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(54) Zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability.

(57) A zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability, which comprises: a steel sheet; a first zinc-silica composite plating layer, formed on at least one surface of the steel sheet, in which silica particles are uniformly dispersed; and a second zinc-silica composite plating layer, formed on the first zinc-silica composite plating layer, in which silica particles are uniformly dispersed. The first zinc-silica composite plating layer has a content of silica particles within a range of from 0.1 to 20.0 wt.% relative to the first zinc-silica composite plating layer; the silica particles in the first zinc-silica composite plating layer have an average particle size within a range of from 20 nm to 1.0 μm; and the first zinc-silica composite plating layer has a weight within a range of from over 10 g/m^2 to up to 90 g/m^2 per surface of the steel sheet. The second zinc-silica composite plating layer has a content of silica particles within a range of from 1 to 20 wt.% relative to the second zinc-silica composite plating layer; the silica particles in the second zinc-silica composite plating layer have an average particle size of under 20 nm; and the second zinc-silica composite plating layer has a weight within a range of from 5 to 10 g/m^2 per surface of the steel sheet.

EP 0 446 727 A1

As far as we know, there is available the following prior art document pertinent to the present invention:

Japanese Patent Provisional Publication No. 54-146,228 dated November 15, 1979.

The contents of the prior art disclosed in the above-mentioned prior art document will be discussed hereafter under the heading of the "BACKGROUND OF THE INVENTION".

FIELD OF THE INVENTION

The present invention relates to a zinc-silica composite electroplated steel sheet excellent in corrosion resistance as well as in a property of inhibiting an excessive heat generation upon the spot-welding and thus improving the service life of electrode tips of a spot welding machine (such property being hereinafter referred to as "spot weldability").

BACKGROUND OF THE INVENTION

There is an increasing demand from the automobile manufacturers and other enterprises for the development of an electroplated steel sheet which has an excellent corrosion resistance and can bear use for a long period of time even under a severe corrosive environment.

An electrogalvanized steel sheet has widely been applied as a steel sheet for automobile. For the purpose of improving corrosion resistance of the electrogalvanized steel sheet so as to meet the above-mentioned demand, it has actively been tried to improve corrosion resistance of the electrogalvanized steel sheet by uniformly dispersing silica particles in the galvanizing layer thereof.

For example, Japanese Patent Provisional Publication No. 54-146,228 dated November 15, 1979 discloses a zinc-silica composite electroplated steel sheet having, on at least one surface thereof, a zinc-silica composite plating layer, in which silica particles in an amount within a range of from 2 to 15 wt.% are uniformly dispersed (hereinafter referred to as the "Prior Art").

In the zinc-silica composite electroplated steel sheet of the Prior Art, the silica particles uniformly dispersed in the zinc-silica composite plating layer inhibit corrosion of the zinc-silica composite plating layer, whereby an excellent corrosion resistance is imparted to the zinc-silica composite electroplated steel sheet.

The above-mentioned Japanese Patent Provisional Publication No. 54-146,228 describes that the zinc-silica composite electroplated steel sheet of the Piror Art has a corrosion resistance about two to three times as high as that of a conventional electrogalvanized steel sheet in a salt spray test.

In the Prior Art, however, no regard is paid to spot weldability. In addition, the zinc-silica composite plating layer of the zinc-silica composite electroplated steel sheet of the Prior Art has a high electric resistance due to the fact that the silica particles uniformly dispersed in the zinc-silica composite plating layer are electrically non-conductive.

When spot-welding the above-mentioned zinc-silica composite electroplated steel sheet of the Prior Art, therefore, the zinc-silica composite plating layer produces much heat, thus resulting in serious wear of the electrode tips of the spot welding machine and hence in a shorter service life thereof.

Under such circumstances, there is a strong demand for the development of a zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability, but such a zinc-silica composite electroplated steel sheet has not as yet been proposed.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability.

In accordance with one of the features of the present invention, in a zinc-silica composite electroplated steel sheet, which comprises: a steel sheet; and at least one zinc-silica composite plating layer, formed on at least one surface of said steel sheet, in which silica particles are uniformly dispersed; there is provided the improvement wherein:

said at least one zinc-silica composite plating layer comprises a first zinc-silica composite plating layer formed on said at least one surface of said steel sheet, and a second zinc-silica composite plating layer formed on said first zinc-silica composite plating layer;

said first zinc-silica composite plating layer has a content of said silica particles within a range of from 0.1 to 20.0 wt.% relative to said first zinc-silica composite plating layer;

said silica particles in said first zinc-silica composite plating layer have an average particle size within a range of from 20 nm to 1.0 μm;

said first zinc-silica composite plating layer has a weight within a range of from over 10 g/m^2 to up to 90 g/m^2 per surface of said steel sheet;

said second zinc-silica composite plating layer has a content of said silica particles within a range of from I to 20 wt.% relative to said second zinc-silica composite plating layer;

said silica particles in said second zinc-silica composite plating layer have an averange particle size of under 20 nm, and more preferably, within a range of from 3 to under 20 nm; and

said second zinc-silica composite plating layer has a weight within a range of from 5 to 10 g/m^2 per surface of said steel sheet.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

From the above-mentioned point of view, extensive studies were carried out to develop a zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability.

As a result, the following findings were obtained: It is possible to manufacture a zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability by:

(1) forming a first zinc-silica composite plating layer on at least one surface of a steel sheet, and forming a second zinc-silica composite plating layer on the first zinc-silica composite plating layer;

(2) limiting the content of silica particles in the first zinc-silica composite plating layer within a range of from 0.1 to 20.0 wt.% relative to the first zinc-silica composite plating layer;

(3) limiting the average particle size of the silica particles in the first zinc-silica composite plating layer within a range of from 20 nm to 1.0 μm;

(4) limiting the weight of the first zinc-silica composite plating layer within a range of from over 10 g/m^2 to up to 90 g/m^2 per surface of the steel sheet;

(5) limiting the content of silica particles in the second zinc-silica composite plating layer within a range of from 1 to 20 wt.% relative to the second zinc-silica composite plating layer;

(6) limiting the average particle size of the silica particles in the second zinc-silica composite plating layer to under 20 nm, and more preferably, within a range of from 3 to under 20 nm; and

(7) limiting the weight of the second zinc-silica composite plating layer within a range of from 5 to 10 g/m^2 per surface of the steel sheet.

The present invention was made on the basis of the above-mentioned findings. Now, the zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability of the present invention is described below.

The zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability of the present invention comprises a steel sheet, a first zinc-silica composite plating layer formed on at least one surface of the steel sheet, and a second zinc-silica composite plating layer formed on the first zinc-silica composite plating layer.

The first zinc-silica composite plating layer has a function of making up corrosion resistance of the second zinc-silica composite plating layer described later having a relatively thin thickness, without impairing spot weldability of the zinc-silica composite electroplated steel sheet.

The content of the silica particles in the first zinc-silica composite plating layer exerts an important effect on corrosion resistance, spot weldability and workability of the zinc-silica composite electroplated steel sheet. With a content of the silica particles in the first zinc-silica composite plating layer of under 0.1 wt.% relative to the first zinc-silica composite plating layer, it is impossible to sufficiently make up corrosion resistance of the second zinc-silica composite plating layer having a relatively thin thickness, and hence, to impart an excellent corrosion resistance to the zinc-silica composite electroplated steel sheet. With a content of the silica particles in the first zinc-silica composite plating layer of over 20 wt.% relative to the first zinc-silica composite plating layer, on the other hand, spot weldability and workability of the zinc-silica composite electroplated steel sheet decrease.

The content of the silica particles in the first zinc-silica composite plating layer should therefore be limited within a range of from 0.1 to 20 wt.% relative to the first zinc-silica composite plating layer.

The average particle size of the silica particles in the first zinc-silica composite plating layer exerts an important effect on corrosion resistance and spot weldability of the zinc-silica composite electroplated steel sheet. With an average particle size of the silica particles in the first zinc-silica composite plating layer of under 20 nm, corrosion resistance of the first zinc-silica composite plating layer is improved, whereas electric resistance thereof increases, resulting in a degraded spot weldability of the zinc-silica composite electroplated steel sheet. With an average particle size of the silica particles in the first zinc-silica composite plating layer of over 1.0 μm, it is impossible to sufficiently make up corrosion resistance of the relatively thin second zinc-silica composite plating layer, and therefore, to impart an excellent corrosion resistance to the

zinc-silica composite electroplated steel sheet.

The average particle size of the silica particles in the first zinc-silica composite plating layer should therefore be limited within a range of from 20 nm to up to 1.0 μm.

The weight of the first zinc-silica composite plating layer exerts an important effect on corrosion resistance and workability of the zinc-silica composite electroplated steel sheet. With a weight of the first zinc-silica composite plating layer of 10 g/m^2 or under per surface of the steel sheet, it is impossible to sufficiently make up corrosion resistance of the relatively thin second zinc-silica composite plating layer, and therefore, to impart an excellent corrosion resistance to the zinc-silica composite electroplated steel sheet. With a weight of the first zinc-silica composite plating layer of over 90 g/m^2 per surface of the steel sheet, on the other hand, there is a degradation in workability of the zinc-silica composite electroplated steel sheet.

The weight of the first zinc-silica composite plating layer should therefore be limited within a range of from over 10 g/m^2 to up to 90 g/m^2.

The second zinc-silica composite plating layer has a function of improving corrosion resistance of the zinc-silica composite electroplated steel sheet without degrading spot weldability and workability thereof.

The content of the silica particles in the second zinc-silica composite plating layer exerts an important effect on corrosion resistance, spot weldability and workability of the zinc-silica composite electroplated steel sheet. With a content of the silica particles in the second zinc-silica composite plating layer of under 1 wt.% relative to the second zinc-silica composite plating layer, corrosion resistance of the second zinc-silica composite plating layer itself is low, and as a result, an excellent corrosion resistance cannot be imparted to the zinc-silica composite electroplated steel sheet. With a content of the silica particles in the second zinc-silica composite plating layer of over 20 wt.% relative to the second zinc-silica composite plating layer, on the other hand, spot weldability and workability of the zinc-silica composite electroplated steel sheet decrease.

The content of the silica particles in the seoond zinc-silica composite plating layer should therefore be limited within a range of from 1 to 20 wt.% relative to the second zinc-silica composite plating layer.

The average particle size of the silica particles in the second zinc-silica composite plating layer exerts an important effect on corrosion resistance of the zinc-silica composite electroplated steel sheet. With an average particle size of the silica particles in the second zinc-silica composite plating layer of 20 nm or over, corrosion resistance of the second zinc-silica composite plating layer itself is low, and as a result, an excellent corrosion resistance cannot be imparted to the zinc-silica composite electroplated steel sheet.

The average particle size of the silica particles in the second zinc-silica composite plating layer should therefore be limited within a range of under 20 nm, and more preferably, within a range of from 3 to under 20 nm.

The weight of the second zinc-silica composite plating layer exerts an important effect on corrosion resistance and spot weldability of the zinc-silica composite electroplated steel sheet. With a weight of the second zinc-silica composite plating layer of under 5 g/m^2 per surface of the steel sheet, corrosion resistance of the second zinc-silica composite plating layer itself is low, and as a result, an excellent corrosion resistance cannot be imparted to the zinc-silica composite electroplated steel sheet. With a weight of the second zinc-silica composite plating layer of over 10 g/m^2 per surface of the steel sheet, on the other hand, there is a decrease in spot weldability of the zinc-silica composite electroplated steel sheet.

The weight of the second zinc-silica composite plating layer should therefore be limited within a range of from 5 to 10 g/m^2 per surface of the steel sheet.

The zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability of the present invention is manufactured by:

electroplating a steel sheet in a zinc-silica composite electroplating solution containing silica Particles in a prescribed amount, which have an average particle size within a range of from 20 nm to up to 1.0 μm, to form, on at least one surface of the steel sheet, a first zinc-silica composite plating layer having a weight within a range of from over 10 g/m^2 to up to 90 g/m^2 per surface of the steel sheet, in which the silica particles are uniformly dispersed; and then, applying another electroplating treatment to the steel sheet having the first zinc-silica composite plating layer formed on at least one surface thereof in another zinc-silica composite electroplating solution containing silica particles in a prescribed amount, which have an average particle size of under 20 nm, to form, on the first zinc-silica composite plating layer, a second zinc-silica composite plating layer having a weight within a range of from 5 to 10 g/m^2 per surface of the steel sheet, in which the silica particles are uniformly dispersed.

Now, the zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability of the present invention is described more in detail by means of examples while comparing with examples for comparison.

EXAMPLES

Each of cold-rolled steel sheets having a thickness of 0.8 mm was subjected to a known degreasing treatment and a known pickling treatment to remove rust from the both surfaces thereof. Then, the steel sheet after the removal of rust was electroplated under the conditions shown in Table 1, to form a first zinc-silica composite plating layer on each of the both surfaces of the steel sheet. Then, the steel sheet having the first zinc-silica composite plating layer formed on each of the both surfaces thereof was subjected to another electroplating treatment under another conditions shown also in Table 1, to form a second zinc-silica composite plating layer on the first zinc-silica composite plating layer, thereby preparing samples of the present invention Nos. 1 to 15.

The plating weight per surface of the steel sheet and the content of silica particles of each of the first zinc-silica composite plating layer and the second zinc-silica composite plating layer in each of the samples of the present invention Nos. 1 to 15 are shown also in Table 1.

Then, for each of the samples of the present invention Nos. 1 to 15, corrosion resistance and spot weldability were investigated.

More specifically, for each of the samples of the present invention Nos. 1 to 15, a salt spray test was carried out to measure a salt spray time before the occurrence of red rust, thereby evaluating corrosion resistance of each of the samples of the present invention Nos. 1 to 15 by means of the above-mentioned salt spray time. The thus measured salt spray time are shown also in Table 1.

In view of the fact that the diameter of a nugget formed by the spot welding becomes smaller according as the electrode tips of the spot welding machine wear out, spot welding was continuously applied, with the use of a pair of electrode tips, to two sheets from among the samples of the present invention Nos. 1 to 15, and the number of spot welding runs, at which an appropriate nugget having a diameter larger than a prescribed diameter could be formed on the joint of the above-mentioned two sheets, was counted. Spot weldability of each of the samples of the present invention Nos. 1 to 15 was evaluated by means of the above-mentioned number of spot welding runs. The numbers of spot welding runs thus counted are shown also in Table 1.

Table 1

	No.	Plating conditions for forming the 1st. zinc-silica composite plating layer: Chemical composition of plating bath (g/ℓ) Zinc sulfate	Sodium sulfate	Sodium acetate	Silica particles	Electric current density (A/dm²)	Bath temp. (C°)	pH value	Electroplating time (sec.)	Plating conditions for forming the 2nd. zinc-silica composite plating layer: Chemical composition of plating bath (g/ℓ) Zinc sulfate	Sodium sulfate	Sodium acetate	Silica particles	Electric current density (A/dm²)	Bath temp. (C°)	pH value	Electroplating time (sec.)	1st.zinc-silica composite plating layer: Content of silica particles (wt.%)	Average particle size of silica particles (nm)	Weight of plating layer (g/m²)	2nd zinc-silica composite plating layer: Content of silica particles (wt.%)	Average particle size of silica particles (nm)	Weight of plating layer (g/m²)	Corrosion resistance (Salt spray time) (hr.)	Spot weldability (Number of spot welding runs)
Sample of the present invention	1	300	30	12	20	50	40	2	24	300	30	12	20	50	40	2	7	10	40	35	7	10	5	800	7,000
	2	300	30	12	20	50	40	2	24	300	30	12	20	50	40	2	7	10	40	35	15	10	5	1,400	6,000
	3	300	30	12	20	50	40	2	24	300	30	12	20	50	40	2	7	10	100	35	15	10	5	1,200	6,500
	4	300	30	12	2	50	40	2	24	300	30	12	20	50	40	2	7	1	100	35	15	10	5	900	7,000
	5	300	30	12	20	50	40	2	24	300	30	12	20	50	40	2	7	10	200	35	15	10	5	1,000	6,500
	6	300	30	12	20	50	40	2	20	300	30	12	20	50	40	2	14	10	40	30	7	10	10	1,000	6,000
	7	300	30	12	20	50	40	2	20	300	30	12	20	50	40	2	14	10	40	30	15	10	10	1,400	5,500
	8	300	30	12	20	50	40	2	20	300	30	12	4	50	40	2	14	10	40	30	15	2	10	1,500	5,000
	9	300	30	12	20	50	40	2	24	300	30	12	4	50	40	2	7	10	40	35	15	2	5	1,200	6,500
	10	300	30	12	20	50	40	2	24	300	30	12	4	50	40	2	7	10	40	35	7	2	5	1,100	7,000
	11	300	30	12	15	50	40	2	28	300	30	12	20	50	40	2	14	5	100	40	4	10	10	1,200	7,000
	12	300	30	12	15	50	40	2	28	300	30	12	4	50	40	2	14	5	100	40	7	2	10	1,300	6,500
	13	300	30	12	20	50	40	2	45	300	30	12	4	50	40	2	14	15	100	65	5	2	10	1,400	5,500
	14	300	30	12	20	50	40	2	45	300	30	12	4	50	40	2	14	15	200	65	5	2	10	1,400	6,000
	15	300	30	12	20	50	40	2	59	300	30	12	4	50	40	2	14	10	200	80	10	2	10	1,700	5,000

For comparison purposes, each of the cold-rolled steel sheets identical with those in the samples of the present invention Nos. 1 to 15 was subjected to a known degreasing treatment and a known pickling treatment to remove rust from the both surfaces thereof. Then, the steel sheet after the removal of rust was electroplated under the conditions shown in Table 2, to form a first zinc-silica composite plating layer on each of the both surfaces of the steel sheet. Then, the steel sheet having the first zinc-silica composite

plating layer formed on each of the both surfaces thereof was subjected to another electroplating treatment under another conditions shown also in Table 2, to form a second zinc-silica composite plating layer on the first zinc-silica composite plating layer, thereby preparing samples for comparison Nos. 1 to 13 outside the scope of the present invention.

The plating weight per surface of the steel sheet and the content of silica particles of the zinc-silica composite plating layer as a single layer in each of the samples for comparison Nos. 1 to 4 and the plating weight per surface of the steel sheet and the content of silica particles of each of the first zinc-silica composite plating layer and the second zinc-silica composite plating layer in each of the samples for comparison Nos. 5 to 13 are shown also in Table 2:

Then, for each of the samples for comparison Nos. 1 to 13, corrosion resistance and spot weldability were investigated by the same method as in the samples of the present invention Nos. 1 to 15. The salt spray time measured in the corrosion resistance test and the number of spot welding runs counted in the spot weldability test are shown also in Table 2.

Table 2

No.		Plating conditions for forming the 1st. zinc-silica composite plating layer							Plating conditions for forming the 2nd. zinc-silica composite plating layer							1st.zinc-silica composite plating layer			2nd.zinc-silica composite plating layer			Corrosion resistance (Salt spray time) (hr.)	Spot weldability (Number of spot welding runs)
		Chemical composition of plating bath			Chemical composition of plating (g/ℓ)				Chemical composition of plating bath			Chemical composition of plating (g/ℓ)											
		zinc sulfate	Sodium sulfate	Sodium acetate	silica particles	Electric current density (A/dm²)	Bath temp. (C°)	pH value	Electroplating time (sec.)	zinc sulfate	Sodium sulfate	Sodium acetate	silica particles	Electric current density (A/dm²)	Bath temp. (C°)	pH value	Electroplating time (sec.)	Content of silica particles (wt.%)	Average particle size of silica particles (nm)	Weight of plating layer (g/m²)	Content of silica particles (wt.%)	Average particle size of silica particles (nm)	Weight of plating layer (g/m²)		
Sample for comparison	1	300	30	12	15.0	50	40	2	28	300	30	12	-	-	-	-	-	-	7.00	10	40	-	-	-	1,200	1,000
	2	300	30	12	20.0	50	40	2	28	300	30	12	-	-	-	-	-	-	10.00	100	40	-	-	-	300	8,000
	3	300	30	12	20.0	50	40	2	59	300	30	12	-	-	-	-	-	-	15.00	200	80	-	-	-	200	9,000
	4	300	30	12	20.0	50	40	2	28	300	30	12	-	-	-	-	-	-	15.00	40	40	-	-	-	200	5,000
	5	300	30	12	20.0	50	40	2	28	300	30	12	20	50	40	2	14	15.00	10	40	15	2	10	400	800
	6	300	30	12	10.0	50	40	2	28	300	30	12	5	50	40	2	14	5.00	100	40	4	30	10	800	1,000
	7	300	30	12	20.0	50	40	2	7	300	30	12	20	50	40	2	7	10.00	40	5	15	10	5	30	5,500
	8	300	30	12	20.0	50	40	2	145	300	30	12	20	50	40	2	7	10.00	40	100	15	10	5	1,800	4,100
	9	300	30	12	20.0	50	40	2	25	300	30	12	20	50	40	2	5	10.00	100	37	10	10	3	500	6,000
	10	300	30	12	2.0	50	40	2	15	300	30	12	10	50	40	2	28	1.00	100	20	5	10	20	1,400	500
	11	300	30	12	10.0	50	40	2	24	300	30	12	10	50	40	2	6	5.00	40	36	5	2	4	600	5,500
	12	300	30	12	30.0	50	40	2	25	300	30	12	20	50	40	2	7	25.00	100	35	25	10	5	2,000	100
	13	300	30	12	0.5	50	40	2	25	300	30	12	20	50	40	2	7	0.05	100	35	0.5	10	5	40	7,000

As is clear from Table 1, in each of the samples of the present invention Nos. 1 to 15, the salt spray time of at least 800 hours was required before occurrence of red rust, and the above-mentioned number of spot welding runs was counted as many as at least consecutive 5,000. Thus, all the samples of the present invention Nos. 1 to 15 were found to be excellent both in corrosion resistance and in spot weldability.

As is clear from Table 2, in contrast, none of the samples for comparison Nos. 1 to 13 satisfied at the

same time the following two properties possessed by the samples of the present invention Nos. 1 to 15:

(1) requiring the salt spray time of at least 800 hours before occurrence of red rust; and

(2) permitting the continuous spot welding of at least 5,000 runs before decrease in the diameter of the nugget formed by the spot welding to under the prescribed diameter.

It was therefore found that at least one of corrosion resistance and spot weldability was poor in any of the samples for comparison Nos. 1 to 13.

According to the present invention, as described above in detail, it is possible to provide a zinc-silica composite electroplated steel sheet excellent in corrosion resistance and spot weldability, thus providing many industrially useful effects.

Claims

1. In a zinc-silica composite electroplated steel sheet, which comprises:

a steel sheet; and

at least one zinc-silica composite plating layer, formed on at least one surface of said steel sheet, in which silica particles are uniformly dispersed;

the improvement wherein:

said at least one zinc-silica composite plating layer comprises a first zinc-silica composite plating layer formed on said at least one surface of said steel sheet, and a second zinc-silica composite plating layer formed on said first zinc-silica composite plating layer;

said first zinc-silica composite plating layer has a content of said silica particles within a range of from 0.1 to 20.0 wt.% relative to said first zinc-silica composite plating layer;

said silica particles in said first zinc-silica composite plating layer have an average particle size within a range of from 20 nm to 1.0 μm.

said first zinc-silica composite plating layer has a weight within a range of from over 10 g/m^2 to up to 90 g/m^2 per surface of said steel sheet;

said second zinc-silica composite plating layer has a content of said silica particles within a range of from 1 to 20 wt.% relative to said second zinc-silica composite plating layer;

said silica particles in said second zinc-silica composite plating layer have an average particle size of under 20 nm; and

said second zinc-silica composite plating layer has a weight within a range of from 5 to 10 g/m^2 per surface of said steel sheet.

2. A zinc-silica composite electroplated steel sheet as claimed in Claim 1, wherein:

said silica particles in said second zinc-silica composite plating layer have an average particle size within a range of from 3 to under 20 nm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 3127

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)
A	CHEMICAL ABSTRACTS, vol. 112, no. 22, 28th May 1990, page 541, abstract no. 206711x, Columbus, Ohio, US; & JP-A-01 268 900 (NIPPON KOKAN K.K.) 26-10-1989		C 25 D 15/02
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 501 (C-556)[3348], 27th December 1988; & JP-A-63 210 300 (NKK CORP.) 31-08-1988		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 25 D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	02 May 91	NGUYEN THE NGHIEP

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
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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