(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 November 2006 (23.11.2006)

PCT

(10) International Publication Number
WO 2006/122852 A1

(51) International Patent Classification:
C23G 1/12 (2006.01) *B41N 1/08* (2006.01)
C23G 1/22 (2006.01) *B41N 3/03* (2006.01)
C23G 5/02 (2006.01)

(21) International Application Number:
PCT/EP2006/061358

(22) International Filing Date: 5 April 2006 (05.04.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05010847.1 19 May 2005 (19.05.2005) EP

(71) Applicant *(for all designated States except US)*: **Hydro Aluminium Deutschland GmbH** [DE/DE]; Ettore-bugatti-str. 6-14, 51149 Köln (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **KERNIG, Bernhard** [DE/DE]; Höninger Weg 145, 50969 Köln (DE). **BRINKMAN, Henk Jan** [NL/DE]; Am Kreuter 7, 53177 Bonn (DE).

(74) Agent: **COHAUSZ & FLORACK**; Bleichstrasse 14, 40211 Düsseldorf (DE).

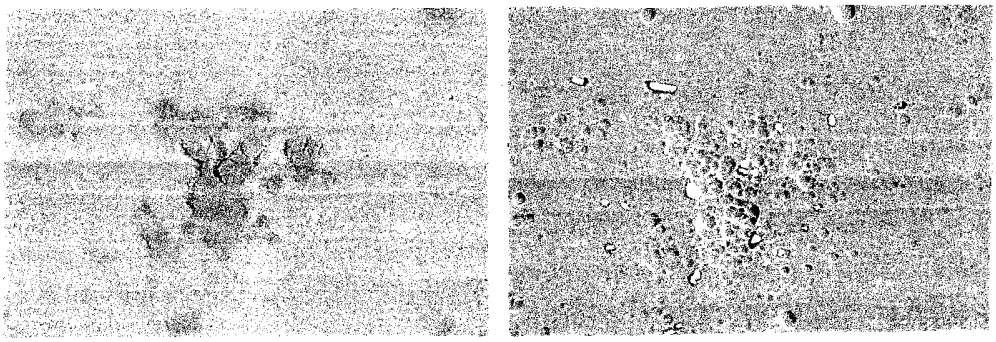
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** CONDITIONING OF A LITHO STRIP



(57) **Abstract:** The invention relates to a method of conditioning the surface of a work piece, particularly of a strip or sheet, more particularly of a lithostrip or lithosheet, consisting of an aluminium alloy. The object of the present invention to provide a method for conditioning the surface of a work piece and a work piece consisting of an aluminium alloy enabling an increasing manufacturing speed in electro-chemically graining and maintaining at the same time a high quality of the grained surface, is solved by a conditioning method which comprises at least the two steps degreasing the surface of the work piece with a degreasing medium and subsequently cleaning the surface of the work piece by pickling.

WO 2006/122852 A1

Conditioning of a litho strip

The invention relates to a method of conditioning the surface of a work piece, particularly of a strip or sheet, more particularly of a lithostrip or lithosheet, consisting of an aluminium alloy.

Work pieces such as strips or sheets consisting of an aluminium alloy are often surface treated after finishing rolling to prepare them for the next manufacturing step. In particular strips or sheet for lithographic printing are conditioned to achieve a predetermined surface roughness in a subsequent graining process. Lithostrips or sheets are usually degreased after finishing rolling. As known from the US-patent specification US 5,997,721, degreasing respectively cleaning of the surface is done in one step by anodising the aluminium alloy sheet with AC current in an acidic electrolyte bath. Another way to degrease or clean aluminium slivers is known from the German patent DE 43 17 815 C1 namely the use of an alkaline medium.

However, prior electro-chemical graining of the lithostrips they are usually subjected to sodium hydroxide in a pre-treatment to degrease and clean the surface again. This step takes place in principle at the side of the manufacture of lithographic printing plates. Due to the increasing manufacturing speed during electro-chemical graining of the lithostrips time for pre-treatment of the surface of the lithostrips and for the electro-chemical

graining itself decreases. It has been found that due to the increasing manufacturing speed the pre-treatment with sodium hydroxide is not sufficient enough to remove all contaminants from the surface of the lithostrip. As a consequence, the results in electro-chemically graining are not stable and surface defects occur on electro-chemically grained lithostrips or sheets. However, a reduction of the manufacturing speed causes higher production costs for lithographic printing plates.

Hence, it is an object of the invention to provide a method for conditioning the surface of a work piece and a work piece consisting of an aluminium alloy enabling an increasing manufacturing speed in electro-chemical graining and maintaining at the same time a high quality of the electro-chemical grained surface of the work piece.

According to a first teaching of the present invention the above mentioned object is solved by a method of conditioning the surface of an aluminium work piece consisting of an aluminium alloy, which method comprises at least the two steps degreasing the surface of the work piece with a degreasing medium and subsequently cleaning the surface of the work piece by pickling.

It has been surprisingly found that a combination of the inventive two step conditioning method with the usually effected pre-treatment with sodium hydroxide prior electro-chemical graining of the lithostrips leads to stable results in the electro-chemical graining even if manufacturing speeds are increased. The inventive conditioning method provides surfaces of an aluminium work piece which are almost free of subsurface oxide particles introduced by rolling without anodising the surface of the

aluminium work piece as known from the prior art. As a result, the surface of the aluminium alloy work piece conditioned with the inventive method is fully grained during electro-chemical graining at charge densities which are distinctly lower than needed in electro-chemical graining after conventional cleaning, i.e. the charge density is less than 900 C/dm^2.

According to a first embodiment of the invention it is preferred to use an alkaline or an acid medium or an organic solvent as degreasing medium to degrease the surface of the work piece. An organic solvent such as isopropyl-alcohol degreases the surface of the aluminium work piece effectively whereas alkaline or acid degreasing media has the additional advantage that the surface of the aluminium work piece is sensitised for the following pickling step.

According to a second embodiment of the inventive conditioning method a further improvement with respect to removal of rolling oil is achieved if the degreasing medium contains at least 1,5 to 3 % by weight of a composite of 5 - 40 % sodium tripolyphosphate, 3 - 10 % sodium gluconate, 30 - 70 % soda and 3 - 8 % of a composite of non-ionic and anionic surfactants. The described degreasing medium removes rolling oil and other contaminants from the surface of the conditioned aluminium work piece with a high effectiveness. Preferably, the degreasing effect of the degreasing medium can be enhanced if the temperature of the degreasing medium increases.

Preferably, sodium hydroxide is utilised for pickling. Using sodium hydroxide in pickling leads to a good removal of oxide islands on the surface of the aluminium work

piece is achieved, in particular at elevated temperatures, i.e. equal or more than 70 °C. However, even at lower temperatures sodium hydroxide supports a stable electro-chemical graining process with increased manufacturing speed. Furthermore, hydrofluoric acid can be used as well for pickling.

According to a further advantages embodiment of the inventive method pickling comprises AC-cleaning with phosphoric acid. During AC-cleaning an alternating current supports pickling process and phosphoric acid is used as electrolyte. Phosphoric acid attacks in particular the oxide islands on the surface of the aluminium work piece which are introduced during rolling. The aluminium of the surface of the lithostrip is not attacked very strongly. Using AC-cleaning with phosphoric acid after the degreasing step of the inventive method a good removal of oxide islands and contaminants from the surface of the aluminium work piece is achieved. However, AC-cleaning is also possible using as electrolyte sulphuric acid.

More preferably, according to a further embodiment of the invention phosphoric acid is utilised for pickling. Phosphoric acid, even in absence of an AC current, has the advantage that it attacks mainly the oxide islands on the surface of the aluminium work piece and leads merely to a removal of small amount of the aluminium of the work piece itself. As a consequence pickling can be accomplished very thoroughly without removing to much aluminium from the surface of the work piece. Surprisingly, it has been found that the results achieved by pickling only with phosphoric acid are superior compared to the pickling with phosphoric acid supported by AC current. It is presumed that the absence of any oxide film, which is build during AC-

cleaning, is the reason for the superior results of phosphoric acid in combination with the degreasing step.

Preferably, the work piece is a strip or a sheet, in particular a lithostrip or a lithosheet. In this case the necessary electro-chemical graining process for manufacturing lithostrips or lithosheets can be accomplished thoroughly within less time and the manufacturing speed can be increased. Furthermore, the charge density needed can be reduced while providing a fully grained strip or sheet surface.

More preferably, the inventive conditioning method is accomplished subsequent the manufacturing of a strip, in particular a lithostrip, and the conditioned strip is reeled on a coil. In this case a coil of a conditioned lithostrip can be provided comprising an optimum performance in further elcectro-chemical graining processes used to manufacture lithographic printing plates.

According to a second teaching of the present invention the above mentioned object is solved by a work piece consisting of an aluminium alloy conditioned by the inventive method. As outlined before, the inventive work piece provides a cleaned surface with an optimum performance for a subsequent electro-chemical graining process.

More preferably, the work piece is a strip or a sheet, in particular a lithostrip or a lithosheet. Lithostrip or sheets are produced for lithographic printing plates and differ from „normal" sheets due to the aluminium alloy they consist of and their specific thickness, which is

typically less than 1 mm. Furthermore, the surface of lithostrips and sheets has to be prepared for a roughening process, since manufacturing of lithographic printing plates generally comprises an electro-chemical graining process to prepare the surface of the lithographic printing plates for the printing process. With the inventive sheets or strips, in particular with the inventive lithosheets or lithostrips, the necessary electro-chemical graining of the surface can be accomplished in shorter time with a reduced charge carrier density.

Beside an optimised surface of the inventive work piece the mechanical features and an improved graining structure during electro-chemical graining can be provided if the aluminium alloy of the work piece is one of the aluminium alloys AA1050, AA1100, AA3103 or AlMg0,5. These aluminium alloys provide the mechanical strength needed for lithographic printing plates while enabling due to the low amount of alloying constituents a homogeneous graining of the surface. However, work pieces consisting of other aluminium alloys may provide the same advantages.

According to a more preferably embodiment of the inventive work piece the aluminium alloy contains the following alloying constituents in percent by weight:

$$
\begin{aligned}
&\text{Si} < 0{,}1 \ \%,\\
0{,}3\ \% \leq\ &\text{Fe} \leq 0{,}4 \ \%,\\
&\text{Cu} < 0{,}01 \ \%,\\
&\text{Mn} < 1{,}1 \ \%,\\
&\text{Mg} < 0{,}2 \ \%,\\
&\text{Zn} < 0{,}01 \ \%,
\end{aligned}
$$

Ti < 0,01 %,
impurities each less than 0,005 % in sum max. 0,15 %,rest Al.

The inventive aluminium alloy has state of the art mechanical and graining properties, in particular when the lithostrip consisting of said aluminium alloy is conditioned with the inventive method.

The inventive method of conditioning the surface of an aluminium work piece as well as the inventive work piece can be designed and developed further in many different ways. In this respect, it is referred to the dependent claims of the independent claims 1 and 8 as well as to the description of embodiments of the present invention in connections with the drawings. The drawings shows in Fig. 1a) to 1c) pictures of a transmission electron microscope (SEM) of the surface of an aluminium alloy work piece conditioned with methods according to three different embodiments of the present invention.

In the present embodiments of the inventions the work piece consist of a cold rolled AlMg0,5 aluminium alloy. However, it has been found that the results achieved with a AlMg0,5 aluminium alloy are representative for the other aluminium alloys mentioned in the claims, too. On the left side Fig. 1a) to 1c) show SEM pictures of a degreased surface of the work piece, whereby degreasing has been accomplished by a medium containing at least 1,5 - 3 % by weight of a composite of 5 - 40 % sodium tripolyphosphate, 3 - 10 % sodium gluconate, 30 - 70 % soda and 3 - 8 % of a composite of non-ionic and anionic surfactants. The dark areas are identified as rolled-in subsurface oxide islands. These oxide islands are typically not removed

during degreasing. However, it has been found that the capability of the pre-treatments prior to the electro-chemical graining to remove subsurface oxide islands is very important to improve the results of electro-chemical graining, since the oxide islands prevent the respective surface area from being grained. In Fig. 1a) on the right side the work piece surface of the left picture of Fig. 1a) is shown after a treatment with sodium hydroxide with a concentration of 50 g/l for 10 s and at a temperature of 80 °C according to a first embodiment of the inventive conditioning method.

On the one hand pickling with sodium hydroxide at the elevated temperature has removed almost completely the oxide island which indicates the interaction between the two conditioning steps of degreasing and pickling. On the other hand the pitted structure indicates that pickling already attacks the bulk material of the work piece surface. However, this pitted structure may be avoided by reducing the temperature or the time of pickling with sodium hydroxide.

Fig. 1b) shows on the right a SEM picture of the surface of the inventive work piece conditioned with an AC-cleaning in an phosphoric acid electrolyte. The AC-cleaning is accomplished in the present embodiment of the invention with a current density of 10 A/dm² with a concentration of phosphoric acid of 20 % at a temperature of 80 °C for 10 s. Comparing left SEM picture after degreasing and the right SEM picture after degreasing and pickling with AC-cleaning in phosphoric acid it can be derived that small parts of the black coloured oxide island has been left on the work piece surface. However, a pitted structure which indicates that the bulk material

has been attacked, has not been observed with AC-cleaning in phosphoric acid in this embodiment of the present invention.

Fig. 1c) presents the surface of the inventive aluminium work piece conditioned with phosphoric acid as second step. In comparison with the degreased work piece surface, pickling with phosphoric acid shows that the oxide islands are attacked mainly and removed from the work piece surface without leaving a pitted structure as shown after a conditioning with sodium hydroxide. The pickling with phosphoric acid shows the best results with respect to removing of subsurface, rolled-in oxide islands. The parameters regarding concentration, temperature and application time are variable and depend on each other. Hence, similar results may be achievable with different parameters.

Anyhow, the inventive two-step method of conditioning the surface of aluminium work pieces provides almost complete removal of rolled-in subsurface oxide islands enabling a reduction of the charge entry during electro-chemical graining to achieved a fully grained surface. Since fully grained surfaces are particularly desired in manufacturing lithosheets and lithostrips an advantageous pre-treatment prior electro-chemical graining is presented with the inventive conditioning method.

To investigate the ability of the inventive two-step conditioning of the aluminium work piece to be applied in a mass production further test with different concentrations, temperatures has been done. As a result, for phosphoric acid with concentrations from 20 % to 50%, at temperatures more or equal than 70 °C an application

time of 0,1s to 10s shows good results with respect to a removal of subsurface oxide islands on the aluminium workpiece. Hence, the inventive two step conditioning method of the surface of aluminium work pieces can be applied even in a mass production of conditioned aluminium work pieces.

Claims

1. Method of conditioning the surface of an aluminium work piece consisting of an aluminium alloy, which method comprises at least the two steps

   - degreasing the surface of the work piece with a degreasing medium and subsequently

   - cleaning the surface of the work piece by pickling.

2. Method according to claim 1, wherein an alkaline or an acid medium or an organic solvent is used as degreasing medium.

3. Method according to claim 1 or 2, wherein the degreasing medium contains at least 1,5 to 3% by weight of a composite of 5 - 40% sodium tripolyphosphate, 3 - 10 % sodium gluconate, 30 - 70% soda and 3 - 8% of a composite of non-ionic and anionic surfactants.

4. Method according to claim 1 to 3, wherein sodium hydroxide is utilised for pickling.

5. Method according to claim 1 to 3, wherein pickling comprises AC-cleaning with phosphoric acid.

6. Method according to claim 1 to 3, wherein phosphoric acid is utilised for pickling.

7. Method according to claim 1 to 6, wherein said work piece is a strip or a sheet, in particular a lithostrip or lithosheet.

8. Method according to claim 1 to 7, wherein the conditioning is accomplished subsequently to manufacturing of the strip and the conditioned strip is reeled on a coil.

9. Work piece conditioned by a method according to claim 1 to 8.

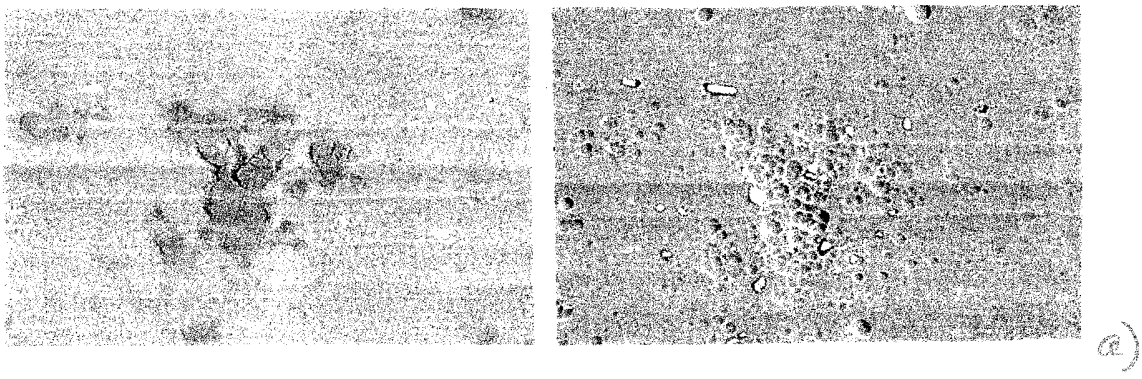
10. Work piece according to claim 8, wherein the work piece is a strip or sheet, in particular a lithostrip or a lithosheet.

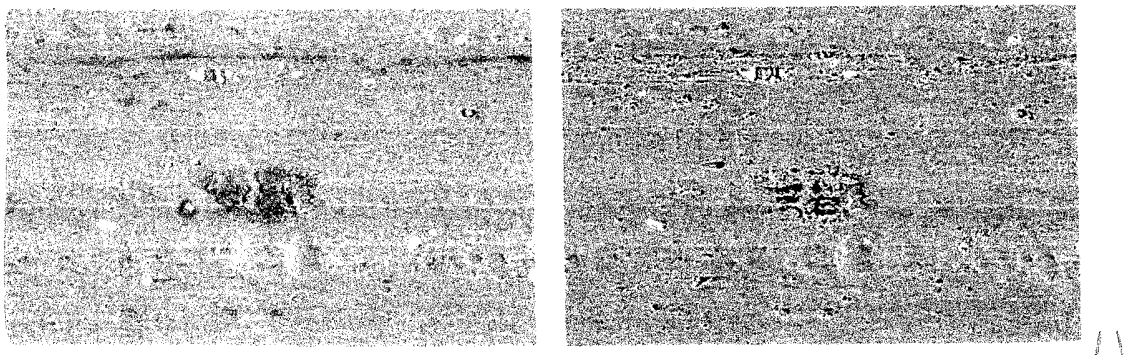
11. Work piece according to claim 9 or 10, wherein the aluminium alloy is one of the aluminium alloys AA 1050, AA 1100, AA 3103 or AlMg0,5.

12. Work piece according to claims 9 to 11, wherein the aluminium alloy contains the following alloying constituents in percent by weight:

	Si	< 0,1	%,
0,3 % ≤	Fe	≤ 0,4	%,
	Cu	< 0,01	%,
	Mn	< 1,1	%,
	Mg	< 0,2	%,
	Zn	< 0,01	%,
	Ti	< 0,01	%,

impurities each less than 0,005% in sum max. 0,15 %, rest Al.





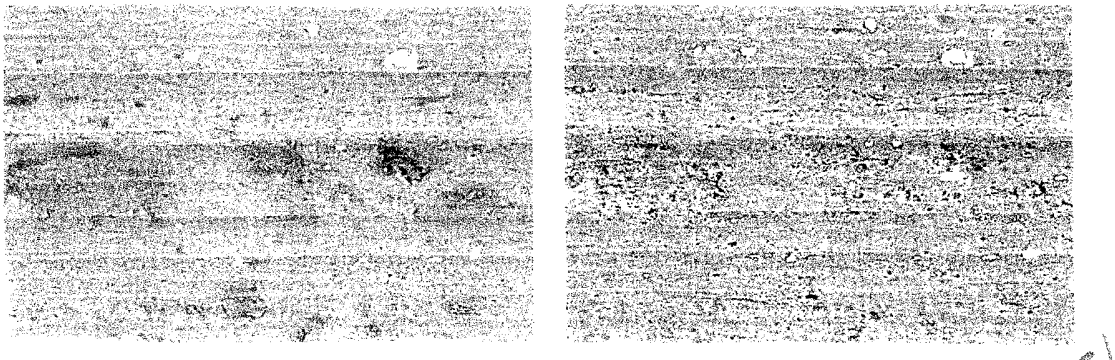


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/061358

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23G1/12 C23G1/22 C23G5/02 B41N1/08 B41N3/03

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)
C23G B41N

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 647 782 A (HERBERT MANFRED FREUD) 20 December 1950 (1950-12-20) page 1, lines 21,22,62-69,78-90 page 2, lines 31-57	1,2,6,7, 9,10
X	US 3 699 013 A (AKIRA MIYATA ET AL) 17 October 1972 (1972-10-17) column 2, lines 34-55 column 3, lines 1-16	1,2,7,9, 10
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 028 (C-471), 27 January 1988 (1988-01-27) & JP 62 177191 A (MITSUI MINING & SMELTING CO LTD), 4 August 1987 (1987-08-04) abstract	1,6,7,9, 10

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 June 2006	13/06/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Patosuo, S

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/061358

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 547 274 A (OHASHI ET AL) 15 October 1985 (1985-10-15) column 2, lines 48-68	1,4-7,9, 10
X	US 4 634 656 A (OHASHI ET AL) 6 January 1987 (1987-01-06) column 3, lines 3-23	1,4-7,9, 10
X	DD 244 363 A1 (VEB STEREMAT "HERMANN SCHLIMME" BERLIN,DD) 1 April 1987 (1987-04-01) page 2	1,2,7,9, 10
X	AT 386 614 B (WILLMITZER HERBERT) 26 September 1988 (1988-09-26) page 2, line 51 - page 3, line 1 page 3, lines 7-17,48-50 page 4, lines 14-30	1,2,5,6, 9
X	DE 36 00 415 A1 (W.CANNING GMBH; W. CANNING GMBH, 4000 DUESSELDORF, DE) 16 July 1987 (1987-07-16)	1,2,4,6, 9
Y	abstract column 2, lines 62-64 column 3, lines 19-41 column 4, paragraph 16-51 column 4, line 65 - column 5, line 23	3
X	US 6 447 982 B1 (VON ASTEN WOLFGANG ET AL) 10 September 2002 (2002-09-10)	1,7-10, 12
Y	column 2, lines 42-50 column 3, paragraph 51-61 column 5, paragraph 53-57 claim 9	3,5,8, 11,12
X	GB 655 737 A (JOHNSON, MATTHEY & COMPANY LIMITED) 1 August 1951 (1951-08-01)	1,2,9
Y	page 1, lines 57-62,79-81	3
Y	US 5 997 721 A (LIMBACH ET AL) 7 December 1999 (1999-12-07) cited in the application column 2, line 48 - column 3, line 21 column 3, line 30	5,8,11, 12
Y	DE 43 17 815 C1 (VAW ALUMINIUM AG, 53117 BONN UND 1000 BERLIN) 1 June 1994 (1994-06-01) cited in the application column 3, lines 15-31 column 4, lines 33-40	3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2006/061358

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 647782 A	20-12-1950	BE 473563 A	
		CH 266114 A	15-01-1950
		FR 966785 A	18-10-1950
		NL 68259 C	
US 3699013 A	17-10-1972	CH 538547 A	30-06-1973
		DE 2041728 A1	08-04-1971
		FR 2059685 A1	04-06-1971
		GB 1312723 A	04-04-1973
		JP 49028572 B	27-07-1974
		SE 367658 B	04-06-1974
		SU 368762 A3	26-01-1973
JP 62177191 A	04-08-1987	NONE	
US 4547274 A	15-10-1985	JP 2008918 B	27-02-1990
		JP 2029317 C	19-03-1996
		JP 58209597 A	06-12-1983
US 4634656 A	06-01-1987	JP 1047544 B	16-10-1989
		JP 1740679 C	15-03-1993
		JP 58210144 A	07-12-1983
DD 244363 A1	01-04-1987	NONE	
AT 386614 B	26-09-1988	AT 295286 A	15-02-1988
DE 3600415 A1	16-07-1987	NONE	
US 6447982 B1	10-09-2002	BR 0002955 A	03-04-2001
		DE 29924474 U1	28-08-2003
		EP 1065071 A1	03-01-2001
		ES 2232347 T3	01-06-2005
		JP 2001049373 A	20-02-2001
		JP 2004250794 A	09-09-2004
GB 655737 A	01-08-1951	NONE	
US 5997721 A	07-12-1999	AT 190678 T	15-04-2000
		AU 4267096 A	10-07-1996
		CA 2208109 A1	27-06-1996
		DE 69515691 D1	20-04-2000
		DE 69515691 T2	20-07-2000
		ES 2143085 T3	01-05-2000
		WO 9619596 A1	27-06-1996
		JP 10510881 T	20-10-1998
		JP 3647461 B2	11-05-2005
DE 4317815 C1	01-06-1994	EP 0626470 A1	30-11-1994