



(51) International Patent Classification:
C07C 309/02 (2006.01)

(21) International Application Number:
PCT/US2012/030850

(22) International Filing Date:
28 March 2012 (28.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/470,767 1 April 2011 (01.04.2011) US
61/597,883 13 February 2012 (13.02.2012) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:
3 January 2013

(54) Title: STABILIZED ACID AMPLIFIERS

(57) Abstract: There are disclosed sulfonic acid precursor compositions, as are methods of using these compositions in, for example, photolithography. Other embodiments are also disclosed.



WO 2012/135286 A3

A. CLASSIFICATION OF SUBJECT MATTER***C07C 309/02(2006.01)i***

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)

C07C 309/02; A61K 31/5383; C07D 225/02; C07D 498/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: PAG, photoacid generator, acid amplifier, acid precursor, lithography.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FRIED, JOSEF et al., "Synthesis and Properties of 7,7-Difluoro Derivatives of the 2,6-Dioxo[3.1.1]bicycloheptane Ring System Present in Thromboxane A ₂ ", J. Am. Chem. Soc. 1984, Vol. 106, 3871-3872.	1,23-24,29
A	See compounds 14 & 15 in page 3871.	2-22,25-28,30-52
A	NUNEZ, ANA et al., "Ring-Closing Metathesis Reactions on Azinium Salts: Straightforward Access to Quinolizinium Cations and Their Dihydro Derivatives", J. Org. Chem. 2009, Vol. 74, 4166-4176. See Table 4.	1-30,38-52
A	HANESSIAN, STEPHEN et al., "Synthetic Studies in the Intramolecular Carbocyclization of N-Acyloxyiminium Ions. Stereoelectronic and Steric Implications of Nucleophilic Alkene, Alkyne, and Allene Tethers", J. Org. Chem. 2005, Vol. 70, 5070-5085. See Scheme 2 and page 5079.	1-30,38-52
A	WANG, JIN et al., "Vinyl Diazophosphonates as Precursors to Quaternary Substituted Indolines and Cyclopentenones", Organic Letters 2011, Vol. 13, 700-702. (14 January 2011) See Table 1.	1-30,38-52



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 application or patent 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 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 OCTOBER 2012 (30.10.2012)

Date of mailing of the international search report

31 OCTOBER 2012 (31.10.2012)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan
City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

KIM, Dongseok

Telephone No. 82-42-481-8647



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/030850

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007-0255055 A1 (VITE, GREGORY D. et al.) 01 November 2007 See paragraph [0093].	1-30,38-52
A	US 2008-0287414 A1 (BERGMAN, JEFFREY M. et al.) 20 November 2008 See paragraph [0399].	1-30,38-52
A	COEFFARD, VINCENT et al., "Mild Electrochemical Deprotection of N-Phenylsulfonyl N-Substituted Amines Derived from (R)-Phenylglycinol", Eur. J. Org. Chem. 2008, 383-391. See page 388, right column, line 33.	1-30,38-52
A	RAGHAVAN, SADAGOPAN et al., "Stereoselective synthesis of (-)-allosedamine and (1R,3R)-HPA-12 from beta-p-toluenesulfonamido-gamma,delta-unsaturated sulfoxide", Tetrahedron 2004, Vol. 60, 5059-5067. See compound 21 in Scheme 5.	1-30,38-52
A	ASENSIO, GREGORIO et al., "H-Bonding Interactions in the Epoxidation of Alkenylammonium Salts with Dimethyldioxirane and m-Chloroperbenzoic Acid: A Kinetic Study", J. Org. Chem. 1999, Vol. 64, 4705-4711. See page 4710, right column, lines 5-6.	1-30,38-52
A	JIANG, ZHONG-XING et al., "Asymmetric synthesis of both enantiomers of syn-(3-trifluoromethyl)cysteine derivatives", J. Fluorine Chem. 2005, Vol. 126, 499-505. See compounds 4a & 4b in Scheme 3.	1-30,38-52
A	CREARY, XAVIER et al., "Response of Triflates to Solvent Ionizing Power. A YOTf Scale Based on 7-Norbornyl Triflate", J. Org. Chem. 1985, Vol. 50, 474-479. See compounds 3-5 in Table I.	1-30,38-52
A	HEIMANN, JENS et al., "Cathodic Cyclisation of N-(Oxoalkyl)pyridinium Salts - Formation of Tricyclic Indolizidine and Quinolizidine Derivatives in Aqueous Medium", Eur. J. Org. Chem. 2003, 2919-2932. See compounds 27-28 in Scheme 5.	1-30,38-52

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2012/030850**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.: 33-37
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:

Claims 33-37 refer to claim(s) which is/are not drafted in accordance with the second and/or third sentence of Rule 6.4(a).
Thus, no meaningful search could be carried out for claims 33-37.
3. ☒ Claims Nos.: 31-32
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 an extra 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 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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/030850

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PCT/US2012/030850

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(Box III.)

Invention group I (Claims 1, 11-22 & 39-52 to the extent that they relate to a compound of formula in claim 1 where A is $R^{40}-M-C(R^{10})(R^{20})-CHR^{50}-$):

A compound of formula in claim 1, a composition for photolithography, a photoresist composition, a photoresist substrate, a method for preparing a substrate for photolithography, or a method for conducting photolithography on a substrate related to the compound.

Invention group II (Claims 1-10, 41-42 & 47-52 to the extent that they relate to a compound of formula in claim 1 where A is $R^{100}-C(R^w)=C(R^x)-CHR^y-$):

A compound of formula in claim 1, a composition for photolithography, a photoresist composition, a photoresist substrate, a method for preparing a substrate for photolithography, or a method for conducting photolithography on a substrate related to the compound.

Invention group III (Claims 1, 23-30, 41 & 47-52 to the extent that they relate to a compound of formula in claim 1 where G1 and A, together with the carbon atom to which they are attached, form a non-aromatic, 5- or 6-membered ring D):

A compound of formula in claim 1, a composition for photolithography, a photoresist composition, a photoresist substrate, a method for preparing a substrate for photolithography, or a method for conducting photolithography on a substrate related to the compound.

Invention group IV (Claims 38 & 47-52 to the extent that they relate to the compound of formula in claim 38):

A compound of formula in claim 38, a composition for photolithography, a photoresist composition, a photoresist substrate, a method for preparing a substrate for photolithography, or a method for conducting photolithography on a substrate related to the compound.

The common technical feature linking invention groups I-III altogether is the $R^{30}-SO_2-O-CG^1G^2-$ structure in claim 1. However, the feature is already disclosed in FRIED, JOSEF et al., J. Am. Chem. Soc. 1984, Vol. 106, 3871-3872 (See compounds 14-15 in page 3871.). There is no common technical feature between invention groups I and IV. Thus, the invention groups I-IV do not relate to a single general inventive concept under PCT Rule 13.1, because there is no common technical feature contributing over the prior art within the meaning of PCT Rule 13.2.