



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 19/08, 23/08, 21/18 C07C 17/00, 17/08, C11D 7/30	A3	(11) International Publication Number: WO 93/05002 (43) International Publication Date: 18 March 1993 (18.03.93)
(21) International Application Number: PCT/US92/07147 (22) International Filing Date: 28 August 1992 (28.08.92) (30) Priority data: 751,019 28 August 1991 (28.08.91) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: RAO, Velliyur, Nott, Mallikarjuna ; 1 Georgetown Avenue, Wilmington, DE 19809 (US). WEIGERT, Frank, Julian ; 3120 Naamans Road, Apartment J-10, Wilmington, DE 19810 (US). KRESPAN, Carl, George ; 8 Mozart Drive West, Wilmington, DE 19807 (US).		(74) Agents: HEISER, David, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 13 May 1993 (13.05.93)
(54) Title: GEM-DIHYDROPOLYFLUOROALKANES AND MONOHYDROPOLYFLUOROALKENES, PROCESSES FOR THEIR PRODUCTION, AND USE OF GEM-DIHYDROPOLYFLUOROALKANES IN CLEANING COMPOSITIONS $\text{—}(\text{CF}_2)_4\text{CH}_2\text{—}$ (a) (57) Abstract A catalytic process is disclosed for producing fluorine-substituted hydrocarbon products of the formulae $\text{RCH}_2\text{CF}_2\text{R}$ and $\text{RFC}=\text{CHR}$ at an elevated temperature, from compounds of the formula RCHFCHFR, where each R is independently selected from the group consisting of $-\text{CF}_3$, $-\text{CF}_2\text{CF}_3$ and $-\text{CF}_2\text{CF}_2\text{CF}_3$ or where both R groups of a formula together are $-(\text{CF}_2)_2-$, $-(\text{CF}_2)_3-$ or $-(\text{CF}_2)_4-$. Suitable catalysts include carbon catalysts and catalysts containing at least one compound of a selected metal (e.g., Na, K, Rb, Cs, Y, La, Ce, Pr, Nd, Sm, Cr, Fe, Co, Rh, Ni, Cu, and/or Zn) supported on carbon. The saturated gem-dihydro-products may also be produced by hydrofluorinating the corresponding olefinic product over such catalysts at an elevated temperature, and can be combined with various other miscible solvents to form compositions useful for cleaning. Compounds such as $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3$, $\text{CF}_3\text{CH}=\text{CF}(\text{CF}_2)_2\text{CF}_3$, $\text{CF}_3\text{CF}=\text{CH}(\text{CF}_2)_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3(\text{CF}_2)_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3$, $\text{CF}_3\text{CH}=\text{CF}(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3\text{CF}=\text{CH}(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3(\text{CF}_2)_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2(\text{CF}_2)_4\text{CF}_3$, $\text{CF}_3\text{CH}=\text{CF}(\text{CF}_2)_4\text{CF}_3$, $\text{CF}_3\text{CF}=\text{CH}(\text{CF}_2)_4\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CH}=\text{CF}(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CF}=\text{CH}(\text{CF}_2)_3\text{CF}_3$ and (a) azeotropic compositions such as azeotropes of $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3$ and/or $\text{CF}_3\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_3$ with methanol, ethanol, or isopropanol are disclosed.		

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FI	Finland				

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/07147

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5 C 07 C 19/08 C 07 C 23/08 C 07 C 21/18 C 07 C 17/00 C 07 C 17/08 C 11 D 7/30		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl.5	C 07 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0431458 (DAIKIN INDUSTRIES) 12 June 1991 see the whole document ---	1-8,25-38
P,A	EP,A,0458279 (NIPPON ZEON) 27 November 1991 ---	1-8,18-38
A	US,A,2975220 (MURRAY HAUPTSCHIEIN ET AL.) 14 March 1961 cited in the application see claims; example 3 ---	1-7,18-38
A	JOURNAL OF THE CHEMICAL SOCIETY 1963, LETCHWORTH GB pages 281 - 289 R. J. HEITZMAN ET AL. 'Fluorocyclopentanes. Part I. The 1H,2H and 1H,3H- Octafluorocyclopentanes, and 1H,3H/2H- Heptafluorocyclopentane.' see the whole document ---	1,8,18-24
-/-		
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18-12-1992	19. 04. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	B. ZERVAS	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0376686 (E.I. DU PONT DE NEMOURS) 4 July 1990 see the whole document ---	18-24
A	BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR DIVISION OF CHEMICAL SCIENCE vol. 31, no. 7, 20 January 1983, NEW YORK US pages 1414 - 1416 V. A. PETROV ET AL. 'Electrophilic Condensation of 1-Hydroperfluoropropylene and 1-Hydroperfluoro-1-butene with Fluoroethylenes' see the whole document -----	9-23

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 92/07147

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims 1-8,9(part.);10-38

2. Claims 9(part.)

For further information please see Form PCT/ISA/206 dated 26/01/93

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8,9(part.); 10-38

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9207147

SA 64033

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/03/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0431458	12-06-91	AU-A- 6691690 CN-A- 1052328 JP-A- 4028798	13-06-91 19-06-91 31-01-92
EP-A- 0458279	27-11-91	JP-A- 4025598	29-01-92
US-A- 2975220		None	
EP-A- 0376686	04-07-90	US-A- 4902838 AU-B- 621439 AU-A- 4731589 AU-B- 634514 AU-A- 4823690 AU-B- 628912 AU-A- 4840590 CA-A- 2006212 EP-A- 0451199 EP-A- 0452363 JP-A- 2231440 JP-T- 4502464 WO-A- 9007481 WO-A- 9007482	20-02-90 12-03-92 05-07-90 25-02-93 01-08-90 24-09-92 01-08-90 28-06-90 16-10-91 23-10-91 13-09-90 07-05-92 12-07-90 12-07-90