

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 January 2008 (10.01.2008)

PCT

(10) International Publication Number  
**WO 2008/003453 A1**

(51) International Patent Classification:  
C11D 1/62 (2006.01)

Aquarecida [BR/BR]; Rua Juquitiba, 74, CEP 09450-000  
Rio Grande da Serra, SP (BR).

(21) International Application Number:  
PCT/EP2007/005860

(74) Agents: HÜTTER, Klaus et al.; Clariant Produkte  
(Deutschland) GmbH, Group Intellectual Property, Am  
Unisys-Park 1, 65843 Sulzbach (DE).

(22) International Filing Date: 3 July 2007 (03.07.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
06013998.7 6 July 2006 (06.07.2006) EP

(71) Applicant (for all designated States except US): CLARI-  
ANT (BRAZIL) S.A. [BR/BR]; Avenida das Nacoes  
Unidas, 180001, CEP-04795-900 Sao Paulo, SP (BR).

(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, 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, 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.

(72) Inventors; and

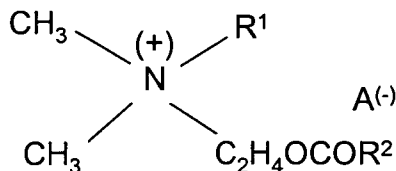
(75) Inventors/Applicants (for US only): GALLOTTI,  
Manlio [IT/BR]; Alameda Itu 1.420 apto 101, Cerqueira  
Cesar, CEP 01421-001 Sao Paulo, SP (BR). NUNES,  
George, Italo, Pitombeira [BR/BR]; Av. Fagundes  
Filho, 789 - apto 55, CEP 04304-011 Sao Paulo, SP  
(BR). DE MORAES, Patricia, Ramos, P. [BR/BR];  
Estrada do Itapeti, 100, Quadra 66, lote 11, CEP 0877-001  
Mogi das Cruzes, SP (BR). DE ALMEIDA, Natanael  
[BR/BR]; Rua Yoshio Honda, 13, CEP 08790-360 Mogi  
das Cruzes, SP (BR). BARGE, Cláudia [BR/BR]; R.  
Estado de Israel, 899, CEP 04022-002 Sao Paulo, SP (BR).  
KUME, Gustavo [BR/BR]; R. Iquiririm, 125 apto 04-B,  
CEP-05586-000 Sao Paulo, SP (BR). ACACIO, Denise,

(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

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: LIQUID SOFTENER COMPOSITION



(57) Abstract: A stable, homogenous and viscous softener formulation  
(I) is claimed which contains less than 50 % by weight of an esterquat  
compound of the formula (I) wherein R<sup>1</sup> is -C<sub>2</sub>H<sub>4</sub>OH or -C<sub>2</sub>H<sub>4</sub>OCOR<sup>2</sup>, R<sup>2</sup> is  
C<sub>11</sub>-C<sub>21</sub>-alkyl or alkenyl and A is an anion, as methylsulfate, bromide, iodide  
and, preferably, chloride, said esterquat being prepared by esterification of  
methyldiethanolamine with fatty acids and subsequent quatemization, with  
preferably methylchloride, the fatty acids containing at least 50 % by weight

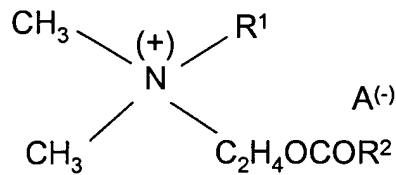
of saturated C<sub>18</sub>-fatty acid, comprising a final product containing at least 50 mol % of diester quat and at least 10 mol % of  
monoesterquat and having an acid value of less than 0.12 meq/g of esterquat active material, the rest being water and an organic  
solvent.

WO 2008/003453 A1

## Summary

## Liquid softener composition

- 5 A stable, homogenous and viscous softener formulation is claimed which contains less than 50 % by weight of an esterquat compound of the formula



- 10 wherein R<sup>1</sup> is -C<sub>2</sub>H<sub>4</sub>OH or -C<sub>2</sub>H<sub>4</sub>OCOR<sup>2</sup>, R<sup>2</sup> is C<sub>11</sub>-C<sub>21</sub>-alkyl or alkenyl and A is an anion, as methylsulfate, bromide, iodide and, preferably, chloride, said esterquat being prepared by esterification of methyldiethanolamine with fatty acids and subsequent quaternization, with preferably methylchloride, the fatty acids containing at least 50 % by weight of saturated C<sub>18</sub>-fatty acid, comprising a final
- 15 product containing at least 50 mol % of diester quat and at least 10 mol % of monoesterquat and having an acid value of less than 0.12 meq/g of esterquat active material, the rest being water and an organic solvent.

## Description

### Liquid softener composition

- 5 This invention relates to a liquid softener composition containing a dimethyldiethanolamine esterquat.

Esterquats are commonly known in the market for presenting problems concerning the production of viscous softeners, obliging the use of thickeners to achieve a  
10 high viscosity in the final product. High viscosities are especially important for some countries, more frequently in Latin America and Asia, where consumers still relate the good quality of a product to its viscosity.

In the present invention, it is shown that it is possible to significantly increase the  
15 viscosity of fabric softeners based on esterquats by lowering the temperature of the process, which allows an expressive reduction or even the complete removal of thickeners from the final formulation. It is basically disclosed a new option for working with esterquats in the production of fabric softeners, consisting of a highly concentrated esterquat composition dispersible in water at temperatures below  
20 60°C.

Many patents have claimed the use of dimethyldiethanolamine esterquats for fabric softener formulations. Patent WO 01/42412 claims the use of a softening compound having a transition temperature of less than 30°C for providing good in-  
25 wear comfort. Unsaturated dimethyldiethanolamine esterquats present a transition temperature below 30°C, but when saturated, which are the preferred composition of the present patent, they present a transition temperature above that. In patent WO 01/34743, dimethyldiethanolamine esterquats are cited among the preferred quaternary ammonium compounds. However, it is also claimed the obligatory use  
30 of metal chelating agents. The patent WO 99/27046 cites dimethyldiethanolamine esterquat as a possible cationic compound for rinse-added fabric softening compositions, including translucent or clear liquid compositions, but it is obligatory to associate it with a polyoxyalkylene alkyl amide surface active agent. A

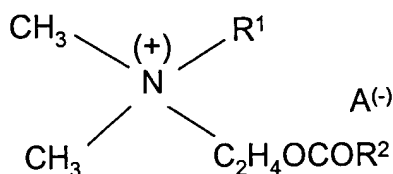
concentrated esterquat composition with water and solvent is disclosed in the patent application JP 10 251 972. However, in this patent is also claimed the obligatory use of alkali and alkaline earth metal salts which are included in the present invention as optional ingredients.

5

It has now been found that are some parameters that are important to optimize the final softener formulation viscosity. As it can be seen in the example, the acid value of the raw material must be less than 0.12 meq/g of esterquat active material, otherwise the viscosity of the final softener formulation will be significantly lower.

10

The invention provides liquid esterquat compositions containing less than 50 % by weight of an esterquat compound of the formula



15

wherein  $\text{R}^1$  is  $-\text{C}_2\text{H}_4\text{OH}$  or  $-\text{C}_2\text{H}_4\text{OCOR}^2$ ,  $\text{R}^2$  is  $\text{C}_{11}$ - $\text{C}_{21}$ -alkyl or alkenyl and A is an anion, as methylsulfate, bromide, iodide and, preferably, chloride, said esterquat being prepared by esterification of methyldiethanolamine with fatty acids and subsequent quaternization, with preferably methylchloride, the fatty acids containing at least 50 % by weight of saturated  $\text{C}_{18}$ -fatty acid, the esterquat containing at least 50 mol % of diester quat and at least 10 mol % of monoesterquat and having an acid value of less than 0.12 meq/g of esterquat active material, the rest being water and an organic solvent.

20

The group  $-\text{COR}^2$  is preferably derived from natural occurring fatty acids such as capronic acid, caprylic acid, caprinic acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic, oleic acid, eluidinic acid, arachinic acid, behenic acid and eruca acid. Preferred acids containing the group  $-\text{COR}^2$  are  $\text{C}_{12}$ / $\text{C}_{18}$  coco fatty acids, tallow fatty acid, fully or partially hydrogenated tallow fatty acid, palm fatty acid, partially or fully hydrogenated palm fatty acid or stearic acid.

30

These esterquats are made by methods known per se, for example by esterification of methyl-diethanolamine with a fatty acid of the formula  $R^2COOH$  and subsequent quaternization with preferably methylchloride or dimethylsulfate or any other quaternization agent introducing a methyl group. The fatty acids used must be of such kind that they contain at least 50 % by weight of saturated  $C_{18}$ -fatty acid. Preferably the fatty acid is derived from vegetable and/or animal fatty acid and contains at least 50 % by weight of saturated fatty  $C_{18}$ -acid, more preferably from 52 to 90 % by weight of saturated  $C_{18}$ -fatty acid and even more preferably from 55 to 85 % by weight of saturated fatty acid. The molar relationship in the esterification between methyldiethanolamine and fatty acid must be such that the relationship of at least 50 mol-% diester quat and at least 10 mol-% monoesterquat is maintained.

In order to decrease the process temperature and consequently increase the viscosity of the final softener formulation, a concentrated pre-mixture of the dimethyldiethanolamine esterquat with water and solvent can be made. The pre-mixture of the dimethyldiethanolamine esterquat molten temperature should be from about 25 to 65°C, most preferably from about 30 to 60°C. Also, the difference in temperature between the molten esterquat pre-mixture and the liquid carrier, preferably water, should be up to 15°C, more preferably up to 12°C, even more preferably up to 10°C.

Due to the presence of organic solvents in the esterification process and also in the pre-mixture of the dimethyldiethanolamine esterquat, the liquid softener composition as claimed herein contain a small amount of such solvents.

In principle, suitable organic solvents in the final esterquat are any mono- or polyhydric alcohols. Preference is given to using alcohols having from 1 to 4 carbon atoms, such as methanol, ethanol, propanol, isopropanol, straight chain and branched butanol, glycerol and mixtures of said alcohols. Other preferred solvents are polyethylene glycols having a relative molecular mass below 2000. The claimed composition may contain these organic solvents in an amount of from 0.13 to 18 % by weight of the whole composition.

Depending on the intended use, the compositions according to the invention comprise, in addition to the mentioned compounds, additives and auxiliaries which are customary and specific in each case such as for example stabilizers, perfumes, colorants, hydrotopes, antifoaming agents, polymeric or other  
5 thickening agents, opacifiers, preservatives, anti-corrosion agents and pH modifiers.

In order to make easier the preparation of the disclosed invention, a concentrated pre-mix containing the same molar and/or mass ratio between the esterquats and  
10 the additives can be prepared in order to be diluted up to 45 times. Other ingredients, such as solvent, water and any other ingredient that could be part of the final formulation may be added.

Stabilizers and/or other additives can be selected from the group of specific  
15 organic and/or inorganic compound, preferably electrolytes and/or short amines derivatives. A problem of aqueous composition containing these esterquats is that they are not stable over prolonged storage since they undergo hydrolysis. It has been found that, apart from alkali and alkaline earth metal salts, there are also other metal salts capable of preventing hydrolysis of esterquats.

20 In order to enhance the stability of the aqueous esterquat compositions, a salt may be added such as alkali or alkaline earth metal salt. Preferred salts, however, are transition metal salts, more preferably zinc and aluminium salts such as  $ZnSO_4$ ,  $ZnCl_2$ ,  $AlCl_3$  or  $Al_2(SO_4)_3$ . These salts may be present in an amount preferably  
25 from 0.002 to 10.0, preferably 0.03 to 5.0, and even more preferably 0.04 to 3.0 % by weight.

The compositions according to the present invention can be made by mixing the cited salts to the dimethyldiethanolamine esterquat disclosed in this invention in  
30 the final softener formulations. The salt can be added at any moment during the softeners process preparation and either in solid form or an aqueous solution. Heating and stirring is recommended for making the claimed compositions.

The compositions according to the invention may have the presence of rare earth metal salts, metal salts of fatty acids, phthalocyanine metal complexes, phthalocyanine metal salts or chelating agents.

- 5 Another option for stabilizers is short amines, which can be selected from the group of amines containing at least one hydroxyethyl group.

Preferred thickeners which may be added if necessary, are fatty alcohols, hydrogenated castor oil, salts of long-chain fatty acids, which are preferably used  
10 in amounts of from 0 to 15 % by weight and in particular in amounts from 0.2 to 14 % by weight, in particular it can be xanthan gum, guar guar, agar agar, alginates and tyloses, Carboxymethylcellulose and Hydroxyethylcellulose, and also relatively high molecular weight polyethylene glycol mono- and -diesters of  
15 fatty acids, polyacrylates, polyvinyl alcohol and Polyvinylpyrrolidone, and also electrolytes. It can also be selected from the group of synthetic and/or natural organic polymers such as modified polyglucopyranoses and/or modified celluloses.

The compositions according to the present invention can be made by heating the  
20 water to the necessary temperature and then adding the melting esterquat pre-mixture, stirring until obtain a homogeneous fabric softener.

An example of the procedure to obtain a stable, homogeneous and viscous fabric softener formulation based on methyldiethanolamine esterquat as described on  
25 claim 1 of the present invention is:

- I. Heating of water to 45°C
- II. Addition of the dimethyldiethanolamine esterquat pre-dispersion at 50°C
- 30 III. Cooling under stirring with approximately 150 rpm for 30 minutes
- IV. Fast cooling under stirring for 15 minutes

The fabric softener formulation prepared according to the procedure and to the

dimethyldiethanolamine esterquat disclosed in this invention exhibits good viscosities results, especially for low active-material levels as shown on tables I and II. Moreover, table I proves the important effect that the acid value content has on the fabric softener formulation viscosity. The acid value, in addition with saturated C18 content and ester distribution are important parameters disclosed in this invention. On table II a comparative with other well-known softener active agents such as DSDMAC and triethanolamine esterquats is shown. For the latter, it was used a pre-dispersion of triethanolamine esterquat as described on Patent EP-1 584 674. This pre-dispersion, as the one prepared for the dimethyldiethanolammonium-chloride esterquat disclosed in this patent, is used to decrease process temperature in order to increase viscosity results.

The results shows that with the dimethyldiethanolamine esterquat disclosed in this invention a viscous softener formulation is obtained, even for fabric softeners containing 2 % am, and the fabric softeners viscosity results are clearly better than fabric softeners prepared through the other two cited softener active agents. It is important to notice that for a softener formulation based on a commercial available triethanolamine esterquat achieve the same viscosity levels of the fabric softener formulation based on the dimethyldiethanolamine esterquat disclosed in this patent, a large amount of thickener would be necessary. This is, in fact, a characteristic of the commercial available triethanolamine esterquats that is the low fabric softeners viscosity values when working with low active material content, even using its pre-dispersion.

Table I

	dimethyl- diethanolamine Esterquat 1	dimethyl- diethanolamine Esterquat 2	dimethyldiethanol- amine Esterquat 3
Saturated C18 Content (%)	> 50%	> 50%	> 50%
Acid Value (meq/g of final product)	0.132	0.031	0.031
Diester Content (mol %)	> 50%	> 50%	> 50%
Monoester Content (mol %)	>10%	>10%	>10%
Fabric Softener with 2% am Viscosity (mPas)	20	1275	1730
Fabric Softener with 4% am Viscosity (mPas)	550	2790	2735

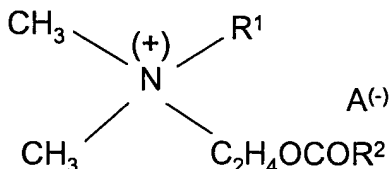
5 Table II

	dimethyldiethanol- amine Esterquat 2	di-stearyl-dimethyl- ammonium-chloride DSDMAC	Triethanolamine esterquat
Fabric Softener with 2% am Viscosity (mPas)	1275	35	20
Fabric Softener with 4% am Viscosity (mPas)	2790	2165	210

## Claims

1. A stable, homogenous and viscous softener formulation containing less than 50 % by weight of an esterquat compound of the formula

5



wherein  $\text{R}^1$  is  $-\text{C}_2\text{H}_4\text{OH}$  or  $-\text{C}_2\text{H}_4\text{OCOR}^2$ ,  $\text{R}^2$  is  $\text{C}_{11}$ - $\text{C}_{21}$ -alkyl or alkenyl and A is an anion, as methylsulfate, bromide, iodide and, preferably, chloride, said

10 esterquat being prepared by esterification of methyldiethanolamine with fatty acids and subsequent quaternization, with preferably methylchloride, the fatty acids containing at least 50 % by weight of saturated  $\text{C}_{18}$ -fatty acid, comprising a final product containing at least 50 mol % of diester quat and at least 10 mol % of monoesterquat and having an acid value of less than 0.12 meq/g of esterquat  
 15 active material, the rest being water and an organic solvent.

2. A composition as claimed in claim 1 wherein the group  $-\text{OCOR}^2$  is derived from a fatty acid mixture containing 52 to 90 % by weight of saturated  $\text{C}_{18}$ -fatty acid.

20

3. A composition as claimed in claim 1 wherein the group  $-\text{OCOR}^2$  is derived from a fatty acid mixture containing 55 to 85 % by weight of saturated  $\text{C}_{18}$ -fatty acid.

25 4. A composition as claimed in claim 1 wherein the group  $-\text{OCOR}^2$  is preferably derived from a fully hydrogenated fatty acid wherein the amount of saturated  $\text{C}_{18}$ -fatty acid is defined as described on claims 2 and 3.

5. A process of making a liquid fabric softener composition as described in  
 30 claim 1, comprising the step of preparing a pre-mixture of the

dimethyldiethanolamine esterquat in order to decrease process temperature and obtain stable, homogeneous and viscous softener formulation.

5 6. The process of claim 5 wherein the pre-mixture molten temperature is from about 25 to 65°C, most preferably from about 30 to 60°C.

7. The process according to claim 5 wherein the temperature difference between the molten pre-mixture and the liquid carrier, preferably water, is up to 15°C, more preferably up to 12°C, even more preferably up to 10°C.

10

8. A liquid, stable and viscous softener formulation as described on claim 1 containing the softener active agent, the dimethyldiethanolmine esterquat disclosed in claim 1, preferably in a level from about 1 to 20% of active material and optionally additional ingredients in order to enhance stability, viscosity and dispersibility, such as stabilizers, electrolytes, thickeners, dispersing agents and pH modifiers.

15

9. A liquid, stable and viscous softener formulation composition according to claim 8 wherein the stabilizers can be selected from the group of inorganic and/or organic compounds such as soluble transition metals salts and short amines derivatives. Preferably metal salts are Zinc and Aluminium salts such as ZnCl<sub>2</sub>, AlCl<sub>3</sub>, ZnSO<sub>4</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and preferably short amines derivatives are the group of amines containing at least one hydroxyethyl group.

20

10. A liquid, stable and viscous softener formulation composition according to claim 8 wherein the thickener is selected from the group of synthetic and/or natural organic polymers such as modified polyglucopyranoses and/or modified celluloses.

25

11. A liquid, stable and viscous softener formulation composition according to claim 8 wherein the pH modifiers are any organic or inorganic acids.

30

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2007/005860

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C11D1/62		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C11D		
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		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 196 42 038 C1 (HENKEL KGAA [DE]) 11 December 1997 (1997-12-11) page 2, lines 21-29; examples V1-V4	1-11
A	US 5 523 433 A (TONEY CHRISTOPHER J [US] ET AL) 4 June 1996 (1996-06-04) column 1, lines 23-42; claims 1-14; example 1	1-11
A	WO 2006/041954 A (PROCTER & GAMBLE [US]; BRUSH LISA GRACE [US]; WAHL ERROL HOFFMAN [US];) 20 April 2006 (2006-04-20) examples XXIX-XXXIV	1-11
A	WO 94/20597 A (PROCTER & GAMBLE [US]) 15 September 1994 (1994-09-15) page 1, lines 23-31; examples I, IA, X	1-11
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> 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	*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	
*E* earlier document but published on or after the international filing date	*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	
*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)	*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.	
*O* document referring to an oral disclosure, use, exhibition or other means	*&* document member of the same patent family	
*P* document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search  <p style="text-align: center; font-weight: bold;">21 September 2007</p>	Date of mailing of the international search report  <p style="text-align: center; font-weight: bold;">01/10/2007</p>	
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  <p style="text-align: center; font-weight: bold;">Klier, Erich</p>	

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2007/005860

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 096 055 A1 (KAO CORP [JP]) 2 May 2001 (2001-05-02) paragraph [0005]; examples 2,3,8,comp.examp,2; tables 1,2 -----	1-11
A	US 2006/089293 A1 (FRANKENBACH GAYLE M [US]) 27 April 2006 (2006-04-27) paragraphs [0002], [0165]; claim 1; examples 1,2 -----	1-11
A	EP 1 103 650 A1 (KAO CORP [JP]) 30 May 2001 (2001-05-30) paragraph [0003]; examples 10,12,comp.,examp.3,comp.,examp.7 -----	1-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2007/005860
---

Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
DE 19642038	C1	11-12-1997	EP 0835863 A1 ES 2188842 T3	15-04-1998 01-07-2003
US 5523433	A	04-06-1996	EP 0710513 A1	08-05-1996
WO 2006041954	A	20-04-2006	CA 2583452 A1 EP 1807496 A1	20-04-2006 18-07-2007
WO 9420597	A	15-09-1994	AT 191743 T AU 6271294 A BR 9405945 A CA 2157178 A1 CN 1288985 A CN 1288986 A CN 1121352 A DE 69423963 D1 DE 69423963 T2 DK 687291 T3 EP 0687291 A1 ES 2144515 T3 FI 954084 A GR 3033212 T3 JP 8507766 T JP 3902783 B2 JP 2006138063 A NO 953415 A PT 687291 T US 5562849 A US 5574179 A US 5545340 A	15-04-2000 26-09-1994 30-01-1996 15-09-1994 28-03-2001 28-03-2001 24-04-1996 18-05-2000 16-11-2000 03-07-2000 20-12-1995 16-06-2000 31-08-1995 31-08-2000 20-08-1996 11-04-2007 01-06-2006 01-11-1995 29-09-2000 08-10-1996 12-11-1996 13-08-1996
EP 1096055	A1	02-05-2001	DE 69927034 D1 DE 69927034 T2 ES 2249006 T3 WO 9964661 A1 US 6521588 B1	06-10-2005 13-07-2006 16-03-2006 16-12-1999 18-02-2003
US 2006089293	A1	27-04-2006	NONE	
EP 1103650	A1	30-05-2001	WO 9964660 A1 US 6410502 B1	16-12-1999 25-06-2002