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- (72) Inventor; and
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- (74) Agents: **GOLOTA, Mary** et al.; BASF Corporation, 26701 Telegraph Road, Southfield, MI 48034-2442 (US).

(54) Title: METHOD OF MAKING A GRAFT POLYMER

(57) Abstract: The invention provides an improved method of making graft polymers. In particular, the invention provides a method of making graft polymers comprising providing an emulsion comprising at least one or more first monomer (a), at least one or more second monomer (b), and at least one graft material (c). The emulsion is subjected to conditions such that it undergoes simultaneous free radical polymerization and grafting. One or more first monomer (a) is unsaturated and is free of any functional groups reactable with functional groups Fb or Fc. Monomer (a) may optionally comprise a functional group Fa which is not reactive with either functional group Fb or Fc. One or more second monomer (b) is unsaturated and comprises a functional group Fb reactive with functional group Fc. Graft material (c) comprises an unsaturated compound comprising a functional group Fc reactive with functional group Fb, and a graft moiety. The unsaturated graft material (c) may be monomeric, oligomeric, or polymeric. Most preferred graft moieties are carbamate groups, groups convertible to carbamate and polyurethane polymers.



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INTERNATIONAL SEARCH REPORT

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| A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G18/67 C08F283/00 C08F290/06 C08F265/10 C09D151/08 | | |
| 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 C08G C09D C08L C09J | | |
| 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. |
| P, X | WO 01 34674 A (ANGERMUELLER HARALD ;WEGNER EGON (DE); BASF COATINGS AG (DE); SCHW) 17 May 2001 (2001-05-17) * (Article 8.2 PCT) : abstract ; claims 6-12, 1-3, 13-19 ; page 8, line 11 - page 11, line 4 ; page 39, line 9 - page 48, line 30 ; page 16, line 15 - page 35, line 27 ; examples * | 1-6, 8, 10 |
| X | GB 899 567 A (BASF AG) 27 June 1962 (1962-06-27) * page 1, line 42-49, 69-79 ; page 2, line 38-52, 114-116 ; page 3, line 5-14, 39-44, 15-38, 95-98 ; claim 3 ; examples * page 2, line 55-68 | 1-5, 10 |
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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 6 040 062 A (CAMPBELL DONALD H ET AL) 21 March 2000 (2000-03-21) * abstract ; column 2, line 25-39, 57-62 ; column 3, line 18-19 ; column 3, line 1 - column 5, line 44 ; column 6, line 39 - column 8, line 9 * column 8, line 32,33; claims 1-12 --- | 1-7,9,10 |
| X | US 6 063 861 A (BLUM HARALD ET AL) 16 May 2000 (2000-05-16) * column 4, line 24-28 ; column 4, line 54 - column 5, line 23 ; column 5, line 43-63 ; column 5, line 35-37 ; abstract ; column 5, line 19-23 ; column 4, line 29-44 * column 3, line 1 -column 4, line 23 --- | 1-6,10 |
| P,X | WO 01 34672 A (FIGGER HANS JUERGEN ;BASF COATINGS AG (DE)) 17 May 2001 (2001-05-17) * (Article 8.2 PCT) : abstract ; page 5, line 16 - page 22, line 7 ; page 14, line 11-20 * page 23, line 21-31 --- | 1-6,8,10 |
| X | US 6 162 506 A (BRUEGGEMANN HERMANN ET AL) 19 December 2000 (2000-12-19) * claims 1-18 ; abstract ; column 10, line 47-54 ; column 11, line 9-10 ; column 9, line 30-38 ; column 3, line 44-47 * column 12, line 6-11 --- | 1-6,8,10 |
| X | US 5 919 972 A (GALLAGHER JAMES A ET AL) 6 July 1999 (1999-07-06) * abstract ; claims 7,8,1-5 ; column 1, line 65 - column 2, line 28 ; column 2, line 48 - column 3, line 23 ; column 8, line 55-56 - particularly "surface-active agents" ; column 9, line 2-4 * column 3, line 39 -column 6, line 60 --- | 1-6 |
| X | EP 0 608 021 A (AKZO NV) 27 July 1994 (1994-07-27) * page 4, line 5 - page 5, line 8 ; claims 7, 1-10 ; abstract * page 2, line 38 -page 3, line 54 --- | 1-8,10 |
| X | EP 0 841 357 A (BASF AG) 13 May 1998 (1998-05-13) * claims 1,2,6,9 ; abstract * page 3, line 16 -page 10, line 40 --- | 1-6,8,10 |
| X | US 5 334 420 A (HARTUNG MICHAEL ET AL) 2 August 1994 (1994-08-02) * column 7, line 1 - column 8, line 33 * column 2, line 33,34; claims 1-16 --- | 1-6,8,10 |
| | -/-- | |

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/48631

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | WO 00 71505 A (BASF CORP ;OHRBOM WALTER (US); HERREL PATRICIA (US)) 30 November 2000 (2000-11-30) * claims 8-16 ; abstract * page 6, line 10 -page 8, line 15 ---- | 1-6,8-10 |
| Y | WO 00 26315 A (BASF CORP ;BOISSEAU JOHN (US); OHRBOM WALTER (US); REHFUSS JOHN (U)) 11 May 2000 (2000-05-11) * claims 1-37 ; page 5, line 36 - page 34, line 17 ; examples * ---- | 1-6,8-10 |
| A | EP 0 767 187 A (BASF CORP) 9 April 1997 (1997-04-09) abstract; claims 1-27 ---- | 1-10 |
| A | WO 00 31195 A (BASF CORP ;OHRBOM WALTER (US); REHFUSS JOHN (US); ST AUBIN DONALD) 2 June 2000 (2000-06-02) claims 1-18; example 2 ---- | 1-10 |
| A | US 5 356 669 A (ST AUBIN DONALD L ET AL) 18 October 1994 (1994-10-18) abstract; claims 1-14 ---- | 1-10 |
| A | US 6 037 441 A (ST AUBIN DONALD L ET AL) 14 March 2000 (2000-03-14) * claims 1-10 ; abstract ; column 11, line 6-33 * column 10, line 10-19 ---- | 1-10 |
| A | US 4 532 266 A (RASSHOFER WERNER ET AL) 30 July 1985 (1985-07-30) claims 1-13 ----- | 1-10 |

INTERNATIONAL SEARCH REPORT

International application No.
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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.:

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: 1-5

A method of making graft copolymers, comprising providing an emulsion comprising, (a) optionally, at least one or more first monomer which is unsaturated and is free of any functional groups reactable with the (b) or (c) functional groups ; (b) at least one or more second monomer which is unsaturated and comprises a functional group reactive with the (c) functional group ; (c) at least one graft material which comprises an unsaturated compound comprising a functional group reactive with the (b) functional group, and a graft moiety ; subjecting the emulsion to simultaneous free radical polymerisation and grafting.

2. Claim : 6

Method of making a graft copolymer, comprising providing an emulsion comprising, (a) optionally, at least one or more first monomer as disclosed in claim 1 ; (b) specifically a hydroxyalkyl(meth)acrylate ; (c) at least one graft material as disclosed in claim 1 ; subjecting the emulsion to simultaneous free radical polymerisation and grafting.

3. Claim : 7

Method of making a graft copolymer, comprising providing an emulsion comprising, (a) optionally, at least one or more first monomer as disclosed in claim 1 ; (b) specifically meta-isopropenyl alpha,alpha-dimethylbenzyl isocyanate ; (c) at least one graft material as disclosed in claim 1 ; subjecting the emulsion to simultaneous free radical polymerisation and grafting.

4. Claim : 8

Method of making graft copolymer, comprising providing an emulsion comprising, (a) optionally, at least one or more first monomer as disclosed in claim 1 ; (b) at least one or more second monomer as disclosed in claim 1 ; (c) specifically an isocyanate functional polyurethane polymer or oligomer ; subjecting the emulsion to simultaneous free radical polymerisation and grafting.

5. Claim : 9

Method of making a graft copolymer, comprising providing an emulsion comprising, (a) optionally, at least one or more first monomer as disclosed in claim 1 ; (b) at least one or

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

more second monomer as disclosed in claim 1 ; (c)
specifically a hydroxyalkyl carbamate ; subjecting the
emulsion to simultaneous free radical polymerisation and
grafting.

6. Claim : 10

A coating composition comprising a graft copolymer, obtained
from a process comprising an emulsion as disclosed in claim
1.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/48631

| Patent document cited in search report | | Publication date | | Patent family member(s) | Publication date |
|--|-----------|------------------|----|-------------------------|------------------|
| WO 0134674 | A | 17-05-2001 | DE | 19953445 A1 | 17-05-2001 |
| | | | AU | 7916000 A | 06-06-2001 |
| | | | WO | 0134674 A1 | 17-05-2001 |
| | | | EP | 1226198 A1 | 31-07-2002 |
| GB 899567 | A | 27-06-1962 | DE | 1138934 B | 31-10-1962 |
| | | | FR | 1277263 A | 24-11-1961 |
| | | | BE | 598869 A | |
| | | | NL | 259698 A | |
| US 6040062 | A | 21-03-2000 | US | 5726244 A | 10-03-1998 |
| | | | US | 6084038 A | 04-07-2000 |
| | | | US | 6160058 A | 12-12-2000 |
| | | | US | 6080825 A | 27-06-2000 |
| | | | US | 5994479 A | 30-11-1999 |
| | | | AU | 703033 B2 | 11-03-1999 |
| | | | AU | 6198796 A | 13-02-1997 |
| | | | BR | 9603381 A | 12-05-1998 |
| | | | CA | 2182901 A1 | 11-02-1997 |
| | | | CN | 1148612 A ,B | 30-04-1997 |
| | | | DE | 69610805 D1 | 07-12-2000 |
| | | | DE | 69610805 T2 | 12-04-2001 |
| | | | EP | 0761695 A2 | 12-03-1997 |
| | | | ES | 2153523 T3 | 01-03-2001 |
| JP | 9221578 A | 26-08-1997 | | | |
| US 6063861 | A | 16-05-2000 | DE | 19753222 A1 | 02-06-1999 |
| | | | EP | 0919579 A1 | 02-06-1999 |
| | | | JP | 11256033 A | 21-09-1999 |
| WO 0134672 | A | 17-05-2001 | DE | 19953446 A1 | 17-05-2001 |
| | | | AU | 7663200 A | 06-06-2001 |
| | | | WO | 0134672 A1 | 17-05-2001 |
| | | | EP | 1230283 A1 | 14-08-2002 |
| US 6162506 | A | 19-12-2000 | DE | 19722862 C1 | 14-01-1999 |
| | | | WO | 9854266 A1 | 03-12-1998 |
| | | | EP | 0986617 A1 | 22-03-2000 |
| | | | JP | 2002502451 T | 22-01-2002 |
| US 5919972 | A | 06-07-1999 | US | 5863959 A | 26-01-1999 |
| | | | US | 5741851 A | 21-04-1998 |
| | | | AT | 200905 T | 15-05-2001 |
| | | | CA | 2140706 A1 | 22-07-1995 |
| | | | DE | 69520802 D1 | 07-06-2001 |
| | | | DE | 69520802 T2 | 09-08-2001 |
| | | | EP | 0664306 A2 | 26-07-1995 |
| | | | ES | 2156164 T3 | 16-06-2001 |
| | | | US | 5710220 A | 20-01-1998 |
| EP 0608021 | A | 27-07-1994 | AT | 152740 T | 15-05-1997 |
| | | | CA | 2113964 A1 | 22-07-1994 |
| | | | DE | 69402993 D1 | 12-06-1997 |
| | | | DE | 69402993 T2 | 23-10-1997 |
| | | | DK | 608021 T3 | 20-10-1997 |
| | | | EP | 0608021 A1 | 27-07-1994 |
| | | | ES | 2101428 T3 | 01-07-1997 |
| | | | GR | 3024210 T3 | 31-10-1997 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/48631

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|--|---|------------------|---|--|
| EP 0608021 | A | | JP 3195486 B2 JP 6299039 A US 5494980 A | 06-08-2001 25-10-1994 27-02-1996 |
| EP 0841357 | A | 13-05-1998 | DE 19645761 A1 EP 0841357 A2 JP 10158345 A | 07-05-1998 13-05-1998 16-06-1998 |
| US 5334420 | A | 02-08-1994 | DE 4010176 A1 AT 110749 T BR 9106292 A DE 59102754 D1 DK 521928 T3 WO 9115528 A1 EP 0521928 A1 ES 2064096 T3 JP 7033490 B JP 5501124 T | 02-10-1991 15-09-1994 13-04-1993 06-10-1994 09-01-1995 17-10-1991 13-01-1993 16-01-1995 12-04-1995 04-03-1993 |
| WO 0071505 | A | 30-11-2000 | US 6346591 B1 AU 5006300 A BR 0009024 A EP 1178957 A1 WO 0071505 A1 US 2002103319 A1 US 2002086966 A1 US 2002035289 A1 | 12-02-2002 12-12-2000 26-12-2001 13-02-2002 30-11-2000 01-08-2002 04-07-2002 21-03-2002 |
| WO 0026315 | A | 11-05-2000 | US 6160058 A AU 1449400 A BR 9914152 A EP 1124909 A1 WO 0026315 A1 | 12-12-2000 22-05-2000 30-10-2001 22-08-2001 11-05-2000 |
| EP 0767187 | A | 09-04-1997 | US 5854385 A AU 721833 B2 AU 6805096 A BR 9605018 A CA 2187225 A1 CN 1150965 A ,B EP 0767187 A1 JP 9221636 A US 6084038 A US 6160058 A US 6080825 A US 5994479 A | 29-12-1998 13-07-2000 10-04-1997 23-06-1998 07-04-1997 04-06-1997 09-04-1997 26-08-1997 04-07-2000 12-12-2000 27-06-2000 30-11-1999 |
| WO 0031195 | A | 02-06-2000 | US 6106951 A AU 1465100 A BR 9914106 A EP 1141149 A1 WO 0031195 A1 | 22-08-2000 13-06-2000 16-10-2001 10-10-2001 02-06-2000 |
| US 5356669 | A | 18-10-1994 | AU 659037 B2 AU 4897893 A BR 9304313 A CA 2108993 A1 CN 1085928 A ,B | 04-05-1995 19-05-1994 03-05-1994 24-04-1994 27-04-1994 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/48631

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 5356669 | A | | EP 0594068 A1 | 27-04-1994 |
| | | | JP 2680564 B2 | 19-11-1997 |
| | | | JP 8332456 A | 17-12-1996 |
| | | | JP 2575597 B2 | 29-01-1997 |
| | | | JP 6210243 A | 02-08-1994 |
| | | | KR 137438 B1 | 28-04-1998 |
| | | | KR 137480 B1 | 28-04-1998 |
| | | | MX 9306562 A1 | 30-06-1994 |
| | | | US 5474811 A | 12-12-1995 |
| | | | US 5605965 A | 25-02-1997 |
| | | | US 5726246 A | 10-03-1998 |
| US 6037441 | A | 14-03-2000 | AU 730540 B2 | 08-03-2001 |
| | | | AU 5603698 A | 15-07-1998 |
| | | | BR 9711428 A | 24-08-1999 |
| | | | CA 2253202 A1 | 25-06-1998 |
| | | | CN 1233264 A | 27-10-1999 |
| | | | EP 0946631 A1 | 06-10-1999 |
| | | | JP 2001511823 T | 14-08-2001 |
| | | | WO 9827146 A1 | 25-06-1998 |
| US 4532266 | A | 30-07-1985 | DE 3112118 A1 | 07-10-1982 |
| | | | DE 3269276 D1 | 03-04-1986 |
| | | | EP 0061627 A2 | 06-10-1982 |