

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 November 2007 (01.11.2007)

PCT

(10) International Publication Number  
WO 2007/123932 A3

- (51) **International Patent Classification:**  
**B01J 21/04** (2006.01)      **B01J 37/02** (2006.01)  
**B01J 23/68** (2006.01)
- (21) **International Application Number:**  
PCT/US2007/009446
- (22) **International Filing Date:** 17 April 2007 (17.04.2007)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
60/792,712                      18 April 2006 (18.04.2006)      US
- (71) **Applicant (for all designated States except US):** **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **NATAL, Manuel, A.W.** [US/US]; 314 Rosemary Lane, Lake Jackson, TX 77566 (US). **BHASIN, Madan, M.** [US/US]; 9 Carriage Road, Charleston, WV 25314 (US). **SOO, Hwaiii** [US/US]; 116 East Ridge Road, Charleston, WV 25314 (US). **LIU, Albert, C.** [US/US]; 1534 Quarrier Street, Charleston, WV 25311 (US).
- (74) **Agent:** **RUHR, Paula, Sanders;** The Dow Chemical Company, Intellectual Property Law, P.O. Box 1967, Midland, MI 48641-1967 (US).

- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**  
— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

[Continued on next page]

(54) **Title:** ALKYLENE OXIDE CATALYST AND USE THEREOF

CATALYST SELECTIVITY AT HIGH WORKRATE

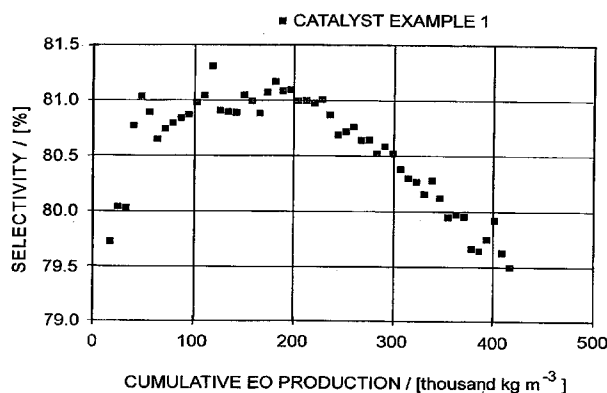


Fig. 1

(57) **Abstract:** A supported silver catalyst and use thereof in a process for producing an alkylene oxide, such as ethylene oxide, by the direct oxidation of an alkylene with oxygen or an oxygen-containing gas, wherein the catalyst provides improved stability and improved resilience to reactor upsets and timely recovery to substantially pre-upset levels of catalyst activity and/or efficiency. In some embodiments, the catalyst also exhibits improved activity. A catalyst capable of producing ethylene oxide at a selectivity of at least 87 percent while achieving a work rate of at least 184 kg/h/m<sup>3</sup> at a temperature of no greater than 235°C when operated in a process where the inlet feed to a reactor containing the catalyst comprises ethylene, oxygen, and carbon dioxide, wherein the concentration of carbon dioxide in the inlet feed is greater than or equal to 2 mole percent.

WO 2007/123932 A3



---

**(88) Date of publication of the international search report:**  
28 August 2008

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2007/009446

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. B01J21/04 B01J23/68 B01J37/02

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)  
B01J

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/023418 A (UNION CARBIDE CHEM PLASTIC [US]; THORSTEINSON ERLIND M [US]; BHASIN MA) 17 March 2005 (2005-03-17) page 4, line 23 - page 6, line 12 page 16, line 25 - page 24, line 31; claims; examples; tables page 7, line 6 - line 15 page 28, line 4 - line 30 page 31, line 6 - page 33, line 2	1-47,51
X	US 2004/198993 A1 (MATUSZ MAREK [US] ET AL) 7 October 2004 (2004-10-07) paragraph [0014] - paragraph [0026] paragraph [0049]; claims; examples paragraph [0048] - paragraph [0051] ----- -/--	1-47,50, 51

Further documents are listed in the continuation of Box C.

See patent family 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.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

19 June 2008

30/06/2008

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

de Cauwer, Robby

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2007/009446

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97/40933 A (SHELL INT RESEARCH [NL]) 6 November 1997 (1997-11-06) claims; examples; tables -----	1-47,51
X	WO 2004/078736 A (SHELL OIL CO [US]; EVANS WAYNE ERROL [US]; MATUSZ MAREK [US]) 16 September 2004 (2004-09-16) page 11 - page 12; figure 1; example 1; tables page 7, line 8 - line 20 page 9, line 6 - line 9 page 12, line 15 - line 31 page 13, line 18 - page 14, line 19 -----	26-28, 45-50
P;X	WO 2006/133187 A (SAINT GOBAIN CERAMICS [US]; SZYMANSKI THOMAS [US]; REMUS DONALD J [US]) 14 December 2006 (2006-12-14) page 19, line 7 - page 26, line 7; claims; examples; tables -----	1-47,50, 51
X	WO 03/074171 A (SCIENT DESIGN CO [US]) 12 September 2003 (2003-09-12)  page 4, line 19 - page 5, line 21; examples; tables -----	1-4,6-9, 11-16, 22-25, 29,51
X	EP 0 764 464 A2 (MITSUBISHI CHEM CORP [JP]) 26 March 1997 (1997-03-26)  page 2, line 55 - page 4, line 53; claims; examples; tables -----	1-4,6-9, 11-16, 22-25, 29,51
A	US 6 511 938 B1 (LIU ALBERT CHENG-YU [US] ET AL) 28 January 2003 (2003-01-28) the whole document -----	

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2007/009446

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 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 No. III Observations where unity of invention is lacking (Continuation of item 3 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 allsearchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
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 and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- 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: 1-4, 6-9, 11-16, 22-25 (in as far as the dependent claims relate to incorporating Ce and/or Rb, Na and/or Li) and 51

a catalyst comprising a carrier comprising > 80 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, rubidium or mixtures thereof, (c) sodium, lithium or mixtures thereof, (d) optionally one or more solid promoters and a process for producing said supported silver catalyst

- 1.1. claim: 29

a catalyst comprising silver and promoters deposited on a support comprising alpha-alumina

2. claims: 5, 6-9, 11-15, 19-25 (in as far as the dependent claims relate to incorporating Ce, Na, Li, and Mn and S)

a catalyst comprising a carrier comprising > 98 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, (c) sodium and lithium, (d) manganese, (e) sulfur and (f) optionally rhenium, tungsten, molybdenum or mixtures thereof.

3. claims: 10, 11-16, 21-25 (in as far as the claims relate to incorporating Ce and/or Rb, Na and/or Li, and S)

a catalyst comprising a carrier comprising > 80 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, rubidium or mixtures thereof, (c) sodium, lithium or mixtures thereof, and (d) sulfur

4. claims: 17, 21-25 (in as far as the claims relate to incorporating Ce and/or Rb, Na and/or Li, and Re)

a catalyst comprising a carrier comprising > 80 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, rubidium or mixtures thereof, (c) sodium, lithium or mixtures thereof, and (d) rhenium

5. claims: claim 18, 20-25 (in as far as the claims relate to incorporating Ce and/or Rb, Na and/or Li and Mn)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

a catalyst comprising a carrier comprising > 80 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, rubidium or mixtures thereof, (c) sodium, lithium or mixtures thereof, and (d) manganese  
---

6. claims: 26-28,45-49

a process for the production of alkylene oxides comprising contacting an alkylene with oxygen or an oxygen containing gas in the presence of a supported silver catalyst  
---

7. claims: 30,31,33-44

a catalyst comprising a carrier comprising > 95 wt% alpha-alumina, with deposited thereon (a) silver, (b) cesium, rubidium or mixtures thereof, (c) sodium, lithium or mixtures thereof, and (d) rhenium (e) at least one of sulfur, molybdenum, tungsten and mixtures thereof.  
---

8. claim: 50

a process for producing an ethylene glycol, an ethylene amine or an ethylene glycol ether  
---

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/009446

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2005023418	A	17-03-2005	CA 2538992 A1	17-03-2005
			CN 1838991 A	27-09-2006
			EP 1658136 A1	24-05-2006
			JP 2007503305 T	22-02-2007
US 2004198993	A1	07-10-2004	NONE	
WO 9740933	A	06-11-1997	AU 711973 B2	28-10-1999
			AU 2776097 A	19-11-1997
			CA 2252780 A1	06-11-1997
			CN 1216940 A	19-05-1999
			DE 69705309 D1	26-07-2001
			DE 69705309 T2	15-11-2001
			EP 0900128 A1	10-03-1999
			ES 2158559 T3	01-09-2001
			JP 4052673 B2	27-02-2008
			JP 2000508969 T	18-07-2000
			US 5801259 A	01-09-1998
WO 2004078736	A	16-09-2004	BR PI0407801 A	14-02-2006
			CA 2517359 A1	16-09-2004
			CN 1768048 A	03-05-2006
			EP 1603892 A1	14-12-2005
			JP 2006520816 T	14-09-2006
			KR 20060033857 A	20-04-2006
			MX PA05009001 A	18-10-2005
WO 2006133187	A	14-12-2006	AU 2006255037 A1	14-12-2006
			CA 2609199 A1	14-12-2006
			CN 101193699 A	04-06-2008
			EP 1901842 A2	26-03-2008
			KR 20080011225 A	31-01-2008
WO 03074171	A	12-09-2003	AU 2003213248 A1	16-09-2003
			BR 0308078 A	21-12-2004
			CA 2505929 A1	12-09-2003
			CN 1638862 A	13-07-2005
			EP 1480742 A1	01-12-2004
			JP 2005518927 T	30-06-2005
			KR 20040088563 A	16-10-2004
			MX PA04008462 A	06-12-2004
			US 2003171215 A1	11-09-2003
EP 0764464	A2	26-03-1997	CA 2186331 A1	26-03-1997
			DE 69634623 D1	25-05-2005
			DE 69634623 T2	02-03-2006
			EP 1529565 A1	11-05-2005
			US 5705661 A	06-01-1998
US 6511938	B1	28-01-2003	NONE	