

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 May 2003 (08.05.2003)

PCT

(10) International Publication Number
WO 03/037938 A3

- (51) International Patent Classification⁷: C08F 4/642, 210/16
- (21) International Application Number: PCT/US02/31049
- (22) International Filing Date:
28 September 2002 (28.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/000,665 31 October 2001 (31.10.2001) US
- (71) Applicant: UNIVATION TECHNOLOGIES, LLC
[US/US]; Suite 1950, 5555 San Felipe, Houston, TX 77056 (US).
- (72) Inventors: CROWTHER, Donna, Jean; 2725 Moss Court, Seabrook, TX 77586 (US). LUE, Ching-Tai; 14938 Redwood Bend Trail, Houston, TX 77062 (US). MATSUNAGA, Phillip, Thomas; 16403 Heatherdale Drive, Houston, TX 77059 (US).
- (74) Agents: FAULKNER, Kevin, M. et al.; Suite 1950, 5555 San Felipe, Houston, TX 77056 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report:
13 November 2003
- 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.*



WO 03/037938 A3

(54) Title: METHODS FOR ADJUSTING MELT PROPERTIES OF METALLOCENE CATALYZED OLEFIN COPOLYMERS

(57) Abstract: The melt strength and the melt index ratio of ethylene-based polyolefins are controlled by the lower alkyl substitution pattern of the bridged cyclopentadienyl ligands of metallocene polymerization catalyst precursor compounds.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/31049

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F4/642 C08F210/16

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 7 C08F

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)

CHEM ABS Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 40622 A (UNIVATION TECH LLC) 13 July 2000 (2000-07-13) page 15 -page 20; tables 1,3 ---	1-3, 5-11, 13-31
X	BURKHARDT, TERRY J. ET AL: "Molecular modeling of metallocenes catalysts for isotactic polypropylene" POLYOLEFINS XI, INTERNATIONAL CONFERENCE -- HOUSTON, FEB. 21-24, 1999 (1999), 333-345 PUBLISHER: SOCIETY OF PLASTICS ENGINEERS, BROOKFIELD, CONN. , XP008015104 page 334 -page 335; tables 1,2 --- -/--	1-31

Further documents are listed in the continuation of box C.

Patent 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 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 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.
- "&" document member of the same patent family

Date of the actual completion of the international search

30 June 2003

Date of mailing of the international search report

28. 07. 2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Parry, J

INTERNATIONAL SEARCH REPORT

Inter al Application No

PCT/US 02/31049

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MISE, TAKAYA ET AL: "Excellent stereoregular isotactic polymerizations of propylene with C2-symmetric silylene-bridged metallocene catalysts" CHEMISTRY LETTERS (1989), (10), 1853-6, XP000914711 page 1854 -page 1855; table 1 ---	1-31
X	WO 00 68279 A (UNIVATION TECH LLC) 16 November 2000 (2000-11-16) examples 2,4,5,8,11,A,B; tables 1-3 ---	1,5-11, 13
X	EP 0 589 364 A (SPHERILENE SRL) 30 March 1994 (1994-03-30) page 6; example 1 page 9; table 1 ---	1,5-11, 13
X	US 5 767 208 A (CROWTHER DONNA JEAN ET AL) 16 June 1998 (1998-06-16) example 1.18; table 1 ---	1,5-9, 11,13
X	US 5 854 362 A (SPENCER LEE ET AL) 29 December 1998 (1998-12-29) page 15 -page 16; example 1 ---	1,5-9, 11,13
X	EP 1 026 177 A (CHISSO CORP) 9 August 2000 (2000-08-09) page 12; example 2 page 20; example 6 ---	1,5-11, 13
X	WO 99 41294 A (EXXON CHEMICAL PATENTS INC) 19 August 1999 (1999-08-19) page 25 -page 26; examples 1,2 ---	1,5-11, 13
X	WO 99 60032 A (UNIVATION TECH LLC) 25 November 1999 (1999-11-25) page 24 -page 29; examples CE1,6-9C; tables 1-3 ---	1,5-11, 13
X	WO 99 64476 A (UNIVATION TECH LLC) 16 December 1999 (1999-12-16) page 25; example 9 page 26; example 9; table 2 ---	1,5-9, 11,13
X	WO 00 37513 A (UNIVATION TECH LLC) 29 June 2000 (2000-06-29) page 14; examples 3,4 page 15; examples 9,10 page 16 -page 17; examples 14,15 ---	1,5-11, 13
	-/--	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/31049

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WATANABE, TAKESHI ET AL: "Metallocene polymerization catalysts and manufacture of olefin polymers by using them" retrieved from STN Database accession no. 133:267229 XP002235240 abstract & JP 2000 281709 A (SUMITOMO CHEMICAL CO., LTD., JAPAN) 10 October 2000 (2000-10-10)</p>	1,5-9, 11,13
X	<p>WO 01 40324 A (UNIVATION TECH LLC) 7 June 2001 (2001-06-07) page 24 -page 30; tables 1,2</p>	1,5-11, 13-16
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YAMAZAKI, HIROSHI ET AL: ".mu.-Oxobismetallocene complexes, olefin polymerization catalysts containing them, and polymerization method" retrieved from STN Database accession no. 132:166734 XP002235241 abstract & WO 2000 008036 A (CHISSO CORPORATION, JAPAN) 17 February 2000 (2000-02-17)</p>	1-31

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/31049

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.: 1-31 (in part)
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:
see FURTHER INFORMATION sheet PCT/ISA/210

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:

see additional sheet

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.:

Remark on Protest

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

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of three C1-C2 alkyl substituents.

2. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of four C1-C2 alkyl substituents.

3. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of five C1-C2 alkyl substituents.

4. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of six C1-C2 alkyl substituents.

5. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of seven C1-C2 alkyl substituents.

6. Claims: 1-31 (in part)

The subject matter of claims 1-31 within the scope of the incomplete search insofar as it relates to a total of eight C1-C2 alkyl substituents.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-31 (in part)

Present claims 1-31 relate to an extremely large number of possible compounds and methods. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds and methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds and methods relating to claim 1 and 17 wherein one cyclopentadienyl ring possesses at least a 2,3,5-substitution pattern, further substitution being possible. Such compounds embrace all the present examples.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/31049

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0040622	A	13-07-2000	US 6034192 A	07-03-2000
			AU 754627 B2	21-11-2002
			AU 1749500 A	24-07-2000
			BR 9916734 A	25-09-2001
			CA 2350447 A1	13-07-2000
			EP 1151019 A1	07-11-2001
			JP 2002534536 T	15-10-2002
			WO 0040622 A1	13-07-2000
			US 2002058766 A1	16-05-2002
WO 0068279	A	16-11-2000	US 6339134 B1	15-01-2002
			AU 4246400 A	21-11-2000
			CA 2372636 A1	16-11-2000
			EP 1189951 A1	27-03-2002
			JP 2002544296 T	24-12-2002
			WO 0068279 A1	16-11-2000
			US 6388115 B1	14-05-2002
			US 2002058828 A1	16-05-2002
EP 0589364	A	30-03-1994	IT 1255514 B	09-11-1995
			AU 672425 B2	03-10-1996
			AU 4756993 A	31-03-1994
			BR 9303880 A	21-06-1994
			CA 2106733 A1	25-03-1994
			CN 1088588 A , B	29-06-1994
			EP 0589364 A2	30-03-1994
			FI 934167 A	25-03-1994
			JP 6192340 A	12-07-1994
			NO 933386 A	25-03-1994
			NO 980486 A	25-03-1994
			PL 300469 A1	18-04-1994
			RU 2140930 C1	10-11-1999
			US 6034196 A	07-03-2000
			ZA 9307012 A	18-04-1994
US 5767208	A	16-06-1998	US 5625016 A	29-04-1997
			US 5907021 A	25-05-1999
			CA 2234816 A1	26-06-1997
			CA 2344994 A1	26-06-1997
			DE 69619548 D1	04-04-2002
			DE 69619548 T2	26-09-2002
			EP 1063244 A2	27-12-2000
			EP 0868445 A1	07-10-1998
			JP 2000502384 T	29-02-2000
			WO 9722639 A1	26-06-1997
			WO 9722635 A1	26-06-1997
US 5854362	A	29-12-1998	NONE	
EP 1026177	A	09-08-2000	AU 9464198 A	10-05-1999
			EP 1026177 A1	09-08-2000
			US 6420501 B1	16-07-2002
			CN 1279694 T	10-01-2001
			WO 9920661 A1	29-04-1999
			TW 430675 B	21-04-2001
WO 9941294	A	19-08-1999	BR 9907267 A	14-11-2000
			CA 2319008 A1	19-08-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/31049

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9941294	A		CN 1291206 T EP 1056792 A1 JP 2002503736 T WO 9941294 A1 US 2003060578 A1 US 6486278 B1	11-04-2001 06-12-2000 05-02-2002 19-08-1999 27-03-2003 26-11-2002
WO 9960032	A	25-11-1999	US 6207606 B1 AU 743509 B2 AU 3983599 A BR 9910482 A CA 2329438 A1 EP 1084153 A1 JP 2002515521 T WO 9960032 A1 US 2002010077 A1	27-03-2001 24-01-2002 06-12-1999 09-01-2001 25-11-1999 21-03-2001 28-05-2002 25-11-1999 24-01-2002
WO 9964476	A	16-12-1999	AU 743376 B2 AU 4333399 A BR 9911158 A CA 2330529 A1 EP 1090045 A1 JP 2002517571 T WO 9964476 A1 US 6211312 B1	24-01-2002 30-12-1999 03-04-2001 16-12-1999 11-04-2001 18-06-2002 16-12-1999 03-04-2001
WO 0037513	A	29-06-2000	AU 1836200 A BR 9915769 A CA 2332056 A1 EP 1144467 A1 JP 2002533484 T WO 0037513 A1 US 6291610 B1 US 2001044509 A1	12-07-2000 13-11-2001 29-06-2000 17-10-2001 08-10-2002 29-06-2000 18-09-2001 22-11-2001
JP 2000281709	A	10-10-2000	NONE	
WO 0140324	A	07-06-2001	AU 7845100 A BR 0016146 A CA 2392949 A1 EP 1255782 A1 JP 2003515627 T WO 0140324 A1 US 2002058766 A1	12-06-2001 13-08-2002 07-06-2001 13-11-2002 07-05-2003 07-06-2001 16-05-2002
WO 2000008036	A		NONE	