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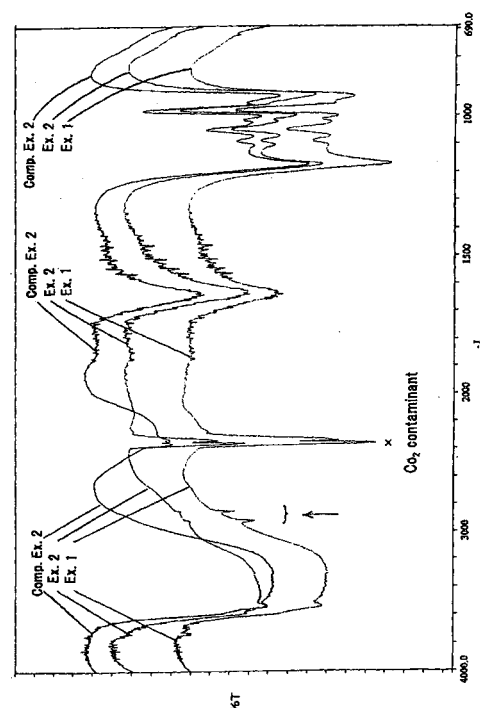
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(54) **ZINC-BASED METAL PLATED STEEL SHEET TREATED WITH PHOSPHATE EXCELLENT IN FORMABILITY AND METHOD FOR PRODUCING THE SAME**

(57) The objective of the present invention is to provide a phosphate-treated galvanized steel sheet that exhibits improved workability. The present invention provides a phosphate-treated galvanized steel sheet with improved workability having a phosphate layer deposited on the surface thereof. The steel sheet is characterized in that the phosphate layer contains a polyolefin wax or a modified polyolefin wax. Also provided is a method for producing such a phosphate-treated galvanized steel sheet. The method is characterized in that, following the application of phosphate onto the surface of the galvanized steel sheet, an aqueous solution containing a polyolefin wax or a modified polyolefin wax along with phosphate ions and polyvalent metal ions is applied over the phosphate layer and is then dried.

FIG.4



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to galvanized steel sheets having improved workability that makes them suitable for use in applications such as automobiles, home electric appliances and building materials.

TECHNICAL BACKGROUND

10 **[0002]** Galvanized steel sheets that are used in applications such as automobiles, home electric appliances, and building materials have often been treated with phosphate, chromate and organic coating prior to their use in order to impart desired properties such as corrosion resistance and workability, and to thereby improve their value. Since chromate-treated steel sheets may contain chromium (VI) and may be harmful to the environment, they have become less favored, and instead, demands are increasing for phosphate-treated steel sheets. On the other hand, Zn-Ni alloy-electrogalvanized steel sheets, now widely in use because of their high workability, contain Ni and therefore lead to increased manufacturing costs. For these reasons, attempts have been made to apply phosphate treatments to less costly electrogalvanized steel sheets, hot-dip galvanized steel sheets, or alloy hot-dip galvanized steel sheets to improve their value.

15 **[0003]** However, when Zn electrogalvanized steel sheets, hot-dip galvanized steel sheets, or alloy hot-dip galvanized steel sheets are treated with phosphate in a conventional manner, the resulting workability tends to be insufficient as compared to the workability attainable by Zn-Ni alloy-electrogalvanized steel sheets. This is particularly the case in an increasingly common application in which steel sheets are drawn while the amount of the steel sheet fed to a die is regulated by means of beading. In light of this, a zinc phosphate-treated galvanized steel sheet disclosed in Japanese Patent Laid-open Publication No. Hei 7-138764 contains at least one of Fe, Co, Ni, Ca, Mg and Mn and exhibits an improved pressability. Even this type of steel sheet fails to provide sufficient performance required in the aforementioned drawing process that takes advantage of beading.

DISCLOSURE OF THE INVENTION

30 **[0004]** Accordingly, it is an objective of the present invention to provide a phosphate-treated galvanized steel sheet that has overcome the above-described drawbacks of the prior art and exhibits an improved workability.

[0005] In an effort to improve the workability of phosphate-treated galvanized steel sheets, the present inventors have conceived of adding a wax to the phosphate coating. This has proven difficult, however, because of the manner by which conventional phosphate treatment is carried out: applying an acidic aqueous solution containing phosphate ions and metal cations to the galvanized surface either by spraying or by immersion in the solution. In this manner, the pH of the phosphate-treatment solution is increased on the galvanized surface, causing phosphate crystals to deposit on the surface. The present inventors have also attempted to deposit a wax layer on top of the phosphate coating. This approach failed to provide necessary workability and coat adhesion due to insufficient fixation of the wax to the coating layer. In the search for a way to solve these problems, the present inventors have discovered that a phosphate layer containing a polyolefin wax or a modified polyolefin wax can be obtained by first applying a phosphate coating onto the surface of a galvanized steel sheet using a known technique and subsequently applying and drying an aqueous solution containing the polyolefin wax or the modified polyolefin wax along with phosphate ions and polyvalent metal ions. The steel sheets manufactured in this manner achieve excellent workability. Collectively, these findings led the present inventors to devise the present invention.

40 **[0006]** Accordingly, one aspect of the present invention provides a phosphate-treated galvanized steel sheet with improved workability having a phosphate layer deposited on the surface thereof. The steel sheet is characterized in that the phosphate layer contains a polyolefin wax or a modified polyolefin wax. Also provided is a method for producing such a phosphate-treated galvanized steel sheet. The method is characterized in that, following the application of phosphate onto the surface of the galvanized steel sheet, an aqueous solution containing a polyolefin wax or a modified polyolefin wax along with phosphate ions and polyvalent metal ions is applied over the phosphate layer and is then dried.

50 **[0007]** The galvanized steel sheet for use in the present invention may be a steel sheet plated either with pure zinc or a zinc alloy, which in each case serves to improve the workability of the steel sheet. Among different types of galvanization, Zn electrogalvanization, hot-dip galvanization, and alloy hot-dip galvanization are preferred in view of manufacturing costs.

55 **[0008]** Also, the phosphate coating applied over the zinc plating may be any phosphate coating although a zinc phosphate coating that forms "hopite crystals" or a zinc phosphate coating modified by Fe, Ni, Co, Mn, Mg, Ca, Cu and other elements are generally preferred.

[0009] It is essential that the aqueous solution to be applied over the phosphate layer deposited on top of the zinc

plating contain a polyolefin wax or a modified polyolefin wax, along with phosphate ions and polyvalent metal ions. The wax-containing phosphate layer can be formed by applying the aqueous solution in which all of the above components coexist.

[0010] Preferably, the polyvalent metal ion is Mg^{2+} , Mn^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , or Al^{3+} . These metal ions may be used either individually or as a mixture of two or more. Of these, Mg^{2+} or Mn^{2+} is most preferred in view of corrosion-resistance.

[0011] It should be noted that a mixed aqueous solution of a polyolefin wax or a modified polyolefin wax (which may be referred to simply as "wax," hereinafter) and a dihydrogenphosphate is most convenient for the production of the galvanized steel sheet.

[0012] Examples of the dihydrogenphosphate include magnesium dihydrogenphosphate, aluminum dihydrogenphosphate, manganese dihydrogenphosphate, and calcium dihydrogenphosphate. Of these, magnesium dihydrogenphosphate is most preferred in view of corrosion resistance.

[0013] Preferably, the wax is either cationic or nonionic wax so that it can stably mix with phosphate ions and polyvalent metal ions.

[0014] While the wax may be added in any amount, it is preferably added in an amount of about 10% or less with respect to the total weight of the phosphate layer, considering the adhesion of the coating.

[0015] Figs. 1 and 2 each show a scanning electron micrography (SEM) of a wax-containing phosphate layer (15kV, X5000) made by the methods described below in Examples 1 and 2, respectively, whereas Fig. 3 shows a SEM image of a wax-free phosphate layer (15kV, X5000) made by the method described below in Comparative Example 2. The results of FT-IR spectroscopy (PERKIN-ELMER, high-sensitivity reflection) of respective samples are also shown in Fig. 4. Each layer was observed after sonicating each of the steel sheets in n-hexane solvent for 5 minutes. The comparison between Figs. 1, 2, and 3 reveals that each of the wax-containing phosphate layers of the present invention has a uniform, fine crystal structure similar to that of the typical wax-free phosphate layer. It is thus difficult to know from the surface appearance if a given layer contains the wax. In comparison, it is known from Fig. 4 that each of the wax-containing phosphate layers has absorption peaks at 2800 to 3000 cm^{-1} , indicative of C-H bonds present in the wax. Thus, by this approach, it can be determined if the layer contains the wax.

[0016] These peaks at 2800 to 3000 cm^{-1} can also be detected by FT-IR when the wax alone is applied over the wax-free phosphate layer to form film over the phosphate layer. In this case, however, the peak intensity significantly decreases over time and the peaks eventually disappear as the phosphate layer is degreased in a solvent such as n-hexane. In this manner, the wax-free phosphate layer with independently applied wax can be distinguished from the wax-containing phosphate layer of the present invention (Alternatively, with the solvent applied, the surface of a given layer may be rubbed to see if visible scratches will be formed on the surface. Scratches are hardly visible if the layer is the wax-containing phosphate layer of the present invention.). In addition, wax layer independently applied to the wax-free phosphate layer is readily removed by the solvent component present in a typical wash oil and the steel sheet does not exhibit a high workability when the actual procedures for press are simulated (*i.e.*, wash oil applied before pressing). Furthermore, the wax-free phosphate layer tends to show a reduced coat adhesion and thus is not preferred.

[0017] If the surface of the layer is not completely degreased and the rust proof oil or dust particles remain on the surface, then the absorption at 2800 to 3000 cm^{-1} may be observed for the wax-free phosphate layer in FT-IR analysis. Thus, the surface of the layer must be completely degreased prior to FT-IR using n-hexane or other solvents.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

Fig. 1 is a SEM image (X5000) showing the surface of a galvanized steel sheet treated with a wax-containing phosphate in accordance with Example 1.

Fig. 2 is a SEM image (X5000) showing the surface of another galvanized steel sheet treated with a wax-containing phosphate in accordance with Example 2.

Fig. 3 is a SEM image (X5000) showing the surface of another galvanized steel sheet treated with a wax-free phosphate in accordance with Comparative Example 2.

Fig. 4 is the result of FT-IR spectroscopy of the phosphate-treated galvanized steel sheets of Example 1, Example 2, and Comparative Example 2.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] The present invention will now be described in detail with reference to Examples, which are not intended to limit the scope of the invention in any way.

[0020] In each of Examples and Comparative Examples, a 0.7mm thick electrogalvanized steel sheet that has an r-

value (Lankford value) of 1.9 and has been plated to an amount of 30g/m² (per one side) was used to make a sample sheet.

Example 1

[0021] A piece of the steel sheet was surface-conditioned (PI-Zn manufactured by NIHON PARKERIZING Co., Ltd.) and was then treated with zinc phosphate (PB-3322 manufactured by NIHON PARKERIZING Co., Ltd.) to prepare a zinc phosphate-treated galvanized steel sheet with a coating amount of 0.7g/m². Meanwhile, an aqueous solution of magnesium dihydrogenphosphate (YONEYAMA CHEMICAL INDUSTRIES Co., Ltd.) and an emulsion of modified non-ionic polyethylene wax (Chemicerac SH5200 manufactured by SANYO CHEMICAL INDUSTRIES Co., Ltd.) were mixed with each other so that the ratio of magnesium dihydrogenphosphate to wax in the resulting mixture was 100:5 as measured by the weight of solid content. Using a roll coater, the mixture was applied onto the zinc phosphate-treated galvanized steel sheet. The sheet was then dried while the temperature of the sheet was maintained at 100°C. The weight of the applied coating as determined by the difference between the weight of the sheet before coating and the weight of the sheet after coating was adjusted to 0.7g/m².

Example 2

[0022] A sample sheet was prepared in the same manner as in Example 1, except that the ratio of magnesium dihydrogenphosphate to wax is 100:1 as measured by the weight of solid content.

Example 3

[0023] A sample sheet was prepared in the same manner as in Example 1, except that the ratio of magnesium dihydrogenphosphate to wax is 100:10 as measured by the weight of solid content.

Example 4

[0024] A sample sheet was prepared in the same manner as in Example 1, except that an aqueous solution of aluminum dihydrogenphosphate (YONEYAMA CHEMICAL INDUSTRIES Co., Ltd.) was used in place of magnesium dihydrogenphosphate solution.

Example 5

[0025] A sample sheet was prepared in the same manner as in Example 1, except that an aqueous solution of manganese dihydrogenphosphate (YONEYAMA CHEMICAL INDUSTRIES Co., Ltd.) was used in place of magnesium dihydrogenphosphate solution.

Example 6

[0026] A sample sheet was prepared in the same manner as in Example 1, except that an aqueous solution of calcium dihydrogenphosphate (YONEYAMA CHEMICAL INDUSTRIES Co., Ltd.) was used in place of magnesium dihydrogenphosphate solution.

Comparative Example 1

[0027] A piece of the steel sheet was surface-conditioned (PI-Zn manufactured by NIHON PARKERIZING Co., Ltd.) and was then treated with zinc phosphate (PB-3322 manufactured by NIHON PARKERIZING Co., Ltd.) to prepare a zinc phosphate-treated galvanized steel sheet with a coating amount of 0.7g/m².

Comparative Example 2

[0028] Using a roll coater, the aqueous solution of magnesium dihydrogenphosphate was applied onto the zinc phosphate-treated galvanized steel sheet of Comparative Example 1, and the sheet was dried while the temperature of the sheet was maintained at 100°C. The weight of the applied coating as determined by the difference between the weight of the sheet before coating and the weight of the sheet after coating was adjusted to 0.7g/m².

Comparative Example 3

[0029] Using a roll coater, an emulsion of modified nonionic polyethylene wax (Chemicerac SH5200 manufactured by SANYO CHEMICAL INDUSTRIES Co., Ltd.) was applied onto the zinc phosphate-treated galvanized steel sheet of Comparative Example 1, and the sheet was dried while the temperature of the sheet was maintained at 100°C. The weight of the applied coating as determined by the difference between the weight of the sheet before coating and the weight of the sheet after coating was adjusted to 0.1g/m².

Procedure for Performance Evaluation

[0030] Presence/absence of wax: The sample sheets of Examples 1 through 6 and Comparative Examples 1 through 3 were each degreased by sonication in a solvent (n-hexane) for 5 minutes and were subjected to analysis by FT-IR. The presence of wax was determined by whether peaks appeared at 2800 to 3000cm⁻¹.

[0031] Workability for forming a U-bead: Rust proof oil (nox-rust 550HN manufactured by PARKER INDUSTRIES Co., Ltd.) was applied to each sample sheet in an amount of about 1.5g/m²(per one side). The sample sheets were then left overnight and were each cut into 30mm x 300mm strips, which were then immersed in a wash oil (Daphne oil coat manufactured by IDEMITSU KOSAN Co., Ltd.) and were subsequently wiped by sponge roll. The rolled strips were sequentially beaded under the following conditions: BHF = 1 ton; height of bead = 40mm; beading punch R = 5mm; beading die R = 1mm; punch R = 5mm; and work speed = 25spm. Ratings were given as follows: a cross indicates that formation of a single bead caused cracking; a triangle indicates that formation of 2 to 10 beads caused cracking; a circle indicates that 10 or more beads could be formed, but only with some scuffs; and a double circle indicates that 10 or more beads could be formed without causing any cracks or scuffs.

[0032] Coat adhesion: Each sample sheet was degreased in a commercial alkaline degreasing solution (pH = 10.5, 40°C, immersed for 1 minute) and was subjected to electrodeposition coating (V20 manufactured by NIPPON PAINT Co., Ltd., 20μ, 170°, baked for 20 minutes). After being left for one day and night, the samples were immersed in warm water at 50°C. After 10 days, the samples were taken out of the water bath and cuts were made in a 1mm grid pattern. Using a strip of adhesive tape, how easy the coating can be peeled was determined. Ratings were given as follows: a double circle indicates that the coating peeled in 0% of the area; a circle indicates that the coating peeled in less than 5% of the area; a triangle indicates that the coating peeled in 5 to 50% of the area; and a cross indicates that the coating peeled in more than 50% of the area.

[0033] The results are shown in Table 1 below. As can be seen, each of the sample sheets of Examples of the present invention exhibited better workability than did the sample sheets of Comparative Examples. The workability, as well as the coat adhesion, was significantly low for the sample sheets of Comparative Examples.

Table 1

No		Presence /Absence of wax	Workability	Coat adhesion
Ex.	1	Present	⊙	⊙
	2	"	⊙	⊙
	3	"	⊙	⊙
	4	"	⊙	⊙
	5	"	⊙	⊙
	6	"	⊙	⊙
Comp. Ex.	1	Absent	Δ	⊙
	2	"	×	⊙
	3	"	Δ	×

INDUSTRIAL APPLICABILITY

[0034] The present invention provides a phosphate-treated galvanized steel sheet that has better workability than ever before. Not only are the steel sheets of the present invention free of hazardous substances such as chromium (VI), but they also are easy to make, are less expensive, and thus are suited for various applications, including automobiles, home electric appliances, and building materials.

Claims

1. A phosphate-treated galvanized steel sheet with improved workability having a phosphate layer deposited on the surface thereof, **characterized in that** the phosphate layer contains a polyolefin wax or a modified polyolefin wax.
2. A method for producing the phosphate-treated galvanized steel sheet of claim 1, **characterized in that**, subsequent to the application of phosphate onto the surface of the galvanized steel sheet, an aqueous solution containing a polyolefin wax or a modified polyolefin wax along with phosphate ions and polyvalent metal ions is applied over the phosphate layer and is then dried.
3. The method according to claim 2 for producing the phosphate-treated galvanized steel sheet, **characterized in that** the polyvalent metal ion is one or two or more selected from the group consisting of Mg^{2+} , Mn^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Al^{3+} .

FIG. 1

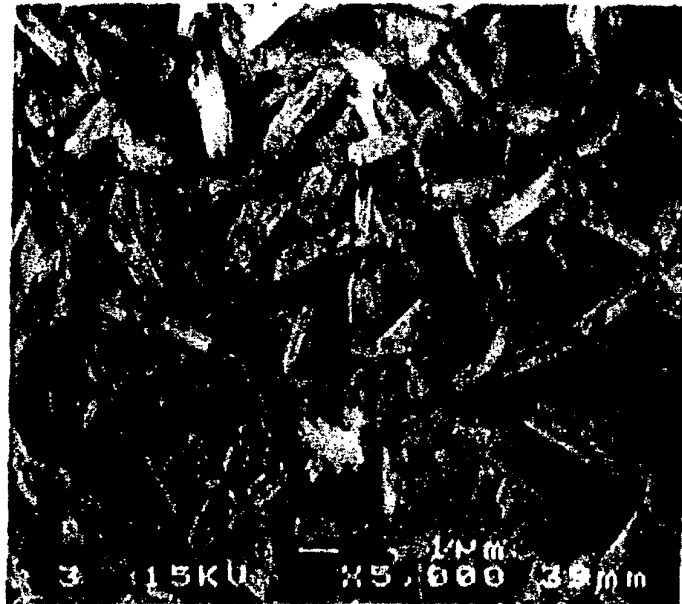


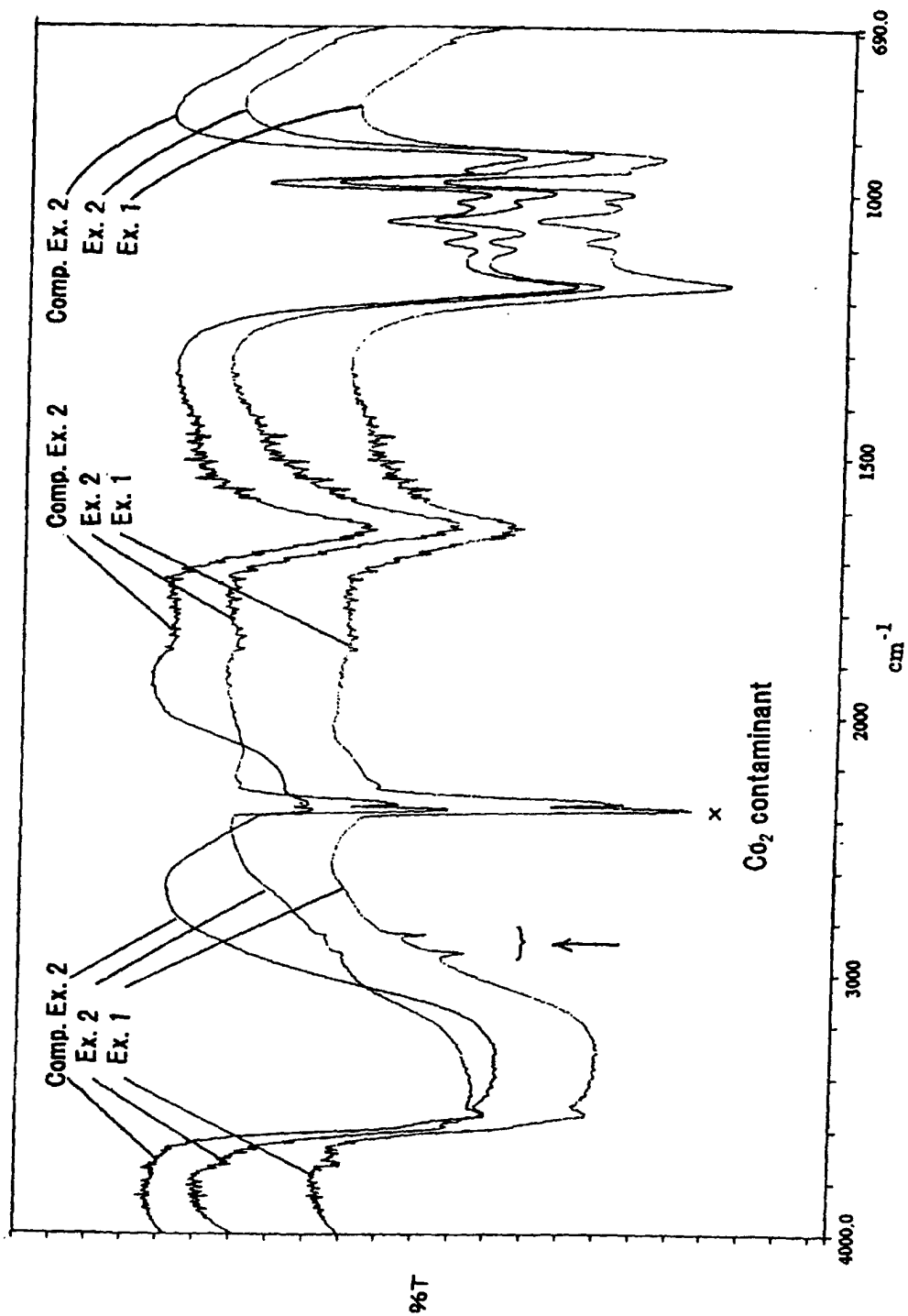
FIG. 2



FIG. 3



FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/07774

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ C23C 22/07, 22/12, 22/18, 22/20, 22/22, 22/78,
C23C 22/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ C23C22/00-22/86

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1999 Toroku Jitsuyo Shinan Koho 1994-2000
Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 653502 A (NIHON PARKERISING CO LTD), 30 May, 1995 (30.05.1995) & JP 7-138764 A	1-3
A	JP 6-299367 A (Nippon Steel Corporation), 08 October, 1994 (08.10.1994) (Family: none)	1-3
A	JP 8-252520 A (Nippon Steel Corporation), 01 October, 1996 (01.10.1996) (Family: none)	1-3

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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considered to be of particular relevance
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