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(56) Documents Cited
**GB 2302824 A EP 0638351 A2 WO 96/23726 A1
WO 91/04096 A1 US 5464598 A US 5314852 A
US 5252528 A US 4999175 A
Japio Abstract No. 03835642 & JP 040200742 A**

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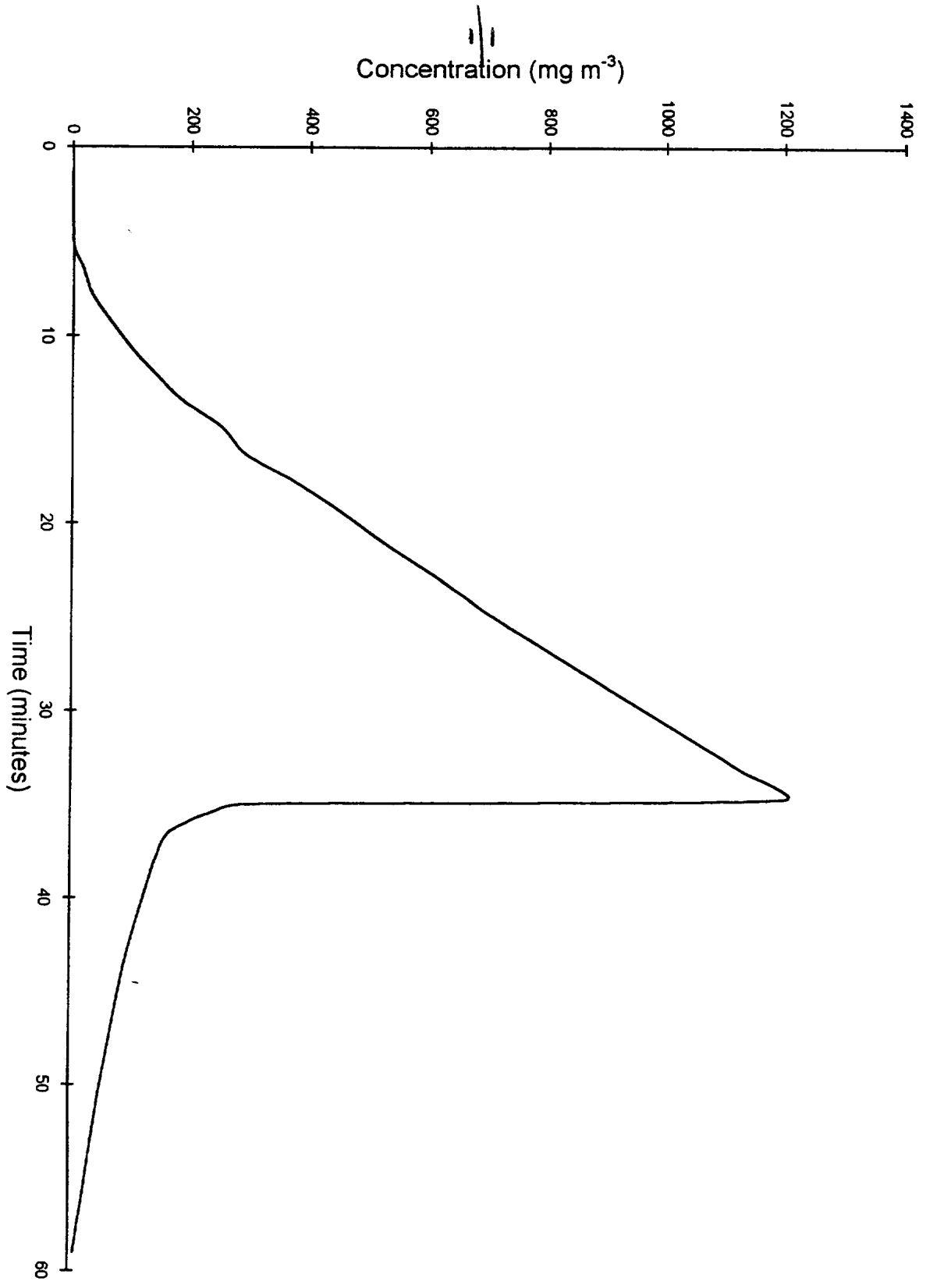
Adsorbent zeolite composition

(57) Adsorbent compositions comprise a zeolite impregnated with a compound which reacts with and/or sequesters a volatile gas or vapour. The compositions are useful in filters of breathing apparatus or in situations where toxic volatile gases or vapours such as toxic perfluorocarbons or methyl iodide are likely to be encountered. Suitable impregnant compounds include organic amines, in particular piperazine or triethylenediamine. The zeolites used are suitably either microporous or mesoporous granules.

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Figure 1

Breakthrough Profile of Cyanogen chloride through PRSV/PPZ (5%)



Adsorbent Materials

The invention relates to adsorbent materials for volatile gases and in particular for toxic toxic gases and vapours.

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The removal of toxic vapours from contaminated airstreams can be achieved by the use of a suitable adsorbent. Often that adsorbent is activated carbon. This is due to its high surface area and wide pore size distribution, enabling the sorption of a wide range of gaseous molecules. However the use of activated carbon is not without certain disadvantages. The tendency for the surface of activated carbon to chemisorb oxygen upon exposure to humid air has been reported (R. Burstein and A. Frumkin, Physik.Chem., (Leipzig), A141, (1929)219). As a result of this, these filters show a decrease in adsorption capacity in the presence of high humidity and a degradation of filter performance if the filter is exposed to air at high humidities for extended periods of time. Furthermore, they have a low adsorption capacity for highly volatile gases and liquids.

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The latter deficiency is often overcome by the use of impregnants which allow for the chemisorption of highly volatile gases. The use of piperazine as an impregnant on activated carbon for the removal of toxic vapours was identified previously (U.S. Pat. No. 4,531,955) and other organic amine impregnants are described in EP-A-629437.

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However, in such systems the interaction of the carbon with the impregnant can cause deleterious effects. It has also been shown that impregnants decompose on the carbon surface (Brown P.N, Jayson G.G and Wilkinson M.C. Carbon, 27, (1989),821). Both these factors affect the filter performance of the adsorbent. The stability of piperazine on activated carbon has been studied by the applicants. It has been observed that piperazine decomposes slowly on the surface of activated carbon to liberate ammonia which desorbs readily. The propensity for BPL impregnated with piperazine (BPL/PPZ) to liberate ammonia prevents the use of this impregnated carbon if inhalation of the effluent air intended. The degradation of piperazine also causes problems associated with long term storage of filters containing BPL/PPZ this has been shown to be critical even in dry storage conditions.

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This invention relates to the discovery of an alternative to carbon for use as an impregnant support, which has improved performance against certain vapours.

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The present invention provides an adsorbent composition, said composition comprising a zeolite which has been impregnated with a

compound which reacts with and/or sequesters said volatile gas or vapour.

5 These compositions have been found to be very effective absorbents. They are not to the same degree of subject to deterioration or decrease in performance in humid conditions as activated carbon, neither does decomposition of impregnants such as piperazine occur.

10 The compositions are useful as filters, for example in breathing apparatus where they can be used to remove unwanted or harmful gases.

15 Suitable compounds for use as impregnants are organic amines which react with toxic vapours such as toxic perfluorocarbons or alkyl halides such as methyl iodide. Particular amines include secondary and tertiary alkyl amines such as piperazine or triethylenediamine (TEDA). Transition metal salts are also suitable impregnants, although these have been shown to be unstable on activated carbon.

20 Zeolites are readily available materials, used as molecular sieves and catalysts in various industries. They comprise a porous structure made up of aluminium silicates of various aluminium to silicon ratios.

25 Suitably, the zeolite used in the composition of the invention has a pore size which is sufficiently large to accommodate the impregnant molecule but small enough to ensure that the impregnant is stably incorporated in the pore structure and presents a large surface area for reaction. For most purposes therefore, it is preferred that zeolites which are microporous (pore size 0-20Å diameter) or
30 mesoporous (pore size 20-50Å diameter) in nature are used. This means that the average diameter of the pore sizes may be in the range of from 3-50Å, suitably from 4-10Å, and most preferably from 5-7Å.

35 The amount of impregnant incorporated into the zeolite support varies depending upon factors such as the precise constitution of the zeolite, the nature of the impregnant and the purpose for which the composition is to be used. However, in general, compositions of the invention comprise up to about 15%w/w impregnant.

40 The impregnant may be applied to the zeolite support material using sublimation methods as illustrated hereinafter. In this method, the impregnant is incubated with the impregnant under conditions whereby the impregnant will sublime. The absorbent nature of the zeolite means that after a sufficient period, the impregnant becomes adsorbed
45 into the zeolite.

Alternatively, a solution of the impregnant may be sprayed directly onto the zeolite using conventional spray apparatus, for example in a fluidised bed. After this, solvent is driven off, for instance by heating. The solvent used may be any organic or inorganic solvent in which the impregnant is soluble but which is more volatile than the impregnant. A preferred solvent is water.

Compositions of the invention may be used in filters, for example for use in breathing apparatus. Such filters may be utilised in any situation where there is a risk of either deliberate or accidental exposure to toxic vapour. For example, they may be used to protect solidiers or civilians against the effects of chemical warfare agents, or industrial workers, for example in the chemical or nuclear industries, where there may be a risk of accidental leakage of toxic or radioactive materials.

The physical form of the compositions of the invention will vary depending upon the requirements of the end product in which they will be used. For many filter applications, the composition is in the form of relatively uniform granules. The optimum size of the granules will again depend upon the precise application. The granules should be small enough to present a large surface area as an absorbent surface. However, if they are too small, they may become too tightly packed to the extent that they may inhibit the flow of gas through them, which could be a problem with, say filters used in breathing apparatus. For breathing apparatus, an average particle size of from 300µm to 3mm, preferably from 500µm to 1.5mm would be utilised.

Zeolites may be subject to grinding and granulation and sieving techniques as is understood in the art. Preferably the zeolites are subject to granulation, grinding etc. prior to impregatation to prevent loss of impregnant.

The use of zeolites as a base for piperazine has been investigated and the results are described hereinafter. Zeolites tested included 13X and PRSV. Both are microporous crystalline alumino silicates of differing Al/Si ratio. 13X has an average pore diameter ~8Å whereas PRSV's average pore diameter is 5.5Å. Adsorbents were tested with gases which normally require an impregnated activated carbon for efficient removal. The gases had a range of boiling points and physiochemical properties including cyanogen chloride (CK); BP 12°C, trifluoronitrosomethane (TFN); BP-85°C and 3-chloropentafluoropropene (CPFP); 7°C.

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The performance of compositions of the invention against the above-mentioned highly volatile compounds was assessed and compared against BPL impregnated with the same amine compounds at the same loading. The amine impregnated zeolites performed better than the corresponding amine impregnated BPL. Furthermore, the deleterious effects on filter performance caused by prolonged exposure to high humidity has been found to be significantly reduced with PRSV/PPZ and 13X/PPZ compared to BPL/PPZ. The degradation of piperazine, resulting in ammonia liberation, associated with carbons impregnated with piperazine, does not occur if zeolites such as PRSV or 13X are used as impregnant supports.

The invention will now be particularly described by way of example with reference to the accompanying drawing in which:

Figure 1 shows a graph illustrating a breakthrough profile used in calculating breakthrough C_t values for the compositions.

Example 1

Impregnation procedure

Zeolites (13X and PRSV) were heated in a muffle furnace at 550 °C. The product was then ground and sieved to produce respirator grade particle sizes. The sieving results are shown in Table 1

Table 1

Sieve Size	Specification required	Amount Retained (%)	
		13X	PRSV
1.18mm	10-30	29.1	24.3
850µm	40-60	54.7	54.6
600µm	10-35	13.9	20.3

Sieved zeolite samples were then dried at 120°C under vacuum (<3mbar) for 3 hours. Impregnation was carried out by sublimation. TEDA and piperazine sublime readily at room temperature. In the presence of a suitable material adsorption occurs and the adsorbent becomes impregnated. Dried zeolite (approx 50g) was accurately weighed into a 1 litre round bottomed flask. The required amount of impregnant was added to the flask and the two solids mixed. A vacuum (0.1mbar) was applied and the flask sealed, the sample was then heated to approximately 40°C and left sealed for 16 hours. The level of uptake

was determined by weight gain. For comparison studies respirator grade carbon was dried at 120°C under vacuum (<3mbar) for 3 hours and impregnated using the same procedure as that used for zeolites.

5 Example 2

Adsorbent testing

Adsorbent samples were loaded into 2cm diameter brass volume activity tubes of the required bed depth. Prior to testing samples were equilibrated with air at relative humidity 80% and 22°C. For some
 10 experiments the exposure to humid air was prolonged to study the effect this has on filter performance. Samples were exposed to a mixture of challenge gas in air at RH80% at specific concentrations for a finite time. The effluent from the filter was monitored using
 15 gas chromatography or mass spectrometry. The flow rate used in all tests was 1.0 lmin⁻¹. At the end of the challenge clean air of the same relative humidity was drawn through the sample until complete desorption of any observed gases was complete.

The filter tests used in this study monitor the concentration of
 20 challenge gas in the effluent of selected novel adsorbents during and after exposure to the challenge gas. If the concentration of the challenge gas observed in the effluent of the filters is plotted against the duration of the test a breakthrough profile can be constructed (figure 1). Integration of this curve allows calculation
 25 of the breakthrough Ct, this in turn can be compared to the challenge Ct and the % of challenge removed from the airstream derived. This is how the data in this study are presented.

The results are shown in Table 2 which shows filter test results from
 30 impregnated adsorbents challenged with trifluoronitrosomethane (15000mg m⁻³, 13mm bed depth, for a series of two minute pulses).

Table 2

Pulse Number	% Of challenged adsorbed			
	BPL/PPZ (15%)	13X/PPZ (10%)	PRSV/PPZ (11%)	PRSV/PPZ (15%)
1	85.0	91.1	97.5	97
2	80.1	64.8	92.8	95.7
3	70.1	38.7	82.0	92.8
4	52.9	-	66.3	86.7
5	41.4	-	35.4	75.0

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The data in table 2 shows that in all cases the zeolite impregnated adsorbents performed better than BPL/PPZ this was even observed with

zeolites containing considerably lower piperazine loadings. PRSV appeared to perform better in this test than 13X. This may be due to the average pore size being smaller or a result of different surface chemistry associated with the aluminium to silicon ratios.

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Example 3

Affect of Humidity on Absorbency

To compare the effect of exposure to humid air in the case of piperazine impregnated zeolites and BPL/PPZ, samples of both were stored under such conditions. The samples were then subjected to absorbency tests as described in Example 2. The filter test results as described above from impregnated adsorbents which have been exposed to RH80%air and the challenged with trifluoronitrosomethane (15000mg m-3, 13mm bed depth, for a series of two minute pulses) are shown in Table 3.

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Table 3

RH80% exposure time	16 hrs	14 days	16 hrs	14 days	16hrs	14 days
Pulse number	BPL/PPZ (15%)		PRSV/PPZ (11%)		PRSV/PPZ (11%)	
	Amount of challenge adsorbed (%)					
1	85%	73%	97.5%	92.8%	97%	92.7%
2	80.1%	41.8%	92.8%	88.3%	95.7%	92.6%
3	70.1%	22.1%	82.0%	58%	92.8%	81.5%
4	52.9%	-	66.4%	33.8%	86.7%	64.5%

It is clear that although the performance of piperazine impregnated zeolites degrade after two weeks exposure, this degradation is far less than that observed with BPL/PPZ; the performance of PRSV/PPZ after 14 days humid air exposure is still better than its unaged BPL/PPZ counterparts. As the surface of zeolites are not prone to oxidation under conditions of high humidity at ambient temperature the degradation in performance may be attributed to sintering of the impregnant.

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Example 4

Absorbency Tests with TEDA Impregnant

Filter test results from unimpregnated adsorbents or adsorbents impregnated with TEDA challenged as described in Example 2 above with cyanogen chloride (4000mg m-3, 20mm bed depth, for a 30 minute challenge duration) are shown in Table 4.

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Table 4

Adsorbent	Amount of challenge adsorbed
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	(%)
BPL/T (2%)	74.8
13X/T (2%)	76.5
PRSZ/T (2%)	81.5
BPL (unimpregnated)	17.8
13X (unimpregnated)	0.5%
PRSV (unimpregnated)	1.2%

The zeolites impregnated with TEDA perform better than the BPL/TEDA with PRSV performing best. It is interesting to note that whereas unimpregnated zeolites offer practically no activity to this compound unimpregnated carbon has the ability to remove 17.8% of the challenge indicating that the improvement on filter performance achieved by impregnating BPL with 2% TEDA is only 54%.

Example 5

10 Comparison of Impregnated and Unimpregnated Adsorbents

The filter test results from impregnated and unimpregnated adsorbents challenged with cyanogen chloride (4000mg m⁻³, 20mm bed depth, for a 30 minute challenge duration) as described above are shown in Table 5.

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Table 5

Adsorbent	Amount of challenge adsorbed (%)
BPL/ppz (5%)	75.3
13X/ppz (5%)	85.6
BPL (unimpregnated)	17.8
13X (unimpregnated)	0.5%

Similar filter test results from impregnated and unimpregnated adsorbents challenged with 3-chloropentafluoropropene (4000mg m⁻³, 20mm bed depth, for a 30 minute challenge duration) are shown in Table 6.

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Table 6

Adsorbent	Amount of challenge adsorbed (%)
BPL/ppz (5%)	49.2
13X/ppz (5%)	52.3
BPL (unimpregnated)	0
13X (unimpregnated)	0

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Data in table 5 show that performance of 13X/PPZ against cyanogen chloride is better than that of BPL/PPZ. Impregnation of BPL with piperazine results in a 57.5% improvement compared to 85.1% obtained upon impregnation of 13X. Data in table 6 shows that the performance of BPL/PPZ and 13X/PPZ against 3-chloropentafluoropropene. Impregnation of both substrates results in significant activity against CFPF which is similar in magnitude.

Throughout the Examples described above, the desorption of ammonia from zeolite/ppz was monitored. There was no noticeable odour from zeolite/ppz after dry storage for 7 months. Ammonia desorption from BPL/PPZ can be observed within a week of dry storage and steadily increases with storage time.

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Claims

1. An adsorbent composition comprising a zeolite which has been impregnated with a compound which reacts with and/or sequesters a volatile gas or vapour.
5
2. A composition according to claim 1 wherein the said compound comprises an organic amine.
- 10 3. A composition according to claim 2 wherein the organic amine comprises piperazine or triethylenediamine (TEDA).
4. A composition according to any one of the preceding claims wherein the zeolite is a microporous zeolite.
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5. A composition according to any one of claims 1 to 3 wherein the zeolite is a mesoporous zeolite.
6. A composition according to claim 4 wherein the zeolite has an average pore diameter of from from 4-10Å.
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7. A composition according to claim 6 wherein the average pore diameter of the zeolite is from 5-7Å.
- 25 8. A composition according to any one of claims 1 to 6 wherein the zeolite is PRSV or 13X.
9. A composition according to claim 8 wherein the zeolite is PRSV.
- 30 10. A composition according to any one of the preceding claims wherein the composition comprises up to 15%w/w of impregnant.
11. A composition according to any one of the preceding claims which is in the form of granules.
35
12. A composition according to claim 11 wherein the granules are of average size of from from 300µm to 3mm.
13. A composition according to claim 12 wherein the granules are of average size of from 500µm to 1.5mm.
40
14. A method of preparing a composition according to any one of the preceding claims wherein either (a) the impregant is allowed to sublime in the presence of the zeolite or (b) a solution of impregnant is sprayed onto the zeolite and the solvent removed.
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15. A filter comprising a composition according to any one of claims 1 to 14.

5 16. Breathing apparatus comprising a filter according to claim 15.

17. A method of removing toxic volatile substances from the air, said method comprising causing the air to pass through a composition according to any one of claims 1 to 13.

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18. A method according to claim 16 wherein the toxic volatile substance comprises a perfluorocarbon compound.

15 19. A method according to claim 17 wherein the toxic volatile substance comprises methyl iodide.

20. An absorbent composition substantially as hereinbefore described with reference to the Examples.

Amendments to the claims have been filed as follows

1. A method of removing toxic volatile substances from the air, said method comprising causing the air to pass through
5 a composition an adsorbent composition comprising a zeolite which has been impregnated with an organic amine which reacts with and/or sequesters said toxic substance.
2. A method according to claim 1 wherein the organic amine
10 comprises piperazine or triethylenediamine (TEDA).
3. A method according to claim 1 or claim 2 wherein the zeolite is a microporous zeolite.
- 15 4. A method according to claim 1 or claim 2 wherein the zeolite is a mesoporous zeolite.
5. A method according to claim 4 wherein the zeolite has an average pore diameter of from from 4-10Å.
20
6. A method according to claim 5 wherein the average pore diameter of the zeolite is from 5-7Å.
7. A method according to any one of claims 1 to 6 wherein
25 the zeolite is PRSV or 13X.
8. A method according to claim 7 wherein the zeolite is PRSV.
- 30 9. A method according to any one of the preceding claims wherein the composition comprises up to 15%w/w of impregnant.

10. A method according to any one of the preceding claims wherein the composition is in the form of granules.
11. A method according to claim 10 wherein the granules are
5 of average size of from 300 μ m to 3mm.
12. A method according to claim 11 wherein the granules are of average size of from 500 μ m to 1.5mm.
- 10 13. A method according to any one of the preceding claims wherein the toxic volatile substance comprises a perfluorocarbon compound.
14. A method according to any one of the preceding claims
15 wherein the toxic volatile substance comprises methyl iodide.
15. A method of preparing a composition for use in a method according to any one of the preceding claims wherein either
20 (a) the impregnant is allowed to sublime in the presence of the zeolite or (b) a solution of impregnant is sprayed onto the zeolite and the solvent removed.
16. A filter for use in a method according to any one of
25 claims 1 to 14, said filter comprising a composition as described in any one of claims 1 to 14.
17. Breathing apparatus comprising a filter according to claim 16.
- 30 18. A method of removing toxic volatile substances from the air, substantially as hereinbefore described.



Application No: GB 9714346.5
Claims searched: 1 - 20

Examiner: Michael R. Wendt
Date of search: 8 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): B1L (LAE)
Int CI (Ed.6): B01J 20/18, 20/32
Other: Online: WPI, Claims, Japio

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2302824 A (I. F. du Pet.) e.g. see Page 4 lines 5 - 19. Claim 1 and Tables 1 & 2.	1, 11, 13
X	EP 0638351 A2 (METALLGESELLS) e.g. see Claims 1 & 3.	1, 11
X	WO 96/23726 A1 (KLATTE) e.g. see Abstract. Page 5 lines 7 - 17. Claims 1 & 21.	1, 11
X	WO 91/04096 A1 (MOBIL) e.g. see Claims 1, 2, 14 & 16.	1
X	US 5464598 (KLATTE) e.g. see Column 4 lines 57 etc. Column 3 lines 37 etc.	1, 14, 15
X	US 5314852 (KLATTE) e.g. see Abstract. Column 4 lines 20 etc.	1, 14, 15
X	US 5252528 (CALIF. I. T.) e.g. Abstract. Column 7 lines 48 etc.	1
X	US 4999175 (EURATOM) e.g. see Claim 1.	1, 2
X	Japio Abstract No. 03835642 & JP 040200742 A (MITSUBISHI) See Abstract.	1, 2, 3

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.