1/1000 to 1/20.

2. The method according to claim 1 wherein the fluoride is selected from the group consisting of H_2SiF_6, HBF_4, HF and salts thereof, and $KAlF_4$.

3. 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.

4. 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.

1/2

FIG. 1

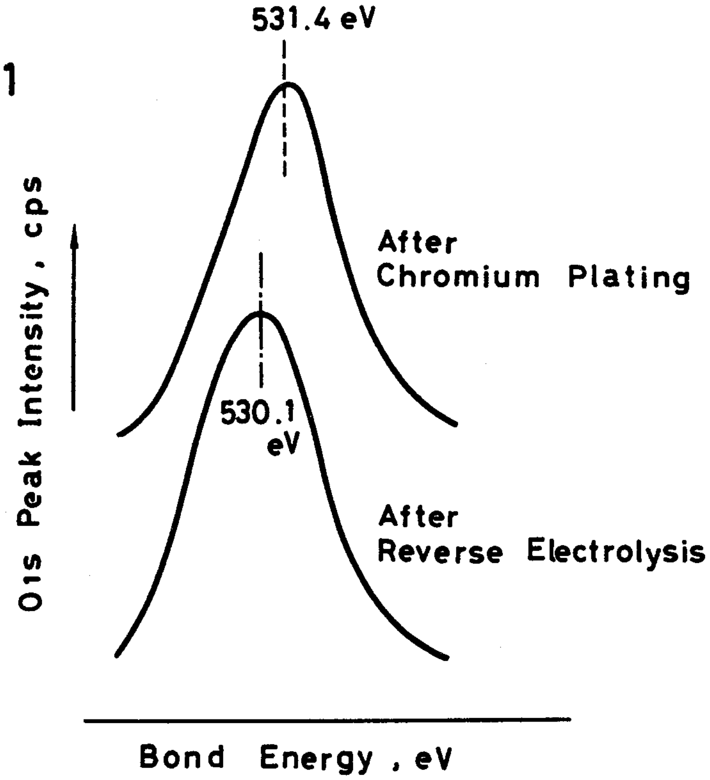

531.4 eV
O1s Peak Intensity, cps
After
Chromium Plating
530.1
eV
After
Reverse Electrolysis
Bond Energy, eV

FIG. 2

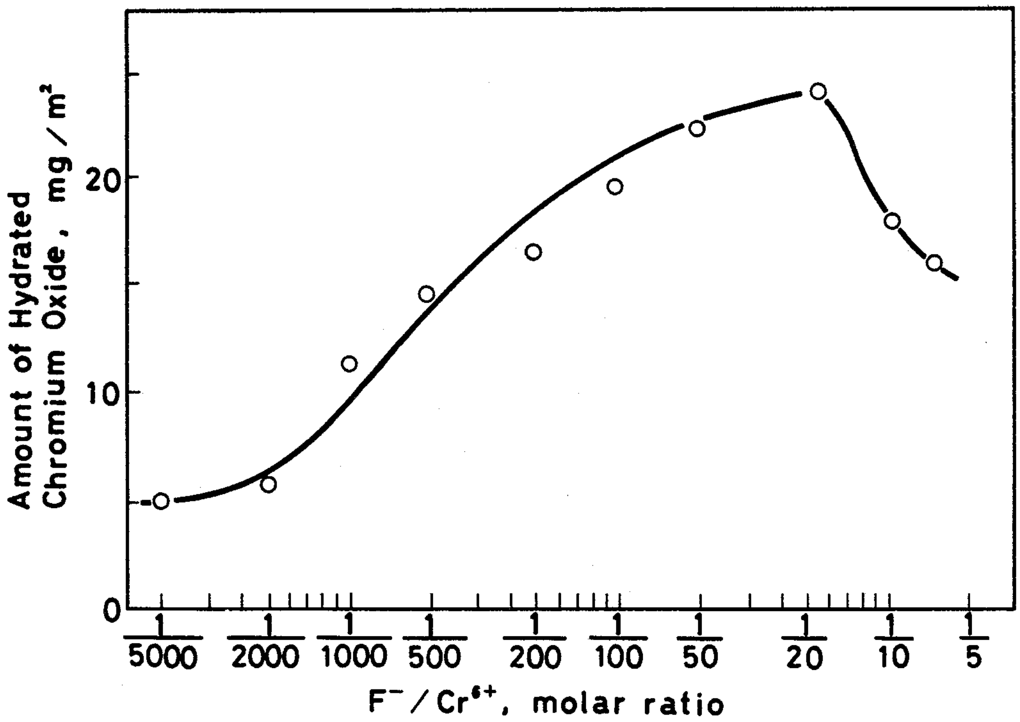

Amount of Hydrated
Chromium Oxide, mg/m²
0
10
20
1/5000
1/2000
1/1000
1/500
1/200
1/100
1/50
1/20
1/10
1/5
F⁻/Cr⁶⁺, molar ratio

FIG. 3

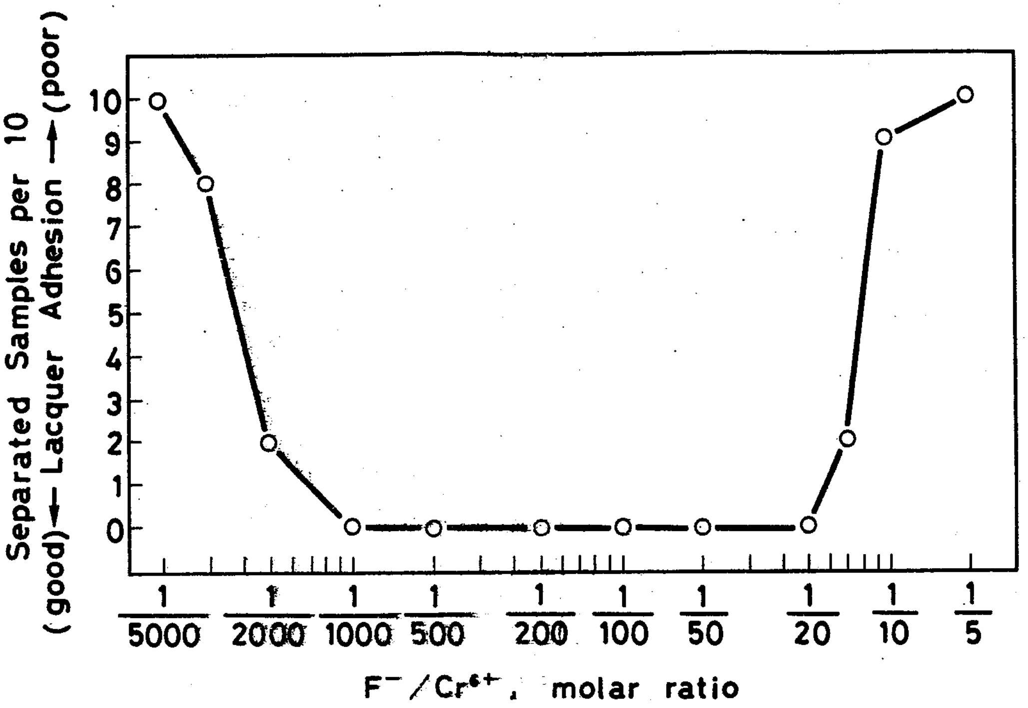


FIG. 4a

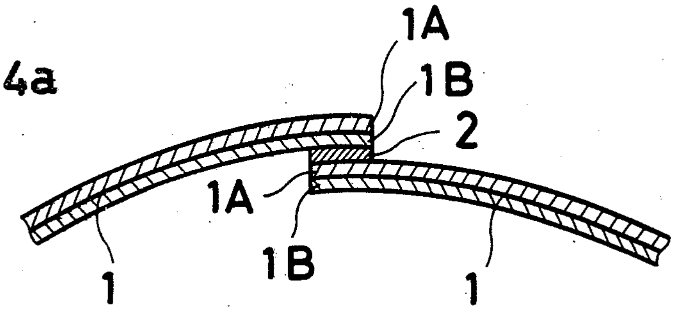
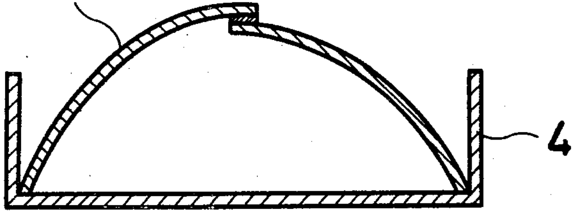


FIG. 4b



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EUROPEAN SEARCH REPORT

Application number
EP 84 10 2797

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. ³)
Y,P	EP-A-0 101 871 (KAWASAKI) * Claim 1; page 6, lines 1-4 * ---	1,3,4	C 25 D 11/38 C 25 D 5/48
Y	GB-A-1 436 150 (INTERNATIONAL NICKEL) * Claims 1-7 * ---	1,2	
Y	CHEMICAL ABSTRACTS, vol. 98, no. 12, March 1983, page 531, no. 97966d, Columbus, Ohio, USA; & JP - A - 57 45479 (KAWASAKI STEEL CORP.) 28-09-1982 ---	1,2	
Y	CHEMICAL ABSTRACTS, vol. 97, no. 12, September 1982, page 569, no. 100694a, Columbus, Ohio, USA; & JP - A - 82 57893 (NIPPON STEEL CORP.) 07-04-1982 -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 25 D 11/38

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04-07-1984	VAN LEEUWEN R.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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