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(54) **Title:** METHOD FOR RECOVERY OF THALLIUM FROM AN AQUEOUS SOLUTION

(57) **Abstract:** The present invention relates to a method of removing impurities, especially thallium from an aqueous solution from an industrial process, using a chelating agent, especially an aminophosphonic or an iminodiacetic chelating resin. According to the present method, monovalent and trivalent thallium ions, which were difficult to remove in one process before the present invention, can be simply removed in one process. In addition, the present invention is very useful in the treatment of an aqueous solution containing a low concentration of thallium and a high concentration of other ingredients due to its high removal yield. The resulting purified aqueous solution treated with the present method contains preferably less than 0.1 ppm of thallium. After removing thallium from the solution, the thallium can be recovered selectively as thallium trihydroxide precipitate by oxidation and pH adjustment of the resin regeneration sludge, and then it can be reused in other processes.



Method for recovery of thallium from an aqueous solution

TECHNICAL FIELD

This application claims priority to European patent application No. 11163265.9 filed April 20, 2011, the whole content of this application being incorporated herein by reference for all purposes.

5 The present invention relates to a method of removing impurities, especially thallium, from an aqueous solution from an industrial process, in particular, obtained from rice hull ashes, ashes of wood combustion plants, ashes of coal combustion plants, cement kiln residue, steel industry dust, or dust from iron sintering processes, preferably using an aminophosphonic or an
10 iminodiacetic chelating resin. The present invention also provides a process of removing impurities, especially thallium, and recovering and recycling the insoluble or removed species.

BACKGROUND

15 The residues from many industrial processes contain salts which make the disposal of these residues more difficult and expensive insofar that these salts run the risk of being leached out and contaminating the subsoil of the disposal site.

20 It would therefore be desirable to have processes that make it possible to remove, recover, and recycle these salts contained in industrial residues with high purity and low cost on an industrial scale.

Particularly, representative of such salts are alkali metals. This is disclosed in French patent application No. 2951383 corresponding to WO 2011048135 both published after the priority date of the current invention.

25 However the desirable salts are often polluted with alkaline earth metals, and other heavy metals, especially barium, calcium, chromium, strontium, and thallium. These metals often remain in the form of a mixture of different salts, for example, chloride, sulfate, hydroxide, or carbonate. Since these metals will have a bad effect on the usage, moreover these metals (especially thallium) can be very expensive, they are needed for removal, recovery, and recycle with high
30 purity.

Several methods for the removal of thallium from waste waters are known. For example, metals can be recovered from aqueous solutions electrolytically or

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by precipitation with precipitating agents, if necessary in the presence of bases like NaOH.

In typical industrial processes, the treated aqueous solution obtained from a conventional purification process other than the present method is still polluted by some amount of thallium. German patent application DE102009018959A describes brine comprising potassium chloride which contains dissolved thallium. By co-precipitation of potassium chloride and thallium, the content of thallium in the brine can be reduced. This process has the disadvantages that valuable product, namely the potassium chloride with a high content of precipitated thallium is lost, and that the precipitated thallium has no real value because it is dissipated in a great amount of potassium chloride. A very high thallium recovery is therefore needed.

However, all of the processes above fail to provide an effective method of removing thallium at sufficient level and recovering pure thallium, without the addition of complicated processes, with high purity and low cost on an industrial scale. Moreover, although some of these processes provide a removal method of thallium, a removal method for monovalent thallium ions has not yet been disclosed.

The only identified case where monovalent thallium may be purified is described in patent application EP-A-0 442778, the entire contents of which are incorporated by reference into the present patent application, provide a method of recovering thallium by contacting the thallium with an ion-exchange resin containing thiol groups. According to one example in EP-A-0 442778, the Tl content of an aqueous solution is reduced at acidic pH from 340 ppm to 57 ppm in a first treatment and to 6 ppm in the second step. The resin captures other metals contained in the starting solution, e.g. Cd and As.

However, possibly due to the strong complexation of Cl or OH ions with thallium, effective purification could not be obtained in our case (see Example 1 and Example 2 below). In addition purification occurs at pH lower than 3, which would mean a huge consumption of acid because an aqueous solution according to the present invention preferably has pH higher than 10.

Another case where thallium purification is mentioned by contacting with resin is in the articles : Mikrochimica Acta Volume 96, Issue 1-6, January 1988, Pages 341-347 New polymeric sorbent for preconcentration of metals, Tsisin, G.I., Malofeeva, G.I., Petrukhin, O.M., Zolotov, Y.A. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, GSP-1,

Moscow, SU-117975, Russia However, the publication appears to focus on aminocarboxylic acids and it refers only to trivalent thallium.

Therefore, the need for simple and cheaper processes which make it possible to purify industrial residues and recover valuable metals, especially all
5 monovalent thallium ions, which are difficult to remove selectively, still exists.

The present invention provides a high removal yield of thallium compared to other impurities, and thallium can be selectively removed from the residue, recovered, and reused. With other resins, for example, thiol-based resins disclosed in patent EP 442778 above, they have poor removal yield of thallium
10 while eliminating most other metals, most of which are divalent or trivalent, so it is impossible to obtain thallium with high purity.

SUMMARY

The present invention is directed to a simple method of removing impurities, especially thallium, from an aqueous solution, to obtain a purified
15 aqueous solution with a very low concentration of thallium, especially preferably of about 0.1 ppm or less, and for recovery and recycling especially of the removed thallium content.

Consequently, the method according to the invention includes a step of removing impurities, especially thallium, from an aqueous solution from an
20 industrial process, using a chelating agent capable of complexing thallium ions, preferably an aminophosphonic or an iminodiacetic chelating resin, to obtain a purified aqueous solution.

The present method works well with a starting aqueous solution which has a small amount of thallium, for example, about 2 ppm or less due to high
25 removal efficiency. The method of the invention can be performed, for example, to treat a solution comprising potassium chloride and Tl ions. Therefore, the resulting potassium chloride obtained by crystallization of the residue has a thallium content of 2 ppm or less, preferably equal to or less than 1 ppm, and even more preferably, equal to or lower than 0.5 ppm, which is suitable for most
30 common applications. The term "ppm" denotes ppm by weight unless other wise indicated.

DETAILED DESCRIPTION

The present inventors discovered that especially an aminophosphonic or an iminodiacetic chelating resin is very useful in the treatment of an aqueous
35 solution, especially for selective removal of thallium. It is therefore possible to

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recover thallium at a lower concentration when sludge recovered during regeneration of the aminophosphonic or the iminodiacetic resin is treated.

Consequently, according to a preferred embodiment, the present invention provides : (1) a purification method of thallium from an aqueous solution using
5 an aminophosphonic or an iminodiacetic chelating resin, (2) a recovery method of the adsorbed thallium onto the an aminophosphonic or an iminodiacetic chelating resin ; and (3) a recycling method of the recovered thallium.

Consequently, one of the essential features of the invention resides in a method of removing impurities, especially thallium from an aqueous solution
10 from an industrial process, preferably using an aminophosphonic or an iminodiacetic chelating resin, more preferably an iminodiacetic resin to obtain a purified aqueous solution. The aqueous solution may, in particular, contain potassium chloride, which will be purified by this process and used for other processes.

15 In some embodiments, one or more other ingredients, which are selected from alkali metals, alkali earth metals, or other heavy metals, as well as thallium, are removed from the aqueous solution. The other ingredients are selected from one or more of barium, calcium, chromium, lithium, silicon or strontium, especially barium, calcium, lithium, or strontium. It is clear for the expert that
20 commonly, those other ingredients are present in the form of salts, e.g. in the form of the chlorides.

The method of the invention may further comprise one or more steps of removing one or more other ingredients before the removal of thallium. Thus, in some embodiments, the aqueous solution is subjected to pre-treatment, one or
25 more times, to remove one or more other ingredients.

In some embodiments, the aqueous solution contains 2 ppm or less of thallium and 30 weight % or more of other ingredients based on the total weight of aqueous solution.

30 In some embodiments, monovalent thallium ions are removed from the aqueous solution along with trivalent thallium ions.

In any event, the resulting aqueous solution contains less thallium than before the purification treatment. In some embodiments, the resulting purified aqueous solution contains 2 ppm or less, preferably 0.1 ppm or less, more preferably 0.02 ppm or less of thallium ions. With the use of other prior methods,
35 such as oxidation and pH adjustment for the removal of thallium ions, the content of thallium dropped to at least 0.4 ppm. However, removal efficiency is

much lower than that using the present method. Moreover, if the starting aqueous solution has a small amount of thallium, for example, about 2 ppm, the prior methods do not work well. However, with the present method, even a small amount of thallium can be removed from the aqueous solution.

5 In some embodiments, the pH of the aqueous solution is at least 9, preferably at least 10, more preferably at least 11. The term “at least” denotes “equal to or higher than”.

In some embodiments, the process temperature is between 10 and 80°C, preferably between 40 and 80°C, still more preferably between 45 and 55°C, and most preferably about 50°C.

The method preferably further comprises one or more steps of recovering thallium from the chelating agent, especially from the aminophosphonic chelating resin or from the iminodiacetic chelating resin. In some embodiments, an acid is used in the recovery steps. Said method further comprises one or more steps of precipitating and isolating thallium from the acid. The recovery steps may comprise :

- 20 (a) treating the resin with water, an acid such as hydrochloric acid, water, a base such as sodium hydroxide, and then water again ;
- (b) adjusting the pH of a sludge recovered during said treatment with a base such as sodium hydroxide, sodium carbonate, and oxidized with an appropriate oxidant, such as sodium hypochlorite or peroxide ; and
- (c) filtering and washing the precipitate to recover thallium trihydroxide.

In some embodiments, the aminophosphonic or the iminodiacetic chelating resin is reused after removing adsorbed ingredients.

25 In some embodiments, the purified solution is subjected to one or more further processes, such as crystallization or electrolysis.

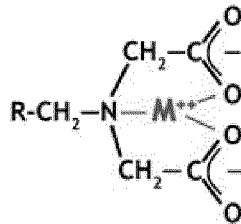
In the present specification, the plural form and the singular form are used interchangeably. Thus, it should be understood that the plural form also includes the singular form and vice-versa.

30 Some types of functional groups comprised in the resins usually used in the field are as follows :

- | | |
|------------------------|--|
| ● Thiol | -SH |
| ● Iminodiacetic acid | $-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ |
| ● Aminophosphonic acid | $-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{PO}_3\text{H}$ |
| ● N-Methylglucamine | $-\text{CH}_2\text{N}-(\text{CHOH})_4\text{CH}_2\text{OH}$ $\quad \quad \quad $ $\quad \quad \quad \text{CH}_3$ |
| ● N-bis-picolylamine | $-\text{CH}_2\text{N}(\text{CH}_2-\text{C}_5\text{H}_4\text{N})_2$ |

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Most of the resins above are of the chelating type. They are able to form complexes with one or more metals. For example, the following chemical formula shows the complex of an iminodiacetic functional group of a chelating resin with a metal.



10 The iminodiacetic groups of a chelating resin only make complexes with multivalent metals. These complexes are very stable. Therefore, these resins have high selectivity and are capable of removing metals from a solution selectively.

The residue, an aqueous extract solution of which is purified according to the process of the present invention, is obtained by, for example, treating by-products from metallurgical manufacture, preferably from steel manufacture, or by treating cement kiln dust from cement production. Cement kiln dust (CKD) is preferably a fine-grained, solid, highly alkali metal waste removed from cement kiln exhaust gas by air pollution control devices. Other residues from industrial processes of rice hull ashes, ashes of wood combustion plants, ashes of coal combustion plants, cement kiln residue, steel industry dust, or dust from iron sintering processes can be purified using the present process. A suitable treatment may comprise, for example, contacting the residue with an aqueous solution to provide a suspension of solids in a solution of water soluble impurities.

The method according to the invention makes it possible to remove impurities contained in a residue, especially thallium, resulting in a purified aqueous solution having high purity and a very low concentration of thallium. The residue may contain various impurities, including polyvalent metals, inorganic compounds, and/or organic compounds, as well as thallium. Said residue may contain impurities from 10000 ppm to 0.001 ppm, preferably from 100 ppm to 0.001 ppm, more preferably from 1 to 0.001 ppm by weight of the residue.

The concentration of thallium in undisturbed natural soil is 2.2 to 29 ppm (See Xiao, "Environmental impact of thallium related to the mercury-thallium-gold mineralization in southwest Guizhou Province, China," Chicoutimi,

Universit du Qu bec Chicoutimi, 2001). The thallium containing aqueous solution to be purified by the present invention has a concentration of thallium from 0.001 ppm to 100 ppm preferably from 0.1 ppm to 10 ppm, more preferably from 0.5 ppm to 2 ppm by weight of the total solution.

5 The preferred resin which can be used in the present invention can be any aminophosphonic-based or iminodiacetic-based resin. The appropriate resins, identified by tests by inventors, include, but are not limited to, LEWATIT[®] TP 260 or LEWATIT[®] TP208 (available from LANXESS SA), which are weakly acidic, macroporous cation exchange resins with chelating
10 respectively aminophosphonic or iminodiacetic groups. It comprises monodisperse beads mechanically and osmotically superior stable. More details can be found at *www.lanxess.com*.

Other suppliers than Lanxess offer the same type of resins like Dow Chemicals (Amberlite[®] IRC747 and Amberlite[®] IRC748), Mitsubishi
15 (Diaion[®] CR11), or Purolite Corp (Purolite[®] S940 and Purolite[®] S930).

According to the invention, the aqueous solution may be pre-treated with any one of known methods in this field. For example, the residue can be pre-treated with, but is not limited to, iron salts and carbonates, especially FeCl₂ and Na₂CO₃. This pre-treatment can decrease the other elements by precipitation,
20 filtration, and/or decantation.

In a preferred embodiment, the aqueous solution is pretreated. This preferred pretreatment serves to remove metal ions which might interfere with the method of the present invention to remove and, especially, to remove and recover thallium ions selectively, or which are undesired because they may
25 contaminate the recovered thallium which desiredly should be pure. Thus, especially alkaline earth metals and heavy metal cations, such as the ions of Cd are removed in a pretreatment step. This pretreatment step can be performed, for example, with an aminophosphonic acid resin. The pretreated aqueous solution then contains essentially only monovalent cations, e.g. potassium ions in the
30 form of potassium chloride, and thallium ions. The thallium ions are then selectively removed from the pretreated solution, especially by contacting the solution with aminophosphonic-based or, especially, with iminodiacetic-based resin.

It has also been observed that the present method works well when the pH
35 of the aqueous solution to be purified is at least 9, preferably at least 10, more preferably at least 11, and the process temperature is between 10 and 80°C,

preferably between 40 and 80°C, still more preferably between 45 and 55°C, and most preferably around 50°C.

The resin may be mixed with the aqueous solution in various ways, such as blending or stirring. After adsorption of thallium onto the resin, the adsorbed
5 thallium can be separated from the resin for recycling. Any separating means in the field can be used.

The used resin can be recycled by a method where the removed impurities, especially thallium from an aqueous solution from an industrial process, are isolated as follows : (a) regenerating the resin as recommended by the producer
10 (generally by countercurrent flow with water, an acid such as HCl, water, a base such as NaOH, and then water again, (b) adjusting the pH of the sludge recovered during the regeneration of the resin and oxidize the sludge with an appropriate oxidant, such as sodium hypochlorite or peroxide salt ; and (c)
15 filtrating and washing of the precipitate, which is thallium trihydroxide ($Tl(OH)_3$).

The present inventors have found that aminophosphonic resin can also be used in the previous treatment of the aqueous solution.

Most other metals can be removed from the aqueous solution. However, according to some tests performed by the present inventors, the recovery yield of
20 thallium is poorer when aminophosphonic resin is used. For example, in one experiment, 50 % of thallium present in the aqueous solution was retained on an aminophosphonic chelating resin. However, more than 75 % of thallium present in aqueous solution was retained on an iminodiacetic chelating resin.

When the solution after a first treatment is treated in a second step with an
25 aminophosphonic or an iminodiacetic chelating resin, thallium is captured on the chelating resin, and the content of thallium in solution falls to 2 ppm or less, preferably 0.1 ppm or less, more preferably 0.02 ppm or less.

The method of the invention allows for the removal especially of thallium from an aqueous solution from an industrial process, in particular, obtained from
30 rice hull ashes, ashes of wood combustion plants, ashes of coal combustion plants, cement kiln residue, steel industry dust, or dust from iron sintering processes. It is principally possible to remove and recover the thallium content of any residue where the removal of thallium is desirable. For example, earth contaminated with thallium or fertilizer (mainly potassium chloride) which
35 contains an undesired amount of thallium salt can be treated : first, the residue (earth or fertilizer) is extracted with water to obtain an aqueous solution

containing thallium, and then, the method of the invention is performed. Thus, a residue containing even low amounts of thallium, e.g. less than 30 ppm, and even less than 2 ppm, can be treated efficiently. The thallium content removed can be recovered in the form of a very pure thallium salt which is a further advantage.

- 5 The purified aqueous solution can be further treated to recover the remaining contents of other salts present, for example, to recover potassium chloride with an extremely low content of thallium.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present
10 description shall take precedence.

Example 1 : Equilibrium with chelating resins

Trial A : 1080 g of initial solution in contact with 180 mL of resin Lewatit TP208 stirred during 1 h in a reactor at 50°C.

- 15 Trial B : 186.5g of initial solution in contact with 40 mL of resin Duolite GT73 stirred during 50 min in a reactor at 50°C.

		Initial	Trial A Iminodiacetic Lewatit TP208	Trial B Thiol Duolite GT74
NaCl	g/kg	111		
KCl	g/kg	165.5		
Na ₂ SO ₄	g/kg	2.7		
Ba	mg/kg	0.08	<0.04	0.08
Ca	mg/kg	3.5	1.5	3.5
Sr	mg/kg	0.28	<0.04	0.28
Tl	mg/kg	1.8	0.46	1.5

The amount of thallium remaining in the solution is 0.46 mg/kg for iminodiacetic-based resin, which is much less than 1.5 mg/kg for the thiol-based resin.

- 20 *Example 2 : Equilibrium with chelating resins*

Trial C : 244g of initial solution in contact with 40 mL of resin Lewatit TP208 stirred during 60 min in a reactor at 50°C.

Trial D : 244g of initial solution in contact with 40 mL of resin Amberset GT74 stirred during 60 min in a reactor at 50°C.

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		Initial	Trial C Iminodiacetic Lewatit TP208	Trial D Thiol Duolite GT74
NaCl	g/kg	106.6		
KCl	g/kg	155.3		
Na ₂ SO ₄	g/kg	2.7		
pH		11.3	9.96	1.77
Redox	mV	191		
Ba	mg/kg	0.33	<0.04	0.33
Ca	mg/kg	2.8	0.55	2.8
Sr	mg/kg	2	<0.04	2
Tl	mg/kg	1.7	0.46	1.2

The amount of thallium remaining in the solution is 0.46 mg/kg for iminodiacetic-based resin, which is much less than 1.2 mg/kg for the thiol-based resin.

Example 3 : Influence of oxidation and pH

- 5 Trial E : 3.49 g of NaOH solution of concentration 1 N.
1.04 g of NaOCl solution of concentration 0.203 N
61.9 g of initial solution

		Initial	Filtered solution
NaCl	g/kg	106.6	
KCl	g/kg	155.3	
Na ₂ SO ₄	g/kg	2.7	
pH		11.3	11.97
Redox	mV	191	640
Tl	mg/kg	1.7	0.19

- 10 By oxidation and pH adjustment of the initial solution, thallium can efficiently be removed from the solution and a precipitate of thallium hydroxide can be recovered.

Example 4 : Efficiency of a purification in column

Column diameter : 25 mm

Height of resin bed : 0.8 m

Sample was taken after 1 h flow.

		Initial	Trial F Iminodiacetic Lewatit TP208	Trial G Iminodiacetic Lewatit TP208	Trial H Aminophosphonic Lewatit TP260
NaCl	g/kg	106.6			
KCl	g/kg	155.3			
Na ₂ SO ₄	g/kg	2.7			
Flow rate	L/h		2	16	16
Temp	°C		50	20	20
Tl	mg/kg	1.7	0.04	0.2	0.36

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The work with continuous flow in a column gives better results than the equilibrium obtained in batch. A slow flow rate can enhance the removal yield of thallium from an aqueous solution. The thallium remaining in the solution is lower when using the imininodiacetic resin than the aminophosphonic resin.

5 *Example 5 : Purification in a pilot plant column*

Column diameter : 100 mm

Height of resin bed : 2.4 m

Sample was taken after 6 h flow.

		Initial	Trial G Iminodiacetic Lewatit TP208
NaCl	g/kg	95.8	95.8
KCl	g/kg	155.3	153.3
Na ₂ SO ₄	g/kg	4.3	4.3
Flow rate	L/h		94
Temp	°C		20
Tl	mg/kg	0.41	<0.02

C L A I M S

1. A method of removing impurities, especially thallium from an aqueous solution from an industrial process, using a chelating agent capable of complexing thallium ions to obtain a purified aqueous solution.
- 5 2. The method of claim 1 wherein the chelating agent is an aminophosphonic or an iminodiacetic chelating resin.
3. The method according to Claim 1 or 2, characterized in that one or more other ingredients selected from the group consisting of alkali metals, alkali earth metals, and other heavy metals, as well as thallium, are removed from the
10 aqueous solution.
4. The method according to Claim 1, 2 or 3, wherein said method further comprises one or more steps of removing one or more other ingredients before the removal of the thallium.
5. The method according to anyone of Claims 1 to 4, wherein the
15 aqueous solution is subjected to a pre-treatment, one or more times, to remove one or more other ingredients.
6. The method of anyone of Claims 1 to 5 where the resin is an iminodiacetic chelating resin.
7. The method according to anyone of Claims 1 to 6, wherein the
20 aqueous solution contains 2 ppm or less of thallium and 30 weight % or more of other ingredients based on the total weight of the aqueous solution.
8. The method according to Claim 1, characterized in that monovalent thallium ions are removed from the aqueous solution along with trivalent thallium ions.
- 25 9. The method according to anyone of Claims 1 to 8, characterized in that the resulting purified aqueous solution contains 2 ppm or less, preferably 0.1 ppm or less, more preferably 0.02 ppm or less thallium ions.
10. The method according to Claim 1, characterized in that the pH of the aqueous solution is at least 9, preferably at least 10, more preferably at least 11.

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11. The method according to Claim 1, characterized in that process temperature is between 10 and 80, preferably between 40 and 80, more preferably about 50°C.

5 12. The method according to Claim 1, wherein said method further comprises one or more steps of recovering thallium from the chelating agent, especially from the aminophosphonic or the iminodiacetic chelating resin.

13. The method of Claim 12, wherein an acid is used in the recovery steps.

14. The method of Claim 13, wherein said method further comprises one or more steps of precipitating and isolating thallium from the acid.

10 15. The method according to Claim 12, wherein the recovery steps comprise :

(a) treating the resin with water, an acid such as hydrochloric acid, water, a base such as sodium hydroxide, and then water again ;

15 (b) adjusting the pH of the sludge recovered during said treatment with a base such as sodium hydroxide, sodium carbonate, and oxidized with an appropriate oxidant, such as sodium hypochlorite or peroxide ; and

(c) filtering and washing the precipitate to recover thallium trihydroxide.

20 16. The method according to anyone of Claims 1 to 15, wherein the aminophosphonic or the iminodiacetic chelating resin is reused after removing adsorbed ingredients.

17. The method according to anyone of Claims 1 to 16, wherein the purified aqueous solution is subjected to one or more further processes, such as crystallization or electrolysis.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/057079

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B61/00 C22B3/24
ADD.

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)
C22B

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 practicable, search terms used)

EPO-Internal, COMPENDEX, 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 A	EP 0 224 209 A2 (SUMITOMO CHEMICAL CO [JP]) 3 June 1987 (1987-06-03) page 4, line 49 - line 50; example 16; table 3	1-5,7-9, 11-15,17 6,16
X	----- JP 56 069226 A (KOGYO GIJUTSUIN) 10 June 1981 (1981-06-10) Patent Abstracts of Japan ----- -/--	1-16



Further documents are listed in the continuation of Box C.



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

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

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