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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 August 2014 (07.08.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/118372 A1

(51) International Patent Classification:
B01J 35/00 (2006.01) *B01J 21/06* (2006.01)

(21) International Application Number:
PCT/EP2014/052060

(22) International Filing Date:
3 February 2014 (03.02.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/760,067 2 February 2013 (02.02.2013) US

(71) Applicant: **JOMA INTERNATIONAL A/S** [NO/NO]; Bergenstråhle & Lindvall AB, Heiane 2b, N-5131 Nyborg (NO).

(72) Inventors: **CORKERY, Robert William**; Skinnarviksringen 22, S-117 27 Stockholm (SE). **WESTERMOEN, Andreas**; Schriverhaugen 2, N-5918 Frekhaug (NO). **BEN-MOSHE, Matti**; Sheizaf St.2, 71799 Reut (IL). **KHEYFETZ, Michael**; Heyl Haavir st 67/24, 97535 Jerusalem (IL).

(74) Agent: **CARLSSON, Fredrik**; Bergenstrahle & Lindwall AB, P.O. Box 17704, S-118 93 Stockholm (SE).

(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, BN, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: AN AQUEOUS DISPERSION COMPRISING TiO_2 PARTICLES

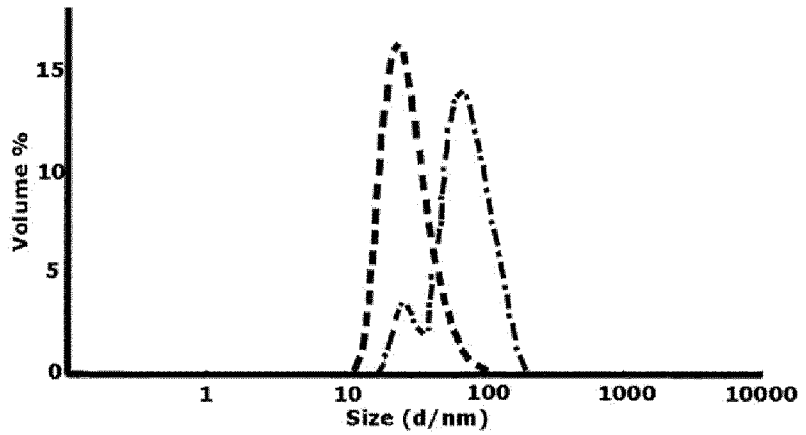

Fig. 1

(57) Abstract: There is disclosed an aqueous dispersion comprising TiO_2 particles, the have a size in the range 2-500 nm, wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the aqueous dispersion comprises at least one amine, and wherein the pH of the aqueous dispersion is above the iso-electric point of the particles comprising TiO_2. One advantage is that it is possible to adjust the pH of the dispersion to adapt the pH to sensitive materials, in particular materials sensitive for low pH values. Another advantage is that the higher fraction of Ti leachable in 37% HCl gives better transparency and dispersion stability. Further it gives better redispersability.

WO 2014/118372 A1

AN AQUEOUS DISPERSION COMPRISING TiO_2 PARTICLES

Technical field

[0001]The present invention relates generally to an aqueous dispersion comprising TiO_2 nanoparticles and which further comprises an amine. The invention also provides a method of manufacturing the dispersion.

Background

[0002]TiO_2 nanoparticles are useful for a range of applications, including photocatalytic breakdown of organic pollutants. However in order to add the active particles to the desired system, the particles must usually be modified in ways that decrease their performance such as drying to powder.

[0003]Hüsken et al (2007) teaches that for air purifying paving stones, having well dispersed and small particles is more important than the amount of TiO_2 added, and that adding the nanoparticles as dispersion increases the performance compared to powders. However TiO_2 dispersions produced by hydrolysis of $TiCl_4$ or $TiOCl_2$ are strongly acidic due to the excess of HCl, and unsuitable for insertion into systems such as cement or paints. Increasing the pH towards the iso-electric point eliminates electrostatic stabilization and leads to aggregation unless stabilized by other means. The process of aggregation irreversibly affects to the surface, so that aggregating and re-dispersing a product generally gives a different particle size distribution with larger particles.

[0004]Several disclosures detail dispersions of TiO_2 nanoparticles at non-acidic pH, but do not give methods to go from acidic to non-acidic pH without changing the particle size distribution.

[0005]EP 2130587 discloses a method to achieve well dispersed TiO_2 at pH above the iso-electric point using phosphoric acid as stabilizer. This method however is limited to pH below 7 and also requires the presence of tungsten oxide nanoparticles.

[0006]EP1997860 and EP202448 disclose dispersions based on re-dispersing TiO_2 powders. EP1997860 discloses the presence of an amine in a well dispersed photocatalytic coating precursor, but teaches dispersion of the TiO_2 particles from powder using a polymer dispersant.

[0007]WO 2007/074436 discloses a method for production of TiO_2 particles comprising the steps of providing an aqueous solution comprising titanium ions or titanium complexes, keeping the temperature lower than 70°C and hydrolyzing, adjusting the conditions by at least one of a) heating at least 1°C, b) changing pH at least 0.1 units, and c) diluting by at least 20%. There is disclosed a step to dehydrate particles at a calcination temperature in a range 90-900°C.

[0008]US 2,819,174 discloses a process for manufacturing a titania hydrate dispersion. The pH is increased from below about 5 to a value between 5 and 11 by addition of an alkalizing agent such as acyclic alkonol monoamines.

[0009]US 7,763,565 discloses a method of preparing stable, transparent photocatalytic titanium dioxide sols which involves thermal treatment of a dispersion of amorphous titanium dioxide in the presence of certain alpha-hydroxy acids. The sots comprise titanium dioxide particles in the anatase form having a crystallite size less than about 10 μm.

[0010]US2010234209 discloses a nano-particle comprising: a core of a size having a first electrically conducting or semiconducting material, a shell of a thickness having a second dielectric or semiconducting material, wherein the composition of said second material is different from the composition of said first material, and wherein the shell thickness is less than or equal to the core size.

[0011]Even if dispersions according to the prior art are used today there is still room for an improvement regarding for instance the pH of the aqueous dispersion. Further the stability of a dispersion of particles is also desired to improve.

Summary

[0012]It is an object of the present invention to obviate at least some of the disadvantages in the prior art and to provide an improved dispersion as well as a method for manufacturing the dispersion.

[0013]In a first aspect there is provided an aqueous dispersion comprising particles, wherein the particles have a size in the range 2-500 nm wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the aqueous dispersion comprises at least one amine and wherein the pH of the aqueous dispersion is above the iso-electric point of the particles comprising TiO_2.

[0014]In a second aspect there is provided a method of manufacturing an aqueous dispersion, said method comprising the steps of:

a) providing an acidic aqueous dispersion comprising particles wherein the particles have a size in the range 2-500 nm, wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl,

b) adding at least one amine to the aqueous dispersion and adjusting the pH value to above the iso-electric point of the TiO_2 particles.

[0015]Further aspects and embodiments are defined in the appended claims, which are specifically incorporated herein by reference.

[0016]One advantage is that it is possible to adjust the pH of the dispersion to adapt the pH to sensitive materials, in particular materials sensitive for low pH values.

[0017]Another advantage is that the higher fraction of Ti leachable in 37% HCl gives better transparency and dispersion stability. Further it gives better redispersability.

Brief description of the drawings

[0018] The invention is now described, by way of example, with reference to the accompanying drawings, in which:

[0019] Fig. 1 shows the volumetric distribution of colloidal particle sizes (hydrodynamic diameter) measured by DLS. The dashed line indicates the neutral dispersion according to the invention, diluted with acid to prepare the DLS sample. The dots-and-dashed line indicates an initially stable acidic solution where simple dilution with water has led to formation of aggregates.

Detailed description

[0020] Before the invention is disclosed and described in detail, it is to be understood that this invention is not limited to particular compounds, configurations, method steps, substrates, and materials disclosed herein as such compounds, configurations, method steps, substrates, and materials may vary somewhat. It is also to be understood that the terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting since the scope of the present invention is limited only by the appended claims and equivalents thereof.

[0021] It must be noted that, as used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise.

[0022] If nothing else is defined, any terms and scientific terminology used herein are intended to have the meanings commonly understood by those of skill in the art to which this invention pertains.

[0023] A dispersion as used herein refers to a system in which particles are dispersed in a continuous phase of a different composition. The term dispersion includes but is not limited to suspensions, colloids, and sols.

[0024] The particle dispersion can be used for many different purposes. One purpose is for preparing a surface with adsorbed particles where the catalytic

properties of the particles are utilized. The catalytic properties of the particles in the dispersion can also be utilized even if the particles are not adsorbed onto a surface. The inventors believe that the catalytic action of the particles can be described as a two-step process, in particular for particles comprising at least one core and an at least partially surrounding layer. The compound to be reacted is in a first step adsorbed to the surrounding layer. Subsequently the compound to be reacted is transported to the core(s). The majority of the molecules to be reacted react at the core(s). A good catalytic particle should thus have a surrounding layer where the adsorption of the compound to be reacted is adsorbed in a good way and a core(s) at which the catalyzed reaction can take place. The high fraction (50wt% or more, even 60wt% or more)

[0025]According to the invention, the particles contain a significant fraction of Ti leachable in HCl 37%. The leachability is determined by treating TiO_2 particles in 37% HCl at 55°C for an extended period of several hours, such as at least 5 hours or more such as 17 hours. The treatment time should be sufficiently long to reach a plateau value for the concentration of leached material in the HCl. The skilled person can perform a routine experiment as already described in this application and verify a sufficiently long treatment time to reach equilibrium. The particles should be leached until equilibrium. A skilled person realizes that in theory equilibrium may not be reached even after many hours, but in practice a value of ±1wt% within the true equilibrium value is considered to be equilibrium. The leached Ti in solution is measured and the fraction of leached Ti can be calculated. All fractions are calculated by weight.

[0026] The leached Ti in solution is measured and the fraction of leached Ti can be calculated. All fractions are calculated by weight. The leachable fraction does to a large extent comprise amorphous material. As shown in example 4, the fraction of amorphous material can be reduced by thermal treatment. Since the particles can show a high leachable fraction while XRD analysis of the crystalline material shows 100wt% anatase, this leachable fraction is

concluded to consist of one of more amorphous forms of titanium oxides (TiO_2 or substochiometric $TiO_{(2-x)}$) and/or hydrated TiO_2, containing –Ti-OH moieties.

[0027]The layer with a high content of Ti leachable in 37% HCl is rich in hydroxyl groups.

[0028]The high fraction of Ti leachable in 37% HCl at 55°C is obtained by carefully controlling the growth of nanoparticles. It is possible to start with a solution/dispersion of titanic acid which is heated to initiate growth of nanoparticles. When the nanoparticles are formed the layer which to a large extent is leachable in 37% HCl at 55°C grows first and when the material which is leachable in 37% HCl has formed the crystalline material starts to grow. The crystalline material is not or only to a very minor extent leachable in 37% HCl. Thus it is possible to abort the heating early in order to obtain particles with a high fraction of leachable material.

[0029]The high amorphous content nanoparticles, i.e. particles with a high fraction of Ti leachable in 37% HCl are observed to give better transparency and dispersion stability in the precursor dispersion. Powders with high amorphous content in the nanoparticles are also observed have better redispersability than highly crystalline powders. When the particles have for instance been standing, and/or exposed to heat they may form a gel, but the gelation process is reversible and by shaking it is possible to regain the aqueous dispersion. A model of the particles as at least one crystalline core surrounded by a layer of amorphous material can explain the advantages in crosslinking, dispersion stability and powder redispersability since all of these are connected to surface mechanisms and not bulk composition.

[0030]There is disclosed a concentrated stable aqueous dispersion of TiO_2 particles at pH above the iso-electric point, comprising at least one amine.

[0031]The ability to provide stable nanoparticle dispersion at basic pH is useful for adding active nanoparticles to materials, where adding acidic TiO_2 dispersions would cause a reaction that typically leads to unwanted aggregation of the TiO_2

nanoparticles and degradation. Examples of such materials include but are not limited to cement. The ability to provide stable nanoparticle dispersion at neutral pH or at a pH slightly above neutral allows the application of active nanoparticles via equipment that is vulnerable to corrosion, allows application of active nanoparticles to substrates, binders and formulations were acid pH is undesirable.

[0032]The claimed dispersion can be made with solid concentrations at least up to 30wt%, but concentrations up to about 15wt% give added advantages in transparency, sprayability and colloidal stability. The dispersion can easily be diluted to obtain lower concentrations. In one embodiment the concentration of the particles in the aqueous dispersion is 1-45wt%. In an alternative embodiment the concentration of the particles in the aqueous dispersion is 10-20wt%.

[0033]The transparency of the dispersion is an indication of aggregation stability, since large aggregates will scatter visible light and make the dispersion turbid. In one embodiment of the invention, the dispersion is transparent. In one embodiment the dispersion is semi-transparent.

[0034]In one embodiment of the invention, the dispersion shows no visible sign of nanoparticle aggregation. In one embodiment of the invention, the dispersion shows no visible sign of nanoparticle aggregation and the DLS size distribution of the dispersion is similar to that of the starting aqueous solution.

[0035]In one embodiment the particles have at least one core which is at least partially surrounded by a surrounding layer. Since most of the crystalline material is in the at least one core, the at least one core can also be referred to as the crystal phase. In an embodiment with particles having at least one core surrounded at least partially by a layer, the at least one core of the particles comprises at least 75wt% anatase. In an alternative embodiment of the invention, the at least one core of the TiO_2 particles comprises at least 95wt% anatase. In another embodiment of the invention, the at least one core of the TiO_2 nanoparticles comprises 100wt% anatase, or essentially 100wt% anatase.

In one embodiment of the invention the at least one core of the TiO_2 nanoparticles comprises 99wt% anatase

[0036]In an embodiment of the invention, the TiO_2 nanoparticles contain at least 50wt% Ti that is leachable in 37% HCl. In an embodiment of the invention, the TiO_2 nanoparticles contain at least 50wt% Ti that is leachable in 37% HCl.

[0037]The pH of the final dispersion can be modified to any target pH at least in the range 6-12 by adjusting the amount of amine and base added.

[0038]In one embodiment of the invention, the pH is neutral or near neutral. In an alternative embodiment the pH is in the range 9-10. In one embodiment the pH is matched to a cementitous substrate.

[0039]The dispersion has controlled viscosity and is sprayable with generic equipment at least up to 20wt% solid content. The solid concentration can easily be reduced by dilution, which is observed to decrease the viscosity.

[0040]The dispersion can be produced by increasing the pH value of an acidic TiO_2 dispersion. Taking the pH through the isoelectric point can be done with or without the presence of amines, but addition of amines gives significantly improved transparency in the final dispersions.

[0041]In a first aspect there is provided an aqueous dispersion comprising particles, wherein the particles have a size in the range 2-500 nm wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the aqueous dispersion comprises at least one amine and wherein the pH of the aqueous dispersion is above the iso-electric point of the particles comprising TiO_2.

[0042]It is understood that the beneficial effects of a high fraction of Ti leachable in 37% HCl start already at 50wt%, but that the beneficial effects are improved at 55wt% and more pronounced at 60wt%. At even higher fractions of leachable material the advantages can be further pronounced. However one drawback of a very high fraction of leachable material (such as 70-80wt% Ti) is that the

yield during the manufacturing process is impaired. Thus in one embodiment at least 50wt% of the Ti in the particles is leachable in 37% HCl. In another embodiment at least 55wt% of the Ti in the particles is leachable in 37% HCl. In yet another embodiment at least 60wt% of the Ti in the particles is leachable in 37% HCl. In a further embodiment at least 65wt% of the Ti in the particles is leachable in 37% HCl. In another embodiment at least 70wt% of the Ti in the particles is leachable in 37% HCl.

[0043]In one embodiment at least of part of said particles comprise at least one core and an at least partially surrounding layer, wherein more than 90wt% of the total amount of Ti leachable in 37% HCl is in the surrounding layer. In an alternative embodiment more than 95wt% of the total amount of Ti leachable in 37% HCl is in the surrounding layer. The embodiments with at least one core and a surrounding layer is often several cores embedded in a surrounding layer.

[0044]In one embodiment the average size of the particles is in the range 5-50 nm.

[0045]In one embodiment the particles in the dispersion are titanium oxide particles with primary particle size in the range 5-50 nm as measured by XRD and where the crystal form comprises mainly anatase TiO_2. In one embodiment the particles comprise sub stoichiometric TiO_2.

[0046]The preparation of the dispersion is not observed to have any significant effect on the basic nanoparticle properties such as crystal phase, crystal size, specific surface and porosity, only on what additives and/or stabilizers are present on the particle surface.

[0047]In one embodiment of the invention, the TiO_2 nanoparticles are in the XRD size range 5-50 nm. In another embodiment of the invention, the TiO_2 nanoparticles are in the XRD size range 10-30 nm.

[0048]In one embodiment of the invention, the TiO_2 nanoparticles are in the DLS size range 5-50 nm. In another embodiment of the invention, the TiO2 nanoparticles are in the DLS size range 15-30 nm.

[0049]In one embodiment at least a part of the particles comprise at least one core and an at least partially surrounding layer, and wherein the at least one core comprises at least 95wt% anatase.

[0050]In one embodiment the dispersion comprises at least one selected from the group consisting of monoethanolamine, diethanolamine, and triethanolamine. In one embodiment the dispersion comprises ethanolamine.

[0051]In one embodiment the dispersion comprises at least one alpha hydroxy acid.

[0052]In one embodiment the dispersion comprises at least one molecule, wherein said molecule comprises at least one chemical group selected from the group consisting of a carboxylic group, a sulphate group, and a phosphate group.

[0053]In one embodiment the pH of the aqueous dispersion is in the range 6-8. In an alternative embodiment the pH is in the range 8-12. In yet another embodiment the pH is in the range 9-10.

[0054]In one embodiment the particles have a monomodal size distribution. Monomodal is interpreted so that at least 99wt% of the particles fall within the monomodal size distribution. I.e. 1wt% of the particles can have sizes which are not monomodal.

[0055]In one embodiment the concentration of said particles is 1-45wt%, preferably 10-20wt%. In an embodiment of the invention the aqueous dispersion comprises up to 10wt% amines. In an alternative embodiment of the invention, the dispersion comprises 2-8wt% amines. In one embodiment the concentration is at least 1wt%. In one embodiment the concentration is at least 5wt%. In one embodiment the concentration is at least 10wt%. In one embodiment the concentration is at least 20wt%. In another embodiment of the invention, the dispersion comprises 3wt% MEA. In yet another embodiment of the invention, the dispersion comprises 3wt% MEA and 3wt% TEA.

[0056] In a second aspect there is provided a method of manufacturing an aqueous dispersion, said method comprising the steps of:

a) providing an acidic aqueous dispersion comprising particles wherein the particles have a size in the range 2-500 nm, wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the pH of the acidic aqueous dispersion is below the isoelectric point of the particles comprising TiO_2,

b) adding at least one amine to the aqueous dispersion and adjusting the pH value to above the iso-electric point of the TiO_2 particles.

[0057] In one embodiment the particles have not undergone a powder stage.

[0058] In one embodiment the pH value is adjusted by adding at least one selected from the group consisting of an organic amine and an inorganic base.

[0059] In one embodiment of the invention, an inorganic base is used to increase the pH above the iso-electric point. In one embodiment of the invention, amines are used to increase the pH from below neutral to the final pH.

[0060] In one embodiment at least one alpha hydroxyl acid is added.

[0061] In one embodiment at least one molecule is added, wherein said molecule comprises at least one chemical group selected from the group consisting of a carboxylic group, a sulphate group, and a phosphate group.

[0062] Other features and uses of the invention and their associated advantages will be evident to a person skilled in the art upon reading the description and the examples.

[0063] It is to be understood that this invention is not limited to the particular embodiments shown here. The embodiments are provided for illustrative purposes and are not intended to limit the scope of the invention since the scope of the present invention is limited only by the appended claims and equivalents thereof.

Examples

[0064]All percentages are calculated by weight if not clearly stated otherwise.

[0065]27.1 kg of $TiOCl_2$ was diluted with 13.8 kg deionized water and left overnight. The diluted $TiOCl_2$ solution was neutralized with 77.2 kg of aqueous NaOH and 16.2 kg of $(Na)_2CO_3$ in a stirred reactor to yield a final solution pH below 5. To this was added a solution of 63.7 kg $TiOCl_2$ and 1.9 kg surfactant yielding a transparent solution with a temperature of 40.4°C. To this clear solution, 1.9 kg of acetylacetone was added followed by heating for 35 minutes until the temperature was 81.9° C. The temperature was held constant for a further 75 minutes, followed by cooling from 81.7°C to 50.9°C. The resulting 198.8 kg nanotitania dispersion yielded 196.6 kg of reaction product. The product was filtered through a nanofiltration unit combining washing and concentration steps to obtain a final pH of 1.1 and approximately 20% weight concentration of TiO_2. These particles were utilized for the following examples unless otherwise is clearly stated.

Example 1: preparation of high stability neutral 15% TiO_2 dispersion

[0066]To 840g of a Joma acidic (pH=1) 18% TiO_2 dispersion was added 30g lactic acid, 70g of 20% KOH, 30g of water and 30g of MEA (Monoethanolamine), bringing the final pH to neutral and the TiO_2 content to 15%. All additions were done slowly and with good stirring in order to homogenize the dispersion between each step. The dispersion remained translucent or semi-transparent during the whole process with no signs of particle sedimentation or visible aggregation.

Example 2: preparation of high stability basic 15% TiO_2 dispersion

[0067]To 840g of a Joma acidic (pH=1) 18% TiO_2 dispersion was added 30g lactic acid, 70g of 20% KOH, 30g of MEA (Monoethanolamine) and 30g of TEA (Triethanolamine), bringing the final pH to 10 and the TiO_2 content to 15%. All additions were done slowly and with good stirring in order to homogenize the dispersion between each step. The dispersion remained translucent or semi-

transparent during the whole process with no signs of particle sedimentation or visible aggregation.

Example 3: sprayability of high stability 15% and 20% TiO_2 dispersions

[0068]In one experiment, a dispersion containing 15%wt TiO_2, 3% TEA and 3% MEA was sprayed onto a brick surface using a generic spraying unit. The dispersion showed good sprayability with no clogging of the equipment, and the resulting liquid layer appeared homogeneous.

[0069]In a different experiment, a dispersion containing 20%wt TiO_2, TEA and MEA was sprayed onto a substrate using a consumer spray pump. The dispersion showed good sprayability with no clogging of

[0070]the equipment, suggesting that even higher concentrations are sprayable and the resulting liquid layer appeared homogeneous.

Example 4: investigation of amorphous content of nanoparticles

[0071]Various samples containing TiO_2 nanoparticles were dissolved in concentrated HCl in an amount of ca 10g HCl 37% per gram of TiO2-containing product, enough to leach any amorphous TiO_2 present in the product.

[0072]Two different Joma acidic TiO_2 dispersions were treated with nano filtration, cationic and anionic exchangers until a pH=6.2 was reached. Excess amounts of 37% HCl was added to the samples. The vials were shaken at 55°C for 17 hours.

[0073]Two samples of the second Joma dispersion, after treatment to pH=6.2, were dried at 60°C and sintered at different temperatures. The sintered samples were added to excess amounts of 37% HCl. The vials were shaken at 55°C for 17 hours.

[0074]A third Joma dispersion, after treatment to pH=6.2, was dried at 100 °C and sintered at 200 °C. The samples were added to excess amounts of 37% HCl.

The vials were shaken at 55°C for 18 hours and the solid fraction weighed after washing and air drying for 96 hours followed by heating at 50°C for 1 hour.

[0075]Two different Cristal Millennium product samples (dispersion) were mixed with excess amounts of 37% HCl. The vials were shaken at 55°C for 6-40 hours.

[0076]Evonik Degussa P25 powder was added to excess amounts of 37% HCl. The vial was shaken at 55°C for 24 hours.

In all the cases the resulting almost clear samples were analysed for Ti content Sample	Initial TiOwt%	Leaching time	Clear solution Ti[aq]wt%	Unleached/initial TiO2
Joma sample A	0.68	17h	0.30	0.25
Joma sample B	1.02	17h	0.44	0.27
Joma sample B sintered at 300°C for 90min	2.44	17h	0.72	0.71
Joma sample B sintered at 500°C for 30min	2.19	17h	0.24	0.89

Joma sample C	7.75	18h	-	0.54
Joma sample C sintered at 200°C for 18h	7.75	18h	-	0.64
Cristal Millennium s5300A	4.09	6h	0.386	0.84
"	2.95	24h	0.616	0.64
"	"	40h	0.637	0.63
Cristal Milennium PC500	4,45	18h	0.69	0.73
Degussa P25	17.5	24h	0.27	0.974
In all the cases the resulting almost clear solutions were analysed for Ti content Sample	Initial TiO_2wt%	Leaching time	Clear solution Ti[aq]wt%	Unleached/initial TiO_2
Joma sample A	0.68	17h	0.30	0.25
Joma sample B	1.02	17h	0.44	0.27
Joma sample B sintered at 300°C for 90min	2.44	17h	0.72	0.71
Joma sample B sintered at 500°C for 30min	2.19	17h	0.24	0.89

Cristal Millennium s5300A	4.09	6h	0.386	0.84
"	2.95	24h	0.616	0.64
"	"	40h	0.637	0.63
Cristal Milennium PC500	4.45	18h	0.69	0.73
Degussa P25	17.5	24h	0.27	0.974

[0077]The results show that Joma TiO_2 nanoparticles have a significantly higher fraction of leachable Ti than other tested products, but that this fraction can be reduced by thermal treatment.

Example 5: comparative investigation of colloidal particle size and stability

[0078]A sample of neutral dispersion prepared according to example 1 was diluted with water and analyzed by DLS. A single peak was observed in the volumetric size distribution with the maximum value in the around 23 nm, as shown by the solid lines in figure 1. The experiment was repeated and reproduced the result.

[0079]A sample of acidic dispersion at pH=1 identical to the starting dispersion used in example 1 was diluted with water and analyzed by DLS. The dilution corresponds to a pH increase to about pH=3.5. Two peaks were observed in the volumetric size distribution, shown by the dashed lines in figure 1, with the dominant peak having a maximum value around 70nm range and a smaller peak having a maximum around 25nm. The experiment was repeated and reproduced the result.

[0080]To the diluted acidic dispersion sample was added a few drops of NaOH, quickly bringing it to basic pH. Instant aggregation was visually observed. The resulting dispersion was too polydisperse to be analyzed by DLS, with aggregate sizes up to several microns.

- - -

CLAIMS

1. An aqueous dispersion comprising particles, wherein the particles have a size in the range 2-500 nm, wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the aqueous dispersion comprises at least one amine and wherein the pH of the aqueous dispersion is above the iso-electric point of the particles comprising TiO_2.

2. The aqueous dispersion according to claim 1 wherein at least of part of said particles comprise at least one core and a surrounding layer, at least partially surrounding the at least one core, wherein more than 90wt% of the total amount of Ti leachable in 37% HCl is in the surrounding layer.

3. The aqueous dispersion according to any one of claims 1-2, wherein the average size of the particles is in the range 5-50 nm.

4. The aqueous dispersion according to any one of claims 1-3, wherein at least a part of the particles comprise at least one core and a surrounding layer, at least partially surrounding the at least one core, and wherein the at least one core comprises at least 95wt% anatase.

5. The aqueous dispersion according to any one of claims 1-4, wherein the dispersion comprises at least one selected from the group consisting of monoethanolamine, diethanolamine, and triethanolamine.

6. The aqueous dispersion according to any one of claims 1-5, wherein the dispersion comprises ethanolamine.

7. The aqueous dispersion according to any one of claims 1-6, wherein the dispersion comprises at least one alpha hydroxy acid.

8. The aqueous dispersion according to any one of claims 1-7, wherein the dispersion comprises at least one molecule, wherein said molecule comprises at least one chemical group selected from the group consisting of a carboxylic group, a sulphate group, and a phosphate group.

9. The aqueous dispersion according to any one of claims 1-7, wherein the pH is in the range 6-8.

10. The aqueous dispersion according to any one of claims 1-7, wherein the pH is in the range 8-12.

11. The aqueous dispersion according to any one of claims 1-7, wherein the pH is in the range 9-10.

12. The aqueous dispersion according to any one of claims 1-11, wherein the particles have a monomodal size distribution.

13. The aqueous dispersion according to any one of claims 1-12, wherein the concentration of said particles is 1-45wt%, preferably 10-20wt%.

14. A method of manufacturing an aqueous dispersion, said method comprising the steps of:

a) providing an acidic aqueous dispersion comprising particles wherein the particles have a size in the range 2-500 nm, wherein the particles comprise TiO_2, wherein at least 50wt% of the Ti in the particles is leachable in 37% HCl, wherein the pH of the acidic aqueous dispersion is below the isoelectric point of the particles comprising TiO_2,

b) adding at least one amine to the aqueous dispersion and adjusting the pH value to above the iso-electric point of the TiO_2 particles.

15. The method according to claim 14, wherein the pH of the aqueous dispersion in step a) is below 3.

16. The method according to claim 14, wherein the pH of the aqueous dispersion is adjusted to a value of 9 or higher in step b).

17. The method according to claim 14, wherein the pH of the aqueous dispersion is adjusted to a value in the range 6-8 in step b).

18. The method according to claim 14, wherein the pH of the aqueous dispersion is adjusted to a value in the range 8-12 in step b).

19. The method according to any one of claims 14-18, wherein the particles have not undergone a powder stage.

20. The method according to any one of claims 14-19, wherein the particles have a monomodal size distribution.

21. The method according to any one of claims 14-20, wherein the concentration of said particles is 1-45wt%, preferably 10-20wt%.

22. The method according to any one of claims 14-21, wherein the pH value is adjusted by adding at least one selected from the group consisting of an organic amine and an inorganic base.

23. The method according to any one of claims 14-22, wherein at least one alpha hydroxyl acid is added.

24. The method according to any one of claims 14-23, wherein at least one molecule is added, wherein said molecule comprises at least one chemical group selected from the group consisting of a carboxylic group, a sulphate group, and a phosphate group.

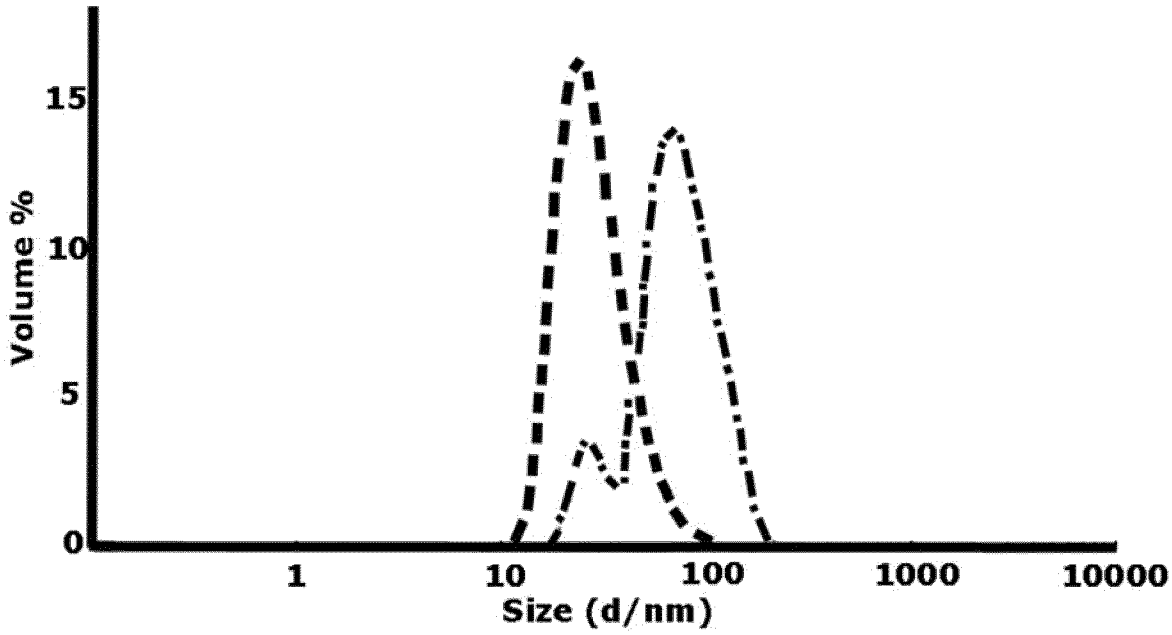

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/052060

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J35/00 B01J21/06
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)
B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, 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 Y	US 2011/183838 A1 (FU GUOYI [US] ET AL) 28 July 2011 (2011-07-28) paragraphs [0021] - [0026]; claims; examples 1,6,9 -----	1-24 1-24
X Y	EP 1 052 225 A1 (NIHON PARKERIZING [JP]) 15 November 2000 (2000-11-15) paragraphs [0012] - [0014], [0022] - [0024], [0027] paragraphs [0047], [0049]; examples; tables 1,2 colloid A: examples 1-7, 12, 14, 16, 18 claims 1,2,8,9,11 -----	1-24 1-24
X	US 2012/283092 A1 (CHAPMAN DAVID M [US]) 8 November 2012 (2012-11-08) paragraphs [0008], [0028], [0029]; examples; tables 1,3,5 -----	1-24
	-/--	

[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
10 April 2014	25/04/2014

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	Holzwarth, Arnold

3

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

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/005145 A1 (SHERMAN JONATHAN [US]) 17 January 2002 (2002-01-17) paragraphs [0008], [0064] - [0074], [0173]	1-24
X,P	WO 2013/074984 A1 (CRISTAL USA INC [US]) 23 May 2013 (2013-05-23) paragraphs [0034] - [0036], [0049] - [0050]	1-24
Y	KR 2012 0084438 A (MK CO LTD [KR]) 30 July 2012 (2012-07-30) paragraphs [0001], [0028]; claims 1,2,6	1-24
Y	AHMET FAIK DEMIRORS ET AL: "Seeded Growth of Titania Colloids with Refractive Index Tunability and Fluorophore-Free Luminescence", LANGMUIR, vol. 27, no. 5, 1 March 2011 (2011-03-01), pages 1626-1634, XP055112069, ISSN: 0743-7463, DOI: 10.1021/la103717m abstract paragraph [2.Experimetal]	1-24
Y	JAYASANKAR M ET AL: "Al2O3 @ TiO2-A simple sol-gel strategy to the synthesis of low temperature sintered alumina-aluminium titanate composites through a core-shell approach", JOURNAL OF SOLID STATE CHEMISTRY, ORLANDO, FL, US, vol. 181, no. 10, 1 October 2008 (2008-10-01), pages 2748-2754, XP025534738, ISSN: 0022-4596, DOI: 10.1016/J.JSSC.2008.06.057 [retrieved on 2008-07-15] paragraph [03.1]; figures 1,3,5	1-24
X,P	US 2013/164444 A1 (TOKUMITSU SHUZO [JP] ET AL) 27 June 2013 (2013-06-27) paragraphs [0052], [0081], [0122]; figure 2	1-24
X	& WO 2012/032868 A1 (HOYA CORP [JP]; TOKUMITSU SHUZO [JP]; KAWAKAMI MASAKO [JP]) 15 March 2012 (2012-03-15)	1-24
A	EP 1 160 202 A1 (SUMITOMO CHEMICAL CO [JP]) 5 December 2001 (2001-12-05) claims 1,3-8; example 1	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/052060

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011183838 A1	28-07-2011	AR 069730 A1	17-02-2010
		AU 2008292827 A1	05-03-2009
		CA 2697542 A1	05-03-2009
		CN 101827650 A	08-09-2010
		EP 2200742 A1	30-06-2010
		JP 5231553 B2	10-07-2013
		JP 2010537809 A	09-12-2010
		KR 20100080509 A	08-07-2010
		NZ 583550 A	25-02-2011
		RU 2010107391 A	10-10-2011
		TW 200927662 A	01-07-2009
		US 2009062111 A1	05-03-2009
		US 2010267550 A1	21-10-2010
		US 2011183838 A1	28-07-2011
		WO 2009029856 A1	05-03-2009
EP 1052225 A1	15-11-2000	DE 69920172 D1	21-10-2004
		DE 69920172 T2	27-01-2005
		EP 1052225 A1	15-11-2000
		JP 3080162 B2	21-08-2000
		JP H11278843 A	12-10-1999
		TW 443992 B	01-07-2001
		US 6420437 B1	16-07-2002
		WO 9937582 A1	29-07-1999
US 2012283092 A1	08-11-2012	AU 2010318634 A1	17-05-2012
		CA 2778778 A1	19-05-2011
		CN 102596813 A	18-07-2012
		EP 2499096 A2	19-09-2012
		JP 2013510707 A	28-03-2013
		KR 20120101386 A	13-09-2012
		TW 201132592 A	01-10-2011
		US 2011118109 A1	19-05-2011
		US 2012283092 A1	08-11-2012
		WO 2011059606 A2	19-05-2011
US 2002005145 A1	17-01-2002	US 2002005145 A1	17-01-2002
		US 2004120884 A1	24-06-2004
		WO 0142140 A1	14-06-2001
WO 2013074984 A1	23-05-2013	TW 201328779 A	16-07-2013
		US 2013122074 A1	16-05-2013
		WO 2013074984 A1	23-05-2013
KR 20120084438 A	30-07-2012	NONE	
US 2013164444 A1	27-06-2013	US 2013164444 A1	27-06-2013
		WO 2012032868 A1	15-03-2012
EP 1160202 A1	05-12-2001	AU 778656 B2	16-12-2004
		AU 3140501 A	29-11-2001
		CA 2342523 A1	24-11-2001
		CN 1324766 A	05-12-2001
		EP 1160202 A1	05-12-2001
		JP 2001335321 A	04-12-2001
		TW 593153 B	21-06-2004
		US 2001056037 A1	27-12-2001