International Application Published under the Patent Cooperation Treaty (PCT)

International Publication Number
WO 2005/018781 A1

International Patent Classification
B01D 53/54, 53/50, 53/52, A62D 3/00

International Application Number
PCT/GB2004/003606

International Filing Date
23 August 2004 (23.08.2004)

Filing Language
English

Publication Language
English

Priority Data
0319886.8 23 August 2003 (23.08.2003) GB

Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; DSTL, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB).

Inventors/Applicants (for US only): CHINN, Matthew, Joseph [GB/GB]; DSTL, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB); WARD, Jessica, Lucy [GB/GB]; DSTL, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB); JACKSON, Dominic, Bairstow [GB/GB]; University of Reading, Whiteknights RG6 6AD (GB).

Agent: BECKHAM, Robert, William; D/TPR Formalities Section, Poplar 2, MOD Abbey Wood#2218, Bristol BS34 8JH (GB).


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, IT, LU, 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.

Title: MATERIAL AND ITS USE FOR TOXIC VAPOUR REMOVAL

Abstract: A material suitable for the adsorption and decomposition of toxic vapours, comprising a highly-ordered silica and an oxidising agent. The material is efficient in adsorbing and oxidising toxic vapours and is suitable for use in a filtration device. Methods of preparing the material and methods of using them are also described and claimed.
MATERIAL AND ITS USE FOR TOXIC VAPOUR REMOVAL

This invention relates to a new material suitable for the adsorption and/or decomposition of toxic vapours, to a method for the preparation of said material and to its use for the removal of toxic vapours from an atmosphere.

Vapour filtration systems find widespread use in areas such as the chemical and mining industries, where the filtration system can be incorporated as part of a large production plant. They can also be used for environmental monitoring and/or remediation where the filter may be incorporated into a waste gas stream. They may also be found in defence applications, where the filtration system is likely to be part of a small personal protection device, such as a respirator fitted with filtration canister.

Currently, many filtration devices contain activated carbon or charcoal. These carbon-based materials are useful for adsorbing toxic gases and vapours, such as hydrogen sulphide or hydrogen cyanide, and removing them from atmospheres and airflows. In order to enhance the adsorption and decomposition of volatile species the carbon is often impregnated with reactive species. The overall activity of these types of filtration devices is attributed to a combination of two factors. Firstly, the carbon provides a very large surface area for efficient adsorption of gases and vapours and secondly, the impregnants are chemically reactive such that they improve chemisorption and/or decomposition of the adsorbed species.
An example of such a filtration device is the military vapour filtration adsorbent. This adsorbent comprises activated carbon that is impregnated with triethylenediamine, to enhance the adsorption and decomposition of cyanogen chloride and with copper and chromium salts to enhance the adsorption and decomposition of hydrogen cyanide. Herein, the decomposition of HCN by the copper salt results in the formation of the toxic by-product, cyanogen, which is in turn decomposed by the chromium salt.

However there are several known problems associated with this type of carbon-based filtration device. For example, they can suffer deactivation from prolonged exposure to humid air, which can limit filter performance. There are also particular health and safety concerns over the use of chromium-based oxidising agents, because Cr(VI) is a known carcinogen and its use is becoming increasingly restricted. In addition, there are environmental considerations for the disposal of the chromium-containing filters after use.

There is a requirement to improve upon these carbon-based materials and to identify improved materials that are able to overcome the above problems. Such replacements should be equally, if not more, stable to humid environments than the carbon filters. Such materials will ideally use less or no toxic oxidising agents. They should also have fewer or no environmental considerations associated with their use and/or disposal. Any new material should have at least similar or improved adsorbent properties to the carbon-based materials. It is also desirable to find such a material that can adsorb and decompose toxic vapours without the production of toxic by-products.
Previously reported work has investigated alternatives to carbon-based materials. One example is an oxidiser gel, comprising silica or alumina and peroxydisulphate anions, for the detoxification of chemical agents (US6455751). However, these materials are unsuitable for use in filtration systems since, in order to achieve the required result, it is necessary to apply the gel directly to the chemical agents. In addition, the types of silica and alumina used are less efficient adsorbers than activated carbon because they have much lower surface areas. Other work describes the synthesis and use of a silica with a high surface area (Elings JA, Ait-Meddour R, Clark JH, Macquarrie DJ, *Chem. Commun.* 24 (1998) 2707-2708). This silica is used as a liquid phase catalyst, where the high surface area of the silica provides a reaction site for an epoxidation reaction. However, although this provides a useful development in the field of catalysis, it relies on the immersion of the catalyst in a reaction mixture and is not applicable to the vapour phase. Therefore, the needs remains to develop an alternative material that is suitable for use in a vapour phase filtration system.

There is also an opportunity to develop alternative oxidising agents for use in vapour filters. It is generally known that alternatives to chromium and other transition metal containing oxidising agents can be found within the peroxo family of compounds. These include the persulphates, perborates, permanganates and percacarboxylates. Of these compounds, the persulphates are some of the strongest oxidants known in aqueous solution. In particular, the peroxydisulphate anion \( \text{S}_2\text{O}_8^{2-} \) has a redox potential that is comparable to that of Cr(VI) but without the associated health and environmental hazards. As a result, the use of peroxydisulphate compounds for oxidation of several organic and inorganic species has been documented. For example, EP0614690 describes a method of
treating incinerator waste gas, which comprises feeding solid ammonium persulphate directly into the incinerator to reduce or remove dioxin, heavy metals and NO\textsubscript{x} from the waste gas; US6019548 describes the use of an aqueous solution of sodium persulphate to oxidise volatile organic species in soil; US4747728 describes the use of persulphate and perborate anions in solution to purify clay samples; and US3725530 describes the use of a dilute acid solution containing persulphate ions to remove mercury vapour from electrolytic cells. These examples highlight the effectiveness of peroxyo compounds in redox reactions and they provide useful developments in the field of purification. However there remains a problem of developing a new material suitable for the adsorption and decomposition of toxic chemicals in the vapour phase that comprises a non-toxic oxidising agent.

Therefore, the need remains to develop a material for use in a filtration system, which has a high surface area, so that it is capable of efficient gas-phase adsorption and which is stable to water and other solvent exposure. In order to enhance the decomposition of adsorbed vapours, this material should contain an oxidising agent or agents, such that the vapours are decomposed with little or no production of toxic by-products. The oxidising agent itself should not be carcinogenic or damaging to the environment. Ideally, such a material with these improved properties would be suitable for use in a filtration system, including a respirator to provide personal protection from toxic vapours.

According to this invention, a new material has been developed which addresses the needs outlined above. The material comprises a highly-ordered silica, which is impregnated with an oxidising agent. The oxidising agent will preferably be one which has one or more of
the following features: it has a high redox potential; is readily soluble and stable in aqueous or organic solution and is easily impregnated into the silica. Preferably, the oxidising agent is evenly distributed throughout the material to maximise the reactivity of the surface. The material should be sufficiently porous to allow the rapid diffusion of vapours into the material; it has been demonstrated that vapours are easily adsorbed on to the material and are retained within the pores long enough for complete reaction with the oxidising agent.

This material has several advantages over those described in the prior art. It is at least as stable to moisture as the carbon-based materials. The material does not contain toxic chromium salts and does produce toxic by-products. As a result, the material does not suffer from the environmental problems associated with the use of chromium species. Finally, it is at least, if not more, efficient in removing toxic vapours than carbon-based materials.

It is an object of this invention to provide a new material, suitable for use in a vapour filtration system, which is efficient in the adsorption, oxidation and/or decomposition of toxic materials in the vapour phase. It is another object of this invention to provide a replacement for carbon-based adsorbents which exhibit, at least similar or better stability to moisture. It is a further object of this invention to provide a filtration material that does not rely on the use of toxic oxidising agents. It is also an object of this invention that the material has little or no environmental considerations associated with its formulation, preparation, use or disposal. It is an additional object of this invention to develop a device
suitable for the filtration of toxic vapours. These, and other objects of this invention, will become apparent in light of the following disclosure.

Summary of the Invention

According to a first aspect, this invention relates to a material, suitable for the removal of toxic vapours, comprising a highly-ordered silica and an oxidising agent.

According to a second aspect this invention relates to a method for the preparation of such a material.

According to a third aspect this invention relates to use of the material according to the present invention for the adsorption and decomposition of vapours from toxic substances.

According to a fourth aspect this invention relates to a filter device comprising a material according to the invention.

According to a fifth aspect this invention relates to a breathing apparatus which comprises such a filter device.

Detailed Description of the Invention

All publications cited herein are hereby incorporated by reference in their entirety, unless otherwise indicated.
The elements of the invention are described in more detail below. Examples of a specific embodiment of the invention are provided and the efficiency of the material in the adsorption of a toxic gas is shown by means of a figure.

This invention relates to a material suitable for the adsorption and decomposition of toxic vapours, comprising a highly-ordered silica and an oxidising agent.

As used herein the term highly-ordered shall be taken to mean a material with pores that are structured in a cubic and/or hexagonal arrangement.

As described above, the highly-ordered silica is porous. It is preferred that the silica has pores with an average diameter, as calculated from the nitrogen desorption isotherm according to the Barrett-Joyner-Halenda (BJH) procedure, in the range from about 0.1 to about 100 nm. It is more preferred that the silica has an average pore diameter in the range of from about 2 nm to about 50 nm, which is commonly termed “mesoporous”. It is even more preferred that the average pore diameter is in the range of from about 2 nm to about 9 nm.

The highly-ordered silica has a very high surface area such that large volumes of toxic vapour can be adsorbed and decomposed on the surface. It is preferred that the surface area, as measured by the Brunauer-Emmett-Teller (BET) model, is at least about 800 m²g⁻¹ but it is more preferred that the surface area is greater than about 1000 m²g⁻¹. The highly-ordered silica optionally has surface properties that may be chemically modified to change or optimise the performance of the material, for example, chemical derivatisation of the
surface may increase the hydrophobicity, which reduces water content and improves the activity of the material. Examples of the preferred silica include, but are not limited to, those materials known by those skilled in the art as MCM-48 (as described in US5198203), MCM-41 and SBA-15 (as described in J. Am. Chem. Soc., 120 (1998) 6024 –6036), each of which may be synthesised from any commercially-available silica to give the required pore size and surface area.

As used herein the term oxidising agent shall be taken to mean any chemical species, which brings about oxidation of any other species and is itself reduced.

The oxidising agent can be chosen depending on the intended use of the material, by one skilled in the art. It is preferred that the oxidising agent is sufficiently reactive to oxidise and decompose toxic vapours that are adsorbed on the material. It is also preferred that the oxidising agent has a standard reduction potential (in aqueous solution at 25°C) of at least about +0.15V, more preferably of at least about +1.33V and even more preferably of at least about +2.01V. The oxidising agent may be in any form at room temperature and pressure, but it is preferred that it is a solid or a liquid which is soluble in aqueous solvent, organic solvent or mixtures thereof so that it can be readily processed with the silica. It is also preferred that the concentration of the oxidising agent in solution is at least about 0.000125 mol dm$^{-3}$ and more preferably at least about 0.00125 mol dm$^{-3}$.

For example, in the case of HCN removal, the preferred type of oxidising agent is a peroxo compound, or other carbonyl oxide. Suitable peroxo compounds include but are not limited to peroxides, persulphates, peroxydisulphates, perborates, perchromates, percarboxylates,
permanaganates, peroxy acids and salts thereof and mixtures thereof. The oxidising agent
is preferably a salt of a peroxydisulphate, wherein the salt cation is selected from the group
consisting of sodium, potassium, ammonia and mixtures thereof.

As used herein the term impregnated shall be taken to mean that one material is added to
another such that the surface of one material is coated, either partially or fully, with the
other.

It is preferred that the silica is impregnated with the oxidising agent, such that the pores of
the material contain a high concentration of, or are saturated with, the oxidising agent. The
concentration of the oxidising agent should be such that adsorbed toxic vapours are
oxidised. It is preferred that complete oxidation of the toxic vapours occurs, but it may be
suitable in some cases, for example when the material is used in a filter device, that partial
or incomplete oxidation is sufficient, such that the quantity or volume of toxic vapours is
reduced. The weight ratio of oxidising agent to silica should be high enough to ensure that
the material is active. It is preferred that the ratio is in the range of from about 1:10 to
about 1:100, more preferably in the range from about 1:20 to about 1:75 and even more
preferably in the range from about 1:30 to about 1:40.

This invention also relates to a method of preparing such a material. The method comprises
the highly-ordered silica is stirred with a solution of the oxidising agent, and the solvent
then removed. Before stirring with the oxidising agent, the highly-ordered silica should be
prepared by mixing together suitable quantities of an alkylated silica and one or more long
chain surfactants. Several different types of silica are suitable but it is preferred to use one
of the lower tetraalkoxysilanes, such as tetramethoxysilane and/or tetraethoxysilanes. There are several types of surfactant that are suitable for the preparation of the highly-ordered silica. The actual surfactant used can be readily determined by one skilled in the art by taking account of certain factors such as the required pore size and arrangement. Suitable surfactants include but are not limited to alkylammonium salts with a variety of chain lengths, dimeric surfactant molecules, gemini surfactants, and polyethylene oxides and glycols. The preferred surfactant is cetyltrimethylammonium bromide. The preferred method of preparation is to use the modified Stöber method, as described in Microporous Mesoporous Materials, Volume 27 (1999) by Schumacher, K, Grun, M., and Unger, K.K.

After preparation, it is preferred that the surfactant is removed from the highly-ordered silica. The surfactant may be removed by washing with aqueous or organic solvent or by heating. The preferred method of removing the surfactant is to heat the silica to high temperatures, preferably to about 650 °C.

The highly-ordered silica is then impregnated with the oxidising agent by mixing them together in suitable quantities. It is preferred that they are mixed by adding the silica to a solution of the oxidising agent. The solvent for the oxidising agent can be any one that partially or completely dissolves the oxidising agent, as determined by one skilled in the art. The solvent may be aqueous or may be a polar organic liquid. If organic solvents are used, it may be necessary to use solubilising agents, such as crown ethers, to aid or improve solvation of the oxidising agent. Examples of suitable solvents include but are not limited to water, methanol, dimethyl sulphoxide, dimethyl formamide, acetonitrile, acetic acid, phenol, acetone, pyridine, ethanol and nitrobenzene. The preferred solvent is water. The mixing of the silica and oxidising agent may be achieved by stirring, agitation or other
suitable method readily determined by one skilled in the art. The mixing may be carried out at elevated temperatures and/or reduced pressures, but it is preferred that mixing is carried out at room temperature and pressure. The mixing should occur for a time suitable to allow for impregnation of the oxidising agent into the silica. The preferred mixing time is between about 60 and 120 minutes. After such time, the solvent should be removed to yield the material. The solvent can be removed by evaporation or filtration but the preferred method is evaporation.

This invention also relates to the use of the material for the adsorption and decomposition of toxic vapours. The material is suitable for the adsorption and decomposition of any toxic vapour that is susceptible to oxidation. Such vapours include, but are not restricted to, hydrogen cyanide, cyanogen chloride, hydrogen sulphide and sulphur dioxide. The material may be used in any environment that contains, or is thought to contain, toxic vapours. Such environments include, but are not restricted to, chemical production plants, waste gas treatment facilities and other breathable environments, such as the battlefield where personal protection is required.

This invention also relates to a filter device comprising the material. The device is suitable for the filtration of toxic vapours from gaseous environments. The physical size and shape of the device will take one of many forms, dictated by the situation in which it will be used. For example, a filtration device for use in an exhaust or waste gas pipe of a large scale production plant will need to be of suitable thickness and diameter to fit within the pipe so that all the gas that passes through the pipe are subjected to filtration through the
device. The required form of the device can readily be determined by one skilled in the art.

Optionally, in another embodiment of the invention, the filter device may additionally comprise an indicator material which will provide a visual response when toxic vapours are adsorbed by the filter and/or when the filter material is used up. Examples of suitable indicators include any standard indicator that is compatible with silica, or it may be formulated specifically for this material by one skilled in the art. The indicator may be incorporated into the material but is preferred that the filter comprises an additional layer of indicator. This has the advantage that it provides the user with a visual reference as to the status of the device, for example when the material is used up, without relying on scientific ability or instrumentation.

The present invention also relates to a breathing apparatus that comprises a filter device as described above. The breathing apparatus contains the device in a suitable form, such that it filters the air that is inhaled by the wearer. The breathing apparatus may take the form of a respirator which has the filter device situated over the mouth of the wearer, or it may be a commercially available or military respirator that is modified to contain the filter device. This embodiment of the invention provides personal protection from toxic vapours.

Examples

The following examples further illustrate the preferred embodiment within the scope of the present invention. The examples are given solely for the purpose of illustration and are not
be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit or scope.

Example 1

The highly-ordered silica was prepared by the modified Stöber method as reported by Schumacher, K et al in Microporous Mesoporous Materials, Volume 27 (1999). Cetyltrimethylammonium bromide was used as the templating surfactant. The silica was calcined at 650 °C in order to remove the surfactant. 1 g of the silica was then stirred in 100 mL of an aqueous solution of sodium peroxydisulphate, at a concentration of 0.00125 mol dm$^{-3}$ for 120 minutes. The water was removed by evaporation to yield the dry material.

Example 2

The material, prepared according to Example 1, was tested for efficiency in the removal of hydrogen cyanide from a flow of air. 0.15 g of the material was placed in a vessel through which a controlled air flow could be passed. The material was challenged with toxic vapour at 8000 mg m$^{-3}$ at a flow rate of 50 mL min$^{-1}$ and at 22 °C and 80 % relative humidity. The time elapsed until hydrogen cyanide was detected in the air that had passed through the filter was recorded by mass spectrometry. Samples of the air were collected from the flow after it had passed through the test materials every 60 seconds.
Example 3

The test described in Example 2 was repeated with a standard activated carbon-based material, which comprises approximately 7% copper(II), 3% chromium(VI), 0.03% silver(I) and 2% triethylenediamine.

The response of the two types of material when challenged with toxic vapour are compared in Figure 1.

Figure 1 shows the response of two materials, A and B, when challenged with hydrogen cyanide vapour, exactly as described in Example 2. A represents the reference activated carbon-based formulation as described in Example 3. B represents the highly-ordered silica impregnated with sodium persulphate, which was prepared as per Example 1.

The y-axis of the graph in Figure 1 represents the time, in minutes, until toxic vapour was detected in the air that had been passed through the materials. This is defined as breakthrough time. In the figure, the bars labelled A1 and B1 represent the breakthrough time for hydrogen cyanide, as measured for materials A and B respectively, and the bars labelled A2 and B2 represent the breakthrough time for cyanogen as measured for materials A and B, respectively. With reference to the Figure, material A suffered breakthrough of hydrogen cyanide vapour after approximately 24 minutes (bar A1) and suffered breakthrough of cyanogen vapour after 22 minutes. Material B did not suffer breakthrough of hydrogen cyanide vapour until 28 minutes had passed and did not show breakthrough of cyanogen vapour at any time during the course of the experiment. This indicates that the material of the invention provides equivalent, if not longer, protection
from hydrogen cyanide vapour than a standard carbon formulation and also decomposes the toxic vapour by a route that does not involve the formation of the toxic by-product cyanogen.
Claims

1. A material suitable for the adsorption and decomposition of toxic vapours, comprising a highly-ordered silica and an oxidising agent.

2. A material according to Claim 1, wherein the highly ordered silica has an average pore diameter, as measured by the BJH method, in the range of from about 0.1 to 100 nm.

3. A material according to Claim 2, wherein the average pore diameter is in the range of from about 2 to about 9 nm.

4. A material according to any of Claims 1 to 3, wherein the highly-ordered silica has a surface area, as measured by the BET method, of at least 800 m² g⁻¹.

5. A material according to Claim 4 wherein the surface area is greater than 1000 m² g⁻¹.

6. A material according to any of Claims 1 to 5, wherein the oxidising agent is a peroxydisulphate salt

7. A material, according to Claim 6 wherein the salt cation is selected from the group consisting of sodium, potassium, ammonia and mixtures thereof.

8. A material according to any of Claims 1 to 7 wherein the weight ratio of oxidising agent to silica is in the range of from about 1:10 to about 1:100.
9. A material according to Claim 8 wherein the weight ratio is in the range of from about 1:30 to 1:40.

10. A method of preparing a material, according to Claim 1, wherein the highly-ordered silica is stirred with a solution of an oxidising agent and the solvent removed.

11. Use of the material according to Claim 1 for the adsorption and decomposition of toxic vapours.

12. Use of the material according to Claim 11 where the vapour is oxidisable such as hydrogen cyanide, cyanogen chloride, sulphur dioxide, hydrogen sulphide or mixtures thereof.

13. A filter device comprising a material according to Claim 1.

14. A filter device according to Claim 13, which comprises an indicator material.

15. A breathing apparatus which comprises a filter device according to Claim 13.
Figure 1
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
<thead>
<tr>
<th>IPC</th>
<th>B01D53/54</th>
<th>B01D53/50</th>
<th>B01D53/52</th>
<th>A62D3/00</th>
</tr>
</thead>
</table>

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)

<table>
<thead>
<tr>
<th>IPC</th>
<th>B01D</th>
<th>A62D</th>
</tr>
</thead>
</table>

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, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 4 786 483 A (AUDEH COSTANDI A) 22 November 1988 (1988-11-22) column 1, line 47 - column 2, line 38; claims 1-26</td>
<td>1-15</td>
</tr>
<tr>
<td>X</td>
<td>US 4 070 300 A (MORONI ROLF ET AL) 24 January 1978 (1978-01-24) column 3, line 17 - line 60 column 11, line 22 - column 12, line 2; claims</td>
<td>1,6-15</td>
</tr>
<tr>
<td>X</td>
<td>US 3 873 674 A (ROSENTHAL RUDOLPH ET AL) 25 March 1975 (1975-03-25) column 3, line 42 - line 60; claims 1-5; examples I,III</td>
<td>1,8,9, 11-15</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

Patient 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 prior claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
* Of* 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  
* B* document member of the same patent family

Date of the actual completion of the international search: 24 November 2004  
Date of mailing of the International Search report: 02/12/2004

Name and mailing address of the ISA:  
European Patent Office, P.B. 5816 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel: (+31-70) 340-2640, Tx: 31 651 epo nl,  
Fax: (+31-70) 340-3018

Authorized officer:  
Eijkenboom, A
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>DE 37 17 848 A (RWK RHEIN WESTFAEL KALKWERKE) 8 December 1988 (1988-12-08) column 3, line 26 - line 28; claims 1,8</td>
<td>1,10-15</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 4786483 A</td>
<td>22-11-1988</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 2422574 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE 815788 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR 2232353 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 1473701 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IT 1013833 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 50032089 A</td>
</tr>
<tr>
<td>US 3873674 A</td>
<td>25-03-1975</td>
<td>NONE</td>
</tr>
<tr>
<td>DE 3717848 A</td>
<td>08-12-1988</td>
<td>DE 3717848 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE 1001406 A5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR 2615755 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LU 87213 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL 8801172 A,B</td>
</tr>
</tbody>
</table>