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(54) Title: SURFACE-MODIFIED, PYROGENICALLY PREPARED SILICAS

(57) Abstract: Surface-modified, pyrogenically prepared silica is prepared by subjecting the pyrogenically prepared silica, which is in the form of aggregates of primary particles and possesses a BET surface area of 150 ± 15 m^2/g, the aggregates having an average area of 12 000 - 20 000 nm^2, an average equivalent circle diameter (ECD) of 90 - 120 nm and an average circumference of 1150 - 1700 nm, to surface- modification in a known way. It can be used as a filler for thickening liquid systems.

Surface-modified, pyrogenically prepared silicas

The invention relates to surface-modified, pyrogenically prepared silicas, to a process for preparing them and to their use.

The preparation of surface-modified pyrogenic (fumed) silicas from pyrogenically prepared silicas by surface modification is known. Silicas prepared in this way find use in many fields of application: for example, for controlling the rheology of liquid systems, in resins, and for use in adhesives. In these applications, great importance attaches not only to the thickening effect but also to the ease of incorporation into the liquid system.

The known surface-modified, pyrogenic silicas have the disadvantage that their ease of incorporation into liquid systems is unsatisfactory.

The object was therefore to prepare surface-modified pyrogenic silicas which possess an improved ease of incorporation into liquid systems without detriment to other important properties, such as the thickening effect.

The invention provides surface-modified, pyrogenically prepared silicas which are characterized in that their ease of incorporation into liquid systems is improved without detriment to the thickening effect.

The invention further provides a process for preparing the surface-modified, pyrogenically prepared silica, which is characterized in that the pyrogenically prepared silica, which is in the form of aggregates of primary particles and possesses a BET surface area of 150 ± 15 m^2/g, the aggregates having an average area of 12 000 - 20 000 nm^2, an average equivalent circle

diameter (ECD) of 90 - 120 nm and an average circumference of 1150 - 1700 nm, is surface-modified in a known way.

The pyrogenically prepared silica used as starting material is known from EP 1 681 266 A2.

The surface modification can be accomplished by spraying the silicas where appropriate with water and subsequently with the surface modifier. Spraying may also take place in the opposite order. The water used may have been acidified with an acid, hydrochloric acid, for example, to a pH of 7 to 1. If two or more surface modifiers are employed, they can be applied together, or separately, in succession or as a mixture.

The surface modifier or modifiers may have been dissolved in suitable solvents. The end of spraying may be followed by mixing for 5 to 30 minutes more.

The mixture is subsequently treated thermally at a temperature of 20 to 400°C over a period of 0.1 to 6 h. The thermal treatment may take place under inert gas, such as nitrogen, for example.

An alternative method of surface modification of the silicas can be accomplished by treating the silicas with the surface modifier in vapour form and then thermally treating the mixture at a temperature of 50 to 800°C over a period of 0.1 to 6 h. The thermal treatment may take place under inert gas, such as nitrogen, for example.

The temperature treatment may also take place over a number of stages at different temperatures.

The surface modifier or modifiers can be applied using single-fluid, two-fluid or ultrasound nozzles.

The surface modification can be carried out in heatable mixers and dryers with spraying installations, continuously or batchwise. Suitable apparatus may for example be the following: ploughshare mixers, plate dryers, fluidized-bed dryers or fluid-bed dryers.

As surface modifier it is possible to use at least one compound from the group of the following compounds:

a) organosilanes of type $(RO)_3Si(C_nH_{2n+1})$ and $(RO)_3Si(C_nH_{2n-1})$
   R = alkyl, such as for example, methyl-, ethyl-, n-propyl-, isopropyl-, butyl-
   n = 1 - 20

b) organosilanes of type $R'_x(RO)_ySi(C_nH_{2n+1})$ and $R'_x(RO)_ySi(C_nH_{2n-1})$
   R = alkyl, such as for example, methyl-, ethyl-, n-propyl-, isopropyl-, butyl-
   R' = alkyl, such as for example, methyl-, ethyl-, n-propyl-, isopropyl-, butyl-
   R' = cycloalkyl
   n = 1 - 20
   x+y = 3
   x = 1, 2
   y = 1, 2

c) haloorganosilanes of type $X_3Si(C_nH_{2n+1})$ and $X_3Si(C_nH_{2n-1})$
   X = Cl, Br
   n = 1 - 20

d) haloorganosilanes of type $X_2(R')Si(C_nH_{2n+1})$ and $X_2(R')Si(C_nH_{2n-1})$
   X = Cl, Br
   R' = alkyl, such as for example, methyl-, ethyl-, n-propyl-, isopropyl-, butyl-

R′ = cycloalkyl
n = 1 - 20

e) haloorganosilanes of type $X(R')_2Si(C_nH_{2n+1})$ and $X(R')_2Si(C_nH_{2n-1})$
X = Cl, Br
R′ = alkyl, such as for example, methyl-, ethyl-, n-propyl-, isopropyl-, butyl-
R′ = cycloalkyl
n = 1 - 20

f) organosilanes of type $(RO)_3Si(CH_2)_m-R'$
R = alkyl, such as methyl-, ethyl-, propyl-
m = 0.1 - 20
R′ = methyl-, aryl (for example $-C_6H_5$, substituted phenyl radicals)
$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
$-NH_2$, $-N_3$, -SCN, $-CH=CH_2$, $-NH-CH_2-CH_2-NH_2$,
$-N-(CH_2-CH_2-NH_2)_2$
$-OOC(CH_3)C = CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$
-SH
-NR′R′′R′′′ (R′ = alkyl, aryl; R′′ = H, alkyl, aryl; R′′′ = H, alkyl, aryl, benzyl, C_2H_4NR'''' R′′′′′ with R′′′′ = H, alkyl and R′′′′′ = H, alkyl)

g) organosilanes of type $(R'')_x(RO)_ySi(CH_2)_m-R'$
R″ = alkyl x+y = 3
= cycloalkyl x = 1, 2
y = 1, 2
m = 0.1 to 20
R′ = methyl-, aryl (for example $-C_6H_5$, substituted phenyl radicals)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$, $-NH-CH_2-CH_2-NH_2$,
$-N-(CH_2-CH_2-NH_2)_2$
$-OOC(CH_3)C = CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$
$-SH$
$-NR'R''R'''$ (R′ = alkyl, aryl; R′′ = H, alkyl, aryl; R′′′ = H, alkyl, aryl, benzyl, C_2H_4NR'''' R′′′′′ with R′′′′ = H, alkyl and R′′′′′ = H, alkyl)

h) haloorganosilanes of type $X_3Si(CH_2)_m-R'$
X = Cl, Br
m = 0.1 - 20
R′ = methyl-, aryl (for example $-C_6H_5$, substituted phenyl radicals)
$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,
$-NH-CH_2-CH_2-NH_2$
$-N-(CH_2-CH_2-NH_2)_2$
$-OOC(CH_3)C = CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$
$-SH$

i) haloorganosilanes of type $(R)X_2Si(CH_2)_m-R'$
X = Cl, Br
R = alkyl, such as methyl-, ethyl-, propyl-
m = 0.1 - 20
R = methyl-, aryl (e.g. $-C_6H_5$, substituted phenyl radicals)
$-C_4F_9$,$-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, -SCN, $-CH=CH_2$, $-NH-CH_2-CH_2-NH_2$,
$-N-(CH_2-CH_2-NH_2)_2$
$-OOC(CH_3)C = CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$, it being possible for R to be methyl-, ethyl-, propyl-, butyl-
$-S_x-(CH_2)_3Si(OR)_3$, it being possible for R to be methyl-, ethyl-, propyl-, butyl-
-SH

j) haloorganosilanes of type $(R)_2XSi(CH_2)_m-R'$

X = Cl, Br

R = alkyl

m = 0.1 - 20

R' = methyl-, aryl (e.g. $-C_6H_5$, substituted phenyl radicals)
$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
$-NH_2$, $-N_3$, -SCN, $-CH=CH_2$, $-NH-CH_2-CH_2-NH_2$,
$-N-(CH_2-CH_2-NH_2)_2$
$-OOC(CH_3)C = CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$
-SH

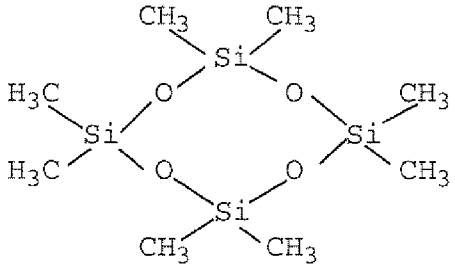
k) silazanes of type $R'R_2Si-N(H)-SiR_2R'$

R = alkyl, vinyl, aryl

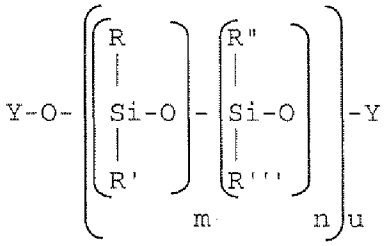
R' = alkyl, vinyl, aryl

l) cyclic polysiloxanes of type D 3, D 4, D 5, with D 3, D 4 and D 5 meaning cyclic polysiloxanes having 3, 4 or 5 units of type $-O-Si(CH_3)_2-$.

e.g. octamethylcyclotetrasiloxane = D 4



m) polysiloxanes or silicone oils of type



m = 0,1,2,3,...∞
n = 0,1,2,3,...∞
u = 0,1,2,3,...∞

Y=CH_3, H, C_nH_{2n+1} n=1-20
Y=$Si(CH_3)_3$, $Si(CH_3)_2H$
$Si(CH_3)_2OH$, $Si(CH_3)_2(OCH_3)$
$Si(CH_3)_2(C_nH_{2n+1})$ n=1-20

R = alkyl such as C_nH_{2n+1}, n being 1 to 20, aryl, such as phenyl radicals and substituted phenyl radicals, $(CH_2)_n$-NH_2, H

R′ = alkyl such as C_nH_{2n+1}, n being 1 to 20, aryl, such as phenyl radicals and substituted phenyl radicals, $(CH_2)_n$-NH_2, H

R′′ = alkyl such as C_nH_{2n+1}, n being 1 to 20, aryl, such as phenyl radicals and substituted phenyl radicals, $(CH_2)_n$-NH_2, H

R′′′ = alkyl such as C_nH_{2n+1}, n being 1 to 20, aryl, such as phenyl radicals and substituted phenyl radicals, $(CH_2)_n$-NH_2, H

As surface modifiers it is preferred to use the following silanes:

octyltrimethoxysilane, octyltriethoxysilane, hexamethyldisilazane, 3-methacryloyloxypropyltrimethoxysilane, 3-methacryloyloxypropyltriethoxysilane, hexadecyltrimethoxysilane, hexadecyltriethoxysilane, dimethylpolysiloxane, glycidyloxypropyltrimethoxy-

silane, glycidyloxypropyltriethoxysilane, nonafluorohexyltrimethoxysilane, tridecafluorooctyltrimethoxysilane, tridecafluorooctyltriethoxysilane, aminopropyltriethoxysilane, hexamethyldisilazane and polydimethylsiloxane.

With particular preference it is possible to use hexamethyldisilazane, dimethylpolysiloxane, octyltrimethoxysilane, octyltriethoxysilane and polydimethylsiloxane

More particularly it is possible to use polydimethylsiloxane.

The surface-modified, pyrogenically prepared silica of the invention can be used as a filler for resins.

The invention further provides resins which comprise the surface-modified, pyrogenically prepared silica of the invention.

The invention features the following advantages: greater ease of incorporation into liquid systems without detriment to the thickening effect.

Examples

Preparation of the comparative silica

2 kg of silica 11 (Table 4 from EP 1681266) were charged to a mixer and, with mixing, were sprayed with 0.42 kg of Rhodorsil oil 47 V 100 (polydimethylsiloxane) by means of a two-fluid nozzle. After the end of spraying, mixing was continued for 15 minutes and the reaction mixture was subsequently heated under a nitrogen atmosphere.

Preparation of the inventive silicas - Example

2 kg of silica 1 (Table 4 from EP 1 681266) were charged to a mixer and, with mixing, were sprayed with 0.42 kg of Rhodorsil oil 47 V 100 (polydimethylsiloxane) by means of a two-fluid nozzle. After the end of spraying, mixing was continued for 15 minutes, and the reaction mixture was subsequently heated under a nitrogen atmosphere.

Physicochemical data

Designation	Tapped density [g/l]	Loss on drying [%]	Loss on ignition [%]	pH	C content [%]	BET specific surface area [m^2/g]
Comparative silica	67	0.1	4.4	5.8	4.6	95
Inventive silica	65	0.1	4.4	5.7	4.6	94

Determination of incorporation characteristics

The incorporation characteristics were determined by measuring the time required for the silica to be homogenized in a resin.

This is done by weighing out 100 g of Palatal A 410 into a 350 ml beaker and heating it at 25°C in a water bath.

The beaker is introduced into the aluminium insert of the mounting device of the dissolver (Getzmann Dispermat).

The stirrer (disc diameter 30 mm) is immersed to its target depth of t = 10 mm above the base of the beaker,

and switched on at a speed n of 500 min^{-1}.

3 g of silica are placed uniformly onto the surface of the resin, and the stopwatch is started.

A measurement is made of the time required for the silica to be homogenized.

The elapsed time is translated into a school-grade system (grade 1 - grade 5). Grade 1 corresponds to very good (rapid) incorporation. Grade 5 corresponds to very poor (slow) incorporation.

Determination of thickening effect in an epoxy resin

201.92 g (92.15%) of Renalm M1 and 8.08 g (3.85%) of silica are weighed out into a 350 ml PE beaker.

The dissolver disc (disc diameter: d = 50 mm) is immersed to the middle point of the beaker and the sample is homogenized at 1000 rpm.

In this case the beaker is sealed with the perforated lid in order to prevent the silica escaping as dust.

As soon as the silica has been fully incorporated, the disc is immersed to a depth of 10 mm above the base of the beaker. Dispersion is carried out for 3 minutes at a speed of 3000 rpm. During this time, air is removed under vacuum.

The dispersed sample is transferred to a 250 ml glass bottle.

The sample is stored in a water bath at 25°C for 90 minutes.

After 90 minutes the sample is agitated with a spatula for 1 minute. Subsequently the viscosity of the sample is determined using a Brookfield DV III.

For this purpose the spindle of the Brookfield rheometer is immersed to the defined mark. Measurement is carried out as follows:

5 rpm - value read off after 60 seconds
50 rpm - value read off after 30 seconds.

The values read off are the viscosities [Pa*s] at the respective rpm.

Incorporation characteristics and thickening effect - results

Designation	Incorporation (grade)	Thickening at 5 rpm [Pa*s]	Thickening at 50 rpm [Pa*s]
Comparative silica	4	70 000	15 760
Inventive silica	1	70 600	15 360

It is clearly apparent that the inventive silica exhibits much better incorporation characteristics. This means that it is incorporated more rapidly than the comparative silica, despite the fact that not only the thickening effect but also the other physico-chemical data are comparable.

Claims:

1. Surface-modified, pyrogenically prepared silica characterized in that it possesses improved ease of incorporation into liquid systems.

2. Process for preparing the surface-modified, pyrogenically prepared silica according to Claim 1, characterized in that the pyrogenically prepared silica, which is in the form of aggregates of primary particles and possesses a BET surface area of 150 ± 15 m^2/g, the aggregates having an average area of 12 000 - 20 000 nm^2, an average equivalent circle diameter (ECD) of 90 - 120 nm and an average circumference of 1150 - 1700 nm, is surface-modified in a known way.

3. Process according to Claim 2, characterized in that dimethylpolysiloxanes are utilized as surface modifier.

4. Process according to Claim 2, characterized in that the silicas are sprayed if appropriate with water and subsequently with the surface modifier.

5. Process according to Claim 2, characterized in that the silicas are treated with the surface modifier in vapour form and the mixture is subsequently treated thermally at a temperature of 50 to 800°C over a period of 0.1 to 6 h.

6. Use of the surface-modified, pyrogenically prepared silica for thickening liquid systems.

7. Use of the surface-modified, pyrogenically prepared silica for thickening resins.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/058416

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/30 C09D7/00 C08K9/06

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)
C09C C08K C09D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 304 332 A (WACKER CHEMIE GMBH [DE]) 23 April 2003 (2003-04-23) paragraphs [0009] - [0072] examples 1-4	1-7
X	US 5 900 315 A (LITTLE CHARLES B [US]) 4 May 1999 (1999-05-04) column 2, line 21 - line 47 column 3, line 9 - column 4, line 8 column 5, line 1 - column 8, line 16	1-7
X	EP 1 681 266 A (DEGUSSA [DE]) 19 July 2006 (2006-07-19) cited in the application paragraphs [0005] - [0019]	1,2,6,7

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[X] Further documents are listed in the continuation of Box C.

[X] 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 January 2009	15/01/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marino, Emanuela

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/058416

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 431 245 A (DEGUSSA [DE]) 23 June 2004 (2004-06-23) paragraphs [0008] - [0048]	1-7
X	US 2003/138715 A1 (BARTHEL HERBERT [DE] ET AL BARTHEL HERBERT [DE] ET AL) 24 July 2003 (2003-07-24) paragraphs [0017] - [0181]	1-7
X	US 2004/131527 A1 (GOTTSCHALK-GAUDIG TORSTEN [DE] ET AL) 8 July 2004 (2004-07-08) paragraphs [0008] - [0097] example 3	1-7
X	EP 1 304 361 A (WACKER CHEMIE GMBH [DE]) 23 April 2003 (2003-04-23) paragraphs [0020] - [0047]	1-7

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1,2

Present claims 1 and 2 relate to an extremely large number of possible products being surface-modified silica. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products claimed.
The application only provides support and disclosure for a silica coated with a polydimethylsiloxane as a surface modifying agent.

Furthermore it has to be realized, that the use of all possible surface treating agents will not always lead to the desirable results. The number of suitable surface treating agents will be limited to those which lead to a hydrophobic surface treated silica.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2008/058416

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.: 1,2
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:
see FURTHER INFORMATION sheet PCT/ISA/210

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:

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 reportcovers 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/EP2008/058416

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1304332 A	23-04-2003	CN 1411916 A	23-04-2003
		DE 10151478 C1	13-03-2003
		JP 4090836 B2	28-05-2008
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