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(54) Title: PHOTOCATALYTIC COMPOSITIONS COMPRISING TITANIUM DIOXIDE AND ANTI-PHOTOGREYING ADDITIVES

(57) Abstract: The present disclosure relates to a photocatalytic composition comprising photocatalytic titanium dioxide particles being dispersed in a continuous phase, and at least one anti-photogreying additive, wherein said at least one anti-photogreying additive is adapted to limit photogreying of said titanium dioxide particles while the photocatalytic activity of said titanium dioxide particles is maintained, and wherein the photo greying index (ΔL) of said composition is less than 6.

Photocatalytic compositions comprising titanium dioxide and anti-photogreying additives

Field of the invention

The present invention relates to formulation of a photocatalytic composition capable of producing colour fast stable and photocatalytic active products. The present invention also 5 relates to a coating of such a photocatalytic composition, a method for applying such a photocatalytic composition, and a building panel having photocatalytic properties.

Background

Photocatalytic materials such as TiO_2 are used in many applications to obtain self-cleaning and air cleaning properties. The largest obstacle with photocatalytic materials is the scaling 10 up to make large industrial productions. Ink jet printing technology is an economic way to apply functional materials using water-based suspensions or solvent-based suspensions. Ink jet printing is a non-contact deposition method, which can be used to obtain large area coverage with direct patterning on almost any substrate. The advantages of using ink jet printing are simplicity, low cost, less material waste, less environmental issues with spray 15 aerosols and control of the coating.

Furthermore, materials and coatings with lasting performances, which are preserved over time, has been lacking. One drawback of using photocatalytic active TiO_2 in for example building materials has been the lack of colour fastness and the change of colour upon light exposure. In the paper and the laminate industry TiO_2 is an often used pigment but special 20 grades of TiO_2 with no or reduced photocatalytic activity are needed as photocatalytic TiO_2 photogrey when exposed to light. Photogreying is an important quality property of pigment TiO_2 used in the décor and paper industry and photogreying is of great practical importance because it can affect the colour of products such as paints, polymers, and cosmetics.

Photogreying is showing as the colour of TiO_2 changes from white to dark violet upon light 25 exposure. It has been suggested that photogreying is caused by reduction of TiO_2 (probably from Ti^{4+} to Ti^{3+}) during light irradiation in the absent of oxygen.

The process of photogreying can be explained by examining the photocatalytic properties of TiO_2 , which is shown in Fig 1. When TiO_2 is irradiated with light with a wavelength shorter than the band gap the absorbed photon can generate an electron/hole pair. 30 Normally the electron travels in the conduction band to the surface where a reduction occurs. In most cases oxygen is reduced by the electron. In low oxygen environment, for example in a melamine formaldehyde resin matrix, the electron cannot be taken by oxygen

and travels to the Ti-centre and creates Ti^{3+} centre. Ti^{3+} centres are purple/blue and create a blue toning of the product. This mechanism is known as photogreying. In for example laminates the high degree of polymerization and density of melamine formaldehyde resin makes the diffusion of oxygen and moisture from the surrounding environment very slowly 5 and the oxidization of grey Ti^{3+} ions to the white Ti^{4+} ions becomes slow. However, the photo reduction of Ti^{4+} to Ti^{3+} is fast and thereby the laminate boards and panels become grey. Another important aspect with laminate boards and panels are the release of 10 formaldehyde during curing. Formaldehyde is known to be a strong reduction agent and formaldehyde in the matrix can lower the overall partial pressure of oxygen and enhance photogreying. When the laminate boards and panels are stored in dark the photocatalytic reduction step is inhibited and within several days up to weeks the slow oxidation step turns the panels back to the original colour.

The photogreying process is reversible and oxygen is known to reverse the photogreying process but the change from dark violet colour to the original colour is much slower than 15 the reverse reaction.

Within paper, décor paper, laminate flooring, laminate panels, foil and film industry photogreying is an important practical problem as the presence of cellulose and melamine formaldehyde resin enhances the photogreying of TiO_2 . Formaldehyde has been shown to enhance photogreying. For example in a melamine formaldehyde resin matrix in a laminate 20 floor, the dark violet Ti^{3+} ions created by light exposure are relative stable as the partial pressure of oxygen is very low. The increasing Ti^{3+} concentration in the system results in greying of the product. Therefore, TiO_2 grades for paper and laminates are surface modified as to be able to eliminate the greying. The TiO_2 grades for laminates are surface coated to inhibit the photocatalytic cycle and thereby suppress photogreying of the products.

25 Various methods and techniques have been developed to overcome photogreying of TiO_2 pigmented products. Common for all of these techniques are that photogreying is eliminated by inhibiting the photocatalytic process, and thereby inactivating the photocatalytic properties of TiO_2 .

Summary of the invention

30 It is an object of embodiments of the present invention to provide an improvement over the above described techniques and known art.

A further object of at least certain embodiments of the present invention is to obtain a composition with reduced photogreying and with maintained photocatalytic activity.

A further object of at least certain embodiments of the present invention is to obtain a composition being photocatalytic and colour stable.

A further object of at least certain embodiments the present invention is to formulate a photocatalytic composition that is stable regarding colour changes upon light exposure and 5 weathering.

A further object of at least certain embodiments the present invention is to provide a photocatalytic composition, which can be applied by digital printing.

At least some of these and other objects and advantages that will be apparent from the description have been achieved by a photocatalytic composition according to a first aspect 10 of the invention. The photocatalytic composition comprises photocatalytic titanium dioxide particles being dispersed in a continuous phase, and at least one anti-photogreying additive. In a preferred embodiment, the photo greying index of said composition is smaller than 6, such as smaller 5, preferably smaller than 4, such as smaller than 3, such as smaller than 2.

15 In embodiments, said at least one anti-photogreying additive is adapted to reduce photogreying while the photocatalytic activity of the composition is essentially maintained. In one embodiment, the photocatalytic activity is maintained to a level of at least 90%.

Composition herein is referred to also as suspension or as dispersion as a system in which particles are dispersed in a continuous phase of a different composition or state.

20 The photocatalytic composition may be used as a photocatalytic coating fluid or a photocatalytic ink.

An advantage of embodiments of the present invention is that it is possible to reduce photogreying but at the same time essentially maintain the photocatalytic activity of the composition, and thereby also provide a photocatalytic coating formed by the composition 25 with reduced photogreying while essentially maintaining the photocatalytic properties.

It has been found that certain additives may be added to a TiO_2 formulation and thereby suppress photogreying while essentially maintaining the photocatalytic activity. Additives suitable for reducing photogreying may be, but are not limited to, a surfactant with a polar and a non-polar part. Whereas additives with the group of glycerine and for example PEG- 30 200, which are often used additives within ink formulation, enhance photogreying.

In embodiments, the additives suitable for reducing photogreying, i.e. the anti-photogreying additives, may be adapted to temporarily coat the photocatalytic titanium

dioxide particles of the composition. The anti-photogreying additive is preferably not chemically bonded to the photocatalytic titanium dioxide particles. A sterical stabilisation between the anti-photogreying additive and the photocatalytic titanium dioxide particles may occur, and/or the anti-photogreying additive may electrostatically coat the 5 photocatalytic titanium dioxide particles. Thereby, a temporary coupling may be obtained.

In embodiments, the anti-photogreying additive may function so that when the photocatalytic titanium dioxide particles are arranged in a matrix such as resin matrix or lacquer matrix, thus being a low oxygen environment, the particles remain coated and the photogreying is reduced. However, the photocatalytic titanium dioxide particles arranged 10 on the surface of a substrate are subjected to external influence such as wear, application of water applied, etc., which may break the temporary coupling. By breaking the temporary coupling, the photocatalytic activity is activated. Thereby, the photocatalytic activity can be controlled to a region of the substrate where the photocatalytic activity is desired, i.e. at the surface of the substrate. The surface of the substrate represents a high oxygen 15 environment. Consequently, photogreying throughout the substrate can be reduced while the photocatalytic activity can be maintained at the surface.

Furthermore, the anti-photogreying additive temporarily coating of the photocatalytic titanium dioxide particles may facilitate orientating the photocatalytic particles at the surface of the composition, such that a major part of the photocatalytic particles are 20 arranged at the surface of the composition when applied to a substrate. The chemical structure of the anti-photogreying additive may orientate the titanium dioxide particles towards the surface of the composition.

The photocatalytic composition may be formulated by adding additives to a TiO_2 dispersion that helps with creating an applicable film of the TiO_2 mixture that dries up without cracks. 25 The photocatalytic composition may be produced by mixing suitable additives to a photocatalytic dispersion. The photocatalytic composition may be applied on a substrate by creating a film or coating. The photocatalytic composition may be dried and/or cured without creating cracks in and/or on the film (for example mud cracks).

The photocatalytic composition may be applied by ink jet technology, thereby being a 30 photocatalytic ink. Known art focus on stabilization of ink jet inks and pigments, for example, by adding a polymer to the particles in suspension. The focus has previously been on the stabilization of the pigments or/and particles to create a stable ink that does not sediment. In embodiments of the present invention the focus is towards obtaining a stable coating that also after application of the ink and/or coating fluid on the substrate obtains a

lasting performance regarding photocatalytic activity and colour fastness. This is achieved by adding different additives in a controlled manner such as to obtain a colour stable and colour fast coating upon light exposure. Traditionally ink jet technology has been used for applying pigment suspensions and recently also waterborne pigments are used as they are 5 environmental safe materials. The pigments are applied to obtain a decorative coating. Surprisingly, embodiments of the present invention show that it is possible to formulate a long lasting photocatalytic ink that instead of having decorative properties is a transparent coating and which has stable colour and photocatalytic properties.

Said at least one anti-photogreying additive may be present in a concentration higher than 10 0.1 wt%. By adding an excess amount of an additive, compared to when used as for example a wetting agent, the additive reduces photogreying while the photocatalytic activity is essentially maintained. The anti-photogreying additive may be present in an amount being sufficient to temporarily coat the titanium dioxide particles.

Said at least one additive may be present in the range of 1-35 wt%, preferably 1-15 wt%, 15 more preferably 5-12 wt%.

Said at least one additive may comprise a wetting agent.

Said at least one additive may comprise a surfactant.

Said surfactant may be or comprise a non-ionic surfactant.

Said surfactant may be or comprise a silicone based surfactant.

20 Said at least one additive may comprise oligomers or polymers.

Said at least one additive may comprise a polyglycol, preferably poly(ethylene glycol) methyl ether. The polyglycol also function as a humectant. The polyglycol may be present in the range of 1-35 wt%, preferably 5-35 wt%.

The titanium dioxide particles may be in anatase form.

25 The titanium dioxide particles may have a primary size in the range between 5 to 250 nm, preferably between 5 to 100 nm, more preferably between 5 to 50 nm, most preferably between 5 and 30 nm. The titanium dioxide particles may have an agglomerate size of < 300 nm < 200 nm < 100 nm, such as < 80 nm preferably an aggregate size of < 60 nm such as of < 40 nm and even more preferably an aggregate < 30 nm such as < 20 nm.

30 The photonic efficiency of the composition may be exceeding 0.025%, preferably exceeding 0.05%, more preferably exceeding 0.1%.

The continuous phase may be a solvent, preferably water.

The titanium dioxide particles may have a concentration in the range between 0.3 wt% to 40 wt%, preferably between 1.0 wt% to 30 wt%.

5 The composition may have a pH higher than 9. The pH of the composition may be stabilized by amines, such as triethylenamine.

The composition may have a pH lower than 4. The pH of the composition may be stabilized by a strong acid such as HCl.

The photocatalytic composition may further comprise a dispersion agent, preferably propylene glycol.

10 The photocatalytic composition may further comprise a binder, preferably a silicon or titanium based material.

The photocatalytic composition may be or form a photocatalytic ink. The photocatalytic composition is printable by means of digital printing, preferably by an ink jet printer.

The photocatalytic composition may further comprise a humectant.

15 The humectant may comprise amines based compounds such as triethanolamine.

The humectant may comprise compounds having a diol group.

The humectant may comprise glycols, preferably poly(ethylene glycol) methyl ether.

The humectant may be present in the range of 1-35 wt%, preferably 5-35 wt%.

20 The colour change (ΔE) index of the composition may be smaller than 6, such as smaller 5, preferably smaller than 4, such as smaller than 3, such as smaller than 2.

The yellowing (ΔB) index of said composition is smaller than 6, such as smaller 5, preferably smaller than 4, such as smaller than 3, such as smaller than 2.

25 According to a second aspect of the invention, a photocatalytic coating formed of a composition according to the first aspect of the invention is provided. The second aspect of the invention may incorporate some or all the advantages of the first aspect of the invention, which previously have been discussed, whereby the previous discussion is applicable also for the coating.

The coating may be provided on a substrate, for example a building panel such as a floor panel or wall panel. The coating may be applied on a surface or a surface layer of a substrate. The surface layer may be a lacquer layer. The surface layer may comprise a binder containing formaldehyde such as melamine formaldehyde resin. The surface layer 5 may be a melamine formaldehyde resin impregnated paper. The surface layer may be a wood powder layer comprising wood fibres and a binder, preferably melamine formaldehyde.

According to a third aspect of the invention, a method for applying a composition according to the first aspect of the invention on a substrate is provided. The method may comprise 10 applying said composition on a substrate for forming a coating, and drying and/or curing said coating.

The composition may be applied by digital printing, preferably by means of an ink jet printer.

According to a fourth aspect of the invention, a building panel is provided. The building 15 panel may have a surface comprising photocatalytic titanium dioxide particles and at least one anti-photogreying additive, and wherein the photo greying index (ΔL) of the surface may be less than 6, such as less 5, preferably less than 4, such as less than 3, such as less than 2. The surface of the building panel is preferably coated with a photocatalytic composition of the type described above. The building panel may have a surface or a 20 surface layer, and a coating comprising photocatalytic titanium dioxide particles and at least one anti-photogreying additive. The surface layer may be a lacquer layer. The surface layer may comprise a binder containing formaldehyde such as melamine formaldehyde resin. The surface layer may be a melamine formaldehyde resin impregnated paper.

According to a fifth aspect of the invention, a photocatalytic ink composition is provided. 25 The photocatalytic ink composition may comprise photocatalytic titanium dioxide particles and a humectant. The humectant may be a glycol, preferably poly(ethylene glycol) methyl ether. The photocatalytic titanium dioxide particles may have a primary size in the range between 5 to 250 nm, preferably between 5 to 100 nm, more preferably between 5 to 50 nm, most preferably between 5 to 30 nm. The titanium dioxide particles may have an 30 agglomerate size of < 300 nm < 200 nm < 100 nm, such as < 80 nm preferably an aggregate size of < 60 nm such as of < 40 nm and even more preferably an aggregate size < 30 nm such as < 20 nm.

According to a sixth aspect of the invention, a method for providing a photocatalytic coating on a substrate is provided. The method may comprise applying a photocatalytic

composition comprising photocatalytic titanium dioxide particles and a humectant by means of digital printing on a substrate, and drying and/or curing said composition for forming a photocatalytic coating. The printing is preferably made by an ink jet printing device. The humectant may be a glycol, preferably poly(ethylene glycol) methyl ether. The 5 photocatalytic titanium dioxide particles may have a primary size in the range between 5 to 250 nm, preferably between 5 to 100 nm, more preferably between 5 to 50 nm, most preferably between 5 to 30 nm. The titanium dioxide particles may have an agglomerate size of < 300 nm < 200 nm < 100 nm, such as < 80 nm, and preferably an aggregate size of < 60 nm, such as of < 40 nm, and even more preferably an aggregate size < 30 nm, such as < 10 20 nm. The substrate may a building panel, for example, a floor panel. The building panel may comprise a surface layer on which the photocatalytic composition is applied by digital printing. The surface layer may be a lacquer layer. The surface layer may be a resin impregnated paper, preferably a melamine formaldehyde resin impregnated paper. The surface layer may be wood powder layer comprising wood fibres and a binder, preferably 15 melamine formaldehyde.

In particular, embodiments of the present invention relate to a method, which allows for production of photocatalytic products without photogreying but with essentially maintained photocatalytic activity. It has been found that it is possible to reduce or eliminate photogreying but at the same time essentially maintain a photocatalytic active 20 product. It was found that a non-photogreying product can be produced by controlling the coating formulation, the procedure of coating the substrate and by controlling the treatment of the coated substrate.

Brief description of the drawings

The present invention will by way of example be described in more detail with reference to 25 the appended schematic drawings, which show embodiments of the present invention.

Fig. 1 shows a photocatalytic process of titanium dioxide.

Fig. 2a shows an example of a non-ionic surfactant in form of a polyether modified polysiloxane.

Fig. 2b shows an example of a non-ionic surfactant in form of a poly(ethylene glycol) 30 monomethyl ether.

Fig. 2c shows an example of a non-ionic surfactant in form of a polyoxyethylene sorbitan.

Fig. 3 shows a wetting process of a composition or coating fluid on a substrate.

Fig. 4 shows a substrate having a coating formed by the photocatalytic composition.

Fig. 5a shows a sample according to example 1A exposed to UVA light.

Fig. 5b shows a sample according to example 1B exposed to UVA light.

Fig. 6 shows a Zisman plot for three different surface tensions of a photocatalytic

5 composition.

Fig. 7 shows wetting of a surface for four different formulations.

Detailed description

A photocatalytic composition according to certain embodiments will now be described in more detail. The photocatalytic composition comprises photocatalytic TiO₂ particles in

10 dispersion. The photocatalytic TiO₂ are preferably in anatase phase. The photocatalytic dispersion may be dispersed in a solvent, preferably water. The concentration of photocatalytic TiO₂ particles in the dispersion is preferably in the range 0.3 wt% to 40 wt%, more preferably in the range 1.0 wt% to 30 wt%.

In an embodiment, the photocatalytic particles may be doped with non-metals and/or

15 metals. The TiO₂ particles may be doped with non-metals and/or elements such as but not limited to the list of C, N, F, S, Mo, V, W, Cu, Ag, Au, Pt, Pd, Fe, Co, La, Eu, WO₂, and PdO or a combination thereof.

The photocatalytic TiO₂ particles may be nanosized TiO₂ particles. The TiO₂ may have a size in the range from 5-250 nm, preferably in the range 5-100 nm, more preferably in the range

20 5-50 nm, most preferably in the range of 5-30 nm.

The photocatalytic composition may be stabilized by pH and/or a dispersant agent. The

photocatalytic composition may be stabilized at pH > 9 by preferably, but not limited to, amines, for example triethylenamine. The photocatalytic composition may also be stabilized at pH < 4 by preferably, but not limited to, a strong acid like HCl. The

25 photocatalytic dispersion may further be stabilized by a dispersion agent to keep the particles in suspension and from re-agglomerating. The dispersion may be stabilized by, but not limited to, propylene glycol. In an embodiment, binders are added to the photocatalytic composition to enable and to improve the adhesion of the TiO₂ particles to the substrate on which the composition is applied. Preferably these binders are non-photocatalytically degradable in the group of preferably, but not limited to, silanes, siloxanes, silicones, SiO₂, surface modified SiO₂, amorphous TiO₂, alkoxides, Ti-alkoxides, Si-alkoxides, UV curable binders and heat curable binders.

In a preferred embodiment, the photocatalytic composition is a stable nanosized TiO₂ dispersion in water with a size in suspension of said photocatalytic particles of less than 50 nm in concentration of said TiO₂ particles up to 40 wt%.

Additives may be added to the photocatalytic composition in order to, for example,

5 enhance the coating and film formation properties and to improve the colourfastness upon light exposure. Additives may be added to the photocatalytic composition as to improve the coating and/or application properties of the photocatalytic composition. Additives may also be added to the photocatalytic composition to improve sprayability. Examples of such additives are humectants. Furthermore, wetting agents may be added to the photocatalytic
10 composition to enhance the wetting of the photocatalytic composition on a substrate. An example of such wetting agent may be, but not limited to, the group of polyether modified siloxanes silicone surfactant such as polyether modified siloxanes.

In a preferred embodiment, the photocatalytic composition is adjusted to be able to reduce photogreying. One or more additives may be added to the photocatalytic composition to

15 reduce photogreying of the photocatalytic particles upon light exposure.

In one embodiment, it was surprisingly found that by adding excess amount (compared to acknowledged recommended quantity of appr. 0.1 wt%) of an additive such as a wetting agent, it was possible to formulate a photocatalytic composition which may be applied on a substrate such as paper, overlay paper, décor paper, foil, or film without experiencing

20 photogreying or with at least reduced photogreying. The additive thereby forms an anti-photogreying additive. The anti-photogreying additive may be chosen from the group of silicone surfactants such as polyether modified siloxanes as shown in fig. 2a. By adding an excess amount of the additive, the additive provides an anti-photogreying properties.

The anti-photogreying additive may be a non-ionic surfactant.

25 The anti-photogreying additive may be a silicone surfactant, preferably a non-ionic silicone surfactant. More preferably, the anti-photogreying additive may be a polyether modified siloxanes. More preferably, the anti-photogreying additive may be a polyether modified polysiloxanes. More preferably, the anti-photogreying additive may be a polyether modified polymethyl siloxane. As an alternative, the anti-photogreying additive may be
30 polydimethylsiloxane co-polymer.

In a further embodiment, the anti-photogreying additive may be a polyglycol, preferably poly(ethylene glycol) methyl ether as shown in fig. 2b.

In a further embodiment, the anti-photogreying additive may be a polyoxyethylene sorbitan as shown in fig. 2c, preferably polyoxyethylene (20) sorbitan. Preferably, the anti-photogreying additive may be a polyoxyethylene (20) sorbitan monooleate.

In a further embodiment, the anti-photogreying additive may be polyvinyl alcohol (PVA) and/or polyvinyl pyrrolidone (PVP), and/or poly(ethylene glycol) methyl ether, preferably combined with a wetting agent.

The anti-photogreying additive is added in an excess amount compared to conventional amounts of additives in order to obtain its anti-photogreying properties. In a preferred embodiment, the anti-photogreying additive may be added in the range of 1-35 % by

10 weight of the composition, preferably 5-35 % by weight of the composition such as 1-15 % by weight of the composition. More preferably, the anti-photogreying additive may be added in the range 5-12 % by weight of the composition.

For a wetting agent acting as an anti-photogreying additive, the wetting agent may be added in an amount of 5x, or 10x or 100x the amount needed to achieve a wetting effect.

15 A de-foaming agent may be added to the photocatalytic composition to suppress foaming.

In one embodiment, the photocatalytic composition is formulated to a photocatalytic coating fluid for spray coating, float coating, impregnation by roller coat application, or printer roll application of, for example, paper, décor paper, overlay paper, foils or films.

20 In one embodiment, the photocatalytic composition is formulated to a photocatalytic ink to be applied by for example an ink jet printer. The photocatalytic ink may be colour and/or weathering stable. The photocatalytic ink may include pigments or may be colourless.

Density, surface tension and viscosity of the fluid are the properties that show the strongest dependence on the ink jet application and spreading of droplets on the substrate. The printability range of an ink can be estimated based as the inverse Ohnesorge number:

$$25 \quad Z = (\alpha \cdot \rho \cdot \gamma)^{1/2} / \eta$$

Where α is the nozzle diameter, ρ is the diameter of the ink, γ is the surface tension of the ink and η is the viscosity of the ink.

In an embodiment, the Ohnesorge number is in the range of $1 \leq Z \leq 30$ and, more preferably in the range of $1 \leq Z \leq 20$ of the photocatalytic ink.

30 In a further embodiment, the photocatalytic composition to be used as a photocatalytic ink has a viscosity below 25 cP.

Controlling drying of the photocatalytic coating or photocatalytic ink formed by the photocatalytic composition facilitates obtaining a good final coating and/or film without cracks. The drying has to be controlled to avoid both drying in the printing head and/or nozzle tip of the ink jet printer, and to minimise stain deposit effect which yields an uneven

- 5 deposit with cracks. An additive, such as a humectant or drying agent, is often added to avoid drying within a spray nozzle or printing nozzle. Often used humectant is glycerol; however, glycerol has shown to be enhancing photogreying when the photocatalytic composition or ink is applied on substrates with tendencies for photogreying. In a preferred embodiment, a humectant is added to the photocatalytic composition and/or
- 10 photocatalytic ink to control the drying of the mixture in the nozzle and on the substrate. In a preferred embodiment, the humectant is chosen such as to prevent or at least reduce photogreying.

In an embodiment, the humectant is chosen from the group of triethanolamine.

In an embodiment, the humectant is chosen from the group of 3-methyl-1,5-pentanediol.

- 15 In an embodiment, a humectant is chosen the group of glycols such as of the group of triethylene glycol, and/or propylene glycol, and/or diethylene glycol, and/or ethylene glycol, and/or poly(ethylene glycol) methyl ether.

In an embodiment of the present invention, the humectant is added in the range of 1-35 wt%, preferably 5-35 wt%.

- 20 In an embodiment, an additive is chosen that has both anti-photogreying properties and functions as a humectant. An example of such an additive is poly(ethylene glycol) methyl ether, both being a humectant and an anti-photogreying additive. An additive such as poly(ethylene glycol) methyl ether may be added in the range of 1-35 wt%, preferably 5-35 wt%.

- 25 The photocatalytic composition may be applied on a substrate or in a substrate matrix. To be able to create a photocatalytic coating or film that is colour stable against light and/or weathering it has been found that is useful to make a film or coating without cracking, like for example mud cracking.

- 30 “Mud cracking” means the occurrence of cracks during the drying phase of paint films, as opposed to crack formation, which can occur through exposure and ageing of the films.

In a preferred embodiment, the film formation process is to be controlled to obtain a non-cracking coating or film. In the coating or application process the time to create a film (t_{open})

may be shorter than the time before drying or curing occurs. Thereby, the applied photocatalytic composition has time enough to create a wet film or coating before the wet film or coating start to dry up.

“ t_{open} ” is the time of full wetting of the substrate by the coating fluid from the impact of the 5 droplet on the substrate to full wetting of the substrate. $t_{open} = t_{final} - t_0$ as illustrated in Fig. 3.

In a preferred embodiment, t_{open} is less than 15 seconds, preferably less than 10 seconds, more preferably less than 5 seconds.

10 In an embodiment, mud cracking may be avoided by adding film forming auxiliary materials. The film forming auxiliary materials and the photocatalytic composition have to be individual adjusted to one another. In a preferred embodiment, the film forming materials are chosen from the group of anti-photogreying additives described above.

15 Furthermore, the photocatalytic composition to be coated or applied on a substrate may be formulated to be able to wet the surface and thereby be able to create a film. Preferably, the photocatalytic composition may have a surface tension which enables a wetting of the surface. More preferably, the surface tension is equal or less than the critical surface tension of the substrate to create a good wetting and create a wet coating or film.

20 It has been discovered that perfect wetting occurs at the point which the surface energy and surface tension are equivalent, and that liquids with low surface tensions wet solids with high surface energies.

In a preferred embodiment, the photocatalytic composition forming a coating or ink has a surface tension smaller than 50 mN/m, preferably less than 40 mN/m, more preferably less than 30 mN/m, and more preferably equal to or less than 25 mN/m.

25 In an embodiment, the surface tension of said photocatalytic composition forming a coating or ink may be achieved by adding an additive from the group of anti-photogreying additives described above. In a further embodiment, the surface tension of the photocatalytic composition forming a coating or ink may be achieved by adding an additive from the group of anti-photogreying additives and adding a wetting agent to the photocatalytic composition forming the coating or ink.

30 In one embodiment, the photocatalytic composition forming a coating or ink may be used to impregnate overlay paper and/or décor paper and/or cellulose paper. The surface tension may be equal to or less than 24 mN/m to create a perfect wetting of the substrate.

In a preferred embodiment, minimum volume of the photocatalytic composition forming a coating or ink is enough to ensure a full wetting of the surface creating a wet film with homogenous covering of the substrate to be coated on and/or impregnated in said matrix.

In one embodiment, the photocatalytic composition is applied by spraying. The

5 photocatalytic composition can be sprayed by nozzles yielding a droplet size small enough to give a homogenous coating. Application droplets of the photocatalytic composition is preferably smaller than 500 µm, more preferably smaller than 250 µm even more preferably smaller than 100 µm and preferably equal to or smaller than 50 µm.

In a preferred embodiment, application of micronized droplets of the photocatalytic

10 composition is obtained by using air-mixed nozzles. In another embodiment, application of micronized droplets of the photocatalytic composition is obtained by using ultrasonic nozzles. In a further embodiment, application of micronized droplets of the photocatalytic composition is obtained by using rotary atomizing nozzle. In a further embodiment, application of micronized droplets of the photocatalytic composition is obtained by using

15 ink jet printer.

In one embodiment, an ink jet printer is used to apply the photocatalytic composition on the substrate or into said substrate matrix.

In a preferred embodiment, the droplets ejected from the nozzles are printed and/or spray coated in an array that ensure an efficient coverage of the substrate. Furthermore, the

20 coverage is in one embodiment made in a way that the inter droplet distance (distance between two neighbouring droplets) in the array is smaller than the wetting capacity of the droplets. Thereby, the inter droplet distance and the spreading of the droplets on the substrate is optimized as to obtain a wet film by overlapping droplets. Furthermore, the diameter of the printed and or spray coated droplets is chosen so as that the inter droplet 25 distance, the spreading of the droplets on the substrate and diameter of each droplet was optimized to obtain a complete wet film.

In one preferred embodiment, the inter droplet distance may be smaller than 5 mm, more preferably smaller than 1 mm, even more preferably smaller than 0.1 mm, and may be smaller than 0.05 mm, smaller than 0.01 mm, and even smaller than 0.001 mm.

30 In a preferred embodiment, the rheological properties of the photocatalytic composition were chosen so as to obtain a homogenous wet film where the droplets spread easily to form a complete layer on the substrate and that the wet film or layer dries up without inhomogeneities.

In a preferred embodiment, the diameter of the droplets is in the range 1-200 μm , preferably in the range 1-100 μm , and more preferably in the range of 1-50 μm .

In a preferred embodiment, the volume of said droplets are in the range of 1 nL – 1 mL.

Controlling drying of the photocatalytic coating and/or photocatalytic ink formed by the photocatalytic composition facilitates obtaining a good final coating and/or film without cracks. The drying has to be controlled to avoid both drying in the printing head and/or nozzle tip and minimizing stain deposit effect which yields an uneven deposit with cracks.

Drying of wet films depends on the thickness of the film, drying temperature and drying profile, humidity and film additives such as leveling agents and film formation agents and humectants.

Previously photocatalytic films have been made ranging from room temperature up to for example 140 °C resulting in cracks limiting their usefulness. To be able to control the cracking during drying of the film and/or coatings is useful as cracking limits the thickness, optical properties, mechanical integrity. Furthermore, as shown in the present invention cracking may also facilitate photogreying on substrates with tendencies for photogreying such as but not limited to melamine impregnated papers and cellulose paper.

Cracking during the drying stage of film formation can often be related to mud cracking.

The film tension produced in the film forming process is often responsible for the occurrence of mud cracking in emulsion paint films and coatings. The film tension develops more or less spontaneously and can be of varying intensity. The cracking of photocatalytic coatings or films has serious consequences for their potential use in viable commercial applications.

In a preferred embodiment, the formation of uncracked photocatalytic films and/or coatings may be obtained by making said film and/or coating below a critical film thickness.

The film thickness is related to the drying conditions and the formulation of said photocatalytic composition. In a preferred embodiment, the film thickness is less than 100 μm , even less than 50 μm , more preferably less than 10 μm , and more preferably less than 1 μm .

In an embodiment, the photocatalytic film and/or coating formed by the photocatalytic composition is dried at a controlled temperature profile. The controlled temperature may in a preferred embodiment be a profile which is adjusted to the film thickness and the formulation of the photocatalytic composition.

In an embodiment, the photocatalytic film and/or coating is applied on a melamine formaldehyde resin impregnated paper. The melamine formaldehyde resin impregnated paper is preferably dry, or semi-dry, such as dried with a relative humidity in the range of 2-10 %.

5 In an embodiment, the photocatalytic film and/or coating formed by the photocatalytic composition is applied on the melamine formaldehyde resin impregnated paper by spray application.

In an embodiment, the photocatalytic film and/or coating formed by the photocatalytic composition is applied on the melamine formaldehyde resin impregnated paper by ink jet printing.

10 In an embodiment, the photocatalytic film and/or coating formed by the photocatalytic composition is applied by roll coating on the melamine formaldehyde resin impregnated paper.

In a further embodiment, the applied film and or coating has a thickness less than 10 µm

15 and maximum drying temperature in the range 20-160 °C.

In a further embodiment, the applied film and or coating may have a thickness of less than 10 µm and drying temperature less than 140 °C.

The photocatalytic composition may be used as a photocatalytic ink or as a photocatalytic fluid. When applied to a substrate, the photocatalytic composition forms a coating or film.

20 The photocatalytic coating or film may be continuous over the substrate, or discontinuous.

Fig. 4 shows a substrate 1 such as a building panel having a core 2 and a surface layer 3 coated by a photocatalytic coating 4 formed of the above described photocatalytic composition. The core 2 may be a wood fibre based core such as HDF. The core may comprise a thermoplastic material. The surface layer 3 may be a lacquer layer. The surface layer 3 may comprise a binder containing formaldehyde, such as melamine formaldehyde resin. The surface layer 3 may be a melamine formaldehyde resin impregnated paper. The surface layer may comprise a thermoplastic material. The surface layer 3 may be a wood powder layer comprising wood fibres and a resin, preferably melamine formaldehyde.

25 The coating may be applied on the surface layer or applied into the surface layer such as into the resin matrix of the surface layer.

The anti-photogreying additive reduces photogreying of the photocatalytic titanium dioxide particles disposed in lacquer layer or resin matrix of the surface layer 3 of the substrate 1.

Even if illustrated as two separate layers, the photocatalytic composition may enter into the underlying surface layer 3 of the substrate 1. However, even if the anti-photogreying additive reduces photogreying of the particles disposed in the surface layer 3, the photocatalytic titanium dioxide particles arranged on the outermost surface of the surface 5 layer 3 remain photocatalytically active.

As an alternative, the composition may be applied into the surface layer before being arranged on the core. As a further alternative, the composition may be added when forming the surface layer. In this embodiment, the photocatalytic coating is integrated in the surface layer. As an example, the photocatalytic composition may be added to a mix 10 comprising wood fibres and a binder.

It is also contemplated that the photocatalytic coating may be applied on a surface of the substrate, i.e. with no intervening layer.

Example 1

Application of the photocatalytic composition to form a 10 μm coating on an overlay paper 15 conforming to abrasion class AC6 (EN 13329). Sample A in fig.5a shows the overlay paper having a coating formed from a waterborne TiO_2 composition comprising 0.5 vol% polyether modified polysiloxanes. Sample B in fig. 5b shows the overlay paper having a coating formed from a waterborne TiO_2 composition comprising 16.6 vol% polyether modified polysiloxanes. Both samples are cured at ambient conditions and irradiated with 1 20 mW/cm^2 UVA light.

Figure 5a shows sample A after UV irradiation. Figure 5b discloses sample B after UV irradiation. Photogreying has occurred of sample A. Sample A also shows mud cracking. Sample B shows no photogreying and no mud cracking.

Example 2

25 Colour and Contact Angle (CA) were measured as a function of time of UVA exposure (ISO) for a reference, a thick film of nanofluid with 10 vol % polyether modified polysiloxanes (A) and a thin film of nanofluid with 12 vol % polyether modified polysiloxanes (B). The colour of a blank white reference and samples were recorded with an NCS Colour Scan before and after UVA radiation. The NCS codes were recalculated to RGB and Lab values with NCS 30 Navigator (www.ncscolour.com). The RGB values (RGB) are used to visually present the colour/colour change and the Lab (L^*a^*b) values are used to calculate the Greying and the Yellowing Index.

The Photogreying index $\Delta L^* = L^*_{(\text{Initial})} - L^*_{(\text{X min})}$

The Yellowing index $\Delta b^* = \text{abs}(b^*_{(\text{Ref})} - b^*_{(\text{Sample})})$

Time	0 hr			16.5 hr			39 hr			60 hr		
	CA	Δb	ΔL	CA	Δb	ΔL	CA	Δb	ΔL	CA	Δb	ΔL
Reference	52.4	0	0	60.4	0	0	64.4	2	0	62.6	2	0
A	11.8	6	0	55.9	8	1	49.5	9	2	42.2	9	2
B	11.9	2	0	68.7	2	0	63.6	2	1	51.7	2	1

Example 3

5 Colour and Contact Angle (CA) were measured as a function of time of UVA exposure (ISO) for a reference, a thin film with 0.5 vol % polyether modified polysiloxanes (A), a thin film of nanofluid with 12 vol % polyether modified polysiloxanes (B), and a thin film TiO₂ particles modified with Pt with 6 vol % polyether modified polysiloxanes (C).

Time	0 hr			16.5 hr			39 hr			60 hr		
	CA	Δb	ΔL	CA	Δb	ΔL	CA	Δb	ΔL	CA	Δb	ΔL
Reference	62.0	0	2	67.0	0	2	69.7	2	0	67.3	2	0
A	57.1	2	0	53.2	3	6	54.1	3	6	47.7	3	6
B	18.2	2	0	65.7	2	0	47.4	2	0	40.0	2	0
C	22.5	2	0	17.1	2	1	14.4	2	1	19.0	2	1

10 Example 4

Figure 6 shows a Zisman plot for three different surface tensions of photocatalytic composition – showing a critical surface tension of overlay paper conforming to abrasion class AC6 (EN 13329) of 24 mN/m. By determining the critical surface tension of the substrate on which the composition is to be applied, a suitable anti-photogreying additive 15 and/or wetting agent may be chosen in order to obtain perfect wetting.

Example 5 - t_{open}

Figure 7 discloses wetting of surface – t_{open} – as described above with reference to fig. 3 for four different formulations:

A) De-ionized water.

20 B) Waterborne nanosized TiO₂ fluid.

C) Waterborne nanosized TiO₂ fluid with 10 wt % polyether modified polysiloxanes.

D) Waterborne nanosized TiO₂ fluid with 10 wt % polyethylglycol monomethyl ether and a wetting agent.

Example 6: Photocatalytic activity

5 An overlay paper conforming to abrasion class AC6 (EN 13329) was impregnated with 25 wt % nanosized photocatalytic anatase TiO₂ composition containing 10 vol % polyether modified polysiloxanes as an anti-photogreying additive. The composition was applied by spray coating on the melamine formaldehyde resin coated overlay paper and a total of 3 g of composition was applied per m². The melamine impregnated and TiO₂ coated overlay 10 paper was pressed together with a decor layer, a core and a backing paper to a laminate structure. The sample was pre-activated in UV light for 3 days where after the photocatalytic activity was measured. The photogreying was measured after 96 hr in Xenon test.

15 The photocatalytic activity was measured according to ISO 22197-2 (removal of acetaldehyde) with a gas flow rate of 1 L/min with 1 ppm acetaldehyde as pollutant a sample size of 45 cm² and an UVA light source of 1 mW/cm².

The photocatalytic activity is measured as removal of pollutant (x ppm) and by the photonic efficiency. The employed UV(A) illumination intensity is 1 mW/cm², with an illuminated sample area of 45 cm² the total power is 45 mW. Taking an average 20 illumination wavelength of 350 nm this can be converted to 1.32×10^{-7} molhv/s. The gas flow contains 1 ppm Acetaldehyde, hence 10^{-6} mol Acetaldehyde flow across the sample within 24 min. During the same time the sample is illuminated with 1.32×10^{-7} molhv / s x 60 s/min x 24 min = 190×10^{-6} molhv. If total oxidation (loss) of the 1 ppm Acetaldehyde is observed, the Photonic Efficiency ζ will be $\zeta = 10^{-6}$ mol Acetaldehyde / 190×10^{-6} molhv = 25 0.0053 = 0.53 %. For a measured degraded amount of x ppm Acetaldehyde the Photonic Efficiency can consequently be calculated with the following formula: $\zeta_x = x \text{ (ppm)} * 0.53 \text{ (\% / ppm)}$.

In the table below the results are listed together with the results of a reference of a pressed laminate without photocatalytic TiO₂.

	Ref	Photocatalytic
ΔL	-1.01	0.12
ζ_x	0.00 % (0.0 ppm)	0.25 % (0.48 ppm)

CLAIMS

1. A photocatalytic composition comprising:
 - photocatalytic titanium dioxide particles being dispersed in a continuous phase, and
 - 5 - at least one anti-photogreying additive being adapted to reduce photogreying while the photocatalytic activity of the composition is substantially maintained, and
 - wherein the photo greying index (ΔL) of said composition is less than 6, such as less 5, preferably less than 4, such as less than 3, such as less than 2.
- 10 2. A photocatalytic composition according to claim 1, wherein the photocatalytic activity of the composition is maintained to a level of at least 90%.
- 15 3. A photocatalytic composition according to claim 1, wherein the photocatalytic activity of the composition is maintained.
- 20 4. A photocatalytic composition according to any of the preceding claims, wherein said at least one anti-photogreying additive is present in a concentration higher than 0.1 wt%.
- 25 5. A photocatalytic composition according to any of the preceding claims, wherein said at least one anti-photogreying additive is present in the range of 1-35 wt%, preferably 1-15 wt%, more preferably 5-12 wt%.
- 30 6. A photocatalytic composition according to any of the preceding claims, wherein said at least one anti-photogreying additive comprises a wetting agent.
- 35 7. A photocatalytic composition according to any of the preceding claims, wherein said at least one anti-photogreying additive comprises a surfactant.
8. A photocatalytic composition according to claim 7, wherein said surfactant is or comprises a non-ionic surfactant.
9. A photocatalytic composition according to claims 7-8, wherein said surfactant is or comprises a silicone based surfactant.

10. A photocatalytic composition according to any one of the preceding claims, wherein said at least one anti-photogreying additive comprises a polyglycol, preferably a poly(ethylene glycol) methyl ether.

5 11. A photocatalytic composition according to any one of the preceding claims, wherein titanium dioxide particles are in anatase form.

10 12. A photocatalytic composition according to any of the preceding claims, wherein said titanium dioxide particles have a size in the range between 5 to 250 nm, preferably between 5 to 100 nm, more preferably between 5 to 50 nm.

15 13. A photocatalytic composition according to any one of the preceding claims, wherein photonic efficiency of the composition is exceeding 0.025%, preferably exceeding 0.05%, more preferably exceeding 0.1%.

15 14. A photocatalytic composition according to any of the preceding claims, wherein said continuous phase is a solvent, preferably water.

20 15. A photocatalytic composition according to any of the preceding claims, wherein said titanium dioxide particles have a concentration in the range between 0.3 wt% to 40 wt%, preferably between 1.0 wt% to 30 wt%.

25 16. A photocatalytic composition according to any of the preceding claims, wherein said composition has a pH higher than 9.

25 17. A photocatalytic composition according to claim 16, wherein said pH is stabilized by amines, such as triethylenamine.

30 18. A photocatalytic composition according to any one of claims 1-16, wherein said composition has a pH lower than 4.

35 19. A photocatalytic composition according to claim 18, wherein said pH is stabilized by a strong acid such as HCl.

35 20. A photocatalytic composition according to any of the preceding claims, further comprising a dispersion agent, preferably propylene glycol.

21. A photocatalytic composition according to any of the preceding claims, further comprising a binder, preferably a silicon or titanium based material.

22. A photocatalytic composition according to any of the preceding claims, 5 wherein said composition is a photocatalytic ink.

23. A photocatalytic composition according to any of the preceding claims, further comprising a humectant.

10 24. A photocatalytic composition according to claim 23, wherein said humectant comprises amines based compounds such as triethanolamine.

25. A photocatalytic composition according to claim 23, wherein said humectant comprises compounds having a diol group.

15 26. A photocatalytic composition according to claim 23, wherein said humectant comprises glycols, preferably a poly(ethylene glycol) methyl ether.

20 27. A photocatalytic composition according to any one of claims 23-26, wherein said humectant is present in the range of 1-35 wt%, preferably 5-35 wt%.

25 28. A photocatalytic composition according to any of the preceding claims, wherein the colour change (ΔE) index of said composition is smaller than 6, such as smaller 5, preferably smaller than 4, such as smaller than 3, such as smaller than 2.

29. A photocatalytic composition according to any of the preceding claims, wherein the yellowing (ΔB) index of said composition is smaller than 6, such as smaller 5, preferably smaller than 4, such as smaller than 3, such as smaller than 2.

30 30. A photocatalytic coating formed of a composition according to any one of the preceding claims.

31. A building panel comprising a photocatalytic coating formed of a photocatalytic composition according to any one of claims 1-29.

32. A method for applying a photocatalytic composition according to claims 1-29 on a substrate, comprising:

- applying said composition on a substrate for forming a coating, and
- drying and/or curing said coating.

5

33. A method according to claim 32, wherein said composition is applied by digital printing.

34. A building panel having a surface, wherein the surface comprises
10 photocatalytic titanium dioxide particles and at least one anti-photogreying additive, and wherein the photo greying index (ΔL) of the surface is less than 6, such as less 5, preferably less than 4, such as less than 3, such as less than 2.

15

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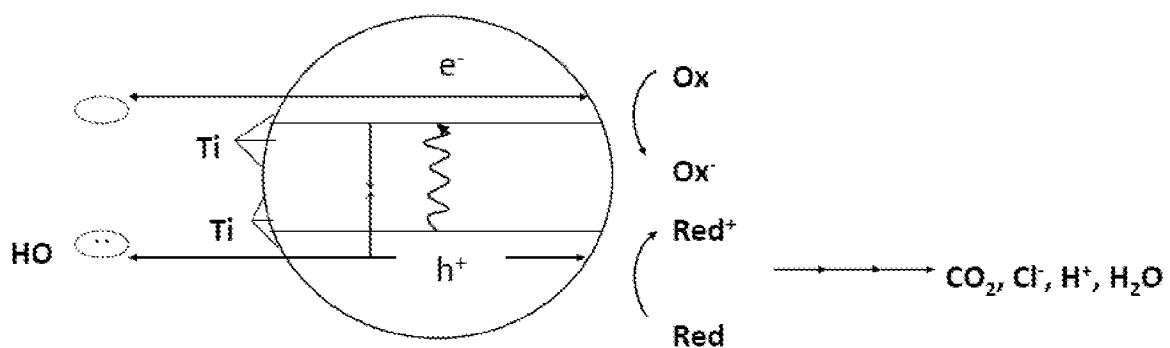


Fig. 1

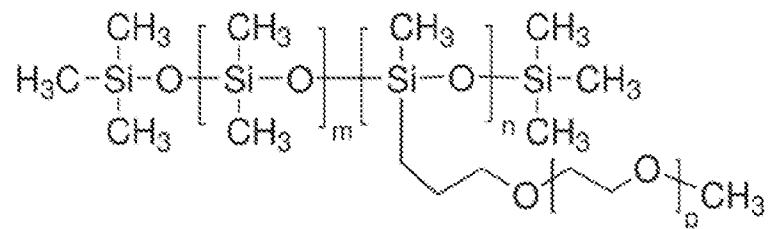


Fig. 2a

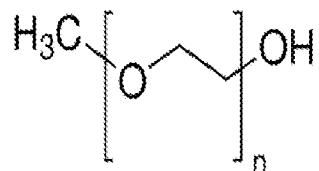


Fig. 2b

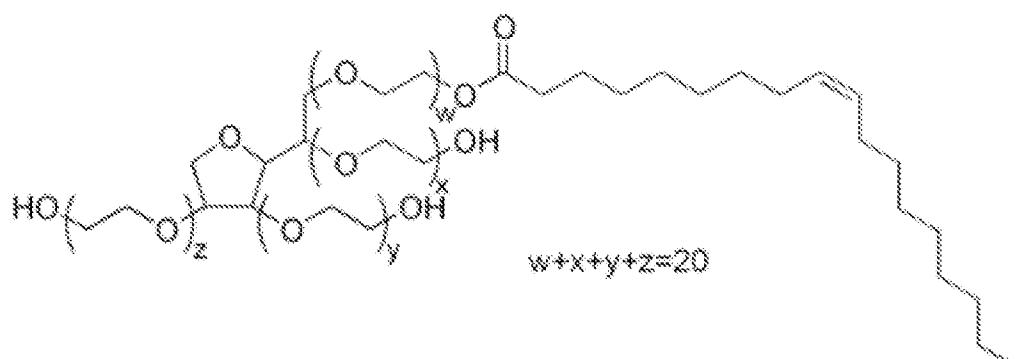


Fig. 2c

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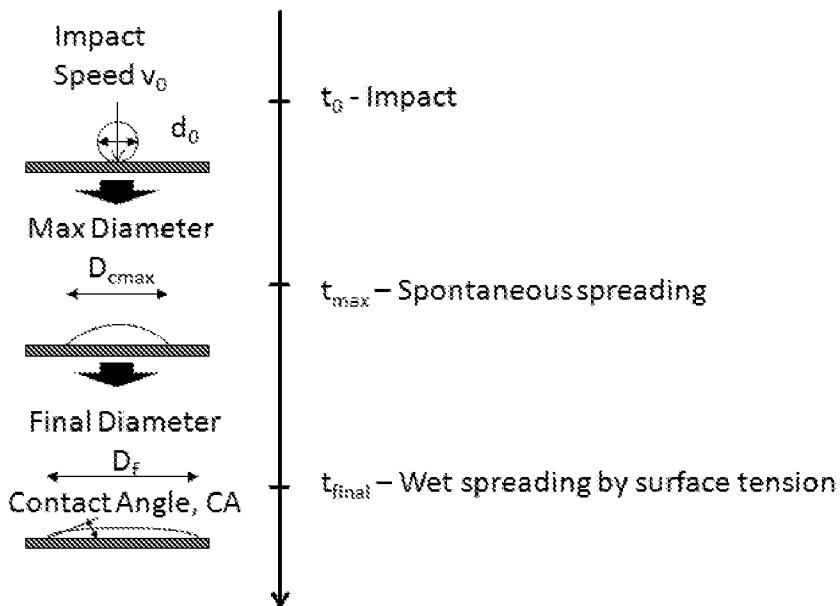


Fig. 3

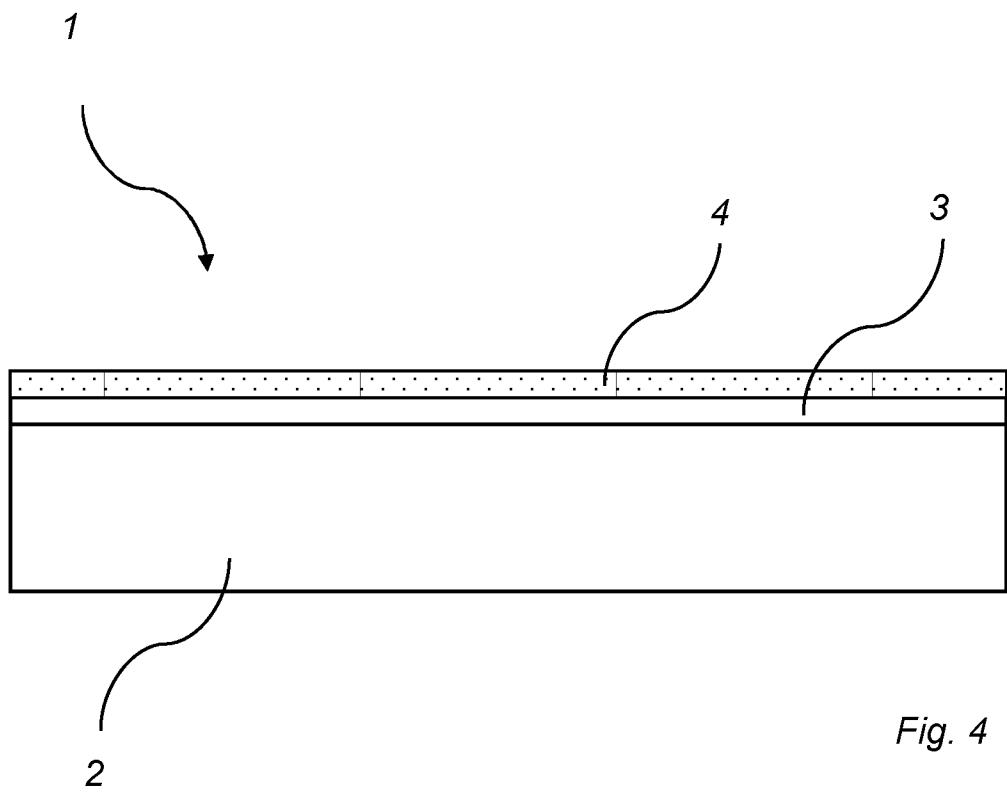


Fig. 4

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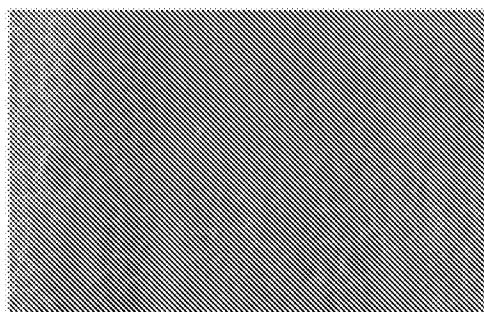


Fig. 5a

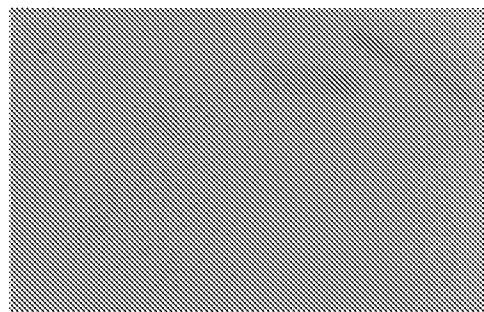


Fig. 5b

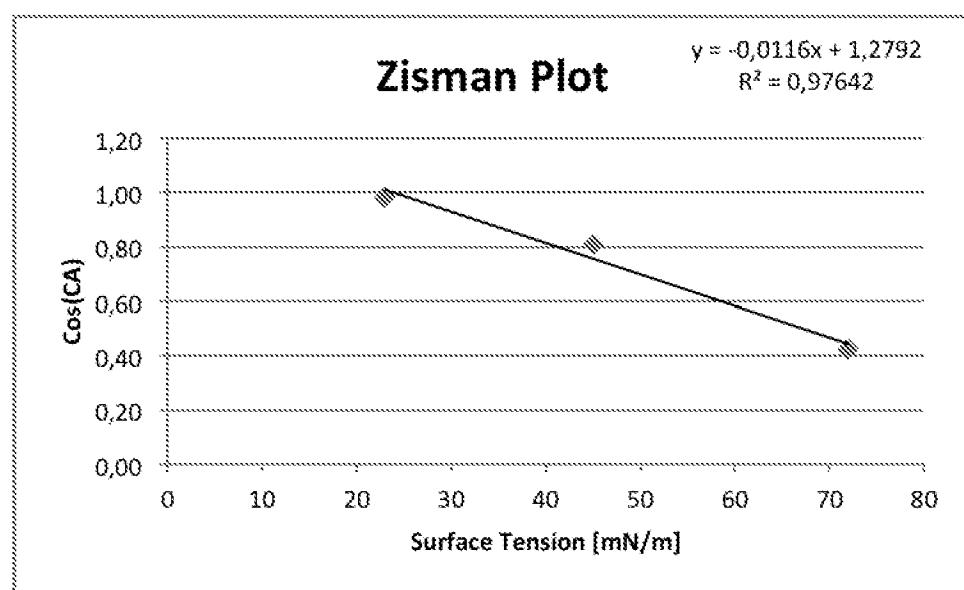


Fig. 6

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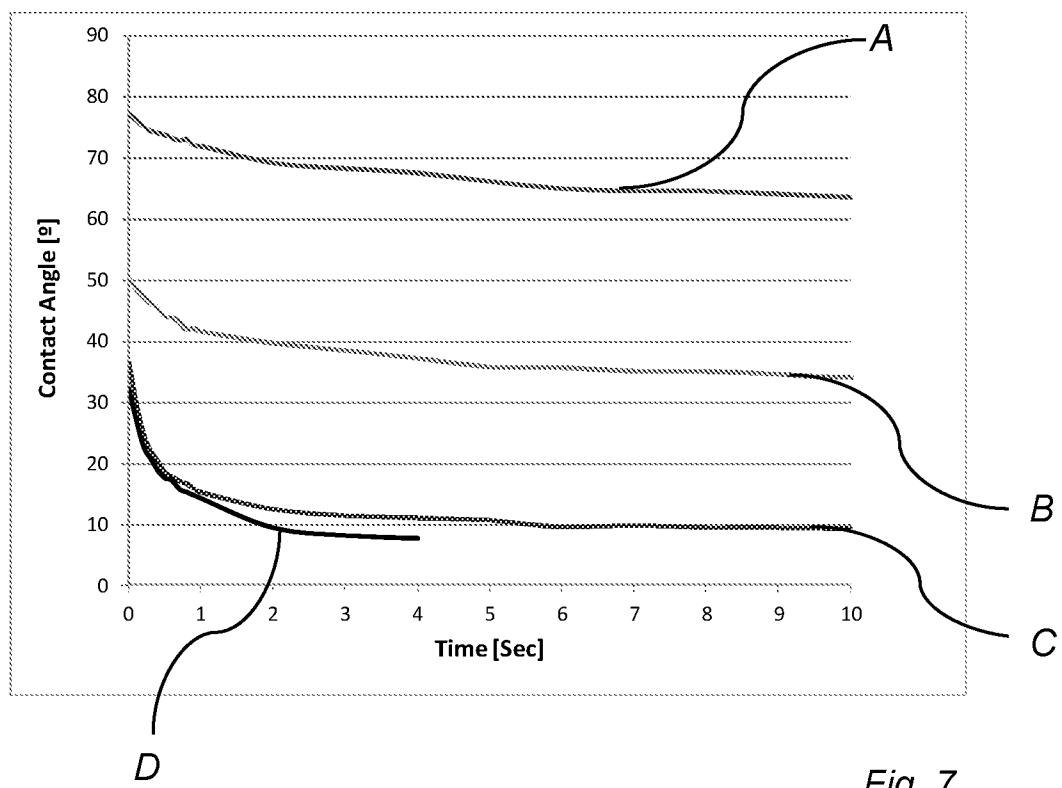


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2013/050283

A. CLASSIFICATION OF SUBJECT MATTER

IPC: 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: B01J, B32B, C09D

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 20110136660 A1 (TERASAKI HIROSHI ET AL), 9 June 2011 (2011-06-09); A1-A5 on page 6; claims 1-15; paragraph [0001] --	1-34
X	EP 0913447 A1 (TOTO LTD), 6 May 1999 (1999-05-06); example B2 on page 14; paragraphs [0001], [0060] -----	1, 4-8, 11, 14-15, 30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	
“A” document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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“O” document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family

Date of the actual completion of the international search

08-07-2013

Date of mailing of the international search report

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Continuation of: second sheet

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B32B 27/18 (2006.01)

C09D 1/00 (2006.01)

C09D 7/12 (2006.01)

INTERNATIONAL SEARCH REPORT
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