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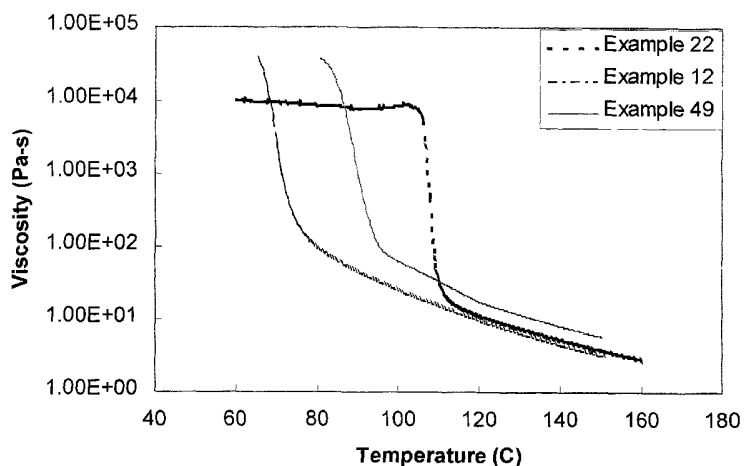
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[Continued on next page]

(54) Title: MULTIPLE CATALYST SYSTEM FOR OLEFIN POLYMERIZATION AND POLYMERS PRODUCED THEREFROM



(57) Abstract: This invention relates to a polymer comprising one or more C3 to C40 olefins, optionally one or more diolefins, and less than 15 mole % of ethylene, where the polymer has: a) a Dot T-Peel of 1 Newton or more; and b) a branching index (g') of 0.95 or less measured at the M_z of the polymer; c) an M_w of 100,000 or less and to a continuous process to produce a branched olefin polymer comprising 1) selecting a first catalyst component capable of producing a polymer having an M_w of 100,000 or less and a crystallinity of 5% or less under selected polymerization conditions; 2) selecting a second catalyst component capable of producing polymer having an M_w of 100,000 or less and a crystallinity of 20% or more at the selected polymerization conditions; 3) contacting the catalyst components in the presence of one or more activators with one or more C3 to C40 olefins, and, optionally one or more diolefins; 4) at a temperature of greater than 100°C; 5) at a residence time of 120 minutes or less; 6) wherein the ratio of the first catalyst to the second catalyst is from 1:1 to 50:1; 7) wherein the activity of the catalyst components is at least 100 kilograms of polymer per gram of the catalyst components; and wherein at least 20% of the olefins are converted to polymer.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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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)

EPO-Internal, WPI Data, 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 00/37514 A (EXXON CHEMICAL PATENTS INC) 29 June 2000 (2000-06-29) cited in the application the whole document	1-54
X	WO 01/46277 A (EXXON CHEMICAL PATENTS INC) 28 June 2001 (2001-06-28) cited in the application claims; examples	1-54
X	WO 95/10575 A (EXXON CHEMICAL PATENTS INC) 20 April 1995 (1995-04-20) cited in the application page 11, line 10 - line 18; claims; examples	1-54
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☒ 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

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"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

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 248 832 B1 (PEACOCK ANDREW J) 19 June 2001 (2001-06-19) cited in the application column 3, line 52 - column 5, line 45	55-77, 79-83
A	column 7, line 56 - column 9, line 31; claims; examples -----	1-54
X	US 5 516 848 A (CANICH JO ANN M ET AL) 14 May 1996 (1996-05-14) cited in the application the whole document -----	55-57, 79-83
X	US 6 323 284 B1 (PEACOCK ANDREW J) 27 November 2001 (2001-11-27) cited in the application the whole document -----	55-77, 79-83
X	WO 02/070572 A (EXXONMOBIL CHEM PATENTS INC) 12 September 2002 (2002-09-12) page 6, line 17 - page 17, line 15 page 25, line 15 - page 27, line 14; claims; examples -----	1-77, 79-83
A	US 2001/007896 A1 (AGARWAL PAWAN KUMAR ET AL) 12 July 2001 (2001-07-12) cited in the application column 2, line 0025; claims; examples -----	1-54
A	WO 99/29742 A (EXXON CHEMICAL PATENTS INC) 17 June 1999 (1999-06-17) claims -----	1-54
A	WO 91/07472 A (EXXON CHEMICAL LTD ;EXXON CHEMICAL PATENTS INC (US)) 30 May 1991 (1991-05-30) cited in the application claims -----	50-54
A	WO 97/20872 A (EXXON CHEMICAL PATENTS INC) 12 June 1997 (1997-06-12) claims -----	50-54

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/32910

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:

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.:

1 - 77, 79 - 83

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: 1-77,79-83

As the common subject-matter of the numerous claims 1 - 77 and 79-83, a special branched bimodal polymer and a process for the preparation thereof can be recognized. The special technical feature of the claimed process is, that two different metallocene catalyst components are used, wherefrom one is stereospecific and the other is not.

2. claim: 78

Subject-matter of claim 78 is a process to prepare an adhesive composition, wherein the special technical feature of claims 1 - 77 and 79 - 83 is not mentioned.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/32910

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0037514	A	29-06-2000	BR 9916426 A CA 2356667 A1 CN 1361795 T EP 1141051 A1 JP 2002533485 T WO 0037514 A1 US 2003060583 A1 US 6573350 B1	04-09-2001 29-06-2000 31-07-2002 10-10-2001 08-10-2002 29-06-2000 27-03-2003 03-06-2003
WO 0146277	A	28-06-2001	AU 2289101 A AU 2592601 A BR 0016618 A CA 2395532 A1 CA 2414498 A1 CN 1433451 T EP 1263815 A2 EP 1263909 A2 JP 2003518171 T WO 0146277 A2 WO 0146278 A2 US 2002019507 A1 US 2002007033 A1 US 2002039623 A1 CA 2388850 A1 EP 1290100 A1 WO 0181493 A1	03-07-2001 03-07-2001 03-09-2002 28-06-2001 08-06-2001 30-07-2003 11-12-2002 11-12-2002 03-06-2003 28-06-2001 28-06-2001 14-02-2002 17-01-2002 04-04-2002 01-11-2001 12-03-2003 01-11-2001
WO 9510575	A	20-04-1995	WO 9510575 A1	20-04-1995
US 6248832	B1	19-06-2001	BR 0016284 A CA 2393481 A1 CN 1408010 T EP 1238008 A1 JP 2003516451 T WO 0142350 A1	24-12-2002 14-06-2001 02-04-2003 11-09-2002 13-05-2003 14-06-2001
US 5516848	A	14-05-1996	CA 2209773 A1 DE 69607147 D1 DE 69607147 T2 EP 0807143 A1 ES 2144725 T3 JP 11500474 T WO 9623838 A1 US 5955625 A	08-08-1996 20-04-2000 28-09-2000 19-11-1997 16-06-2000 12-01-1999 08-08-1996 21-09-1999
US 6323284	B1	27-11-2001	BR 0016272 A CA 2393698 A1 CN 1408011 T EP 1268657 A1 JP 2003516452 T WO 0142351 A1	22-10-2002 14-06-2001 02-04-2003 02-01-2003 13-05-2003 14-06-2001
WO 02070572	A	12-09-2002	US 2001044506 A1 EP 1373337 A2 WO 02070572 A2	22-11-2001 02-01-2004 12-09-2002
US 2001007896	A1	12-07-2001	US 2004087749 A1 US 2004087750 A1	06-05-2004 06-05-2004

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/32910

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001007896 A1		US 2002013440 A1	31-01-2002
		BR 0016286 A	27-08-2002
		CA 2393598 A1	14-06-2001
		CN 1409731 T	09-04-2003
		EP 1237963 A1	11-09-2002
		JP 2003516441 T	13-05-2003
		WO 0142323 A1	14-06-2001

WO 9929742 A	17-06-1999	BR 9813031 A	15-08-2000
		CA 2306352 A1	17-06-1999
		CN 1106408 B	23-04-2003
		DE 69818705 D1	06-11-2003
		EP 1361232 A2	12-11-2003
		EP 1044225 A1	18-10-2000
		JP 2001525460 T	11-12-2001
		US 6197910 B1	06-03-2001
		WO 9929742 A1	17-06-1999
		US 6342574 B1	29-01-2002

WO 9107472 A	30-05-1991	CA 2068658 A1	15-05-1991
		DE 69028210 D1	26-09-1996
		DE 69028210 T2	16-01-1997
		EP 0500646 A1	02-09-1992
		WO 9107472 A1	30-05-1991
		JP 3009460 B2	14-02-2000
		JP 5504983 T	29-07-1993
		KR 170755 B1	20-03-1999

WO 9720872 A	12-06-1997	CN 1427015 A	02-07-2003
		CN 1203605 A ,B	30-12-1998
		DE 69624590 D1	05-12-2002
		DE 69624590 T2	14-08-2003
		EP 0871675 A1	21-10-1998
		JP 2000502130 T	22-02-2000
		WO 9720872 A1	12-06-1997
		US 5874512 A	23-02-1999
