(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2012 (27.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/175529 A1

(51) International Patent Classification:
*C01B 33/148* (2006.01) *C09J 111/02* (2006.01)
*C08L 11/02* (2006.01)

(21) International Application Number:
PCT/EP2012/061776

(22) International Filing Date:
20 June 2012 (20.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11170684.2 21 June 2011 (21.06.2011) EP

(71) Applicant *(for all designated States except US)*: **AKZO NOBEL CHEMICALS INTERNATIONAL B.V.** [NL/NL]; Stationsstraat 77, NL-3811 MH Amersfoort (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **PANSKUS, Knut** [DE/DE]; Grüner Weg 28A, 51375 Leverkusen (DE). **MUSCH, Rüdiger** [DE/DE]; Altenberger Dom Strasse 169, 51467 Bergisch Gladbach (DE). **KIRCHMEYER, Stephan** [DE/DE]; Ernst-Ludwig-Kirchner-Str. 45, 51375 Leverkusen (DE). **PANTKE, Dietrich** [DE/DE]; Eisenhüttenstrasse 30, 40882 Ratingen (DE).

(74) Agent: **DE VRIES, Adriaan, Jacobus c.s.**; Akzo Nobel N.V., Legal, IP & Compliance, P.O. Box 9300, NL-6800 SB Arnhem (NL).

(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, 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))*

WO 2012/175529 A1

(54) Title: METHOD FOR CONCENTRATING AN AQUEOUS SILICON DIOXIDE DISPERSION

(57) Abstract: The invention relates to a method of concentrating an aqueous silicon dioxide dispersion comprising the steps of: a) providing an aqueous dispersion comprising silicon dioxide particles having an initial content of silicon dioxide; b) contacting the dispersion of step a) with a creaming agent to yield an aqueous serum phase and an aqueous concentrated phase, the serum phase having a silicon dioxide content lower than the initial content of silicon dioxide in the dispersion of step a) and the concentrated phase having a silicon dioxide content higher than the initial content of silicon dioxide in the dispersion of step a); and c) separating the serum phase from the concentrated phase, wherein the dispersion of step a) does not comprise organic polymer particles of polychloroprene and/or polyurethane. The invention also relates to a concentrated aqueous silicon dioxide dispersion obtainable by the method, and the use thereof as an adhesive.

# Method for concentrating an aqueous silicon dioxide dispersion

The present invention relates to a method of concentrating an aqueous silicon dioxide dispersion using a creaming agent. The invention further relates to a concentrated aqueous silicon dioxide dispersion which is obtainable by the method according to the invention and to the use of such dispersions as adhesives.

The combination of silicon dioxide dispersions with organic polymer dispersions such as adhesive dispersions is thought to have numerous beneficial effects. Such combinations may be achieved by either polymerizing a monomer in the presence of an inorganic particle dispersion or by mixing inorganic particles and pre-formed organic polymer dispersions.

An example for the first case is given in US 2004/0077761 A1 which discloses a filler-containing organic polymer dispersion. The organic polymer of the dispersion is polymerized in the presence of particles of at least one filler. The ratio of the particle size of the filler particles to the particle size of the polymer particles is in the range of from 1.1:1 to 20:1.

An example of the latter case is given in US 2006/0115642 A1 which provides a process for finishing fibrous products with a preparation based on aqueous dispersions of polychloroprene and a process for preparing textile-reinforced and fiber-reinforced concrete and other cement-based products including those finished products. In the process for reinforcing one of concrete and cement, the improvement disclosed herein includes a fibrous product soaked in a preparation comprising: (a) about 20 to about 99 wt. % of an aqueous dispersion based on polychloroprene; and (b) about 1 to about 80 wt. % of an aqueous suspension based on inorganic solids chosen from oxides, carboxides and silicates; (c) optionally, polymer dispersions chosen from polyacrylates, polyacetates, polyurethanes, polyureas, rubbers and epoxides, and (d) optionally, additives and auxiliaries chosen from resins, stabilizers, antioxidants, cross-linking agents, cross-linking accelerators, fillers, thickening agents and fungicides, wherein the weight percentages of (a) and (b) total 100 wt. % and are based on the weight of non-volatile fractions.

When mixing a commercially available adhesive dispersion with a commercially available silicon dioxide dispersion, an undesired dilution of the resulting mixture, especially with respect to the silicon dioxide content may occur. This necessitates a subsequent concentration step.

Several methods of increasing the solids content of polymer latices such as SBR (styrene butadiene rubber), NBR (acrylonitrile butadiene rubber), polychloroprene,

polybutadiene, polyisoprene, natural rubber, polyvinylchloride or (meth)acrylate dispersions or dispersions of copolymers thereof are known in the art.

A non-exhaustive compilation of such methods is given in Houben-Weyl, vol. XIV/1 "Makromolekulare Stoffe" vol. 1, 4. edition, p. 515 (1961), in Polymer Colloids, Elsevier Applied Science Publishers, p. 272 (1985) or Industrial and Engineering Chemistry, vol. 43, Febr. 1951, pp 406-412, Ernst Schmidt and R. H. Kelsey "Creaming Latex with Ammonium Alginate".

By way of example, US 2009/0234064 A1 discloses an aqueous elastomer dispersion which includes a dispersed phase and an aqueous phase. The dispersed phase includes an elastomer including curable aliphatic conjugated-diene elastomers, such as polyisoprene, and a minor amount of at least one additive. The aqueous phase includes water and other optional components in either a soluble state or a dispersion state. The aqueous elastomer dispersion may be prepared by dissolving an elastomer, such as rubber, and additives in a solvent mixture and then converting the resulting solution into an aqueous emulsion. The aqueous emulsion is concentrated and the solvent is stripped from it to yield a dilute latex. The dilute latex that is obtained is concentrated again. Articles made from the aqueous elastomer dispersion include medical gloves, condoms, probe covers, dental dams, finger cots, catheters and the like.

The disclosed methods of concentrating dispersions of organic substances have the disadvantage that an agglomeration of the particles of the dispersion may take place (when adding electrolytes, freezing, water evaporation), that filter pores may become clogged (ultrafiltration) or that foaming may prevent an effective separation (centrifugation). In the use of creaming agents it has been thought that the particle size of the latex to be treated is of decisive importance. While natural rubber latex with a particle size of 400 nm can be creamed rapidly and without problems, the creaming of, for example, SBR latex with a particle size of 78 nm by ammonium alginate was not successful (Ind. Eng. Chem. 43, 407 (1951)).

It would therefore be desirable to be able to concentrate dispersions of silicon dioxide particles without suffering from the above-mentioned drawbacks. The present invention has the object of providing such a method.

According to the invention this object is achieved by a method of concentrating an aqueous silicon dioxide dispersion, comprising the steps of:

a) providing an aqueous dispersion comprising silicon dioxide particles having an initial content of silicon dioxide;

b) contacting the dispersion of step a) with a creaming agent to yield an aqueous serum phase and an aqueous concentrated phase,

the serum phase having a silicon dioxide content lower than the initial content of silicon dioxide in the dispersion of step a) and

the concentrated phase having a silicon dioxide content higher than the initial content of silicon dioxide in the dispersion of step a); and

c) separating the serum phase from the concentrated phase,

wherein the dispersion of step a) does not comprise organic polymer particles of polychloroprene and/or polyurethane.

According to one embodiment, the dispersion of step a) does not comprise any organic polymer particles.

It has been surprisingly found that the method according to the invention allows for concentrating silicon dioxide dispersions without particle agglomeration during the concentration step. The particle size distribution of the dispersions is virtually unchanged.

Step a) of the method involves providing an aqueous silicon dioxide dispersion with an initial, meaning before the concentration step, content of silicon dioxide. While not strictly necessary, organic co-solvents may also be present in this dispersion, for example in an amount up to 20 wt% based on the dispersion.

Step b) of the method calls for contacting this dispersion with a creaming agent. The creaming agent may be provided in the form of an aqueous solution as an aqueous colloid or in solid form. If needed, co-solvents may also be present.

Different methods of creaming have been reported in the literature which may be used in the method of the invention:
- Stevens AH (1934). Improvements Relating to the Treatment of Rubber Latex B. P. 415, 133; appl. 23.2.33; publ. 23.8.34 / - Rhodes E, Sekaran KC (1937). Concentration of latex. B.P.474, 651; appl. 24.8.36; publ. 4.11.37. / - Dafader NC, Haque ME, Akhtar F, Ahmad MU, Utama MJ (1996),Macromol. Sci., A 33, 1 (2): 73. / - Peethambaran NR, Kuriakose B, Rajan M, Kuriakose APJ (2003).Rheological behaviour of natural rubber latex in the presence of surface-active agents. Appl. Polym. Sci., 41(5-6): 975.

Suitable creaming agents for the method according to the present invention are all creaming agents known in the prior art, but preferably alginates, cellulose derivatives, methyl cellulose, agar-agar, salts of poly(meth)acrylic salts and acids, copolymers of alkyl(meth)acrylates and/or styrene with unsaturated sulfonic acid derivatives or olefinically unsaturated monobasic or polybasic carboxylic acids or salts thereof, and salts of divalent ions, such as e.g. calcium acetate are used. Preferably, the creaming agent is sodium alginate, potassium alginate and/or ammonium alginate. Preferably, the creaming agent has a size which is below the organic polymer particle size as defined herein, i.e. below 10 nm.

The creaming agent has the effect that the silicon dioxide dispersion separates into a solid-rich aqueous phase and a low-solid aqueous phase that contains also a higher percentage of the creaming agent ( serum phase) than the solid-rich aqueous phase. Hence, the (dispersed) silicon dioxide content in the serum phase is lower than in the initially provided dispersion and the (dispersed) silicon dioxide content in the concentrated phase is higher. Due to the high density of the inorganic solids the concentrated phase forms the lower phase and the serum the upper phase. By way of example, in absolute terms the serum phase may have a solids content of ≤ 25 weight-% and preferably ≤ 20 weight-%. The phase boundary may, for instance, be determined by visual inspection or by other optical means.

The separation in step c) can be performed in a settler such as described in DE 10 145 097 A1.

The creaming may be a discontinuous or continuous process at temperatures below, at or above room temperature. Preferably, the method of the invention is performed at about room temperature, i.e. from 0 to 50 °C, most preferably from 10 to 35 °C. It is also possible to wait for a pre-determined time before the separation step c). A pre-determined time may be for example 22 to 26 hours, for example 22 to 24 hours.

While it is possible that dissolved organic substances such as ethylene oxide based emulsifiers are present, one proviso of the method according to the invention is that the dispersion of step a) does not comprise organic polymer particles of polychloroprene and/or polyurethane. According to one embodiment, organic polymer particles (including polymer latices thereof) may be present in the dispersion, e.g. styrene butadiene rubber particles, acrylonitrile butadiene rubber particles, polybutadiene particles, polyisoprene particles, chlorinated polyisoprene particles, natural rubber particles, polyvinylchloride or (meth)acrylate particles and/or particles of copolymers thereof. Such organic particles

are preferably mixed with the silicon dioxide particles prior to step a) of the invention. The present invention is described in further detail in connection with preferred embodiments. They may be combined freely unless the context clearly indicates otherwise.

In one embodiment of the method according to the invention the dispersion of step a) is a silica sol, a silica gel, a pyrogenic silica dispersion, a precipitated silica dispersion or a mixture of these.

Silica sols are colloidal solutions of amorphous silicon dioxide particles in water, which are also referred to as silicon dioxide sols but are usually referred to for short as silica sols. Silica sols may also be dispersed in organic medium such as lower alcohols or mixtures of alcohols and water. The silicon dioxide therein is in the form of spherical, surface-hydroxylated particles. The diameter of the colloidal particles is generally from 1 to 200 nm, with the specific BET surface area that correlates with the particle size (determined by the method of G. N. Sears, Analytical Chemistry Vol. 28, N. 12, 1981-1983, December 1956) being from 15 to 2000 $m^2/g$. The surface of the $SiO_2$ particles has a charge which is compensated by a corresponding counterion, leading to the stabilization of the colloidal solution. The alkali-stabilized silica sols generally possess a pH of from 7 to 11.5 and comprise as alkalifying agents, for example, small amounts of $Na_2O$, $K_2O$, $Li_2O$, ammonia, organic nitrogen bases, tetraalkylammonium hydroxides or alkali metal or ammonium aluminates. Silica sols may also be in weakly acidic form, as semi-stable colloidal solutions. Furthermore, it is possible by coating the surface with $Al_2(OH)_5Cl$ to prepare cationically formulated silica sols. The solids concentrations of the silica sols generally are from 5 to 60% by weight $SiO_2$.

The preparation procedure for silica sols essentially encompasses the production steps of dealkalifying waterglass by ion exchange, setting and stabilizing the particular $SiO_2$ particle size (distribution) desired, setting the particular $SiO_2$ concentration desired, and, where appropriate, modifying the surface of the $SiO_2$ particles, with $Al_2(OH)_5Cl$, for example, or with silane as set out in for example WO 2004/035474. In none of these steps do the $SiO_2$ particles leave the colloidally dissolved state. This explains the presence of the discrete primary particles which are highly effective as binders, for example.

By silica gels are meant colloidally formed or unformed silica of elastic to solid consistency with a pore structure varying from relatively loose to dense. The silica is in the form of highly condensed polysilicic acid. On the surface there are siloxane and/or silanol groups. The silica gels are prepared from waterglass by reaction with mineral

acids. The primary particle size is generally from 3 to 20 nm and the specific surface area is generally from 250 to 1000 $m^2/g$ (according to DIN 66131).

A further distinction is made between pyrogenic silica and precipitated silica. In the precipitation process, water is introduced and then waterglass and acid, such as $H_2SO_4$, are added simultaneously. This produces colloidal primary particles which, as the reaction proceeds, undergo agglomeration and grow together to form agglomerates. The specific surface area is generally from 30 to 800 $m^2/g$ (DIN 66131) and the primary particle size is generally from 5 to 100 nm. The primary particles of these solid silicas are firmly crosslinked to form secondary agglomerates.

Pyrogenic (or fumed) silicas can be prepared by flame hydrolysis or by means of the light arc process. The predominant synthesis process for pyrogenic silicas is flame hydrolysis, in which tetrachlorosilane is decomposed in an oxyhydrogen flame. The silica formed in this process is X-ray-amorphous. Pyrogenic silicas possess significantly fewer OH groups on their virtually pore-free surface than precipitated silica. The pyrogenic silica prepared by flame hydrolysis generally has a specific surface area of from 50 to 600 $m^2/g$ (DIN 66131) and generally a primary particle size of from 5 to 50 nm; the silica prepared by the light arc process generally has a specific surface area of from 25 to 300 $m^2/g$ (DIN 66131) and generally a primary particle size of from 5 to 500 nm.

Further details on synthesis and properties of silicas in solid form can be found, for example, in K. H. Büchel, H.-H. Moretto, P. Woditsch "Industrielle Anorganische Chemie", Wiley VCH Verlag 1999, section 5.8.

Where an $SiO_2$ raw material present in the form of an isolated solid, such as pyrogenic or precipitated silica, is used for the polymer dispersion of the invention, it is converted into an aqueous $SiO_2$ dispersion by dispersing it.

To prepare the silicon dioxide dispersion, known dispersers may be used, preferably those suitable for producing high shear rates, such as Ultraturrax or dissolver discs, for example.

A preferred silicon dioxide dispersion is colloidical silica. It is likewise preferred for the $SiO_2$ particles to possess hydroxyl groups on the particle surface.

In another embodiment of the method according to the invention the initial content of silicon dioxide in the dispersion of step a) is ≥ 1 weight-% to ≤ 60 weight-%. Preferably the initial silicon dioxide content is ≥ 5 weight-% to ≤ 55 weight-%.

In another embodiment of the method according to the invention, in the dispersion of step a) the mean particle size of silicon dioxide particles is ≥ 1 nm to ≤ 400 nm. The mean particle size can also be referred to as the primary average particle diameter and is determined by ultracentrifugation, preferably as set out in H. G. Müller, Progr. Colloid Polym. Sci. 107, 180-188 (1997). It is expressed as the mass average. Preference is given to using those dispersions whose $SiO_2$ particles have a primary average particle diameter of ≥ 3 nm to ≤ 100 nm and with particular preference of ≥ 5 nm to ≤ 70 nm. When precipitated silicas are used, they are ground in order to reduce the particle size.

The silicon dioxide particles preferably have a narrow particle size distribution, i.e. a low relative standard deviation of the particle size. The relative standard deviation of the particle size distribution is the ratio of the standard deviation of the particle size distribution to the mean particle size by numbers. The relative standard deviation of the particle size distribution preferably is lower than about 60 % by numbers, more preferably lower than about 30 % by numbers, and most preferably lower than about 15 % by numbers.

The dispersion comprising silicon dioxide particles preferably has a conductivity of at least about 2.0 mS/cm or at least about 2.5 mS/cm, usually at least about 2.75 mS/cm or at least about 3.0 mS/cm. Sometimes, the conductivity is at least about 4.0 mS/cm or even at least about 5.0 mS/cm. The conductivity is usually up to about 6.0 mS/cm or up to about 8.0 mS/cm, suitably up to about 10.0 mS/cm. The conductivity can be measured by means of known technique, for example using a WTW LF330 portable conductivity meter.

Preferably, the molar ratio of Si:X in the dispersion comprising silicon dioxide particles, where X = alkali metal, is at least about 10:1 or at least about 15:1, more preferably at least about 20:1. The molar ratio is preferably up to 50:1, more preferably up to about 40:1, or even more preferably up to about 30:1, or most preferably up to about 25:1.

Preferably, the dispersion comprising silicon dioxide particles has a viscosity of at least about 1.1 cP or at least about 2 cP, and it may even be at least about 4 cP or at least 6 cP, or at least about 10 cP. Preferably, the viscosity is up to about 100000 cP, or up to about 10000 cP, or up to about 100 cP or up to about 50 cP, or up to about 30 cP. The viscosity can be measured by means of known technique, for example using a Brookfield LVDV II+ viscosimeter equipped with an UL adapter.

In another embodiment of the method according to the invention, in the dispersion of step a) the silicon dioxide particles have a bimodal or multimodal particle size

distribution. For example, in a bimodal case one maximum in the particle size distribution may be in the range of ≥ 5 nm to ≤ 15 nm and another maximum may be in the range of ≥ 45 nm to ≤ 65 nm. The method of the present invention allows for preparing concentrated bimodal or multimodal dispersions that would not have been accessible otherwise.

In another embodiment of the method according to the invention the creaming agent is provided in form of an aqueous solution and the content of the creaming agent in the aqueous solution is ≥ 0.5 weight-% to ≤ 10 weight-%. Preferred concentrations are ≥ 1 weight-% to ≤ 5 weight-% and more preferred ≥ 1.5 weight-% to ≤ 4 weight-%.

In another embodiment of the method according to the invention the creaming agent is present in an amount of ≥ 0.2 weight-% to ≤ 15 weight-%, based on the solids content of the dispersion of step a). Preferred amounts are ≥ 0.3 weight-% to ≤ 8 weight-% and more preferred ≥ 0.4 weight-% to ≤ 7 weight-%.

In another embodiment of the method according to the invention the separation in step c) is at least partially performed by centrifugation. This greatly accelerates the separation of the serum.

The present invention is further directed to a concentrated aqueous silicon dioxide dispersion, obtainable by the method according to the invention, wherein the aqueous silicon dioxide dispersion does not comprise organic polymer particles of polychloroprene and/or polyurethane, and wherein the dispersion comprises a creaming agent in an amount ≥ 0.01 weight-% to ≤ 1 weight-% and silicon dioxide in an amount ≥ 30 weight-% to ≤ 80 weight-% According to one embodiment, the dispersion does not comprise any organic polymer particles.

The present invention is further directed to a concentrated aqueous silicon dioxide dispersion, wherein the aqueous silicon dioxide dispersion does not comprise organic polymer particles of polychloroprene and/or polyurethane and wherein the dispersion comprises a residual amount of creaming agent ≥ 0.01 weight-% to ≤ 1 weight-% and silicon dioxide in an amount ≥ 30 weight-% to ≤ 80 weight-%. By “polymer particles” in this application is meant particles which are not soluble in water. Preferably, by the term “polymer dispersion” or “latex” is meant a colloidal stable dispersion of polymer particles in an aqueous phase. Preferably, the diameter of organic polymer particles as described herein ranges from 10 nm to 100 µm, more preferably from 10 nm to 1 µm. Preferably, the stability of the dispersion is achieved through surface active ingredients such as tensides or protection colloids.

Polymer dispersions can be synthesized directly from the monomers by different polymerization methods as emulsion polymerization or suspension polymerization or by dispersing the polymers. Natural rubber from the rubber tree (Hevea Brasiliensis) is an example of a natural borne polymer dispersion. According to one embodiment, the dispersion prepared according to the method does not comprise any organic polymer particles.

It is of course contemplated that the concentrated dispersion is not only obtainable but also has been obtained by the method according to the invention. Preferably the content of silicon dioxide is ≥ 35 weight-% to ≤ 75 weight-% and more preferred ≥ 50 weight-% to ≤ 67 weight-% in the concentrated dispersion. The creaming agent may also be present in an amount of ≥ 0.05 weight-% to ≤ 0.5 weight-% and more preferred ≥ 0.1 weight-% to ≤ 0.3 weight-% in the concentrated dispersion.

With respect to the other aspects of this dispersion, in the interest of avoiding repetition reference is made to the description in connection with the method according to the invention. The same applies to the description of preferred embodiments as outlined below.

In an embodiment of the dispersion according to the invention the silicon dioxide dispersion is a silica sol, a silica gel, a pyrogenic silica dispersion, a precipitated silica dispersion or a mixture of these.

In another embodiment of the dispersion according to the invention the silicon dioxide particles of the dispersion have a bimodal or multimodal particle size distribution as described herein.

In another embodiment of the dispersion according to the invention the creaming agent is selected from the group comprising alginates, cellulose derivates, methyl cellulose, agar-agar, poly(meth)acrylic acids and salts, and/or copolymers of alkyl(meth)acrylates and/or styrene with unsaturated sulfonic acid derivates or olefinically unsaturated mono- or polycarboxylic acids or salts thereof, and salts of divalent ions, such as e.g. calcium acetate are used. Preferably, the creaming agent is sodium alginate, potassium alginate and/or ammonium alginate.

The dispersion according to the invention may optionally contain further additives and auxiliary agents which are known from adhesive and dispersion technology, e.g. resins, stabilizers, antioxidants, cross-linking agents and cross-linking accelerators. For

example, fillers such as quartz flour, quartz sand, barites, calcium carbonate, chalk, dolomite or talcum, optionally together with cross-linking agents, for example polyphosphates such as sodium hexametaphosphate, naphthalinesulfonic acid, ammonium or sodium polyacrylic acid salts, may be added, wherein the fillers are preferably added in amounts of 10 to 60 wt. %, more preferably 20 to 50 wt. % and the cross-linking agents are preferably added in amounts of 0.2 to 0.6 wt. %, all weight percentages with respect to the non-volatile fractions.

Other suitable auxiliary agents such as for example organic thickening agents may preferably be added in amounts of 0.01 to 1 wt. %, with respect to non-volatile fractions, or inorganic thickening agents such as for example bentonites preferably in amounts of 0.05 to 5 wt. %, with respect to non-volatile fractions, may be added to dispersions (a) or (b) or the entire preparation, wherein the thickening effect in the formulation should preferably not exceed 1000 mPas.

For preservation purposes, fungicides may also be added to compositions according to the invention. These may preferably be used in amounts of 0.02 to 1 wt. %, with respect to non-volatile fractions. Suitable fungicides are for example phenol and cresol derivatives or tin inorganic compounds or azol derivatives such as TEBUCONAZOL or KETOCONAZOL.

Tackifying resins such as e.g. unmodified or modified natural resins such as colophony esters, hydrocarbon resins or synthetic resins such as phthalate resins may also optionally be added to compositions according to the invention or to the components used for preparing these in dispersed form (see e.g. in "Klebharze" R. Jordan, R. Hinterwaldner, p. 75-115, Hinterwaldner Verlag, Munich, 1994). Alkyl phenol resin and terpene phenol resin dispersions with softening points preferably higher than 70 °C, more preferably higher than 110 °C, are preferred.

The present invention also relates to the use of the dispersion according to the invention as an adhesive. The adhesive displays a high storage stability and the viscosity thereof can be tailored to a desired level. The adhesive has a high initial bonding strength despite its water content, an open time before joining pieces and a high thermal stability. The invention also relates to adhesive layers obtainable from the dispersion.

The invention also relates to adhesive layers as well as a substrate obtainable from the dispersion according to the invention as an adhesive. Preferably, the substrate is selected from shoes, foam blocks, wooden structures like furniture and toys, clothing

articles and objects used in the automotive industry like dashboard decoration foils and the like.

The present invention will be further described with reference to the following examples and figures without wishing to be limited by them.

5

Glossary:

Manutex: Sodium alginate (creaming agent), Monsanto, UK

$SiO_2$ dispersions used:

| Product | Supplier | Supplied form | Type | Density | Mean particle size |
|---|---|---|---|---|---|
| Levasil 50 | Akzo-Nobel, Leverkusen, DE | Dispersion, 50 wt.-% solids | Colloidical silica | 1.385 $g/cm^3$ | 55 nm |
| Levasil 200 | Akzo-Nobel, Leverkusen, DE | Dispersion, 30 wt.-% solids | Colloidical silica | 1.205 $g/cm^3$ | 15 nm |
| Levasil 300 | Akzo-Nobel, Leverkusen, DE | Dispersion, 30 wt.-% solids | Colloidical silica | 1.21 $g/cm^3$ | 9 nm |
| Levasil 500 | Akzo-Nobel, Leverkusen, DE | Dispersion, 15 wt.-% solids | Colloidical silica | 1.10 $g/cm^3$ | 6 nm |

Methods:

1. Creaming of silicon dioxide dispersions for determining the optimum amount of creaming agent:

Creaming tests were performed to determine the amount of creaming agent needed to reach the maximum solids concentration in the dispersions. The equipment used was a Brookfield LV DV III viscosimeter, a Knick KR301 pH meter and Sartorius 1364 laboratory scales. Furthermore, the creaming agent Manutex was provided as a 2 wt-% solution (freshly prepared on the previous day) in deionized water.

The pH of the silica dispersions was recorded and 8 samples of 100 g silica dispersion were filled into bottles. To the samples 5, 10, 15, 20, 25, 30, 40, and 50 g, respectively, of the 2% creaming agent solution were added and gently mixed. Visual inspection of the samples was undertaken after storing the samples for 24 hours at room temperature.

The serum formed above the dispersion was measured with a ruler and the result was also recorded. The samples were finally homogenized by shaking at the maximum revolution speed and the pH was recorded again.

2. Particle size distributions:

The mean particle diameter of the silica particles was determined by ultracentrifugation according to H. G. Müller, Progr. Colloid Polym. Sci. 107, 180-188 (1997) and is expressed as the mass average.

3. Solids content:

Solids content was determined by drying the dispersions at 110 °C for 16-18 hours. The amount of $SiO_2$ was determined as ash content after heating the sample at 850 °C-1000 °C for 30 minutes.

Results:

Examples 1-8: determination of the optimum creaming agent

| Example | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Levasil 200 [g] | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2% Manutex solution [g] | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 50 |
| Manutex solid [g] | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.5 |
| observations | No sep.. | No sep. | Visible sep. | Good sep. | Good sep. | Good sep. | Good sep. | Good sep. |
| Solids content of serum after pyrolysis [%] (upper phase) | 0 | 0 | 20.66 | 18.44 | 15.07 | 13.26 | 12.34 | 15.8 |
| Solids content of concentrated phase after pyrolysis [%] | 0 | 0 | 38.18 | 43.05 | 46.82 | 48.09 | 49.74 | 52.66 |

( sep. = separation)

According to these experiments the best amount of creaming agent was found to be 35 g of the 2% solution per 100 g of the silicon dioxide dispersion (Fig 1).

The concentration experiments of 3 silica dispersions are summarized in the table below: 35 g of the 2% solution per 100 g of the silicon dioxide dispersion are used.

| Example Nr. | 9 | 10 | 11 |
|---|---|---|---|
| Levasil 50 [g] | 100 | 50 | 50 |
| Levasil 300 [g] | 0 | 50 | 0 |
| Levasil 500 [g] | 0 | 0 | 50 |
| Solids content before concentration [%] | 50 | 40 | 32.5 |
| Solids content of concentrated phase [%] | 64 | 66 | 58 |
| Solids content of serum after drying at 100 °C [%] ( alginate, $SiO_2$) | 5.7 | 21.6 | 16.4 |
| Solids content of serum after pyrolysis [%] ($SiO_2$ only | 4.3 | 19.4 | 14.3 |
| Solids content serum (alginate) [%] | 1.4 | 2.2 | 2.1 |

The particle size distribution in Levasil 50 before the concentration step is given in FIG. 2 and after the concentration step (example Nr. 9) is given in FIG. 3. It can be seen that the particle size distribution is virtually unchanged.

Likewise, the particle size distribution of Levasil 300 before the concentration step is given in FIG. 4 and after the concentration step of the 50/50 mixture with Levasil 50 (example Nr. 10) is given in FIG. 5. It can also be seen that there is a bimodal particle size distribution and both distributions sizes of the starting materials are virtually unchanged.

In a further example (Nr. 3), a sample of the concentrated dispersion obtained in example Nr. 10 was stored at a temperature of 50 °C for 6 months. Visual inspection revealed that the dispersion still was homogenous and did not show signs of segregation.

Claims

1. A method of concentrating an aqueous silicon dioxide dispersion, comprising the steps of:

a) providing an aqueous dispersion comprising silicon dioxide particles having an initial content of silicon dioxide;

b) contacting the dispersion of step a) with a creaming agent to yield an aqueous serum phase and an aqueous concentrated phase,

the serum phase having a silicon dioxide content lower than the initial content of silicon dioxide in the dispersion of step a) and

the concentrated phase having a silicon dioxide content higher than the initial content of silicon dioxide in the dispersion of step a); and

c) separating the serum phase from the concentrated phase,

wherein the dispersion of step a) does not comprise organic polymer particles of polychloroprene and/or polyurethane.

2. The method according to claim 1, wherein the dispersion of step a) is a silica sol, a silica gel, a pyrogenic silica dispersion, a precipitated silica dispersion or a mixture of these.

3. The method according to claim 1, wherein the creaming agent is selected from the group comprising alginates, cellulose derivates, methyl cellulose, agar-agar, poly(meth)acrylic salts, and/or copolymers of alkyl(meth)acrylates and/or styrene with unsaturated sulfonic acid derivates or olefinically unsaturated mono- or polycarboxylic acids or salts thereof.

4. The method according to claim 3, wherein the creaming agent is sodium alginate, potassium alginate and/or ammonium alginate.

5. The method according to claim 1, wherein the initial content of silicon dioxide in the dispersion of step a) is ≥ 1 weight-% to ≤ 60 weight-%.

6. The method according to claim 1, wherein in the dispersion of step a) the mean particle size of silicon dioxide particles is ≥ 1 nm to ≤ 400 nm determined by ultracentrifugation.

7. The method according to claim 1, wherein in the dispersion of step a) the silicon dioxide particles have a bimodal or multimodal particle size distribution.

8. The method according to claim 1, wherein the creaming agent is provided in form of an aqueous solution and the content of the creaming agent in the aqueous solution is ≥ 0.5 weight-% to ≤ 10 weight-%.

9. The method according to claim 1, wherein the creaming agent is present in an amount of ≥ 0.2 weight-% to ≤ 15 weight-%, based on the solids content of the aqueous silicon dioxide dispersion of step a).

10. The method according to claim 1, wherein the separation in step c) is at least partially performed by centrifugation.

11. A concentrated aqueous silicon dioxide dispersion comprising a creaming agent in an amount ranging from ≥ 0.01 weight-% to ≤ 1 weight-% and silicon dioxide in an amount from ≥ 30 weight-% to ≤ 80 weight-%, wherein the aqueous silicon dioxide dispersion does not comprise organic polymer particles of polychloroprene and/or polyurethane.

12. A concentrated aqueous silicon dioxide dispersion, obtainable by a method according to one or more of claims 1 to 10, comprising silicon dioxide in an amount ≥ 30 weight-% to ≤ 80 weight-% and a creaming agent in an amount being ≥ 0.01 weight-% to ≤ 1 weight-%, wherein the aqueous silicon dioxide dispersion does not comprise organic polymer particles of polychloroprene and/or polyurethane.

13. The dispersion according to claim 11 or 12, wherein the silicon dioxide dispersion is a silica sol, a silica gel, a pyrogenic silica dispersion, a precipitated silica dispersion or a mixture of these.

14. The dispersion according to any one of claims 11 to 13, wherein the silicon dioxide particles of the dispersion have a bimodal or multimodal particle size distribution.

15. The dispersion according to any one of claims 11 to 14, wherein the creaming agent is selected from the group comprising alginates, cellulose derivates, methyl cellulose, agar-agar, poly(meth)acrylic salts, and/or copolymers of alkyl(meth)acrylates and/or styrene with unsaturated sulfonic acid derivates or olefinically unsaturated mono- or polycarboxylic acids or salts thereof; and salts of divalent ions.

16. The dispersion according to any one of claims 11 to 15, wherein the creaming agent is sodium alginate, potassium alginate and/or ammonium alginate.

17. Use of the dispersion according to any one of claims 11 to 16, as an adhesive.

18. Adhesive layer obtainable from the dispersion according to any one of claims 11 to 16.

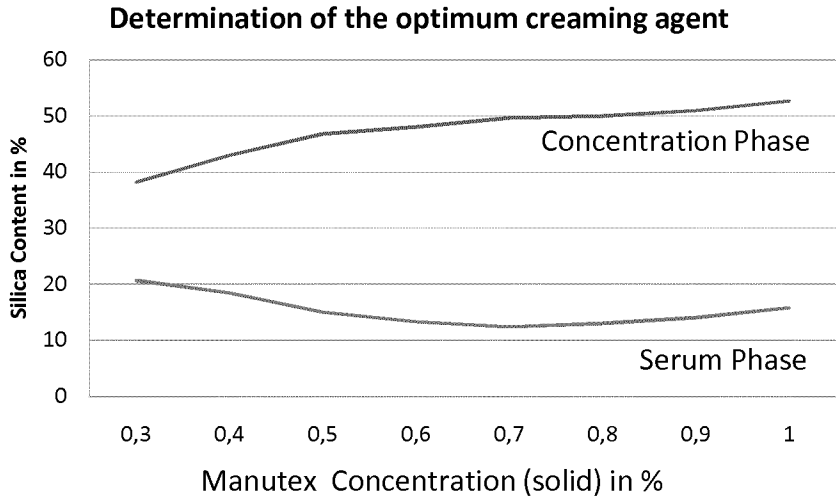
Determination of the optimum creaming agent
Silica Content in %
60
50
40
30
20
10
0
Concentration Phase
Serum Phase
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
Manutex Concentration (solid) in %

Fig 1

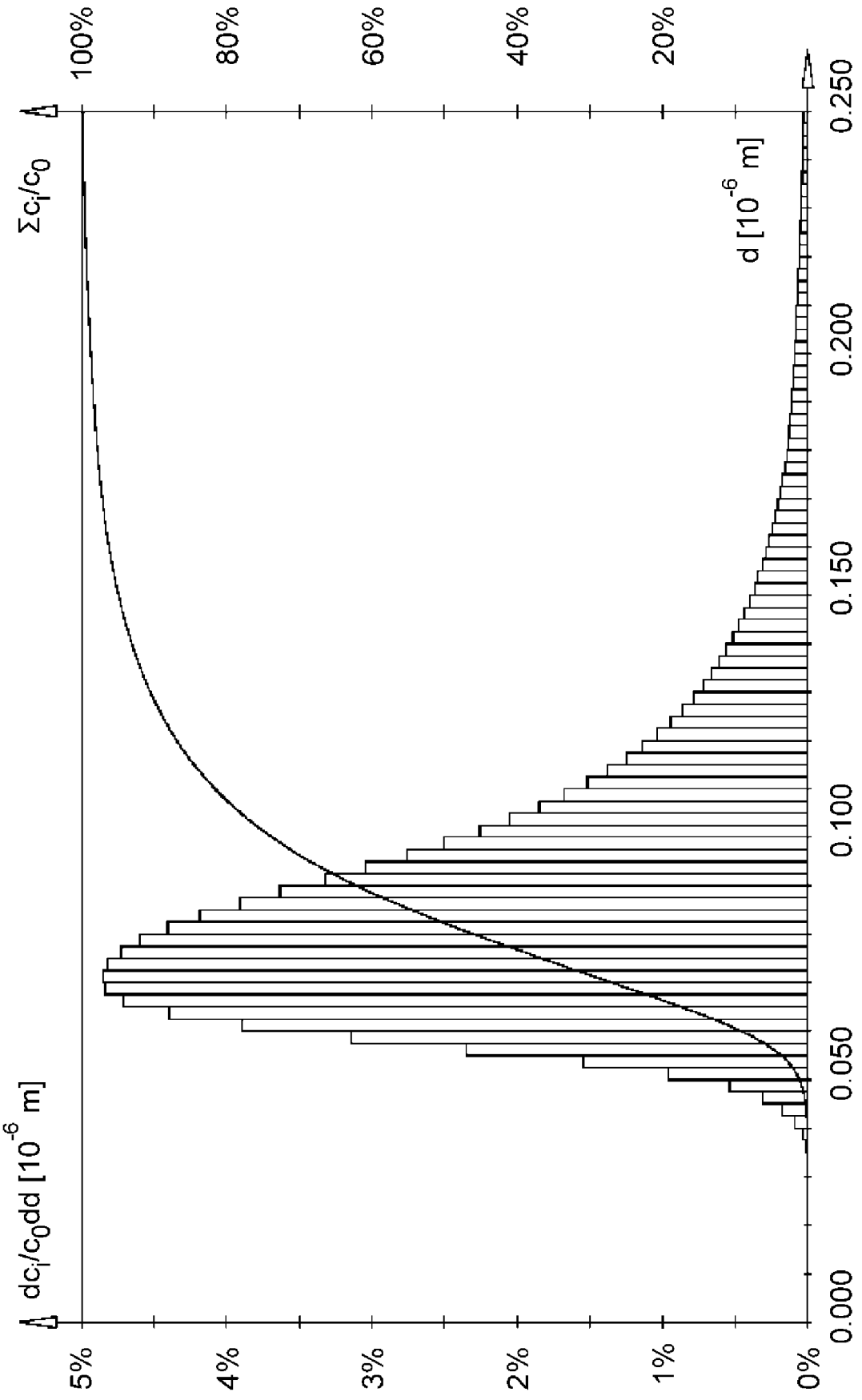
100%
80%
60%
40%
20%
Σc_i/c_0
d [10^-6 m]
0.250
0.200
0.150
0.100
0.050
0.000
dc_i/c_0dd [10^-6 m]
5%
4%
3%
2%
1%
0%

FIG. 2

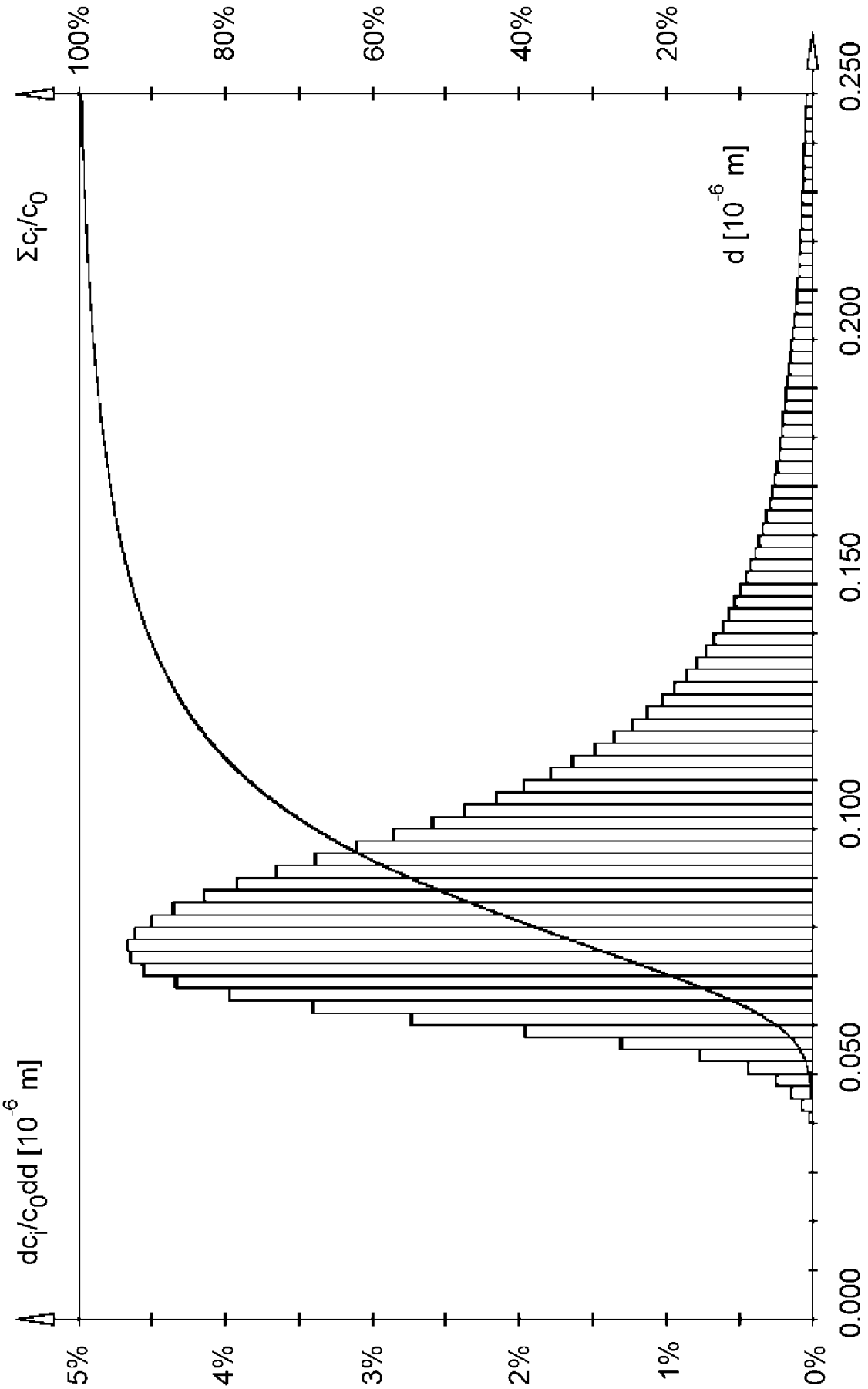
100%
80%
60%
40%
20%
Σc_i/c_0
d [10^-6 m]
0.250
0.200
0.150
0.100
0.050
0.000
dc_i/c_0dd [10^-6 m]
5%
4%
3%
2%
1%
0%

FIG. 3

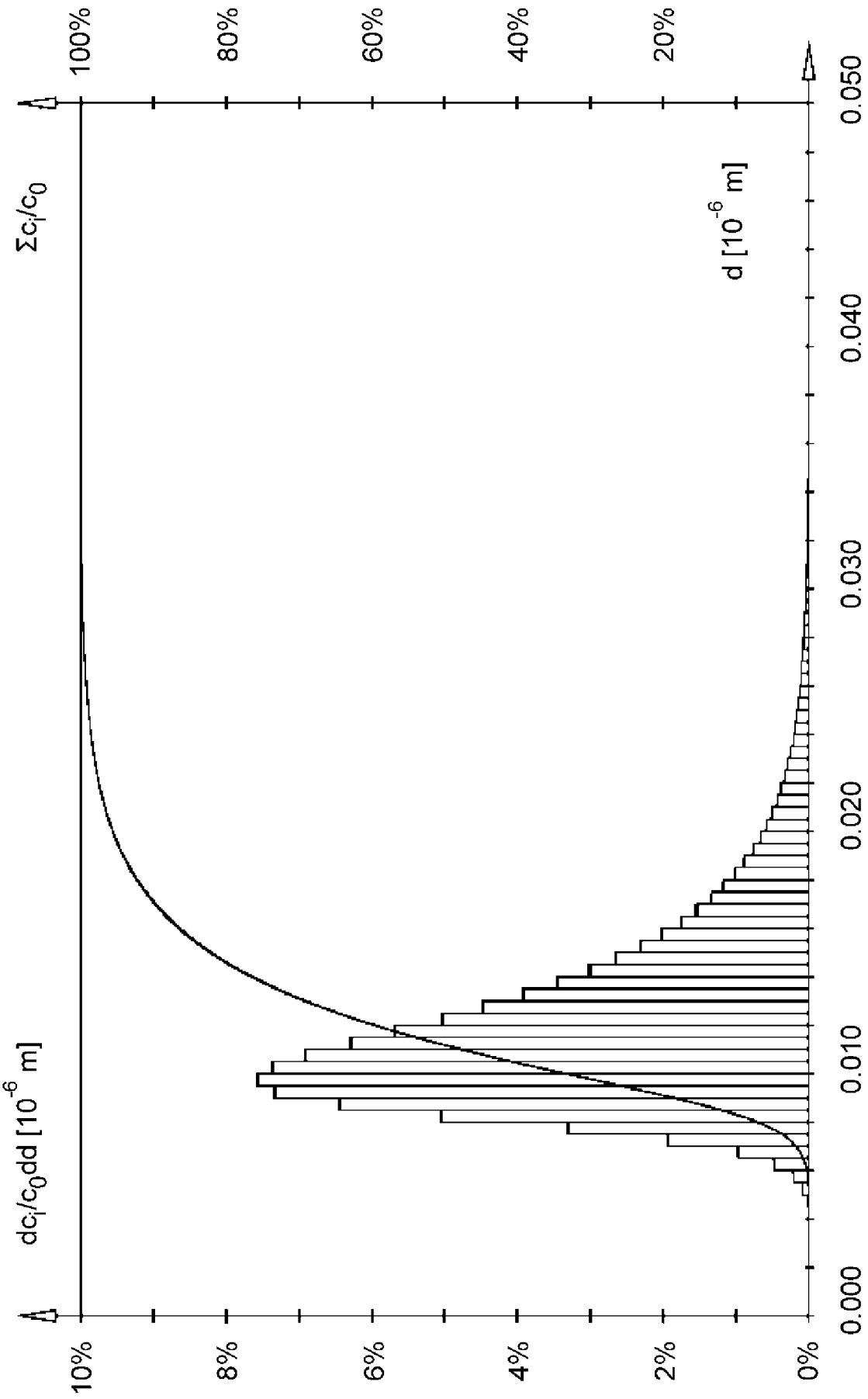
100%
80%
60%
40%
20%
Σc_i/c_0
d [10^-6 m]
0.050
0.040
0.030
0.020
0.010
0.000
dc_i/c_0dd [10^-6 m]
10%
8%
6%
4%
2%
0%

FIG. 4

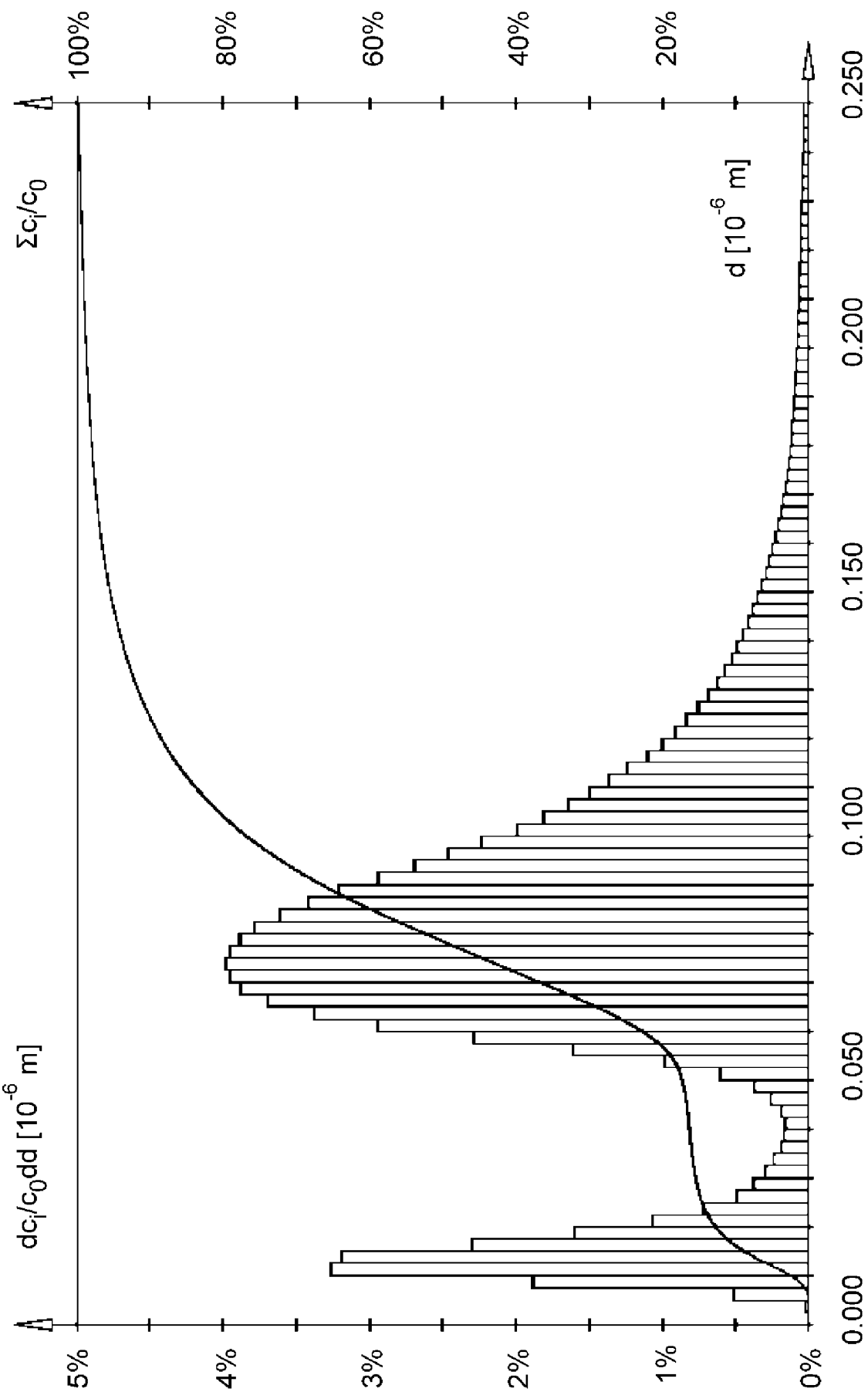
100%
80%
60%
40%
20%
$\Sigma c_i/c_0$
d [$10^{-6}$ m]
0.250
0.200
0.150
0.100
0.050
0.000
$dc_i/c_0dd$ [$10^{-6}$ m]
5%
4%
3%
2%
1%
0%

FIG. 5

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061776

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B33/148 C08L11/02 C09J111/02
ADD.

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)
C01B 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 practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 2009/234064 A1 (WANG SHIPING [US] ET AL) 17 September 2009 (2009-09-17)<br>cited in the application<br>paragraph [0002]<br>paragraph [0018] - paragraph [0038]<br>claims 24, 25, 27, 28, 34-36 | 1-18 |
| A | US 2008/076838 A1 (PUPPE LOTHAR [DE])<br>27 March 2008 (2008-03-27)<br>paragraph [0006]<br>paragraph [0018] - paragraph [0020]<br>examples 1-3 | 1-16 |
| A | WO 99/01377 A1 (KEMPRO ITALIANA S R L [IT]; TODARELLO FRANCESCO [IT])<br>14 January 1999 (1999-01-14)<br>the whole document | 1-16 |

-/--

[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 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 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 |
|---|---|
| 18 October 2012 | 24/10/2012 |

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

1

Form PCT/ISA/210 (second sheet) (April 2005)

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/061776

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 1 664 225 A1 (BAYER MATERIALSCIENCE AG [DE]) 7 June 2006 (2006-06-07) the whole document<br>---<br>S. S. Ochigbo ET AL: "Comparison of two creaming methods for preparation of natural rubber latex concentrates from field latex", African Journal of Agricultural Research, 18 June 2011 (2011-06-18), pages 2916-2919, XP055011817, ISSN: 1991-637X Retrieved from the Internet: URL:http://www.academicjournals.org/ajar/PDF/pdf2011/18 June/Ochigbo et al.pdf [retrieved on 2011-11-10] Introduction Experimental<br>--- | 1-18 |
| A | | 1-10 |

1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/061776

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 2009234064 A1 | 17-09-2009 | AU 2009223247 A1 | 17-09-2009 |
| | | CA 2716805 A1 | 17-09-2009 |
| | | CN 101970548 A | 09-02-2011 |
| | | EP 2257595 A2 | 08-12-2010 |
| | | JP 2011518233 A | 23-06-2011 |
| | | NZ 587607 A | 31-08-2012 |
| | | US 2009234064 A1 | 17-09-2009 |
| | | US 2011178234 A1 | 21-07-2011 |
| | | WO 2009114788 A2 | 17-09-2009 |
| US 2008076838 A1 | 27-03-2008 | DE 102006044520 A1 | 03-04-2008 |
| | | EP 1905741 A1 | 02-04-2008 |
| | | JP 2008074701 A | 03-04-2008 |
| | | US 2008076838 A1 | 27-03-2008 |
| WO 9901377 A1 | 14-01-1999 | AT 208739 T | 15-11-2001 |
| | | AU 8802998 A | 25-01-1999 |
| | | CN 1261860 A | 02-08-2000 |
| | | CZ 9904656 A3 | 14-06-2000 |
| | | DE 69802538 D1 | 20-12-2001 |
| | | DE 69802538 T2 | 23-05-2002 |
| | | EP 0996588 A1 | 03-05-2000 |
| | | IT RM970391 A1 | 04-01-1999 |
| | | WO 9901377 A1 | 14-01-1999 |
| EP 1664225 A1 | 07-06-2006 | AU 2004280360 A1 | 21-04-2005 |
| | | CA 2538955 A1 | 21-04-2005 |
| | | EP 1664225 A1 | 07-06-2006 |
| | | JP 2007533778 A | 22-11-2007 |
| | | KR 20060083211 A | 20-07-2006 |
| | | MX PA06002882 A | 05-06-2006 |
| | | US 2005085584 A1 | 21-04-2005 |
| | | WO 2005035683 A1 | 21-04-2005 |