



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

<p>(51) International Patent Classification <sup>6</sup> : B01D 53/54, 53/86, C01B 31/12, B01J 20/20</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 99/11358</b></p> <p>(43) International Publication Date: 11 March 1999 (11.03.99)</p>
<p>(21) International Application Number: PCT/GB98/02515</p> <p>(22) International Filing Date: 20 August 1998 (20.08.98)</p> <p>(30) Priority Data: 9718314.9 30 August 1997 (30.08.97) GB</p> <p>(71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): CHINN, Matthew, Joseph [GB/GB]; DERA Porton Down, Salisbury, Wilts SP4 0JQ (GB). NORMAN, Paul, Roderick [GB/GB]; DERA Porton Down, Salisbury, Wilts SP4 0JQ (GB). BARNES, Philip, Andrew [GB/GB]; Leeds Metropolitan University, Catalysis Research Unit, Calverley Street, Leeds LS1 3HE (GB). DAWSON, Elizabeth, Anne [GB/GB]; Leeds Metropolitan University, Catalysis Research Unit, Calverley Street, Leeds LS1 3HE (GB).</p> <p>(74) Agent: BOWDERY, A., O.; D/IPR, Formalities Section (DERA), Poplar 2, MOD Abbey Wood #19, Bristol BS34 8JH (GB).</p>	<p>(81) Designated States: CA, GB, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: ACTIVATED CARBON FILTER AND PROCESS FOR THE SEPARATION OF NOXIOUS GASES</p>		
<p>(57) Abstract</p> <p>The filtration of hydrogen cyanide from an atmosphere is accomplished, according to this invention, by a filter comprising activated carbon containing at least one of copper, cobalt and silver to between 3 and 18 % in total by weight, when the filter material has been prepared from an ion exchange material in the form of a sodium salt carboxymethyl cellulose. The metal is then incorporated into the carbon by an ion exchange reaction of the cellulose with a suitable salt of the metals concerned. The activation which then follows may be supplemented by a secondary oxidation. Where the suppression of cyanogen generation is also required the carbon may also be arranged to contain chromium, with copper, chromium and silver having been found particularly effective.</p>		

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## ACTIVATED CARBON FILTER AND PROCESS FOR THE SEPARATION OF NOXIOUS GASES

The present invention relates to filtration processes. It is particularly concerned with the use of activated carbon filters to remove toxic chemicals from a breathable atmosphere.

According to the present invention a method of filtering an atmosphere containing a gaseous contaminant comprising passing said atmosphere through an activated carbon filter containing at least one transition metal, the filter material having been prepared in a process including, *inter alia*, the exchange of the metal ion with a cellulose ion exchange resin.

Preferably the transition metal is copper, cobalt, chromium or silver. A suitable process for the production of the activated carbon filter containing one or more of these metals is described by P A Barnes and E A Dawson in "A New Method for the Production of Metal-Carbon Catalysts" published in the Proceedings of the 6th International Symposium on Catalyst Preparation, University of Louvain-la-Neuve, September 1994. In general terms in this process the starting material is typically an ion exchange material in the form of carboxymethyl cellulose (Whatman, CM32) as an alkali metal salt such as a sodium salt. Hydroxyl groups on the cellulose chain are modified to form an ether group which carries a metal carboxylic substituent, for example of formula  $O(CH_2)_nCOO_m$  where  $n$  is an integer of from 1 to 6 and  $m$  is an exchangeable cation. A particular group is  $OCH_2COONa$ , with sodium as an exchangeable cation. An ion exchange reaction is set up with a suitable metal salt, preferably a nitrate or sulphate of the metal, for example copper sulphate, and the resulting residue is dried and then charred in an inert gas flow. It is then cooled under an inert gas and this is followed by activation in a nitrogen stream containing steam, to result in a carbon matrix holding the metal relatively uniformly dispersed throughout. This primary activation may be followed by a secondary oxidation by heating in a flow of oxygen in helium to chemisorb oxygen on the carbon surface. The resulting pore widening improves access to the metal by the gases being filtered.

The amount of metal present is preferably arranged to be between 3% and 18% by weight. Preferably the metal is copper, but cobalt and silver are also effective, singly or in combinations with one another or copper. When such combinations are contemplated the ion exchange process for each may take place simultaneously. The percentage ion exchange and the carbon activation time both have significant effect on the property of the resultant filter to adsorb hydrogen cyanide. Low ion exchange, less than 50% and preferably about 25% or less has been found to favour dispersion of the metal and

to increase the capacity of the filter to adsorb HCN. Long activation times, for example 6 to 12 hours or more increase the capacity to adsorb HCN very considerably. The activation is catalysed by the presence of copper, and the metal then becomes a centre for evolved gases and in the final product the nucleus for transport passages through which reacting gases may diffuse. Cobalt and silver are also both capable of this catalytic effect.

The reaction of hydrogen cyanide with copper and copper salts on activated carbon results in the release of cyanogen (CN<sub>2</sub>) as a volatile reaction product. Due to the toxic nature of cyanogen additional measures may need to be taken for its removal, particularly when copper is the primary metal present. This is much less the case when cobalt is the primary metal.

The filter material may be arranged to contain chromium, in addition to the copper, cobalt or silver. Where copper and chromium are employed, the presence also of silver is particularly useful. There is no lower limit for the secondary metal. The upper limit may be of the order of 11% by weight.

Particularly good results in terms of the removal of both hydrogen cyanide and the product cyanogen are achieved in activated carbon filters containing copper, chromium and silver.

Various examples of filtration and the construction of filters suitable for use in processes according to the invention will now be described, by way of example, with reference to the accompanying drawings and tables, of which:

Figure 1 illustrates an ion exchange process;

Figure 2 is a graph comparing water adsorption properties; and

Figure 3 is a graph comparing water desorption properties.

Table 1 below lists a number of samples of filter materials which were tested for their ability to remove HCN.

**Table 1**

Sample	Exchanged metal ion	Percentage metal by weight	Number of HCN pulses removed	Pulses before cyanogen breakthrough
502	Cu <sup>2+</sup>	2	6	-
505	Cr <sup>2072-</sup>	13	8	-
506	Ag <sup>2+</sup>	5	60	-
507	Cu <sup>2+</sup>	10	80	-

5070	Cu <sup>2+</sup>	10	120	-
508	Cu <sup>2+</sup>	17	46	-
510	Cu <sup>2+</sup> /Cr <sup>2+</sup>	8/9	98	-
511	Co <sup>2+</sup>	16	85	62
512	Cu <sup>2+</sup> /Co <sup>2+</sup>	8/8	53	60
513	Cu <sup>2+</sup> /Cr <sup>3+</sup> /Ag <sup>+</sup>	5/1/3.5	141	120
515	Cu <sup>2+</sup> /Ag <sup>+</sup>	5/1	25	12
517	Ag <sup>+</sup>	18	15	
518	Cu <sup>2+</sup> /Co <sup>2+</sup> /Ag <sup>+</sup>	6/-/1	54	40
ASC	Cu/Cr/Ag (whetlerite)	6-9/1.5-3.5/0- 0.5	120	85

Samples 506 to 518 represent examples of filter materials in accordance with the invention, while samples 502, 505 and ASC are outside the scope of the invention and are included for the purposes of comparison.

Thus sample 506 is a filter carbon containing 5% by weight silver, 507 contains 10% by weight copper etc. These samples 506 to 518 were prepared as now described below.

10 The starting material for the creation of filter carbon was carboxymethyl cellulose (Whatman, CM32), this being a sodium salt ion exchange medium. Hydroxyl groups on the cellulose chain were modified to OCH<sub>2</sub>COONa, with sodium as the exchangeable cation. Ion exchange was then conducted using copper sulphate, cobalt nitrate and silver nitrate to give the desired metal content, the ion exchange process being as illustrated in Figure 1.

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The exchange process was conducted at room temperature by stirring the metal salt solution into a mixture of 1gm cellulose per 100 cm<sup>3</sup> water, then leaving to stand for several hours. Afterwards the solid was filtered off, washed thoroughly in deionised water and dried. The dried material was then charred at 400°C for one hour under a nitrogen flow. After cooling under nitrogen the carbon was activated by heating to 600°C for 2 hours in an atmosphere of flowing nitrogen saturated with water vapour at 25°C. A relatively low temperature could be used for the activation because of the catalytic effect of the metal on carbon gasification, and one advantage of this low temperature was the minimisation of sintering of surface metal particles. The standard activation time was 2 hours.

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This then was the process employed for the production of samples 506 to 518. Sample 5070 however was then subjected to a further oxydation by heating to 150°C in a flow of 5% oxygen in helium to chemisorb oxygen on the carbon surface. Removal of surface carbon

as CO<sub>2</sub> was then achieved by heating to 350°C in a pure helium flow. The oxygen/helium cycling procedure was repeated four times to give a controlled stepwise removal of carbon throughout the pore network. This results in a carbon structure in which there is, so to speak, a lattice of interconnecting pores, with the metal trapped at the pore junctions and uniformly distributed throughout the carbon.

Table 2 below shows the effect of activation time and percentage ion exchange upon the total and copper surface areas, and upon HCN adsorption, of various samples of filter material according to the invention, all of which comprised only copper in carbon.

**Table 2**

Sample	Activation time (h)	% ion exchange	% copper	Total surface area	Dispersion	Cu area	HCN pulses removed
521	2	100	10.1	372	4.0	3.8	9
522	4	100	10.6	344	14.2	14.3	17
523	6	100	10.2	437	16.5	16	25
524	2	50	6.4	449	15.2	9.2	20
525	4	50	6.5	443	26.1	16.1	29
526	6	50	6.5	497	35.5	21.9	47
527	2	25	3.4	389	13.3	4.3	19
528	4	25	3.4	359	9.3	3.0	28
529	6	25	3.5	468	17.5	5.8	57
530	12	25	3.5	518	67.8	22.5	110

The carbons were tested against pulses of 10,000 mg/m<sup>3</sup> HCN/air mixture, the air having been at a relative humidity of 80%. Prior to testing the carbons were sieved, with the fractions between 600µm and 150µm being used. Carbon samples (10mg) were loaded into glass tubes 60mm in length and 2mm in internal diameter with a glass fibre plug at each end. Each sample was then compressed to the same degree by applying a weight to the carbon. The glass tubes were then loaded into a Chrompack CP9001 packed gas chromatography oven at 140°C with a nitrogen carrier flow of 10ml/min and a head pressure of 175 KPA. The effluent from the sample tubes was split; 0.75 ml/min being transferred by capillary cfm to a mass spectrometer and 9.25 ml/min passing through a flame ionisation detector (FID). Once the baseline from the FID had settled the samples were pulsed with the HCN vapour using an automated gas sampling valve fitted with a 1ml sample loop. Pulses were supplied every minute until breakthrough was observed.

It is clear from the Tables that carbon filter materials formed with copper, cobalt or silver introduced by an ion exchange mechanism as above described perform significantly well in the removal of HCN from an atmosphere. Those outside the preferred range performed much less well. The most significant results were obtained with sample 513 which  
5 contained chromium and silver as secondary metals. This showed a very high HCN adsorption coupled with a high retention of  $(CN)_2$ .

Sample 513 was deliberately created to compare with the sample labelled ASC. ASC was a conventional coal-based carbon impregnated with an ammoniacal solution of copper,  
10 chromium and silver, so that the final product contained the metals as salts on the carbon surface. Sample 513 performed significantly well in the adsorption of hydrogen cyanide and in withholding cyanogen. The ASC sample however, whilst exhibiting quite good hydrogen cyanide adsorption, demonstrated an extremely sharp cyanogen breakthrough which resulted in detector overload.

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The results in Table 2 show that for samples containing the same amount of copper, increase in activation time caused an increase in the total Langmuir  $m^2/g$  surface area. Sample 530 demonstrates in particular how important an effect activation time can have upon hydrogen cyanide adsorbability. The Table demonstrates that while an activation time  
20 of 6 hours produces a significant improvement over lower times, 12 hours gives particularly good results.

It is also discernible from Table 2 in comparison with Table 1, that the lower percentage ion exchange of 25% gave better results than 50% and certainly than 100%.

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Figures 2 and 3 show that there was no great difference in water adsorption and desorption between the carbon filter materials according to the invention and SCII and ASC carbon at levels of  $P/P_0$  below 0.5. Above that level however carbon materials in accordance with the invention performed significantly better.

## CLAIMS

1. A method of filtering an atmosphere containing a gaseous contaminant comprising passing said atmosphere through an activated carbon filter containing at least one transition metal, the filter material having been prepared in a process including, *inter alia*, the exchange of the metal ion with a cellulose ion exchange resin.
2. A method as claimed in claim 1 wherein said gaseous contaminant is hydrogen cyanide.
3. A method of producing an activated carbon filter which contains at least one transition metal, the filter material having been prepared in a process including, *inter alia*, the exchange of the metal ion with a cellulose ion exchange resin.
4. An activated carbon filter containing at least one transition metal, the filter material having been prepared in a process including, *inter alia*, the exchange of the metal ion with a cellulose ion exchange resin.
5. A filter as claimed in claim 4 wherein the transition metal is copper, cobalt chromium or silver.
6. A filter as claimed in claims 4 or 5 wherein the cellulose ion exchange resin used in the process is an alkali metal salt carboxymethyl cellulose
7. A filter as claimed in claim 6 wherein the alkali metal is sodium.
8. A filter as claimed in any one of claims 4 to 7 and comprising also the step of modifying hydroxy groups on the cellulose chain to form an ether group having the formula  $\text{OCH}_n\text{COO}_m$  where n is an integer from 1 to 6 and m is an exchangeable cation.
9. A filter as claimed in any one of claims 4 to 8 and wherein the ion exchange reaction used in the process is set up with a salt of the required metal or metals.

10. A filter as claimed in claim 9 and wherein the salt is a sulphate or nitrate.
11. A filter as claimed in claim 10 and wherein the salt is copper sulphate, cobalt nitrate and/or silver nitrate.
12. A filter as claimed in any of claims 4 to 11 and wherein the process for preparing the filter material comprises also the steps of washing, filtering, drying and charring the material resulting from the ion exchange, followed by activation in a nitrogen containing stream.
13. A filter as claimed in any one of claims 4 to 12 the preceding claims and wherein the amount of metal present is arranged to be between 3% and 18% by weight.
14. A filter as claimed in any one of claims 4 to 13 wherein the filter material also includes chromium.
15. A filter as claimed in any of claim 4 to 14 and wherein the filter material includes up to 11 % chromium by weight.

Fig. 1.

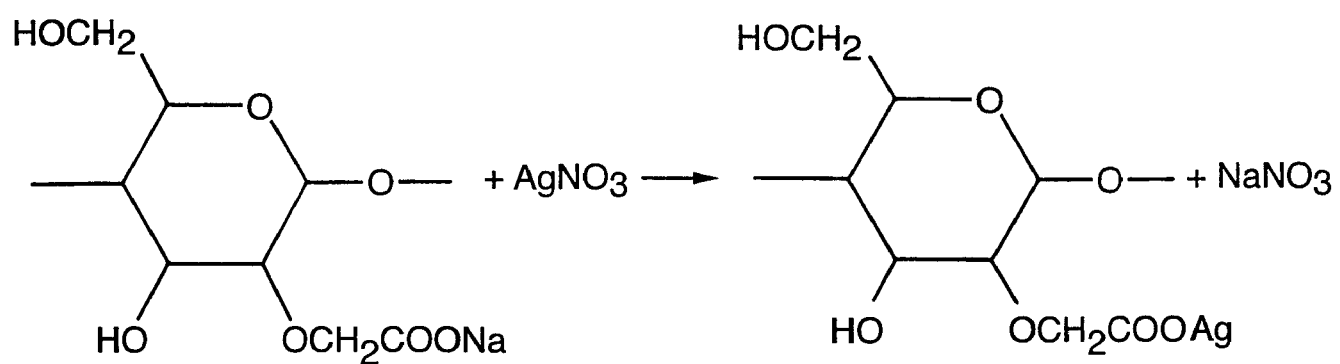


Fig.2.

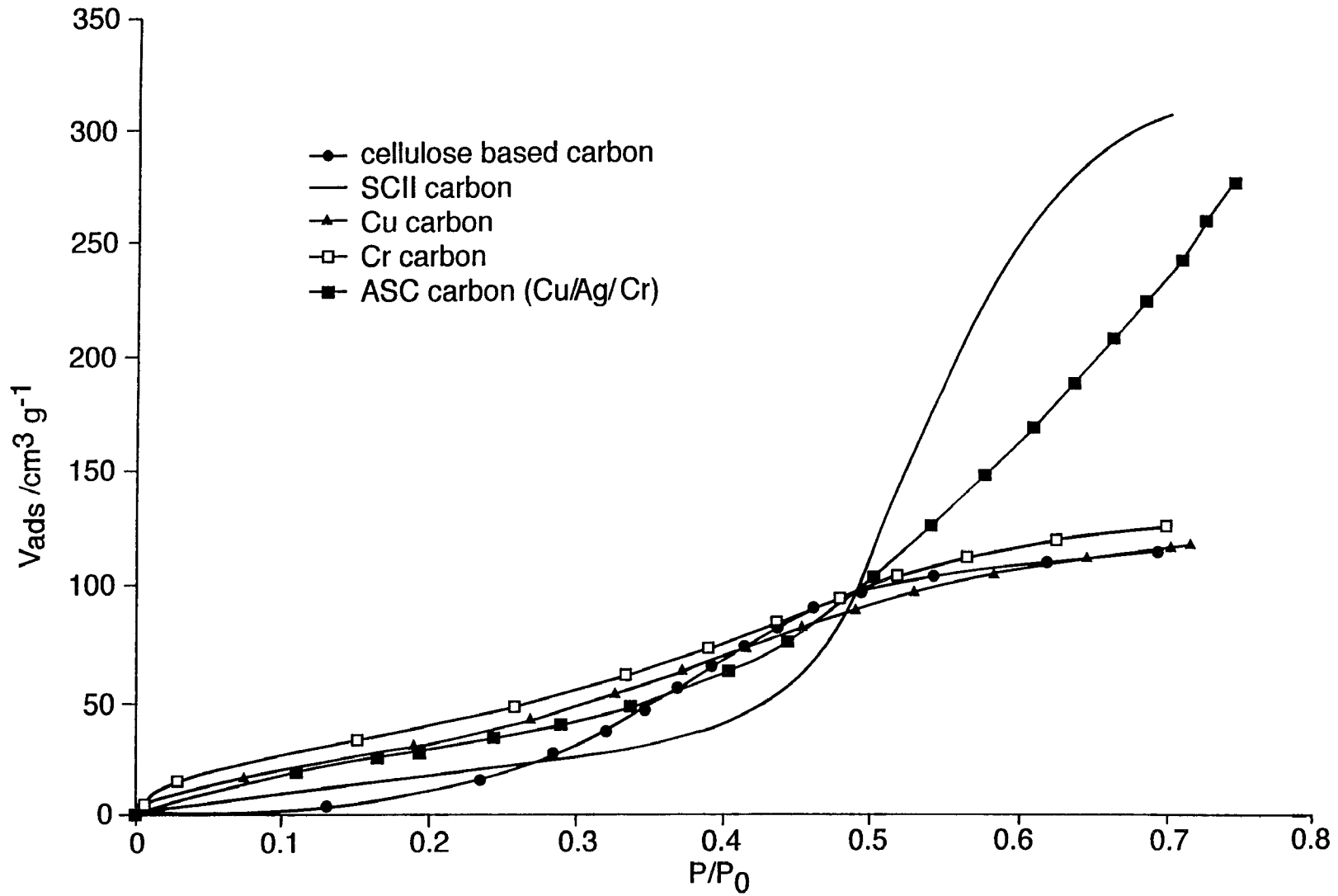
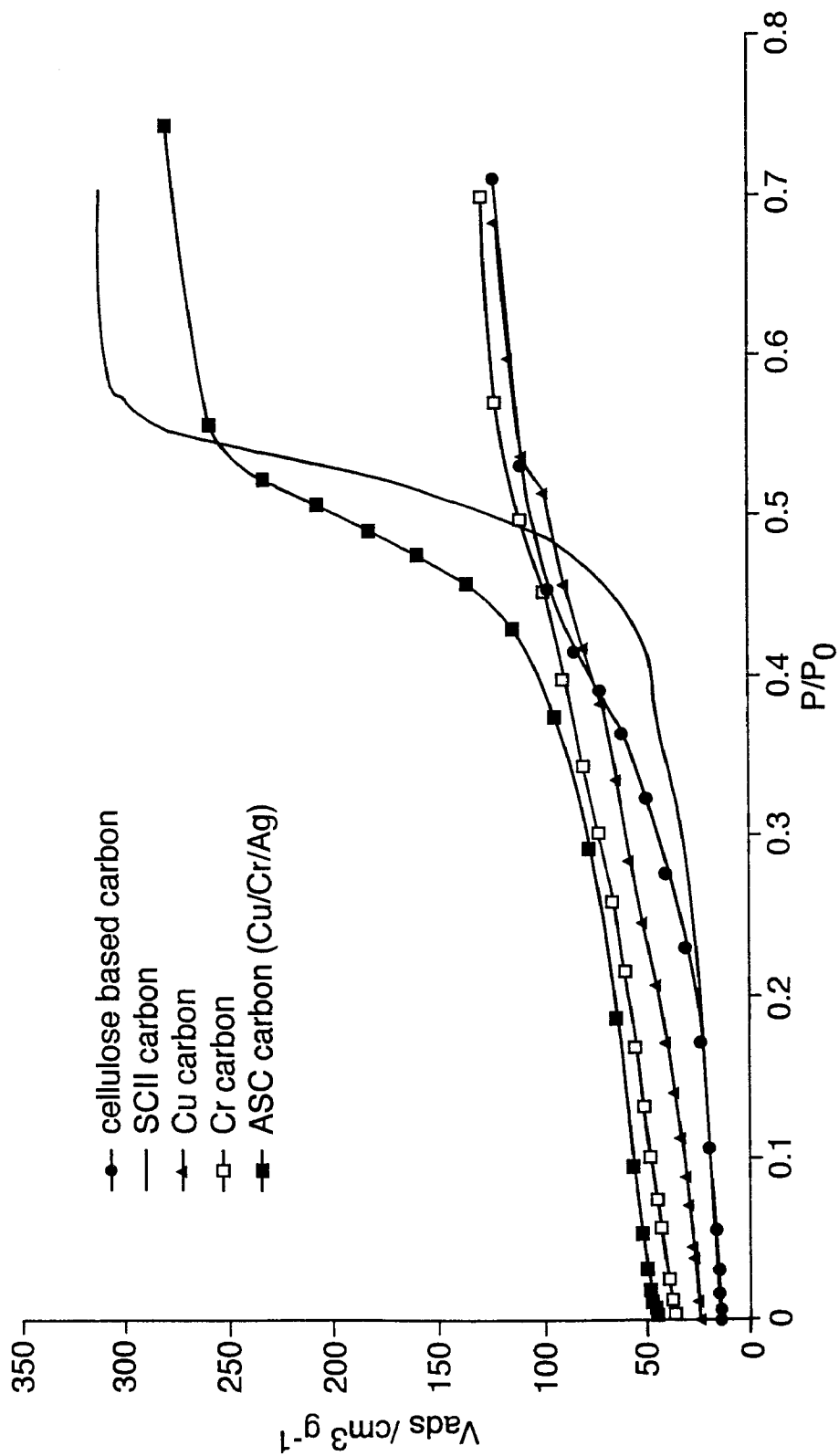


Fig.3.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 98/02515

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 B01D53/54 B01D53/86 C01B31/12 B01J20/20

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 6 B01D C01B

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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A	DATABASE WPI Section Ch, Week 9737 Derwent Publications Ltd., London, GB; Class A21, AN 97-397642 XP002090496 & JP 09 173829 A (NIPPON CHEM IND CO LTD) , 8 July 1997 see abstract -----	5
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Information on patent family members

International Application No

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