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(54) Title: A PHOTOCATALYTIC POLYMER CONTAINING PRODUCT AND A METHOD TO PRODUCE A PHOTOCATALYTIC POLYMER CONTAINING PRODUCT

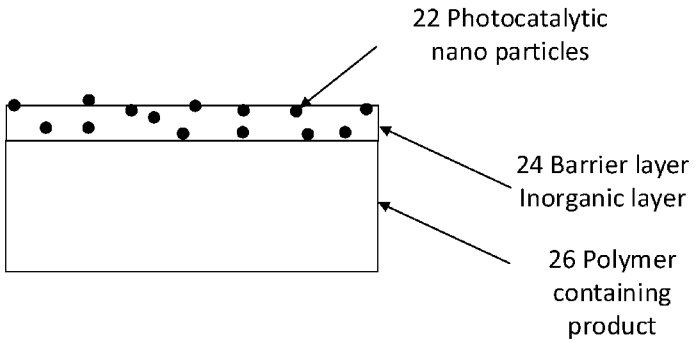

Fig. 1

(57) Abstract: The present invention relates to a photocatalytic polymer containing product and a method to produce a photocatalytic polymer containing product.

A PHOTOCATALYTIC POLYMER CONTAINING PRODUCT AND A METHOD TO PRODUCE A PHOTOCATALYTIC POLYMER CONTAINING PRODUCT

FIELD OF THE INVENTION

The present invention relates to a photocatalytic polymer containing product and a method to produce a photocatalytic polymer containing product.

BACKGROUND OF THE INVENTION

Air pollution and surface contamination as well as algae growth are major problems in e.g. buildings. Photocatalytic compounds such as TiO_2 can be used to produce smart building materials that can reduce, e.g. the high level of pollutant that poses a threat to the human health in big cities.

A common strategy is to apply photocatalytic compounds to building surfaces that are irradiated by the sun light during the day. For example, plastic surfaces that are exposed to sun light for several hours during the day. For example, titanium dioxide powder may be mixed with cement and other binders materials to produce photocatalytic pavement.

One drawback of these materials is the large amount of titanium dioxide powder used. Titanium dioxide powder has to be mixed in large quantity so as to achieve acceptable activity towards the reduction of pollutants as not all the titanium dioxide powder is available for photocatalytic reactions.

Thus, an efficient method to produce photocatalytic materials that are exposed to sunlight for several hours per day, could be advantageous.

In particular, a method of producing photocatalytic materials that are exposed to sunlight for several hours per day, which employs low amount of catalytic materials and achieves high activity in degradation of pollutants, such as NOx, SO_2 or other Volatile Organic Compound (VOC), could be advantageous.

Polymer containing products, such as plastic products generally lack protections, thus are quite sensitive to scratches, abrasions and therefore dust and dirt can easily contaminate their surfaces.

However, photocatalytic materials deposited on polymer surfaces may produce degradation due to light induced photocatalytic reactions.

Hence, there is a need for an improved plastic product that is less sensitive to scratches and to formation of dust and dirt on its surfaces.

OBJECT OF THE INVENTION

It may be seen as an object of the invention to provide a method to produce photocatalytic materials that are exposed to sunlight for several hours per day, having high activity towards degradation of air and water pollutants, reduction of algae growth and reduction of staining.

It may be seen as another object of the invention to provide a photocatalytic material that is exposed to sunlight for several hours per day, having high activity towards degradation of air and/or water pollutants.

It is an object of the present invention to wholly or partly overcome the above disadvantages and drawbacks of the prior art.

An object of the present invention is to provide an alternative to the prior art.

In particular, it may be seen also as an object of the present invention to provide a more efficient and low cost method of production of photocatalytic polymer containing materials for different application.

SUMMARY OF THE INVENTION

In a first aspect the invention relates to a method of producing a photocatalytic polymer containing product, the method comprising: providing a polymer containing product; coating the polymer containing product with an inorganic barrier layer; wherein the inorganic barrier layer forms an internal surface in contact with the polymer containing product and an external surface; modifying the external surface of the inorganic barrier layer by surface treatment; applying a dispersion of inorganic particles to the modified external surface; wherein the inorganic particles of the dispersion of inorganic particles comprises photocatalytic particles.

The photocatalytic particles are deposited on the modified external surface of the inorganic layer. The external surface of the inorganic layer is the one not in contact with polymer containing product, i.e. the one exposed to air before the application of the dispersion of inorganic particles. Thus, the external surface may be generally the surface opposite to the internal surface in contact with the polymer containing product.

As disclosed herein, and as schematically illustrated in figures 1-3, an inorganic barrier layer applied on the surface of a polymer containing product shields the polymer containing product from the environment, thus protecting the polymer containing product from abrasion and scratches that may be caused during use. At the same time, the presence of photocatalytic particles, on the outer surface of the inorganic barrier layer, ensure degradation of undesired chemicals through (sun)light activation of the photocatalytic particles.
Furthermore, the presence of the inorganic barrier layer avoids direct degradation of the polymer containing surface.

The inorganic barrier layer prevents the contact between the photocatalytic particles and the surface of the polymer containing product.
The contact between the photocatalytic particles and the surface of the polymer containing product may lead to degradation of the surface due to photocatalytic reaction induced by the (sun)light irradiation. The presence of the inorganic barrier layer ensure separation between the photocatalytic particles and the surface of the polymer containing product thus avoiding photocatalytic degradation of the surface.

The surface of the polymer containing product may be coated with an organic layer, e.g. a base coat such as a lacquer layer. Also in this case, if the barrier layer was not present, the photocatalytic nanoparticles upon (sun)light excitation may react with the base coat or any other underlying lacquer layer damaging the surface of the base coat and in turn of the polymer containing product

For example, due to the photocatalytic activity of the photocatalytic nanoparticles, if a barrier layer was not present, photocatalytic reactions may degrade the base coat and thus affect the properties of the base coat, providing chromatic variations and/or changing its mechanical resistance.

In that respect, it is advantageous that the inorganic barrier layer is not brittle or stiff but flexible so that it can be applied to the surface of the polymer containing product with no negative impact on the surface substrate avoiding potential cracking that would lead to percolation of photocatalytic particles that may produce the undesired above mentioned effects.
For the same reasons, it is advantageous that the inorganic barrier layer is weather resistant and that does not delaminate or deteriorate thus avoiding cracks formation.

In some embodiments, providing a polymer containing product comprises applying a polymer layer to a sheet as a coating and/or impregnation to provide a polymer containing product.

The polymer containing product may be a product consisting of polymer, such as a hard plastic product.

In some other embodiments, the polymer containing product may be a product made of other materials, such a metal, wood, glass or plastic and then coated with a polymer coating.

The sheet may be a fiber sheet or paper, for example glass fiber dew, or any other base material for roofing felt to make shingles and roll roofing used in building construction.

In some examples, the sheet may also be a plate of cement fibers.

By impregnating is preferably meant that a the polymer at least partially penetrate in the sheet.

In a second aspect, the invention relates to a photocatalytic polymer containing product comprising:
- a polymer containing product;
- an inorganic barrier layer coated onto said polymer containing product;
- inorganic particles comprising photocatalytic particles onto and/or into said inorganic barrier layer.

Further aspects and embodiments of the invention are presented in the following as well as in the accompanying patent claims.

In some other embodiments, the inorganic barrier layer is a continuous inorganic barrier layer.
The inorganic layer may be a compact layer.
The inorganic layer may be impermeable layer.
In some embodiments, the inorganic layer may be a layer of silica.

In some embodiments, the photocatalytic particles have a particle size in the micro and/or nano meter range.

Micro meter range is preferably used to indicate that the dimension of the particle in question is in the range of between $1*10^{-6}$ and $1000*10^{-6}$ meters. Nano meter range is preferably used to indicate that the dimension of the particle in question is in the range of between $1*10^{-9}$ and $1000*10^{-9}$ meters. Such dimension may be determined as an average particle size, as the geometrical average of the size of the particles, or based on an equivalent diameter determined as the cubic root of mass/density*4/3/π (Pi).

In some embodiments, the photocatalytic particles may be provided by depositing on the surface on the inorganic barrier layer.
In some other embodiments, the photocatalytic particles may be embedded in the inorganic barrier layer.

In some further embodiments, the photocatalytic particles are titanium dioxide nanoparticles.

The surface modification may produce changes of the surface properties.

In some embodiments, modifying the external surface changes surface properties by exposing chemical functional groups, such as hydroxyl groups, i.e. OH groups.

Modifying the external surface of the inorganic barrier layer subsequently to being applied to the polymer containing product may comprise priming the inorganic barrier layer for adherence and/or spreading of photocatalytic nano particles to the surface of the inorganic barrier layer.

The priming for adherence of photocatalytic nano particles may be selected from corona exposure, plasma exposure, flame oxidation exposure.

Thus, the surface treatment may comprise air plasma treatment, such as corona discharge treatments.

In some embodiments, the surface treatment of the external surface may comprise chemical treatment, flame treatment, oxidation treatment, corona discharge treatment, ultraviolet irradiation treatment, plasma treatment and ion treatment.

In some further embodiments, priming or surface treatment may be extended to one or more surfaces of the polymer containing product before the application of the inorganic barrier layer.

In some embodiments, the method according to the first aspect further comprises, after coating the polymer containing product with an inorganic barrier layer: drying and/or curing said inorganic barrier layer.

Thus, in some embodiments, the drying and/or curing said inorganic barrier layer occurs before modifying the external surface of the inorganic barrier layer by surface treatment.

In some other embodiments, the method according to the first aspect further comprises, after applying a dispersion of inorganic particles to the modified external surface: drying and/or curing the inorganic particles applied to the modified external surface.

In some further embodiments, the method according to the first aspect further comprises: modifying an external surface of the polymer containing product before coating the polymer containing product with an inorganic barrier layer.

In some embodiments, modifying an external surface of said polymer containing product before coating the polymer containing product with an inorganic barrier layer is a achieve by surface treatment.

Thus, in some embodiments, the surface of polymer containing product to which the inorganic layer is provided as a coating is primed for adherence and/or spreading of the coating, before the coating with the inorganic layer.

In some further embodiments, the priming for adherence and/or spreading of the coating is selected from corona exposure, plasma exposure, flame oxidation exposure.

In some embodiments, drying and/or curing the inorganic barrier layer is provided by heating, such as forced heating, such as convective heating, e.g. by use of a gas flow where the gas has an elevated temperature (e.g. heated air), exposure to infra-red radiation, ultra violet radiation, microwaves or electron beam.

Drying and/or curing may be achieved by low temperature steps, e.g. less than 100, such as less 80, for example less than 60, such as less than 40 degree C, for period of times between 5 minutes down to 30 sec.

According to the invention, fast low temperature steps may be used to obtain efficient drying and/or curing. The thickness and material of the inorganic layer used that allows for efficient fast drying and/or curing at low temperature such as less than 70 degree C.

In some further embodiments, drying and/or curing the dispersion of inorganic particles is provided by heating, such as forced heating, such as convective heating, e.g. by use of a gas flow where the gas has an elevated temperature (e.g. heated air), exposure to infra-red radiation, ultra violet radiation, microwaves or electron beam.

In some embodiments, drying and/or curing may be achieved by exposing said polymer containing product to temperatures less than 100, such as less 80, preferably less than 60, such as less than 40 degree C, for period of times between 5 minutes down to 10 sec, such as less than 4 minutes, less than 3 minutes, less than 2 minutes or less than 1 minutes, such as less than 50 seconds, less than 30 seconds or less than 15 seconds.

In some embodiments, applying the dispersion of inorganic particles to the modified external surface comprises spraying a dispersion comprising photocatalytic titanium dioxide nanoparticles onto the inorganic barrier layer.

The dispersion of inorganic particles may be an aqueous dispersion.

In some embodiments, the dispersion is applied to the inorganic barrier layer in an amount of less than 200 ml/m^2, such as 150 ml/m^2, for example less than 100 ml/m^2, preferably less than 50 ml/m^2, such as less than 40 ml/m^2, preferably less than 30 ml/m^2, such as less than 20 ml/m^2.

In some further embodiments, the photocatalytic particles are embedded in the inorganic barrier layer.

In some embodiments coating the polymer containing product with an inorganic barrier layer comprises coating with an inorganic fluid composition, wherein the inorganic fluid composition is a solution comprising a solvent, preferably selected from alcohols, water and mixture hereof and an inorganic substance is selected from silicone resin, methyl silicone, methylphenyl silicone, PMSQ silicone and mixtures hereof.

The inorganic fluid composition may comprise an of inorganic substance less than 25 wt %, such as between 1 and 10 wt %, preferable in between 4 and 6 wt %, such as 5 wt %.

In some embodiments, coating the polymer containing product with an inorganic barrier layer provides the inorganic barrier layer with a mass per square meter less than 100 g/m^2, such as less than 50 g/m^2, preferably less than 25 g/m^2.

In some further embodiments, coating the polymer containing product with an inorganic barrier layer provides the inorganic barrier layer with a thickness less than 5.0 µm, such as less than 2.5 µm, preferably less than 1.0 µm, such as less than 0.75 µm, preferably less than 0.5 µm, such as less than 0.25 µm.

The photocatalytic particles may be embedded in the inorganic barrier layer.

In some embodiments, the photocatalytic particles are deposited on an outer surface of the inorganic barrier layer.

In some further embodiments, the photocatalytic particles are embedded in the inorganic barrier layer and deposited on an outer surface of the inorganic barrier layer.

The photocatalytic polymer containing product may be used as a consumable plastic product.
The polymer containing product may have the form of a foil that is then coated by the inorganic barrier layer on which photocatalytic particles are deposited.
For example polymer containing product may be furniture foils, outdoor weather resistant foils, polycarbonate (PC) foils, Polyvinyl chloride (PVC) foils, PMMA, polyurethane (PU), Acrylic foils, such as Poly(methyl methacrylate) (PMMA) foils and flexible floors, such as Luxury Vinyl Tile (LVT) floor.

The photocatalytic polymer containing product may thus be foils, such as semi-transparent foils that can be attached to windows or façades so as to provide a photocatalytic surface on a photocatalytic degradable substrate through the use of an inorganic barrier layer.

The photocatalytic particles may be discrete particles.

In some embodiments, the inorganic barrier layer is a continuous inorganic barrier layer.

The photocatalytic particles, such as titanium dioxide nanoparticles, may be in an amount of 10 g/m^{2}or less, such as 5 g/m^2 or less, preferably 3 g/m^2 or less, more preferably 2 g/m^2 or less, most preferably 1 g/m^2 or less.

The photocatalytic particles, such as titanium dioxide nanoparticles, may have a primary size less than 50 nm, preferably less than 30 nm, more preferably less than 20 nm.

The photocatalytic particles, such as titanium dioxide nanoparticles, may have an agglomerate size of less than 300 nm, less than 200 nm, less than 100 nm, such as less than 80 nm preferably an aggregate size of less than 60 nm such as of less than 40 nm and even more preferably an aggregate less than 30 nm such as less than 20 nm.

In some embodiments, the photocatalytic particles, such as titanium dioxide nanoparticles, are in anatase phase.

BRIEF DESCRIPTION OF THE FIGURES

The method of producing polymer containing product and the polymer containing product according to the invention will now be described in more detail with regard to the accompanying figures. The figures show ways of implementing the present invention and are not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figures 1 illustrates schematically a photocatalytic polymer containing product according to a some embodiments of the invention wherein photocatalytic nano particles are embedded in an inorganic barrier layer.

Figure 2 illustrates schematically a photocatalytic polymer containing product according to a some other embodiments of the invention wherein photocatalytic nano particles are deposited onto an inorganic barrier layer.

Figure 3 illustrates schematically a photocatalytic polymer containing product according to further embodiments in which the polymer containing product comprises a sheet coated by a polymer coating.

Figure 4 is a flow-chart of a method of producing photocatalytic polymer containing product according to some embodiments of the invention.

Figure 5 is a schematic drawing of the steps of the method of producing a photocatalytic polymer containing product, according to some embodiments of the invention.

Figure 6 shows polymer containing foils tests related to the photocatalytic air purifying properties tested according to the NOx degrading properties after ISO 22197-1 before and after 300 hours of accelerated weathering according to EN 1297:2004.

DETAILED DESCRIPTION OF AN EMBODIMENT

Reference is made to figures 1-3 schematically illustrating a photocatalytic polymer containing product comprising a polymer containing product 26 and an inorganic barrier layer 24 coated onto said polymer containing product 26. The polymer containing product 26 may be in the form of a sheet impregnated with polymer, or in general a matrix comprising polymer (not shown) or may be in the form of a sheet to which polymer is applied as a layer/coating, e.g. figure 3.

Thus, in the embodiment of figure 3, the product 25 and the layer/coating of polymer 27 forms the polymer containing product 26.

As shown in figure 1, the inorganic barrier layer 24 may comprise photocatalytic particles 22, such as photocatalytic titanium dioxide nanoparticles, having a particle size in the micro- and/or nano meter range.

As illustrated in figure 1, the photocatalytic particles 22 may be embedded in the inorganic barrier layer 24, and as illustrated in figure 2, the photocatalytic particles 22 may be deposited on the outer or external surface (opposite to the surface facing towards the layer in contact with the polymer containing product)

of the inorganic barrier layer 24. A combination of this may be used in connection with the present invention in which the photocatalytic particles 22 are embedded in the inorganic barrier layer 24 and deposited on the outer surface of the inorganic barrier layer 24.

As disclosed herein, and as schematically illustrated in figure 1, a barrier layer applied on the surface of the polymer containing product 26 shields the polymer containing product from the surrounding environment.

In some embodiments, the polymer containing product according to the invention is a roofing felt.

In some other embodiments, the polymer containing product according to the invention is a consumable plastic product.

In a polymer containing product according to the present invention, the photocatalytic particles are discrete particles. However, agglomerates of photocatalytic particles may also be used.

Typically, the inorganic barrier layer 24 is a continuous inorganic barrier layer, preferably in the meaning that the inorganic barrier layer 24 covers fully the polymer containing product with no direct exposure of the surface of the polymer containing product 26.

In many preferred embodiments, the photocatalytic particles, such as titanium dioxide nanoparticles, are in an amount of 10 g/m^2 or less, such as 5 g/m^2 or less, preferably 3 g/m^2 or less, more preferably 2 g/m^2 or less, most preferably 1 g/m^2 or less. The area used in characterizing the amount is typically the outer or external surface area of the inorganic barrier layer 24. It is preferably aimed at providing an evenly distribution of the photocatalytic particles in/on the inorganic barrier layer 24. By evenly is typically meant that the concentration either as g/m^2 or g/m^3 varies less than 25% such as less than 20% preferably less than 15%, such less than 10%, such as less than 5% through-out the inorganic barrier layer 24.

The photocatalytic particles, such as titanium dioxide nanoparticles, have preferably a primary size less than 50 nm, preferably less than 30 nm, more preferably less than 20 nm.

When agglomerates of photocatalytic particles are used, the photocatalytic particles, such as titanium dioxide nanoparticles, preferably have an agglomerate size of less than 300 nm, less than 200 nm, less than 100 nm, such as less than 80 nm preferably an aggregate size of less than 60 nm such as of less than 40 nm and even more preferably an aggregate less than 30 nm such as less than 20 nm.

Preferably, the photocatalytic particles, such as titanium dioxide nanoparticles, are in anatase phase.

Reference is made to figure 4 illustrating in a flow chart a method of producing a photocatalytic polymer containing product according to a preferred embodiment of the invention wherein:

- S1 refers to one or more steps of
  providing a polymer containing product (26) and
- S2 refers to one or more steps of
  coating said polymer containing product with an inorganic barrier layer (24);
  wherein said inorganic barrier layer forms an internal surface in contact with said polymer containing product (26) and an external surface;
  modifying said external surface of said inorganic barrier layer by surface treatment;
  applying a dispersion of inorganic particles to the modified external surface wherein said inorganic particles of said dispersion of inorganic particles comprises photocatalytic particles (22)

Reference is made to figure 5 that is a schematic drawing of the steps of the method of producing polymer containing product according to an embodiment. The schematic drawing of figure 5 shows:

- S3 providing a polymer containing product by either coating a product, such as a fiber cement with a polymer material or proving a product consisting of polymer, such as polycarbonate;

- S4 optionally performing an organic coating onto the surface of the polymer containing product, for example an acrylic coating or PU coating;
- S5 applying an inorganic barrier layer and a dispersion of inorganic particles comprising photocatalytic particles.

Subsequently, the coating of the polymer containing product 26 with an inorganic barrier layer 24 is done. It is noted that a priming or surface treatment may be applied prior to the coating with an inorganic barrier layer to ensure adherence of the inorganic barrier layer 24 to the polymer containing product 26.

If depositing of photocatalytic particles are to be deposited on the surface of the inorganic barrier layer 24, this is typically carried out subsequently to the application of the inorganic barrier layer. Again, a priming or surface treatment may be used prior to application of the photocatalytic particles e.g. to ensure adherence. These steps may be carried out as sprinkling.

In some embodiments, drying in between the process illustrated e.g. in figure 5 may be advantageous.

After the application of the inorganic barrier layer 24, the polymer containing product 26 may need to cool, cure, dry, heated or other setting process prior to e.g. being rolled into a coil.

In embodiments where the photocatalytic particles are deposited on to the surface of the inorganic barrier layer, this can be carried out before a rolling up step.

Coating the polymer containing product comprises: sprinkling, roll application or brush application said polymer containing product with an inorganic liquid composition being harden-able, cure-able, and/or setting-able.

The photocatalytic particles 22 may be in the inorganic liquid composition or be applied onto the surface of the inorganic barrier layer 24.

Such a sprinkling can be air assisted sprinkling, hydraulic assisted sprinkling where the inorganic liquid composition is made into a stream of droplets directed

towards the polymer containing product by use of gas or hydraulic. Alternatively, or in combination thereto, the droplets may be formed by use of ultra sound.

Preferably, the inorganic barrier layer 24 subsequently to being applied to said polymer containing product (26) is dried and/or cured. Such drying and/or curing may be provided by heating, such as forced heating, such as convective heating, e.g. by use of a gas flow where the gas has an elevated temperature (e.g. heated air), exposure to infra-red radiation, ultra violet radiation.

The inorganic barrier layer 24 is preferably, subsequently to being applied to the polymer containing product 26, primed or surface treated for adherence and/or spreading (or at least improvements thereof) of photocatalytic nano particles to the surface of the inorganic barrier layer 24 but also to create a better wetting of the surface to avoid excess amount of wetting agent to be used. The Contact Angle (CA) between water and the corona treated barrier layer surface is preferable lower than 60 º, 40 º, 20 º, 10 º. Such priming of surface treatment for adherence of photocatalytic nano particles may be selected from corona exposure, plasma exposure, flame oxidation exposure.

Priming may typically include, after the barrier layer is dried, hardened or in general set, a corona treatment e.g. to provide

- OH-groups providing chemical bonding cited for TiO_2
- A better wetting (lower contact angle) to allow a dispersion or solution containing the photocatalytic particle 22 to spread out, which also may reduce the amount of wetting agent

Preferably, the photocatalytic particles 22 are provided by depositing on the surface on the inorganic barrier layer 24. Such depositing may comprise spraying a dispersion comprising photocatalytic titanium dioxide nanoparticles onto said inorganic barrier layer 24. Such a dispersion is preferably an aqueous dispersion.

The surface of the polymer containing product 26 to which the inorganic layer 24 is provided e.g. as a coating may preferably be primed for adherence and/or spreading of the coating. Such as priming for adherence and/or spreading may be selected from corona exposure, plasma exposure, flame oxidation exposure.

In a preferred embodiment, the dispersion comprises:

- a solvent, preferably water;
- one or more co-solvents, preferably alcohol, such as isopropanol up to 15 wt%, more preferably up to 10 wt%;
- photocatalytic titanium dioxide nanoparticles in the range between 15 wt% and 2.5 wt%, such as 10 wt% or 5wt%; and
- means for keeping the dispersion stable, such as a dispersion agent, and preferably
- additives such as silica compounds.

The dispersion is preferably applied to the inorganic barrier layer in an amount of less than 200 ml/m^2, such as 150 ml/m^2, for example less than 100 ml/m^2, preferably less than 50 ml/m^2, such as less than 40 ml/m^2, preferably less than 30 ml/m^2, such as less than 20 ml/m^2

In other embodiments, the photocatalytic particles 22 are embedded in the inorganic barrier layer 24. In such embodiments, a liquid containing photocatalytic nano particles 22, and the inorganic substances forming the bulk of the inorganic layer is applied to the surface of the polymer containing product 26. If a priming for adherence and/or spreading is used, this priming is carrier out prior to application of the liquid.

The inorganic fluid composition, which at least partially forms the inorganic barrier layer, is typically a solution comprising a solvent and an inorganic substance is selected from silicone resin, methyl silicone, methylphenyl silicone, PMSQ silicone and mixtures hereof. The solvent can be for example alcohols, water and mixture hereof. Preferably, the amount of inorganic substance in said inorganic fluid composition is less than 25 wt %, such as between 1 and 10 wt %, preferable in between 4 and 6 wt %, such as 5 wt %.

The inorganic particles 25 are preferably selected from silica particles, alumina particles, and/or amorphous TiO2 particles. The size of the inorganic particles is preferably smaller than 250 nm, such as smaller than 100 nm, preferably smaller than 50 nm, such as smaller than 25 nm.

The weight ratio the inorganic particles 25 to the amount of inorganic matter in inorganic liquid composition is in the range of preferably 1:10, such as 1:4, preferably 1:2, such as 1:1, preferably 2:1, such as 4:1, preferably 10:1.

The coating provided by the inorganic barrier layer is typically provided so that the inorganic barrier layer 24 has a mass per square meter less than 100 g/m2, such as less than 50 g/m2, preferably less than 25 g/m2, for example less than 10 g/m2, such as less than 1 g/m2.

The coating is typically coated to provide the inorganic barrier layer 24 with a thickness less than 5.0 µm, such as less than 2.5 µm, preferably less than 1.0 µm, such as less than 0.75 µm, preferably less than 0.5 µm, such as less than 0.25 µm, for example less than 0.10 µm, such as less than 0.01 µm.
In some embodiments, the coating is typically coated to provide the inorganic barrier layer having a thickness of one or more monolayers, such as few monolayers.

After application of the inorganic barrier layer the samples was treated with a corona equipment yielding a hydrophilic surface prepared (primed) for the final coating of the photocatalytic TiO_2 particles.

The photocatalytic TiO_2 particles were for both samples coated with a coating bar yielding a thickness of appr. 50 g/m2. The samples was dried at ambient conditions.

A dispersion comprising 1.25 % of titanium dioxide nanoparticles with an average particle size in the dispersions (measured by Volume with Nanotrac NPA 252) measured to 27 nm was used. Less than 10 wt% of the solvent was isopropanol and the density was 1.04 g/ml. The photocatalytic TiO_2 dispersion was added 0.3 mL of non-ionic surfactant as wetting agent per liter of photocatalytic TiO_2 dispersion.

As disclosed herein (although not explicitly indicated in the figures), a polymeric product according to some embodiments of the invention comprising: a fiber

sheet 20, a polymeric layer 21 deposited onto the fiber sheet 20 and an inorganic barrier layer 24 deposited onto the polymeric layer 21. Photocatalytic titanium dioxide nanoparticles 22 are deposited and thus located in/on the inorganic barrier layer 24 alternatively or in combination thereto, photocatalytic particles may be embedded in the inorganic barrier layer.

In a preferred embodiment, the inorganic barrier layer is made from a resin, such as silicone resin.

The polymeric product is preferably made by a process similar to what is disclosed herein. Advantageously, prior to coating the inorganic barrier layer with a dispersion of photocatalytic substances, the inorganic barrier layer is exposed to a corona treatment in order to generate OH-cites where e.g. TiO_2 can react with to create chemical bonding between the inorganic barrier layer 24 and the photocatalytic substance 22. Alternatively, flame treatment may be applied instead.

Inorganic barrier layer:

According to preferred embodiments of the invention, the inorganic barrier layer is an inorganic silicone resin with good compatibility to organic resins. The inorganic barrier layer is therefore suited for adhering and making chemical bonds to an organic substrate, such as a polymer layer or a polymeric surface. The inorganic barrier layer can be dissolved in different solvents. The weight percentage of silicon resin in the inorganic barrier layer fluid is in the range 0-25 %, 1-10 %, preferably 5%. The inorganic barrier layer may include inorganic particles. The inorganic particles is in one preferred example added to improve the scratch resistance, wear resistance, strength of the layer.

The inorganic particles are preferably silica particles, alumina particles, amorphous TiO2 particles. The size of the inorganic particles is preferably smaller than 250 nm, 100 nm, 50 nm, 25 nm.

The inorganic barrier layer is applied with for example a roll, brush, spray (air, hydraulic, ultrasonic). The inorganic barrier layer is preferably dried and or cured. The drying and or curing could preferably be done with heat, forced heat, such as convective heating, e.g. by use of a gas flow where the gas has an elevated temperature (e.g. heated air), IR, UV. After drying, the inorganic barrier layer is

preferably treated such as to be primed for the TIO2 to adhere to the inorganic barrier layer. The priming could preferably be done with corona, plasma, flame oxidation. The inorganic barrier layer is typically applied with a quantity of less than 100 g/m2, 50 g/m2, 25 g/m2 such as the final thickness of the inorganic barrier layer is less than 5,0; 2,5 µm, 1.0 µm; 0.75 µm; 0.5 µm; 0.25 µm.

Further, it may be preferred that the thickness of the inorganic barrier layer 24 is as little as possible with a thickness approaching a mono layer.

In preferred embodiments, an upper limit of the inorganic barrier layer 24 is less than 100 g/m^2 (produced by use of an applicator bar of approximately 100 micro meter) with 20 wt% silicone resin in iso propanol. This typically provides 20 g/m^2 and a thickness of 20 micro meter.

In still further embodiments, a lower limit of the inorganic barrier layer 24 is less than: 10 g/m^2 (produced by use of an applicator bar of approximately 10 micro meter) with 2.5 wt% silicone resin in iso propanol. This typically provides a thickness of 250 nm (0.25 micro meter)

In still further embodiments, a lower limit of the inorganic barrier layer 24 is less than 75 nano meter.

Preferably, the thickness of the inorganic barrier layer is less 20 micro meter, such as less than 10 micro meter, such as less than 5 micro meter, preferably less than 1 micro meter, such as less than 0.5 micro meter, preferably less than 0.25 micro meter. The thickness preferably refers to the thickness of the dried and/or cured inorganic barrier layer 24.

It is found that although relatively thick inorganic barrier layer 24 is useable in connection with the present invention, it has been found that a relatively thick layer may cause mud cracking, delamination and/or other undesired effects. It is therefore preferred to make the barrier layer relatively thin. Further, as handling of the inorganic barrier layer may involve bending, rolling and other mechanical handlings, the inorganic barrier layer could advantageously be made flexible enough to withstand such mechanical handlings.

Example 1

Two different plastic foils, also referred as plast foils, were produced using an 'Automatic Film Applicator', comprising a base foil with PMMA top layer and a laminated foil with MMA top layer. The samples were made with a 15 µm application bar. A methylphenyl silicone resin was used as inorganic barrier layer using a 5 wt% silicone resin in iso propanol. After application the samples were cured and dried by forced drying (2 min at 60 ºC). Afterwards the samples were surface corona treated (20 W/m^2) until the contact angle with water was lower than 20º. Afterwards the photocatalytic dispersion was applied with a 15 µm application bar. The photocatalytic dispersion comprising 1.25 % of titanium dioxide nanoparticles with an average particle size in the dispersions (measured by Volume with Nanotrac NPA 252) measured to 27 nm was used. Less than 10 wt% of the solvent was isopropanol and the density was 1.04 g/ml. To the photocatalytic TiO_2 dispersion 0.3 mL of non-ionic surfactant as wetting agent per liter of photocatalytic TiO_2 dispersion was added. The photocatalytic coating was dried for 2 min at 60 ºC. After drying the samples were ready to be rolled up.

Example 2

A pilot scale production was performed producing photocatalytic composite façade sheets. The substrate was a fibre cement based material with an organic acrylic coating. To the fibre cement organic coating was applied the inorganic barrier layer which was a 5 % methylphenyl silicone resin. Approximately 20 g/m^2 was applied by a roll coater at a line speed of appr. 30/min. After application of the barrier layer the silicon resin was cured by IR and forced heated air at a temperature of 90 ºC for 30 sec. at a line speed of 3-4 m/min. After the curing the barrier layer was surface corona treated at 1000W 6m/min and until the contact angle with water was lower than 20º. Afterwards the photocatalytic dispersion was applied with a roll coater. Approximately 10g/m^2 was applied by a roll coater at a line speed of appr. 10 m/min. After application of the photocatalytic dispersion the product was dried under the same conditions as before. Hereafter the products were ready to be collected and packed. The photocatalytic dispersion comprising 1.25 % of titanium dioxide nanoparticles with an average particle size in the dispersions (measured by Volume with Nanotrac NPA 252) measured to 27 nm was used. Less than 10 wt% of the solvent was

isopropanol and the density was 1.04 g/ml. The photocatalytic TiO_2 dispersion was added 0.3 mL of non-ionic surfactant as wetting agent per liter of photocatalytic TiO_2 dispersion.

Example 3

Four samples produced according example 1 were tested for photocatalytic air purifying properties tested according to the NOx degrading properties after ISO 22197-1 before and after 300 hours of accelerated weathering according to EN 1297:2004. The results are shown in figure 6.

ISO 22197-1 test procedure: The NOx degrading performance of the sample was tested according to ISO 22197-1. The initial concentration of NO was 1.0 ppm and the flow of NO gas over the sample was 3 l/min. The concentrations of NO, NO_2 and NOx was analysed with a Horiba APNA NOx analyser model 370. The test cell was purchased from an accredited institute. The light intensity was 1.0 mW/cm^2 UVA measured with a PMA 2110 UVA detector and the relative humidity was kept constant at 45% ±5 %. The sample sizes in the test were $49x99mm^2$.

EN 1297:2004 Test Procedure. The EN 1297:2004 test weathering procedure consists of a dry cycle followed by a wet spray cycle. The dry cycle is 300 min of 45 W/cm2 ± 5 w/cm^2 UVA (340 nm) and a chamber temperature of 60 °C (BST). The wet spray cycle is 60 min of spraying de-ionized water (max conductivity of 500 µS/m) at a flow rate of 10 ± 3 $l/min/m^2$ with an initial temperature of the water of 25 ± 5 °C. The test is continued by repeating step 4 and 5 for a predetermined number of hours.

The data in the figure 6 shows that the inorganic barrier layer and the photocatalytic treatment is a robust and durable treatment where the particles are bonded to the inorganic barrier layer and not washed off after 300 hours of accelerated ageing. From the data in Figure 6 it is statistically not possible to detect a difference in the photocatalytic activity before and after 300 hrs of accelerated weathering for all four samples.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to

the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. In addition, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

CLAIMS

1. A method of producing a photocatalytic polymer containing product, said method comprising:

- providing a polymer containing product (26);
- coating said polymer containing product with an inorganic barrier layer (24);

wherein said inorganic barrier layer forms an internal surface in contact with said polymer containing product (26) and an external surface;

- modifying said external surface of said inorganic barrier layer by surface treatment;
- applying a dispersion of inorganic particles to the modified external surface;

wherein said inorganic particles of said dispersion of inorganic particles comprises photocatalytic particles (22).

2. A method according to claim 1, wherein said providing a polymer containing product comprises applying a polymer layer to a sheet as a coating and/or impregnation to provide a polymer containing product.

3. A method according to any of the preceding claims, wherein said photocatalytic particles (22) have a particle size in the micro and/or nano meter range.

4. A method according to any of the preceding claims, wherein said photocatalytic particles (22) are titanium dioxide nanoparticles.

5. A method according to any of the preceding claims, wherein said modifying said external surface changes surface properties by exposing chemical functional groups, such as OH groups.

6. A method according to any of the preceding claims, wherein said surface treatment comprises air plasma treatment, such as corona discharge treatments.

7. A method of producing a photocatalytic polymer containing product according to any of the preceding claims, wherein said coating said polymer containing product comprises:

- sprinkling, roll application or brush application said polymer containing product with an inorganic liquid composition being harden-able, cure-able, and/or setting-able.

8. A method of producing a photocatalytic polymer containing product according to any of the preceding claims further comprising, after coating said polymer containing product with an inorganic barrier layer (24):
- drying and/or curing said inorganic barrier layer (24)

9. A method of producing a photocatalytic polymer containing product according to any of the preceding claims further comprising, after applying a dispersion of inorganic particles to the modified external surface:
- drying and/or curing said inorganic particles (22) applied to the modified external surface.

10. A method of producing a photocatalytic polymer containing product according to any of the preceding claims further comprising:
modifying an external surface of said polymer containing product before coating said polymer containing product with an inorganic barrier layer (24).

11. A method of producing a photocatalytic polymer containing product according to claim 10, wherein modifying an external surface of said polymer containing product before coating said polymer containing product with an inorganic barrier layer (24)is a achieve by surface treatment.

12. A method of producing a photocatalytic polymer containing product according to claim 8, wherein said drying and/or curing said inorganic barrier layer (24) is provided by heating, such as forced heating, exposure to infra-red radiation, ultra violet radiation, microwaves or electron beam.

13. A method of producing a photocatalytic polymer containing product according to claim 9, wherein said drying and/or curing said dispersion of inorganic particles

(22) is provided by heating, such as forced heating, exposure to infra-red radiation, ultra violet radiation, microwaves or electron beam.

14. A method of producing a photocatalytic polymer containing product according to any of the preceding claims, wherein said applying dispersion of inorganic particles to the modified external surface comprises spraying a dispersion comprising photocatalytic titanium dioxide nanoparticles onto said inorganic barrier layer (24).

15. A method of producing a photocatalytic polymer containing product according to any of the preceding claims, wherein said dispersion of inorganic particles is an aqueous dispersion.

16. A method of producing a photocatalytic polymer containing product according to any of the preceding claims, wherein said dispersion comprises:

- a solvent, preferably water;
- one or more co-solvents, preferably alcohol, such as isopropanol up to 15 wt%, more preferably up to 10 wt%;
- photocatalytic titanium dioxide nanoparticles in the range between 15 wt% and 2.5 wt%, such as 10 wt% or 5wt%; and
- means for keeping the dispersion stable, such as a dispersion agent, and preferably
- additives such as silica compounds.

17. A method of producing a photocatalytic polymer containing product according to any of the preceding claims, wherein said dispersion is applied to the inorganic barrier layer in an amount of less than 200 ml/m^2, such as 150 ml/m^2, for example less than 100 ml/m^2, preferably less than 50 ml/m^2, such as less than 40 ml/m^2, preferably less than 30 ml/m^2, such as less than 20 ml/m^2

18. A method according to any of the preceding claims, wherein photocatalytic particles (22) are embedded in the inorganic barrier layer (24).

19. A method according to any of the preceding claims, wherein said coating said polymer containing product with an inorganic barrier layer (24) comprises coating

with an inorganic fluid composition, wherein said inorganic fluid composition is a solution comprising a solvent, preferably selected from alcohols, water and mixture hereof and an inorganic substance is selected from silicone resin, methyl silicone, methylphenyl silicone, PMSQ silicone and mixtures hereof.

20. A method according to claim 19, wherein said inorganic fluid composition comprises an of inorganic substance less than 25 wt %, such as between 1 and 10 wt %, preferable in between 4 and 6 wt %, such as 5 wt %.

21. A method according to any of the preceding claims, wherein said coating said polymer containing product with an inorganic barrier layer (24) provides said inorganic barrier layer (24) with a mass per square meter less than 100 g/m2, such as less than 50 g/m2, preferably less than 25 g/m2.

22. A method according to any of the of the preceding claims, wherein said coating said polymer containing product with an inorganic barrier layer (24) provides said inorganic barrier layer (24) with a thickness less than 5.0 µm, such as less than 2.5 µm, preferably less than 1.0 µm, such as less than 0.75 µm, preferably less than 0.5 µm, such as less than 0.25 µm.

23. A photocatalytic polymer containing product comprising:
- a polymer containing product (26);
- an inorganic barrier layer (24) coated onto said polymer containing product (26);
- inorganic particles comprising photocatalytic particles (22) onto and/or into said inorganic barrier layer (24).

24. A photocatalytic polymer containing product according to claim 23, wherein said photocatalytic particles (22) are embedded in said inorganic barrier layer (24).

25. A photocatalytic polymer containing product according to any of the claims 23-24, wherein the photocatalytic particles (22) are deposited on an outer surface of the inorganic barrier layer (24).

26. A photocatalytic polymer containing product according to any of the claims 23-25, wherein the photocatalytic particles (22) are embedded in said inorganic barrier layer (24) and deposited on an outer surface of said inorganic barrier layer (24).

27. A photocatalytic polymer containing product according to any of the preceding claims 23-26, wherein said photocatalytic polymer containing product is a consumable plastic product.

28. A photocatalytic polymer containing product according to any of the preceding claims 23-27, wherein said photocatalytic particles are discrete particles.

29. A photocatalytic polymer containing product according to any of the preceding claims 23-28, wherein said inorganic barrier layer (24) is a continuous inorganic barrier layer.

30. A photocatalytic polymer containing product according to any of the preceding claims 23-29, wherein said photocatalytic particles, such as titanium dioxide nanoparticles, are in an amount of 10 g/m^2or less, such as 5 g/m^2 or less, preferably 3 g/m^2 or less, more preferably 2 g/m^2 or less, most preferably 1 g/m^2 or less.

31. A photocatalytic polymer containing product according to any of the preceding claims 23-30, wherein said photocatalytic particles, such as titanium dioxide nanoparticles, have a primary size less than 50 nm, preferably less than 30 nm, more preferably less than 20 nm.

32. A photocatalytic polymer containing product according to any of the preceding claims 23-31, wherein said photocatalytic particles, such as titanium dioxide nanoparticles, have an agglomerate size of less than 300 nm, less than 200 nm, less than 100 nm, such as less than 80 nm preferably an aggregate size of less than 60 nm such as of less than 40 nm and even more preferably an aggregate less than 30 nm such as less than 20 nm.

33. A photocatalytic polymer containing product according to any of the preceding claims 23-32, wherein said photocatalytic particles, such as titanium dioxide nanoparticles, are in anatase phase.

34. A method of producing a photocatalytic polymer containing product according to any of the claims 8-9, 12 or 13 wherein said drying and/or curing may be achieved by exposing said polymer containing product to temperatures less than 100, such as less 80, preferably less than 60, such as less than 40 degree C, for period of times between 5 minutes down to 10 sec, such as less than 4 minutes, less than 3 minutes, less than 2 minutes or less than 1 minutes, such as less than 50 seconds, less than 30 seconds or less than 15 seconds.

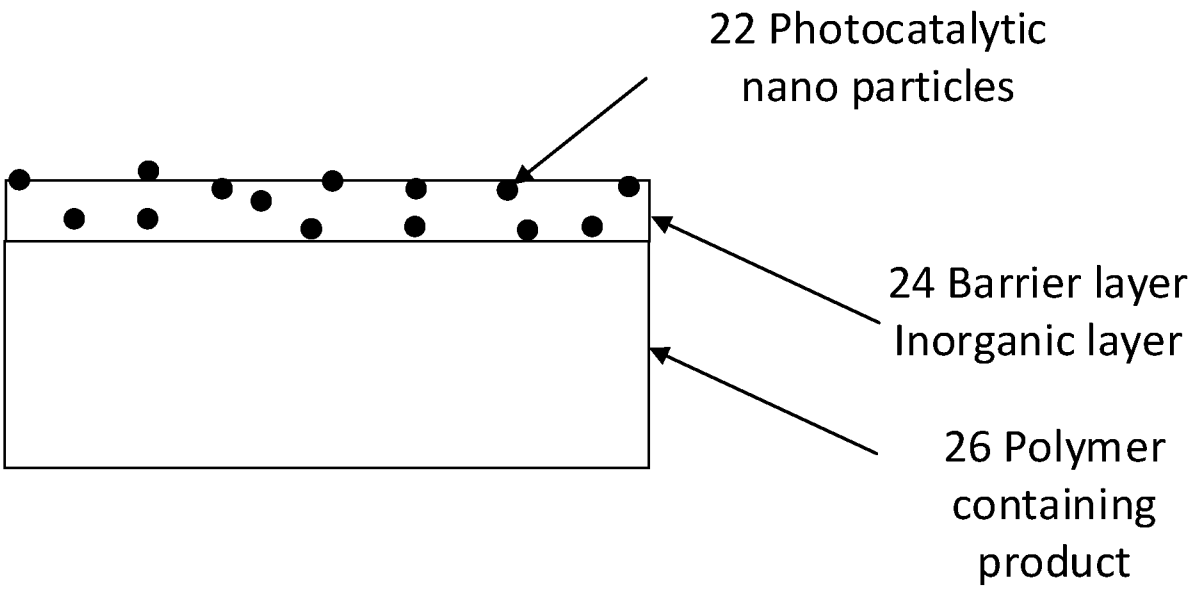
22 Photocatalytic
nano particles
24 Barrier layer
Inorganic layer
26 Polymer
containing
product

Fig. 1

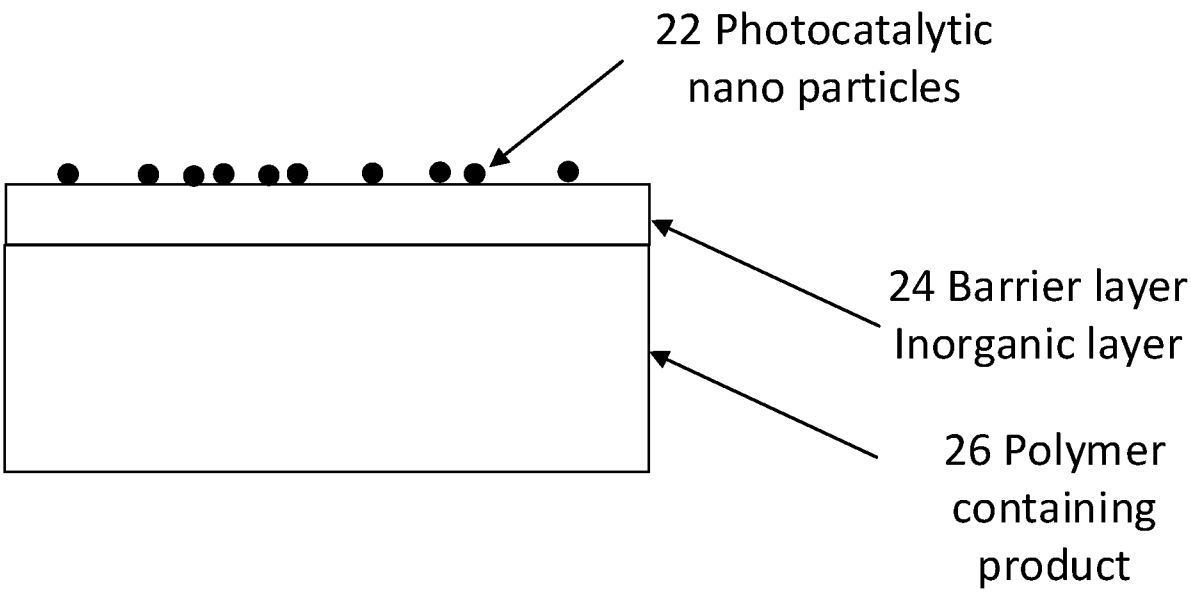
22 Photocatalytic
nano particles
24 Barrier layer
Inorganic layer
26 Polymer
containing
product

Fig. 2

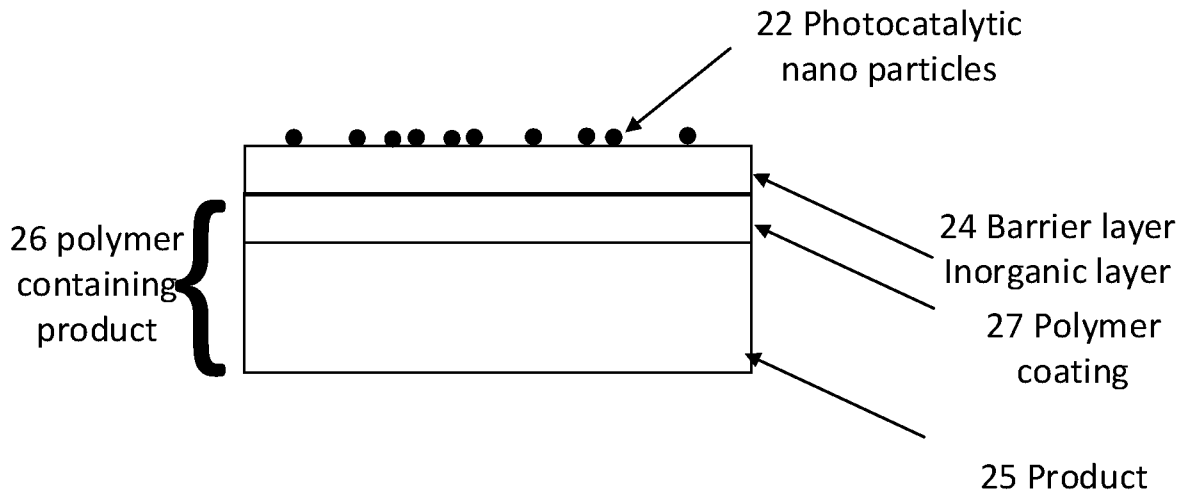

Fig. 3

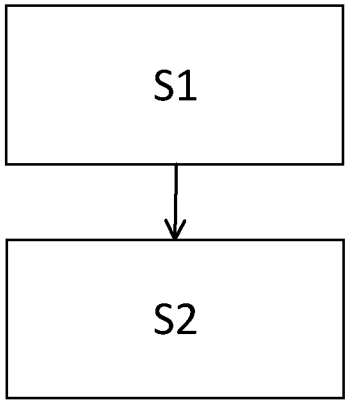

Fig. 4

Fig. 5

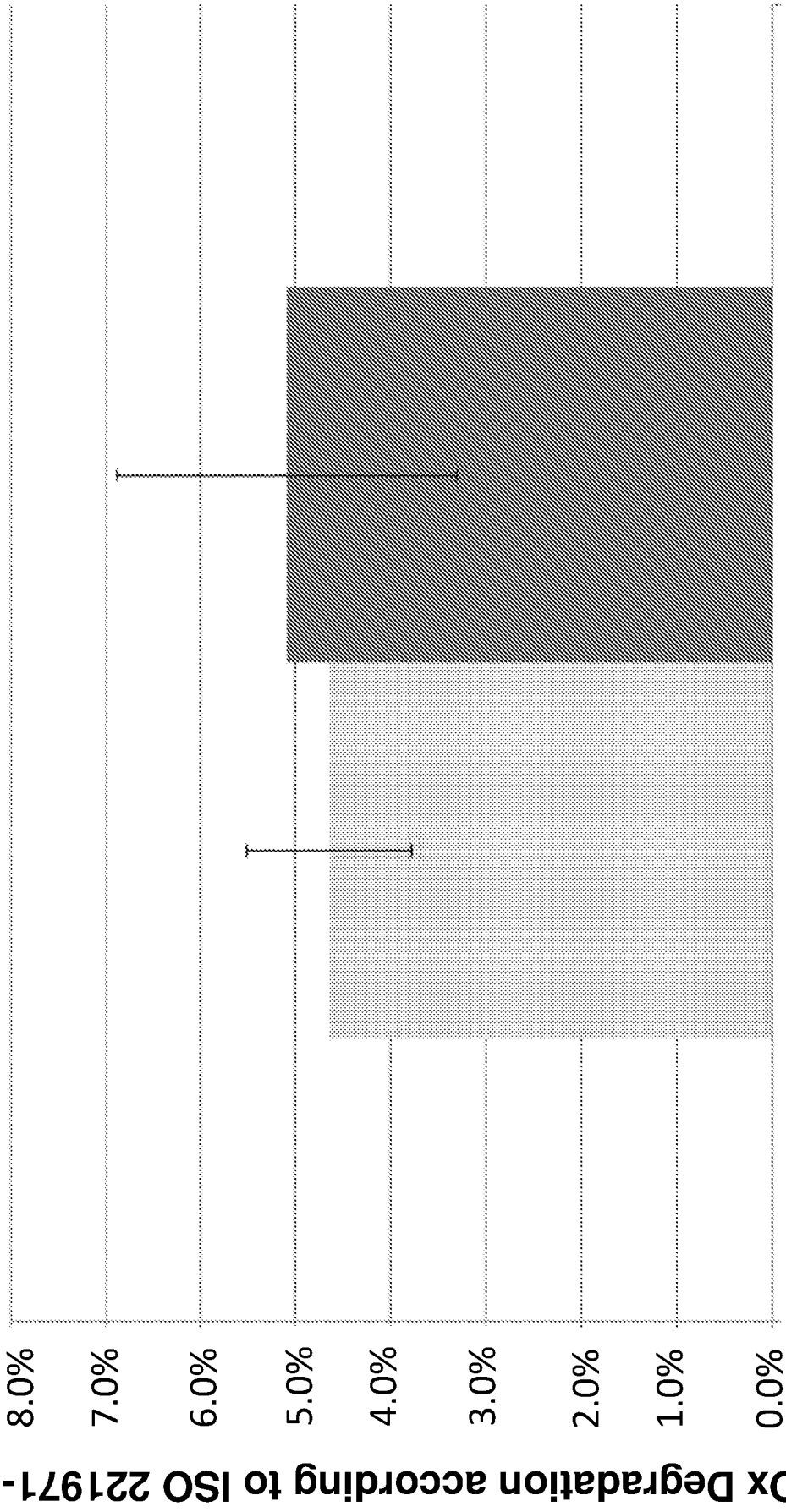
ISO 22197-1 before and after EN 1297:2004
NOx Degradation according to ISO 22197-1[%]
8.0%
7.0%
6.0%
5.0%
4.0%
3.0%
2.0%
1.0%
0.0%
Before Ageing
After 300 hr Ageing

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2017/050117

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J7/06 B01J37/02 B01J21/06 B01J35/00
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)
C08J B01J B01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/011684 A1 (JENSEN HENRIK [DK] ET AL) 10 January 2013 (2013-01-10) paragraph [0046] paragraph [0057]; figure 2 paragraph [0061] paragraph [0063] - paragraph [0072]; figure 3 paragraph [0075] - paragraph [0085]; example 1 ----- -/--	1-4, 7-31,34

[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

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"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
6 July 2017	14/07/2017

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	Meiser, Wibke

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2017/050117

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2004 021425 A1 (INST NEUE MAT GEMEIN GMBH [DE]) 24 November 2005 (2005-11-24) paragraph [0005] paragraph [0007] paragraph [0043] - paragraph [0045] paragraph [0053] paragraph [0059] paragraph [0062] paragraph [0100] - paragraph [0111] paragraph [0113] claims 1-37 -----	1,3-9, 18,21-34
X	WO 2014/098762 A1 (VÄLINGE PHOTOCATALYTIC AB [SE]) 26 June 2014 (2014-06-26) page 12, line 20 - page 21, line 17; figures 1-4 -----	1-4, 7-31,33, 34

1

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Information on patent family members

International application No
PCT/DK2017/050117

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		KR 20150100718 A	02-09-2015
		RU 2015127404 A	26-01-2017
		WO 2014098762 A1	26-06-2014