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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 July 2003 (24.07.2003)

PCT

(10) International Publication Number
WO 03/059922 A1

(51) International Patent Classification[7]: C07F 15/02, C07C 229/76, B01D 53/56, 53/60, 53/14

(21) International Application Number: PCT/EP03/00273

(22) International Filing Date: 8 January 2003 (08.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02075174.9 16 January 2002 (16.01.2002) EP

(71) Applicant *(for all designated States except US)*: **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **NIEUWENHUIZEN, Peter, Jan** [NL/NL]; Looierstraat 56-3, NL-6811 AZ Arnhem (NL). **CARSTENS, Axel** [DE/DE]; Wildgehege 7, 47533 Kleve (DE). **MAY, Rainer** [DE/DE]; Am Senger 15, 63933 Mönchberg (DE).

(74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).

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

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

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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.

WO 03/059922 A1

(54) Title: CONCENTRATED AQUEOUS IRON CHELATE COMPOSITION

(57) Abstract: The invention relates to a concentrated aqueous iron chelate composition containing at least 0.7 wt % of iron, in a molar ratio of iron to chelate of about 1:1, and containing an additive selected from the group consisting of alkali metal, protonated alkali metal, and ammonium salts of carbonate (CO_3^{2-}), phosphate ($P0_4^{3-}$), diphosphate ($P_2O_7^{4-}$), triphosphate ($P_3O_{10}^{5-}$), phosphite (HPO_3^{2-}), hypophosphite ($H_2PO_2^-$), tetraborate ($B_4O_7^{2-}$), disulfite ($S_2O_5^{2-}$), thiosulfate ($S_2O_3^{2-}$), and iminodiacetate ($HN(CH_2CO_2)_2^{2-}$), in a molar ratio of additive to iron of from 0.1:1 to 2.5:1. Most preferably, the additive is sodium carbonate. The invention further relates to a process for preparing said composition and to the use of said composition for the removal of NO_x from a gas stream. Typically, the invention compositions have an increased, high content of iron and are stable for prolonged periods of time.

CONCENTRATED AQUEOUS IRON CHELATE COMPOSITION

The present invention relates to a concentrated aqueous iron chelate composition.

Iron chelates such as ferric ion ethylenediaminetetraacetic acid (NaFeEDTA) are used in many applications. In particular, they can be used for the removal of NO_x compounds from a gas stream, e.g. flue gas.

It is known to scrub nitrogen oxides (NO_x) in combination with sulfur oxides (SO_x) as gaseous components from a gas by causing the gas to rise in a scrubber, the gas being brought into contact with a scrub liquid in the form of an aqueous slurry comprising biomass, a transition metal chelate, such as NaFeEDTA, and a calcium compound suitable for binding sulfur oxides, such as lime or limestone, which rains down from spray bars in the scrubber. The complex formed from NO and transition metal chelate and/or any spent transition metal chelate is regenerated biologically, NO and NO_2 being reduced to molecular nitrogen (N_2). In addition, the sulfur oxides are removed by reacting with the calcium compound to form calcium sulfite, which is oxidized further, inside or outside the scrubber, to calcium sulfate, which is separated and land filled or used in construction.

The water balance of this scrubbing process is important, and it is preferred to only have a limited purge of water used in this process. Hence, the intake of additional water is to be limited. For this reason, the aqueous NaFeEDTA solution should be as concentrated as possible. In order to further decrease the intake of additional water, the aqueous NaFeEDTA solution preferably is prepared using clarified process water.

For the removal of NO_x compounds from a gas stream, iron chelates in different forms can be used, i.e. NaFeEDTA, which is commercially available as a solid

material in a purified form, or KFeEDTA, which is commercially available in a concentrated liquid form (i.e. approx. 6 wt% Fe).

Unfortunately, these commercial sources of iron chelates are relatively expensive. In addition, it is a known problem that handling solid iron chelate materials causes dusting. These drawbacks preclude their use for the removal of NO_x compounds from a gas stream.

US 3,933,993 discloses a chelated iron solution of high concentration that is stable at a pH of 7-10. The formulation is used for removing H_2S and/or mercaptans as pollutants in a gas stream. It is mentioned that in order to provide the requisite sequestering action whereby iron is kept in solution, an excess of EDTA must be used, i.e. the molar ratio of EDTA to Fe must be greater than 1:1, i.e. 1.25:1 in Examples 2, 5, and 6. The preferred ratio of EDTA to Fe is about 1.5:1 (see Examples 3 and 4). In Example 7 of this document a preferred chelated iron formulation having an Fe content of 2.8 wt% and a molar ratio of EDTA to Fe of 1.5:1 is disclosed.

SU 1287346 discloses an absorbent for the purification of gases from hydrogen sulphide comprising an aqueous solution of chelated iron, an organic amine, an alkali metal hydroxide or carbonate, and a sodium, potassium or ammonium phosphate. In the Example, an aqueous FeEDTA solution having a content of about 0.8 wt% Fe is described. The molar ratio of EDTA to Fe is 1.65:1.

Using an excess of EDTA is undesirable, because in various applications the excess EDTA will be degraded, which adds to the cost of the formulation. Furthermore, the excess EDTA can coordinate with (transition) metals, which may deactivate these metals. For example, in the application where NO_x is removed simultaneously with SO_x (see above), an excess of EDTA is known to limit the oxidation of calcium sulfite to calcium sulfate, which is ascribed to the chelation of (trace amounts of) transition metals known to catalyze this oxidation reaction.

DE 4130132 relates to hydrogen sulphide absorption from gas with a high carbon dioxide content using a ferric amino-carboxylate solution stabilized with alkali hydrogen carbonate to avoid oxidative decomposition of the amino-carboxylate. The alkali bicarbonate is added in an amount of 20-80 g/l, preferably 40-60 g/l. The Fe content is 2-5 g/l, i.e. 0.2-0.5 wt%. Hence, the molar ratio of alkali bicarbonate to iron varies between 2.6:1 and 26.5:1. In Example 2 of this document an aqueous FeEDTA solution having an iron content of 0.28 wt% is described.

The iron content of the formulations described in this document is too low, and this adds to the costs for transporting, e.g., shipping, such formulations over long distances and for storing during prolonged periods of time in a cost effective way. Hence, it is desired that the iron content of aqueous iron chelate solutions be increased. Also, using an excess of alkali bicarbonate is undesirable, because it further adds to the cost of the formulation.

Hence, there is a need in the art for an aqueous composition which does not have the aforementioned problems. The present invention provides a composition having an increased, high concentration of soluble chelated iron, which can be shipped and stored for prolonged periods of time.

The concentrated aqueous iron chelate composition of the present invention contains more than 0.7 wt% of iron, in a molar ratio of iron to chelate of about 1:1, and contains an additive selected from the group consisting of alkali metal, protonated alkali metal, and ammonium salts of carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), diphosphate ($P_2O_7^{4-}$), triphosphate ($P_3O_{10}^{5-}$), phosphite (HPO_3^{2-}), hypophosphite ($H_2PO_2^-$), tetraborate ($B_4O_7^{2-}$), disulfite ($S_2O_5^{2-}$), thiosulfate ($S_2O_3^{2-}$), and iminodiacetate ($HN(CH_2CO_2)_2^{2-}$), in a molar ratio of additive to iron of from 0.1:1 to 2.5:1.

The iron chelate to be used in accordance with the present invention may be any single iron chelate or a mixture of two or more iron chelates. Suitable iron chelates for use in accordance with the present invention include iron ethylenediaminetetraacetic acid (FeEDTA), iron nitrilotriacetic acid (FeNTA), iron hydroxyethylenediaminetriacetic acid (FeHEDTA), and iron (propylene-diamino)tetraacetic acid (FePDTA). Preferred iron chelates are FeEDTA, FeNTA, and FePDTA. The most preferred iron chelate is FeEDTA.

The amount of iron present in the composition in accordance with the present invention is at least 0.7 wt%, based on the total weight of the composition. Typically, the iron content is in the range of 0.7 to 6 wt%. Preferably, the iron content is at least 1.5, more preferably at least 1.7, most preferably at least 2 wt%. Preferably, the iron content is at most 4, more preferably at most 3, most preferably at most 2.5 wt%.

The molar ratio of iron to chelate in the composition of the invention is about 1:1, i.e. about equimolar. In the context of the present invention, this means that the molar ratio of iron to chelate is in the range of 0.95:1 to 1.05:1.

Preferably, the additive to be used in accordance with the present invention is an alkali metal or protonated alkali metal salt, more preferably a sodium or protonated sodium salt. Preferably, the additive is selected from the group consisting of alkali metal, protonated alkali metal, and ammonium salts of carbonate, phosphate, diphosphate, triphosphate, phosphite, tetraborate, thiosulfate, and iminodiacetate, more preferably the sodium and protonated sodium salts thereof. More preferably, the additive is selected from the group consisting of sodium carbonate, trisodium phosphate, disodium hydrogen phosphate, sodium dihydrogen phosphate, and disodium iminodiacetate. Most preferably, the additive to be used in accordance with the present invention is sodium carbonate.

The amount of additive to be used in accordance with the present invention is defined by a molar ratio of additive to iron of from 0.1:1 to 2.5:1. Preferably, the additive is added in a molar ratio of at least 0.5:1. Preferably, the additive is added in a molar ratio of at most 2:1, more preferably at most 1.5:1.

Typically, the pH of the composition of the present invention is in the range of 7 to 10. Preferably, the pH is at least 7.5. Preferably, the pH is at most 9.5, more preferably at most 9, most preferably at most 8.5. In order to adjust the pH, for example sodium hydroxide may be added. In general, the higher the pH, the higher the solubility of the iron chelate will be.

The compositions in accordance with the present invention can be prepared using means and equipment known to a person of ordinary skill in the art. For example, conventional stainless steel equipment may be used.

The compositions of the present invention can be prepared, for example, by first contacting an iron salt with a chelate sodium salt in water in a molar ratio of iron to chelate of about 1:1, resulting in a precipitation of the iron chelate salt, and subsequently adding the additive, in the amount which is defined above. It is also possible to dissolve solid sodium iron chelate in water and then add the additive in the amount which is described above. Preferably, if necessary, the pH is adjusted to a pH of 7 to 10 as described above. Preferably, the iron salt is $Fe_2(SO_4)_3$ and the chelate sodium salt is Na_4EDTA.

In a preferred embodiment, an aqueous homogeneous iron chelate solution of a low concentration, i.e. in the range of 0.1 to 0.5 wt% of iron, is prepared by first contacting an aqueous iron salt solution with an aqueous sodium chelate solution, then adding the additive in a molar ratio as defined above, after which iron salt, sodium chelate, and additive in the proper molar ratios (as described above) are added as solids or in an aqueous solution to reach the more preferred concentrations of iron and additive. Alternatively, the aqueous homogeneous iron chelate solution of a low iron concentration is prepared by

dissolving the pure, solid iron chelate or diluting commercially available (aqueous) solutions of the iron chelate with water, and then adding the additive in a molar ratio to iron as defined above, after which the preparation can continue as described in the previous sentence.

Preferably, process water obtained from an installation which is used for the removal of NO_x and/or SO_x from a gas stream is used for preparing the composition in accordance with the present invention.

Preferably, a chelate sodium salt is used for preparing the composition of the present invention. Suitable chelates for use in accordance with the present invention include EDTA, nitrilotriacetic acid (NTA), and (propylenediamino)tetra-acetic acid (PDTA). Most preferably, the chelate is EDTA. A suitable chelate sodium salt is Na_4EDTA.

Suitable iron salts include $Fe_2(SO_4)_3$, $FeSO_4$, $FeCl_3$, and $Fe(NO_3)_3$. Preferably, $Fe_2(SO_4)_3$ is used.

The compositions in accordance with the present invention generally do not contain any further components other than the iron chelate and the additive, as claimed, with the exception of the by-product salt – i.e. Na_2SO_4 in Examples 1 and 2 below - formed from the *in situ* preparation of the iron chelate, as described above, or by-products present in a commercially available iron chelate, and/or a pH adjusting agent.

As described above, the compositions of the present invention can be sufficiently concentrated in iron to be highly useful. We have found that the compositions of the present invention were storage stable for prolonged periods of time, e.g., the composition of Example 1 was stable for more than four months of storage at room temperature, meaning that during this time period no solid material was observed by visual inspection.

The compositions of the present invention are particularly useful for the removal of NO_x from a gas stream, more in particular for the removal of NO_x in combination with SO_x. Apart from providing the ability to limit the intake of additional water as much as possible, the use of the invention composition has the additional advantage that it aids in neutralizing acidic components in the flue gases.

The present invention is illustrated by the following Examples.

EXAMPLES

Example 1

An aqueous solution of NaFeEDTA (20 mmoles) was prepared from 20 mmoles of an aqueous Na_4EDTA solution (Dissolvine E-39, 19.0 g, 39.4 wt%), 10 mmoles of an aqueous $Fe_2(SO_4)_3$ solution (9.0 g, 44.4 wt%), and 18.2 g of extra water. To this solution – which further contained 30 mmoles of Na_2SO_4 – were added 14.1 mmoles of an aqueous Na_2CO_3 solution (13.6 g, 11.0 wt%) at room temperature with stirring. The resulting aqueous solution, having a pH of 7.9 and an Fe content of 2.4 wt%, was stable at room temperature for at least four months.

Example 2

An aqueous solution of NaFeEDTA (100 mmoles) was prepared from 100 mmoles of an aqueous Na_4EDTA solution (Dissolvine E-39, 93.5 g, 40.1 wt%), 50 mmoles of an aqueous $Fe_2(SO_4)_3$ solution (45.0 g, 44.4 wt%), and 35.0 g of process water having the typical composition of clarified process water from a Flue Gas Desulfurization unit (~1,600 ppm Ca, ~1,200 ppm sulfate, ~2,600 ppm chloride, and pH < 5). To this solution – which further contained 150 mmoles of Na_2SO_4 – were added 70 mmoles of an aqueous Na_2CO_3 solution (67.9 g, 11.0 wt% in process water) at room temperature with stirring. The resulting aqueous solution, having a pH of 7.8 and an Fe content of 2.4 wt%, was stable at room temperature for at least three months.

Example 3

To an aqueous solution of 20 mmoles of pure NaFeEDTA (Dissolvine E-Fe-13, 8.43 g) in 38.3 g of water were added 10 mmoles of Na_2CO_3 (1.06 g) at room temperature with stirring. The resulting aqueous solution, having a pH of 7.2 and an Fe content of 2.4 wt%, was stable at room temperature for at least two months.

Example 4

To an aqueous solution of 20 mmoles of pure NaFeEDTA (Dissolvine E-Fe-13, 8.43 g) in 44.3 g of water were added 10 mmoles of Na_3PO_4 (1.64 g) at room temperature with stirring. The resulting aqueous solution, having a pH of 7.2 and an Fe content of 2.1 wt%, was stable at room temperature for at least two months.

Example 5

To an aqueous solution of 20 mmoles of pure NaFeEDTA (Dissolvine E-Fe-13, 8.43 g) in 50.25 g of water were added 20 mmoles of disodium iminodiacetate (3.54 g) at room temperature with stirring. The resulting aqueous solution, having a pH of 7.2 and an Fe content of 1.8 wt%, was stable at room temperature for at least two months.

Example 6

To an aqueous solution of 20 mmoles of pure NaFeEDTA (Dissolvine E-Fe-13, 8.43 g) in 9.8 g of water were added 10 mmoles of Na_2CO_3 (1.06 g) and 8.9 mmoles (8.9 ml) of an aqueous 1N NaOH solution at room temperature with stirring. The resulting aqueous solution, having a pH of 7.9 and an Fe content of 4.0 wt%, was stable at room temperature for at least two months.

Comparative Example A

An aqueous solution of NaFeEDTA (20 mmoles) was prepared from 20 mmoles of an aqueous Na_4EDTA solution (Dissolvine E-39, 19.0 g, 39.4 wt%), 10

mmoles of an aqueous $Fe_2(SO_4)_3$ solution (9.0 g, 44.4 wt%), and 147.8 g of extra water – this solution further contained 30 mmoles of Na_2SO_4. The resulting aqueous solution had a pH of 5.3 and an Fe content of 0.7 wt%.

CLAIMS

1. A concentrated aqueous iron chelate composition containing at least 0.7 wt% of iron, in a molar ratio of iron to chelate of about 1:1, and containing an additive selected from the group consisting of alkali metal, protonated alkali metal, and ammonium salts of carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), diphosphate ($P_2O_7^{4-}$) triphosphate ($P_3O_{10}^{5-}$), phosphite (HPO_3^{2-}), hypophosphite ($H_2PO_2^-$), tetraborate ($B_4O_7^{2-}$), disulfite ($S_2O_5^{2-}$), thiosulfate ($S_2O_3^{2-}$), and iminodiacetate ($HN(CH_2CO_2)_2^{2-}$), in a molar ratio of additive to iron of from 0.1:1 to 2.5:1.

2. A composition according to claim 1, characterized in that the additive is an alkali metal or protonated alkali metal salt.

3. A composition according to claim 1 or 2, characterized in that the iron chelate is selected from the group consisting of iron ethylene diamine tetraacetic acid, iron nitrilotriacetic acid, and iron (propylenediamino)tetraacetic acid.

4. A composition according to any one of claims 1-3, characterized in that the pH of the composition is 7 to 10.

5. A process for preparing the composition according to any one of the preceding claims containing at least 0.7 wt% of iron comprising first contacting an iron salt with a chelate sodium salt in water in a molar ratio of iron to chelate of about 1:1, and subsequently adding the additive in an amount of a molar ratio of additive to iron of from 0.1:1 to 2.5:1.

6. A process according to claim 5, characterized in that the pH of the composition is adjusted to a pH of 7 to 10.

7. A process according to claim 6, characterized in that the pH of the composition is adjusted using sodium hydroxide.

8. A process according to any one of claims 5-7, characterized in that the water is process water obtained from an installation which is used for the removal of NO_x from a gas stream.

9. A process according to any one of claims 5-8, characterized in that the iron salt is $Fe_2(SO_4)_3$ and the chelate sodium salt is Na_4EDTA.

10. Use of the composition according to any one of claims 1-4 for the removal of NO_x, optionally in combination with SO_x, from a gas stream.

INTERNATIONAL SEARCH REPORT

International Application No
P[redacted]/EP 03/00273

A. CLASSIFICATION OF SUBJECT MATTER WO 03/059922 PCT/EP03/00273
IPC 7 C07F15/02 C07C229/76 B01D53/56 B01D53/60 B01D53/14

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)
IPC 7 C07F B01D C07C

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)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 055 623 A (SAITOH SHIGERU ET AL) 25 October 1977 (1977-10-25) examples 4-6 ---	1-10
X	US 4 186 176 A (KITAMURA TAKETSUGU ET AL) 29 January 1980 (1980-01-29) column 2, line 18 - line 65; examples 1,2 ---	1-10
X	EP 0 257 124 A (ARI TECHNOLOGIES INC) 2 March 1988 (1988-03-02) page 2, line 27 - line 31 page 5, line 47 -page 6, line 40 page 7, line 42 - line 46; table 4 --- -/--	1-9

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

[X] Patent family members are listed in 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
13 June 2003	23.06.03

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	Eijkenboom, A

Form PCT/ISA/210 (second sheet) (July 1992)

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 4 518 577 A (KLECKA MIRO E) 21 May 1985 (1985-05-21) column 1, line 22 - line 27 column 5, line 12 -column 6, line 5 column 9, line 24 - line 31 ---	1-9
X	US 4 518 576 A (DIAZ ZAIDA) 21 May 1985 (1985-05-21) column 2, line 64 -column 3, line 30 column 5, line 5 - line 12; examples 1,2 ---	1-9
X	US 5 223 173 A (JEFFREY GAINES C) 29 June 1993 (1993-06-29) column 1, line 35 - line 38 column 10, line 1 -column 11, line 19; claims 1-4 ---	1-9
X	WO 89 06675 A (CHEVRON RES) 27 July 1989 (1989-07-27) page 25, line 18 - line 32; examples -----	1-9

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4055623	A	25-10-1977	JP	50105593 A	20-08-1975
			JP	50144694 A	20-11-1975
			JP	51065078 A	05-06-1976
			JP	1153912 C	30-06-1983
			JP	51065098 A	05-06-1976
			JP	57043527 B	16-09-1982
			CA	1058829 A1	24-07-1979
			CA	1058830 A1	24-07-1979
			CA	1061519 A2	04-09-1979
			DE	2502117 A1	24-07-1975
			DE	2502118 A1	24-07-1975
			FR	2258214 A1	18-08-1975
			FR	2258215 A1	18-08-1975
			GB	1501701 A	22-02-1978
			GB	1501702 A	22-02-1978
			NL	7500672 A	23-07-1975
			NL	7500673 A	23-07-1975
			NO	750153 A ,B,	18-08-1975
			NO	750154 A ,B,	18-08-1975
			NO	771759 A ,B,	22-07-1975
			SE	407790 B	23-04-1979
			SE	7500563 A	22-07-1975
			SE	406190 B	29-01-1979
			SE	7500564 A	22-07-1975
			SE	410303 B	08-10-1979
			SE	7610594 A	24-09-1976
			US	3991161 A	09-11-1976
			US	3992508 A	16-11-1976
US 4186176	A	29-01-1980	JP	54028274 A	02-03-1979
			JP	54072799 A	11-06-1979
			DE	2833440 A1	08-02-1979
EP 0257124	A	02-03-1988	EP	0257124 A1	02-03-1988
			AT	88657 T	15-05-1993
			DE	3688372 D1	03-06-1993
			DE	3688372 T2	12-08-1993
			US	4622212 A	11-11-1986
US 4518577	A	21-05-1985	CA	1207513 A1	15-07-1986
US 4518576	A	21-05-1985	AU	569006 B2	14-01-1988
			AU	3686684 A	04-07-1985
			CA	1221673 A1	12-05-1987
			DE	3465886 D1	15-10-1987
			EP	0152647 A1	28-08-1985
			JP	1802322 C	26-11-1993
			JP	5012965 B	19-02-1993
			JP	60153921 A	13-08-1985
			ZA	8409844 A	28-08-1985
US 5223173	A	29-06-1993	US	4816238 A	28-03-1989
			US	4774071 A	27-09-1988
			AU	605244 B2	10-01-1991
			AU	1179688 A	25-08-1988
			CA	1305464 A1	21-07-1992
			CN	88100739 A ,B	07-09-1988
			DK	85388 A	20-08-1988

INTERNATIONAL SEARCH REPORT

International Application No
P[redacted]/EP 03/00273

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5223173 A		EP 0279667 A2	24-08-1988
		JP 63294924 A	01-12-1988
		MX 166649 B	26-01-1993
		NO 880714 A	22-08-1988
		NZ 223528 A	27-08-1991
		PH 24894 A	26-12-1990
		AU 605764 B2	24-01-1991
		AU 7219987 A	05-11-1987
		CA 1288087 A1	27-08-1991
		CN 87103152 A ,B	23-12-1987
		DK 225387 A	02-11-1987
		EP 0244249 A2	04-11-1987
		JP 62269729 A	24-11-1987
		NO 871807 A ,B,	02-11-1987
		NZ 220088 A	26-10-1990
		PH 23589 A	11-09-1989
		SU 1679970 A3	23-09-1991
		US 4781901 A	01-11-1988
WO 8906675 A	27-07-1989	AU 3043789 A	11-08-1989
		CN 1036545 A	25-10-1989
		EP 0398952 A1	28-11-1990
		JP 3503856 T	29-08-1991
		WO 8906675 A1	27-07-1989
		US 5004588 A	02-04-1991