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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 March 2014 (13.03.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/037623 A1

(51) **International Patent Classification**:
C23C 24/00 (2006.01) *C23C 20/06* (2006.01)

(21) **International Application Number**:
PCT/FI2013/050863

(22) **International Filing Date**:
6 September 2013 (06.09.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
20125923 6 September 2012 (06.09.2012) FI

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, 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, 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))*

— *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 2014/037623 A1

(54) **Title**: DISPERSED NANOPARTICLES IN TRANSPARENT COATINGS

(57) **Abstract**: The present invention concerns a transparent or semi-transparent coating prepared from coating mixture containing conventional coating components mixed with a coating slurry containing dispersed inorganic nano-particles in a content of 1-70w-% of the slurry. Further, the invention concerns a manufacturing process of such a coating, as well as a manufacturing process of said coating slurry.

DISPERSED NANOPARTICLES IN TRANSPARENT COATINGS

Background of the Invention

Field of the Invention

The present invention concerns transparent or semi-transparent coatings and coating slurries that contain dispersed nanoparticles, as well as processes for the manufacture of these. These coatings are intended to be used on solid products, such as concrete, plastic or glass surfaces, or on fibrous structures, such as the surfaces of paper, wood and furniture products.

Description of Related Art

Transparent and semi-transparent coatings are widely used in the paper, wood and furniture coating industry for enhancing surface properties of these products, particularly hardness and gloss.

In non-transparent coatings, fillers are more commonly used in addition to the conventional polymer pigments in order to reduce costs, since polymer pigments are expensive. Nanoparticles have thus been used in coatings in general for various purposes, as in WO 201078071 A1 and in US 2005/0234178 A1. Further, JP 11012497 A relates to the use of colourless microparticles in printing ink.

Such non-transparent coating formulations can contain e.g. nano-sized precipitated calcium carbonate (nano-PCC) as a filler. These formulations have traditionally been manufactured by adding PCC agglomerates into water to a suitable solids content, and mixing thoroughly to provide a fluid consistency, whereafter a drying step is carried out in order to provide a formulation having a higher solids content, which is suitable to be applied on the desired surface to form the coating. However, there is a demand for an improved procedure, since this traditionally used alternative results in a coating formulation that still contains non-dispersed agglomerates, which provide a low transparency.

However, due to the specific requirements of semi-transparent and transparent coatings, and due to the difficulties in dispersing typical filler pigments these coatings are generally formulated with a minimum amount of filler, hence affecting the raw material costs. In fact, in completely transparent applications the aim is to use no fillers.

Particularly in the case of high strength surface applications, which utilize transparent coatings, e.g. in furniture and floor applications, the coating formulation often consists of expensive special polymers enhancing the mechanical properties of the application. Gloss and viscosity of the coatings applied on these products can be adjusted by adding different additives. However, the addition of supplementary components to the coating formulation makes the formulation complex and difficult to handle, which might lead to complex formulations and product inconsistency. Also the transparency is often reduced.

Summary of the Invention

It is an object of the present invention to provide a novel transparent or semi-transparent coating for fibrous products, as well as a manufacturing process thereof.

Particularly, it is an object of the present invention to provide such a transparent or semi-transparent coating having a simple composition and providing a high surface strength.

These and other objects, together with the advantages thereof over known coatings and processes, are achieved by the present invention, as hereinafter described and claimed.

The present invention is based on the development of tailored transparent and semi-transparent coatings for use in concrete, plastic, glass or fibrous end-products to provide them with superior mechanical properties and increased filler content.

Thus, the present invention concerns a transparent coating containing dispersed nanoparticles, the coating having been formed from a coating slurry having a high solids content. Further, the invention concerns a manufacturing process of such a coating slurry, as well as the application of the slurry on said product surfaces to provide the final coating.

More specifically, the coating slurry of the present invention is characterized by what is stated in the characterizing part of Claim 1, while its manufacturing process is characterized by what is stated in Claim 9.

Further, the final coating is characterized by what is stated in the characterizing part of Claim 5, while its manufacturing process is characterized by what is stated in Claim 11.

Considerable advantages are obtained by means of the invention. Thus, the present invention introduces nano-particles evenly and efficiently dispersed in a coating matrix (the slurry) to be formulated into a transparent coating. This gives rise to superior final product properties, simplified formulation as well as higher filler content compared to conventional transparent coatings, thus achieving savings in the cost of the raw material.

Due to a novel procedure for evenly and efficiently dispersing the filler into the slurry, its content can be maximized, thus keeping the particle size below half of the wavelength of visible light and avoiding visible light to be absorbed by the particles. Thereby, the transparency is maintained.

Simultaneously, gloss and viscosity can be optimized via filler addition, as well as an enhanced surface hardness and durability. In optimizing the viscosity and gloss, the thixotropic behavior of the nano-particle slurry can be utilized.

Next, the invention will be described more closely with reference to the attached drawing and a detailed description.

Brief Description of the Drawing

Figure 1 illustrates the opacity of a coating of the present invention on a drawdown card.

Figure 2 illustrates the König hardness of a coating of the present invention on a glass plate.

Figure 3 illustrates the König hardness of a preprocessed or in-situ processed coating of the present invention on a glass plate.

Figure 4 illustrates the gloss of a preprocessed or in-situ processed coating of the present invention on a glass plate.

Detailed Description of the Preferred Embodiments of the Invention

The present invention concerns a transparent coating containing nanoparticles that are formed from an inorganic compound.

In said context, the term "transparent" is intended to include also "semi-transparent" coatings, whereby a completely "transparent" coating is considered to be a coating that exhibits a light transmission of > 90% (for visible light, at a wavelength of 400–800nm), and "semi-transparent", in turn, is used for coatings exhibiting a light transmission of 70–90% (at said wavelengths). Thus, the term "coating" is intended to include also films, lacquers, varnishes, waxes and wood oils. Particularly the water thinnable versions of said coatings are intended.

The transparent coatings can have a thickness of ≤150 μm, preferably 1–80μm, and most suitably about 60 μm, while the semi-transparent coatings can be made thicker, having a thickness of ≤450 μm, and most suitably 80–400μm.

The nanoparticles can be formed from various inorganic compounds, particularly those obtainable from mineral sources. Examples include particles of calcium carbonate, silicate or other minerals derivable from clay or mica, preferably being calcium carbonate, more preferably precipitated or ground calcium carbonate (PCC or GCC), and most suitably being PCC. These materials can contain traces of organic compounds, which can also be transferred to the nanoparticles used in the invention. Due to the negligible contents of these organic compounds, the material of the nano-particles is still referred to as inorganic.

The term "nano-particle" is intended to include any particles having a mean particle diameter of less than 1μm. In the present context, a particle diameter of less than 400nm is preferred, more preferably 3–300nm, and most suitably of 5–80nm, particularly in order to maintain a particle size that is below the wavelength of visible light.

These nanoparticles are generally obtained by the dispersion of agglomerates to separate these into smaller particles. Thus, the present invention also relates to a coating slurry containing said particle dispersion.

Said slurry contains dispersed inorganic nanoparticles in a content of 1-70w-%, preferably 5–70w-%, more preferably 20–60 w-%, and most preferably 40-55w-%, of the slurry.

The slurry can be manufactured by carrying out a mechanical or ultrasonic treatment, or both, on said nanoparticles or their agglomerates at a solids content of 10–100w-%, preferably 15-65 w-%, whereafter solvent is added to provide a coating slurry containing the dispersed nanoparticles at a desired final solids content of 1-70w-% of the slurry, preferably 1–50w-%, more preferably 1–40w-%, and most suitably 1–20 w-%.

The coating slurry is intended to include any dispersions or mixtures formed using solvents or solutions that are based on either an inorganic or an organic solvent. However, the most preferred solvent is water, whereby the slurry containing the nanoparticles is an aqueous solution, dispersion or mixture.

The coating slurry can further contain additives, such as dispersing agents. These can include, in addition to agents commonly used as dispersing agents, also conventional binders.

The optional dispersing agent is used to facilitate the complete dispersion of the nanoparticles into a suitable solids content, while it is preferred to avoid the use of other additives.

Said optional dispersion agent can be added either on-site to the coating slurry during its manufacture, or off-site during nano-particle production or dispersion of agglomerates, whereby the dispersion agent is added to the coating slurry simultaneously with the dispersed nano-particles.

To form the final coating, a coating slurry, such as the one described above, is generally mixed with optional further coating components, to form a coating mixture, and applied onto a surface. The further coating components include one or more agents selected from

the group of binders, dispersing agents, wetting agents, anti-foaming agents, viscosity modifiers and film-forming agents.

The total content of said additives (dispersing agents and optional further coating components) in the final coating is preferably 10–70w-%, more preferably 30-60w-%, and most suitably 35-50-%.

The present invention also concerns a process for manufacturing a transparent coating, particularly the above-described final coating. This process includes the step of treating said inorganic nanoparticles to cause their dispersion and forming a slurry, mixing the slurry with optional firther coating components, as well as applying the mixture onto a desired product surface, and optionally separately drying the formed coating.

The above described coatings can be applied on any surfaces, which generally are surfaces of solid products, such as concrete, plastic, glass or fibrous surfaces. However, it is preferred to use these coatings on fibrous solid products, such as paper, wood or furniture. The coating is preferably applied as a uniform coating on at least one surface of said product, whereby the coating will cover the entire surface. The application is then followed by a step of drying to remove the solvent, or at least to remove excess solvent.

The following non-limiting examples are intended merely to illustrate the advantages obtained with the embodiments of the present invention.

Examples

Example 1

A coating formulation was prepared, based on an aqueous slurry containing 50 w-% of nano-sized calcium carbonate having a mean primary particle diameter of 50 nm (based on SEM-images). The nano-particles were dispersed into the aqueous solution using ultrasonic treatment

The coating formulation was applied with film applicator on a glass plate and drawdown card (opacity chart), and dried, to form uniform layer of 30 – 70 µm thickness

The opacity of the coating on the drawdown card is illustrated in Figure 1. Figure 1 shows how transparency of the coating enhances as dispersion time increases.

The König hardness of the coating on the glass plate is illustrated in Figure 2. Figure 2 shows how damping time increases as function of increasing nanoparticle fraction of the coating.

Example 2

Another coating formulation was prepared, based on an aqueous nanoparticle slurry containing 12 w-% of nano-sized calcium carbonate having a mean primary particle diameter of 50nm. The slurry was predispersed prior to addition to the coting formulation and insitu dispersion in the the coating formulation.

The coating formulation was applied as above

The König hardness and gloss of the coatings are illustrated in Figure 3 and 4, respectively.

Claims

1. A coating slurry containing nanoparticles, **characterized** in that it contains dispersed inorganic nanoparticles in a content of 1-70w-% of the slurry.

2. The coating slurry of Claim 1, **characterized** in that the nanoparticles are particles of calcium carbonate, silicate or other minerals derivable from clay or mica, preferably being calcium carbonate, more preferably ground or precipitated calcium carbonate (GCC or PCC), most suitably PCC.

3. The coating slurry of Claim 1 or 2, **characterized** in that it contains dispersed inorganic nanoparticles in a content of 5–70w-%, preferably 20–60 w-%, most preferably 40-55w-%.

4. The coating slurry of any preceding claim, **characterized** in that it further contains a dispersing agent.

5. A transparent or semi-transparent coating containing nanoparticles, **characterized** in that it has been formed from a coating slurry containing inorganic nanoparticles in a content of 1-70w-% of the slurry, and optional further components, by applying this coating mixture on a surface.

6. The coating of Claim 5, **characterized** in that it has been formed from a coating mixture containing the coating slurry of any of claims 1–4.

7. The coating of Claim 5 or 6, **characterized** in that said coating mixture further contains one or more agents selected from the group of binders, dispersing agents, wetting agents, anti-foaming agents, viscosity modifiers and film-forming agents.

8. The coating of any of claims 5–7, **characterized** in that it has been formed by applying the coating mixture on the surface of a solid product, such as a concrete, plastic, glass or fibrous product, the fibrous product preferably being selected from paper, wood or furniture.

9. The coating of any of claims 5–8, **characterized** in that it, in transparent form, has a thickness of ≤150 μm, more preferably 1–80μm, and most suitably about 60 μm, and in semi-transparent form, has a thickness of ≤450 μm, and most suitably 80–400μm.

10. A process for manufacturing the coating slurry of any of claims 1–4 by dispersion of inorganic nanoparticles, **characterized** by carrying out a mechanical or ultrasonic treatment, or both, on said inorganic nanoparticles or their agglomerates at a solids content of 10–100w-%, whereafter solvent is added to provide a coating slurry containing the dispersed nanoparticles at a desired final solids content of 1-70w-% of the slurry.

11. The process of Claim 10, **characterized** by adding a dispersing agent, preferably prior to any mechanical or ultrasonic treatment.

12. A process for manufacturing a transparent or semi-transparent coating, **characterized** by mixing the coating slurry according to any of claims 1–4 with optional further coating components, and by applying this coating mixture on a surface.

13. The process of Claim 12, **characterized** by applying said coating mixture on a solid product, such as a the surface of a concrete, plastic, glass or fibrous product, the fibrous product preferably being selected from paper, wood or furniture.

14. The process of Claim 12 or 13, **characterized** by applying the coating mixture on the surface using a film applicator.

15. The process of any of claims 12 – 14, **characterized** by carrying out a drying step after the application onto the surface.

Fig. 1

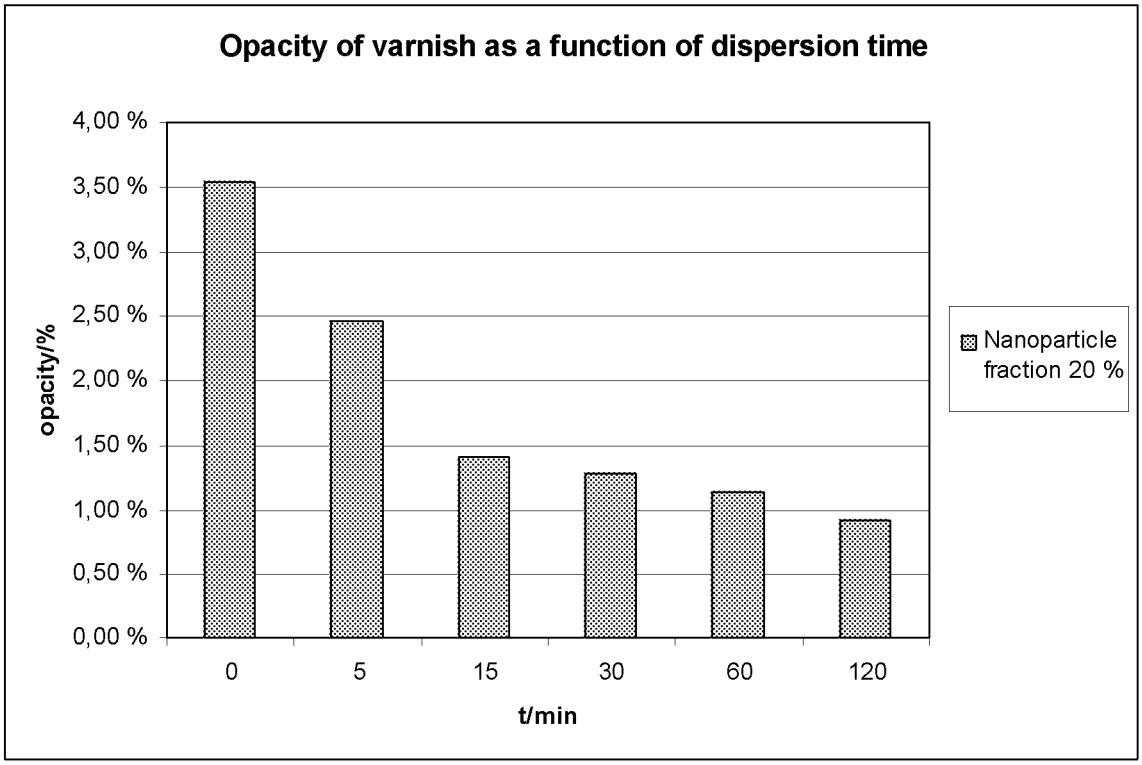

Opacity of varnish as a function of dispersion time
4,00 %
3,50 %
3,00 %
2,50 %
2,00 %
1,50 %
1,00 %
0,50 %
0,00 %
opacity/%
0
5
15
30
60
120
t/min
Nanoparticle fraction 20 %

Fig. 2

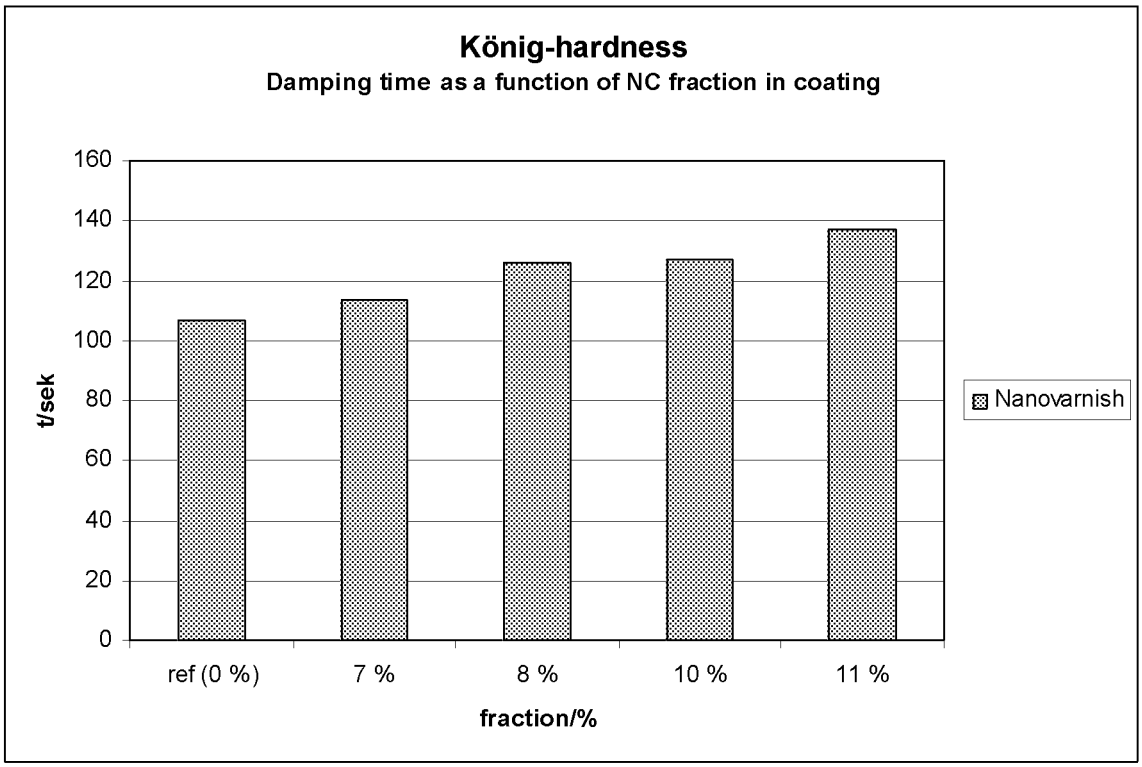

König-hardness
Damping time as a function of NC fraction in coating
160
140
120
100
80
60
40
20
0
t/sek
ref (0 %)
7 %
8 %
10 %
11 %
fraction/%
Nanovarnish

Fig. 3

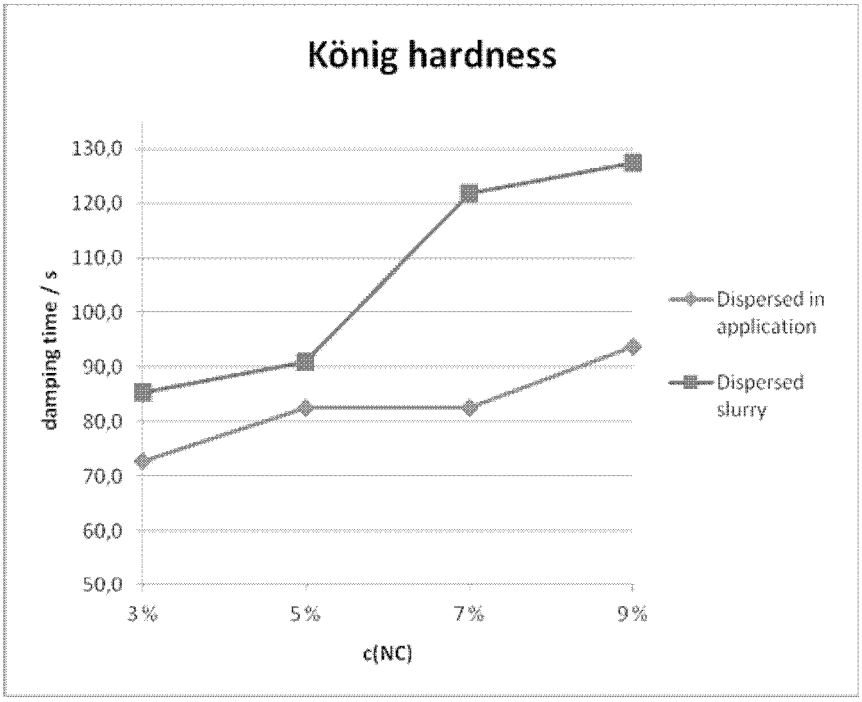
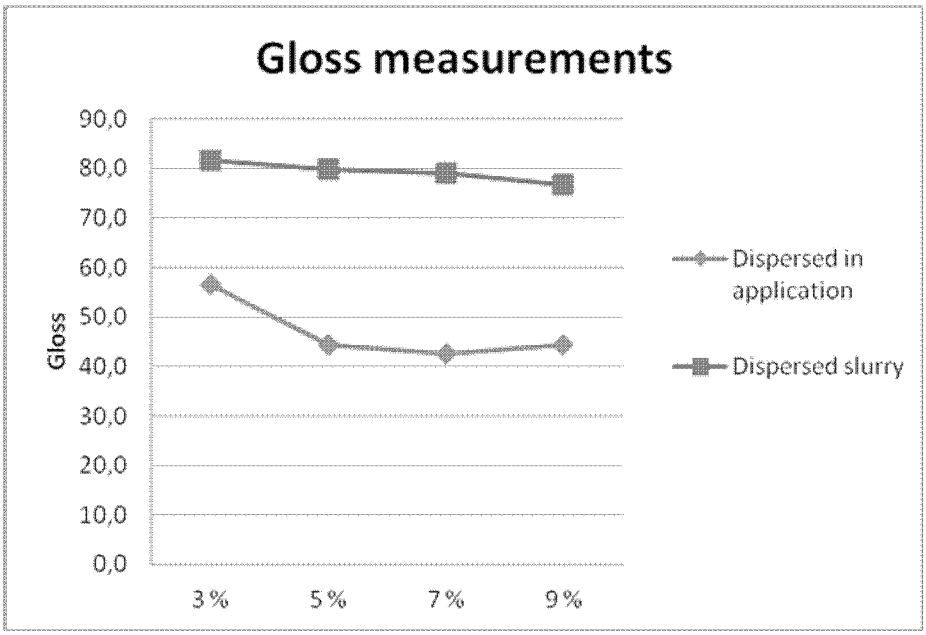

König hardness
130,0
120,0
110,0
100,0
90,0
80,0
70,0
60,0
50,0
damping time / s
3 %
5 %
7 %
9 %
c(NC)
Dispersed in application
Dispersed slurry

Fig. 4


Gloss measurements
90,0
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
Gloss
3 %
5 %
7 %
9 %
Dispersed in application
Dispersed slurry

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/050863

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C01F, C09D, C23C, D21H

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

FI, SE, NO, DK

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

EPO-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1736504 A1 (WEYERHAEUSER CO [US]) 27 December 2006 (27.12.2006) paragraphs [0029]-[0033]; examples	1-3, 5-8, 12-15
X	WO 2012113876 A1 (OMYA DEVLOPMENT AG [CH]) 30 August 2012 (30.08.2012) page 23, line 6 - page 29, line 2; table 4; claims	1-8, 12-13, 15
X	WO 2007050763 A1 (HEWLETT PACKARD DEVELOPMENT CO [US]) 03 May 2007 (03.05.2007) abstract; paragraphs [0020]-[0023]; table 1; claims	1-4
X	US 2005119391 A (MASON GEOFF [GB] et al.) 02 June 2005 (02.06.2005) paragraph [0028]; examples	1-4, 10-11

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"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
14 January 2014 (14.01.2014)	17 January 2014 (17.01.2014)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/050863

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 2007187653 A (SUMITOMO METAL MINING CO [JP]) 16 August 2007 (16.08.2007) abstract; paragraph [0197]-[0205]; examples	1, 3-9, 12-15
X	WO 2008153687 A2 (ASHLAND LICENSING & INTELLECTU [US]) 18 December 2008 (18.12.2008) claims; examples	1, 5-8, 10, 12-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2013/050863

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US 2005119391 A	02/06/2005	None	
US 2007187653 A	16/08/2007	None	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2013/050863

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/050863

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
C23C 24/00 (2006.01)
C23C 20/06 (2006.01)