(54) Title: ELECTRO SPRAYING OF TITANIA FOR NITROGEN OXIDE ABATEMENT

Fig 1a

(57) Abstract: The invention provides a method for the production of a titania coating (80) on a surface (101) of an object (100) comprising electro spraying a titanium comprising liquid (15) to the surface (101) of the object (100) to provide a titanium comprising layer (85); and heating the titanium comprising layer (85) thus obtained to provide the titania coating (80), wherein the object (100) is an object selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element. Such object (100) may especially be used to abate the nitrogen oxide content in a nitrogen oxide comprising fluid (600).

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Electro spraying of titania for nitrogen oxide abatement

Field of the invention

The invention relates to a method for the production of a titania coating on a surface of an object and to the use of such product. The invention also relates to an object comprising a titania coating obtainable by such method.

The invention further relates to a method for the removal of a nitrogen oxide in a nitrogen oxide comprising fluid. The invention also relates to the use of electro spraying a titanium comprising liquid to a surface of an object.

Background of the invention

Photo catalysis is an emerging technology that has gained much attention in air and water pollution control. Photo catalytic oxidation (PCO) uses photo catalyst under UV/visible light illumination to oxidize pollutants to innocuous compounds. Some recent applications include indoor air cleaning, process vent treatment, groundwater treatment, disinfection of hospital rooms, and self-cleaning lamp covers. Recent advancements in visible-light-responsive photo catalysts make this technology even more attractive. Photo catalytic concrete and photo catalytic paints are known in the art.

WO0204569 for instance discloses a coating composition which comprises at least one calcium compound selected from the group consisting of lime, gypsum, calcium phosphate and calcium silicate, a water-soluble or water-dispersible resin, an inorganic oxide having photo catalytic activity and water and optionally an inorganic pigment such as titanium oxide and zinc oxide and a coated article having a coating film formed from the coating composition; and a method for carrying out or repairing the coating of an exterior or interior of a building by the use of the coating composition. The coating composition is capable of forming a coating film which has a photo catalytic function such as deodorizing property, antibacterial activity and air clarifying action, and also self-clarification action, and thus can maintain good appearance for a long period of time.

DE102006039249 for instance discloses a paving stone useful in parking lot and footpath, comprises a photo catalytic substance on its upper side, a material mixture consisting a raw material with doping component, a recess formed at its lower surface and/or at its side panels, and grooves. The photo catalytic substance is formed for
accelerating the dismantling process of a soiling on the upper side of the paving stone under effect of light. The photo-catalytic substance develops a catalytic effect, which is amplified if it is illuminated with UV light. The paving stone useful in parking lot and footpath comprises a photo catalytic substance on its upper side, a material mixture consisting of a raw material with doping component, a recess formed at its lower surface and/or at its side panels, and grooves. The photo catalytic substance is formed for accelerating the dismantling process of a soiling on the upper side of the paving stone under effect of light. The photo-catalytic substance develops a catalytic effect, which is amplified if it is illuminated with UV light. The photo-catalytic substance is concentrated in a layer at the upper side of the paving stone or is formed as a layer. The paving stone is made from concrete and the photo-catalytic material is added to the concrete as aggregate. The soiling is contained in rainfall. The paving stone is formed for liquids in infiltratable or non-infiltratable manner. The doping component in type and in quantity is determined in relation to its activity with certain lighting conditions or with the dismantling of certain types of soiling. The soiling has oil, which is removed under effect of the light. The grooves are deeply formed so that the incident light reaches the base of the recess. An independent claim is included for a surface reinforcement with paving stones.


WO2008010196 proposes a method for applying a nanostructured material onto articles, in particular tiles, glass and the like, includes the following work steps: preparation of a liquid, not gelatinized precursor obtained by solvolysis of titanium compounds (IV); application of a film of the precursor to the surface of an article; heat treatment of the compound formed by the article and the precursor, so as to cause the gelation of the latter, and the subsequent conversion of the precursor in the nanostructured material.
Summary of the invention

A disadvantage of prior art systems may be that the photo catalyst material is embedded in another material, such as concrete or a coating. Further, it is a disadvantage that prior art methods do not easily allow providing an efficient coating to ready or existing products such as elements of an existing road or an existing building. Hence, prior art systems may not efficiently abate nitrogen oxides (including nitrous oxide).

Hence, it is an aspect of the invention to provide an alternative method for the production of a titania coating on a surface of an object, which preferably further obviates one or more of above-described drawbacks. It is yet another aspect of the invention to provide an alternative object comprising a titania coating obtainable by such method, which preferably further obviates one or more of above-described drawbacks. Yet, it is further an aspect of the invention to provide an alternative method for the removal of a nitrogen oxide in a nitrogen oxide comprising fluid, especially air comprising a nitrogen oxide, which preferably further obviates one or more of above-described drawbacks.

To this end, the invention suggest the use of electro spraying titania, since surprisingly, this technique may allow providing relative reactive surfaces, may be applied on existing objects, and does not provide objects with coatings wherein the catalyst material is embedded in substantially non-reactive material.

The invention provides in a first aspect a method for the production of a titania coating on a surface of an object comprising

a. electro spraying a titanium comprising liquid to the surface of the object to provide a titanium comprising layer; and

b. heating the titanium comprising layer thus obtained to provide the titania coating.

This method may advantageously provide objects with a reactive surface for the abatement or removal of nitrogen oxide. Preferred objects of the invention are objects selected from the group of road or building objects such as consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element, in an embodiment, especially existing road or building objects (i.e. yet constructed road or building objects). In an embodiment, the object is a man-made
object. The term quay may also refer to wharf or pier, but especially relates to quays or
wharfs, especially quays.

Further, this method may advantageously provide titania coatings that are
substantially pure, i.e. free of organics (but optionally including inorganic dopants, see
below). Hence, the method may especially provide a titania coating, preferably free of
organic material, with preferably 90-100 wt.% of the metal elements in the titania
coating consisting of Ti, and with preferably a good porosity.

Hence, in an embodiment, the titania coating (thus obtained) is free of organic
material. The term “free of organic material” may especially indicate that the content of
organic material is less than 4 wt.%, especially less than 2 wt.%, even more especially
less than 1 wt.%, yet even more especially less than 0.5 wt.%, more preferably less than
about 0.2 wt.%, relative to the total weight of the titania coating. In an embodiment, the
titania coating comprises 0-2 wt.%, such as 0-0.5 wt.% organic material, relative to the
total weight of the titania coating. This may not exclude that during use of the titania
coating, organic materials may adsorb to the coating; however, such organic material is
not part of the titania coating (structure).

In a further embodiment, the titania coating (thus obtained) comprises at least 70
wt.%, preferably at least 80 wt.%, especially at least 90 wt.%, such as at least 95 wt.%,
especially 98-100 wt.%, such as at least 99.5 wt.% titanium, relative to the total amount
of metal elements in the titania coating. For instance, the titania coating may comprise
98 wt.% Ti (titanium) and 2 wt.% Fe (iron), relative to the total amount of metal
elements in the titania coating. In a specific embodiment, 90-100 wt.%, especially 95-
100 wt.% of the metal elements in the titania coating consists of Ti. The rest may in an
embodiment consist of one or more of Zn, Sn and Fe (see also below).

Further, the titania coating (thus obtained) may be (highly) porous, such as at
least 75% porosity.

This may provide a large free titania surface, in contrast to for instance concrete
tiles wherein titania is mixed with concrete mixture (in such system one could also not
speak of a coating) or in contrast to for instance dyes or paints, that are coated onto
tiles, etc.

Therefore, the invention especially provides the use of a road or a building object
having an electro sprayed titania coating (on its surface), for the abatement, especially
under influence of light, of a nitrogen oxide in a nitrogen oxide comprising fluid,
wherein the road or building object is preferably selected from the group consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element, wherein the titania coating preferably has a porosity of at least 75%. Especially, the titania coating is free of organic material (especially ≤ 4 wt.% organic material) and preferably 95-100 wt.% of the metal elements in the titania coating consists of Ti. Part or the entire surface of the object may be provided with the titania coating.

The light may comprise UV light, visible light or a combination of both. The nitrogen oxide may especially be selected from the group consisting of N₂O, NO, N₂O₃ and N₂O₄.

In a specific embodiment, the electro sprayed road or a building object has been obtained by electro spraying a road or building object after arranging at its predetermined position as road or building object. This is a further advantage, that the electro spray coating may be provided on existing objects (i.e. especially objects at their predetermined position).

The titanium comprising liquid may comprise any liquid that is able to provide a liquid comprising titanium, but especially comprises dissolved titanium, such as a titanium complex in a solvent. In a preferred embodiment, the titanium comprising liquid comprises one or more titanium compounds selected from the group consisting of titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra methoxide, and titanium tetra chloride. As solvent may for instance one or more solvents be used selected from the group consisting of ethanol, propanol and butanol. Such titanium compounds can also be indicated as precursors. Hence, the titanium comprising liquid especially is a titanium dioxide precursor comprising liquid.

Optionally, the titanium comprising liquid may further comprise dissolved zinc and/or dissolved tin. The oxides of the metals, or the mixed oxides of two or more of the metals Ti, Zn and Sn, may also be used to abate nitrogen oxides (in the fluid, see also below). Optionally, the titanium comprising liquid may (further) comprise other dissolved metals, such as dissolved iron. The oxides of such other metals, or the mixed oxides of two or more of the metals Ti, Zn, Sn, and other metals may also be used to abate or to promote abatement of nitrogen oxides (in the fluid, see also below). For instance, it appears that when iron (Fe) is added, the abatement of nitrogen oxides may already occur with visible light (only). Hence, optionally, the titanium comprising
liquid may further comprise a dissolved metal, that, when comprised by the titania coating, especially also allows or promotes abatement of nitrogen oxides. In a specific embodiment, the titanium comprising liquid may further comprise one or more dissolved metals selected from the group consisting of dissolved zinc, dissolved tin and dissolved iron.

Electro spray can for instance be created by an aerosol generator that produces first a conical droplet that breaks up into miniature droplets of nanometer or micrometer size because of electric charge forces. These droplets may contain titanium dioxide and titanium dioxide precursors (i.e. especially the above mentioned titanium compounds) and will be deposited on the surface of the object, such as objects of concrete, ceramic or any other material. Due to this electro spray method a thin layer of pure titanium dioxide remains after evaporation of the liquid carrier, and especially after subsequent heating (calcinations). The layer of titanium dioxide will be heated to (further) fix it on the surface. In this way, a highly porous titania coating may be provided.

The following reactions may take place during the flight of the droplet and/or on the surface of the object and/or during heating of the titanium comprising layer:

\[ \text{titanium comprising liquid} \rightarrow \text{hydrolyzed titania} + \text{liquid} \]

\[ \text{hydrolyzed titania} \rightarrow \text{titania} + \text{water (vapour)} \]

Hence, the process may be enhanced by providing water to the spray or to the layer, especially fluid comprising water vapour. Hence, in a specific embodiment, while electro spraying the titanium comprising liquid, fluid comprising water vapour is provided to a space between a nozzle opening of an electro spray apparatus and the surface of the object.

Optionally, while spraying or after spraying or while spraying and after spraying a fluid comprising $\text{H}_2\text{O}_2$ may be provided to the titanium comprising layer. This may further improve oxidation of the titanium compounds in (of) the titanium comprising liquid to titania or of the titanium compounds (including non-reacted titanium comprising compounds) in the titanium comprising layer.

For further oxidation and/or for further improvement of layer formation and/or for further improving adhesion with the surface of the object, the titanium comprising
layer obtained with electro spraying may be heated, for instance with a burner. Hence, in an embodiment, heating the titanium comprising layer comprises heating at a temperature in the range of 500-1500°C, especially in air (i.e. calcination). Preferably, heating is performed at a temperature of ≥ about 700 °C.

The titania coating obtained preferably comprises a relative highly porous structure. Preferably, the porosity of the titania coating is at least about 40%, such as at least 50%, preferably at least 75%, more preferably at least about 85%, yet even more preferably at least about 90%. Good results may be obtained with a porosity of about 75-95%, like 80-95%.

An advantage of the production method of the invention is that the production method may applied to an object of an existing road or building object, for instance to a sound barrier, a tunnel wall, etc. Of course, as mentioned above, the production method of the invention may also be applied to elements such as a tile, a tunnel wall element, a road element, a runway element, a quay element, a sound barrier element, that may later be applied as a road or building objects. For instance, tiles may be used to make roads, pavements, or walls of buildings such as houses or departments stores (such as façade panelling), quay elements may be used to build the quay roads or quay walls, etc.

In this way, the invention in a further aspect also advantageously provides a method for the removal of a nitrogen oxide in a nitrogen oxide comprising fluid, the method comprising exposing the nitrogen oxide comprising fluid, especially in the presence of light, to an object comprising a titania coating obtainable by a method for the production of a titania coating on a surface of an object comprising

a. electro spraying a titanium comprising liquid to the surface of the object to provide a titanium comprising layer; and

b. heating the titanium comprising layer thus obtained to provide the titania coating,

wherein the titania coating preferably has a porosity of at least 75%, wherein the titania coating is preferably free of organic material (such as 4 wt.% or less, or 2 wt.% or less, relative to the total weight of the titania coating), and wherein preferably 90-100 wt.% (relative to the total weight of the titania coating) of the metal elements in the titania coating consists of Ti.
The fixed titanium dioxide (titania) coating may be irradiated with light (UV light and/or visible light; especially UV light)(artificial or from the sun) and convert NO\(_x\) in dry air situations into nitrogen dioxide (NO\(_2\)) and in humid air or wet conditions into nitric acid and/or nitrous acid (HNO\(_3\), HNO\(_2\)). The latter (in wet conditions) may be converted into artificial fertilizer, because it can react with calcium carbonate granulates after removal. Hence, the removal method may further comprise washing the titania coating with a liquid and collecting the liquid after washing. Washing may be performed by natural washing (rain) or artificial washing, i.e. providing water to the surface. In this way, a substantial amount of the titania converted NO\(_x\) may be collected in for instance a gutter, arranged to collect the acids from the object.

The nitrogen oxide may be any nitrogen oxide, and may especially be selected from the group consisting of N\(_2\)O, NO, N\(_2\)O\(_3\), and N\(_2\)O\(_4\). Hence, the term “nitrogen oxide” may relate to a mixture of two or more types of nitrogen oxides. The fluid comprising the nitrogen oxide may especially be air. Air may comprise nitrogen oxides due to pollution from traffic and industry. With the removal method of the invention, harmful nitrogen oxides may be converted to NO\(_2\), and in the presence of water to acids, which may be collected (and reused). Hence, the fluid is especially a gas, even more especially air (or more precisely, especially nitrogen oxide polluted air).

Again, the object is preferably an object selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element. In a specific embodiment, the object is a tunnel wall element.

To enhance the conversion / abatement of the nitrogen oxides, the removal method may further comprise providing artificial UV and/or visible light to the titania coating. Herein, the term UV light relates to light having a wavelength in the range of about 190-400 nm. Hence, for instance a mercury lamp having an emission in the range of about 254 and/or about 365 nm might be applied as artificial UV light source. Also Xe discharge lamps might be applied. Such lamps are known in the art. Herein, the term visible (VIS) light relates to light having a wavelength in the range of larger than about 400 and up to about 780 nm. Herein, the term “light” relates UV and/or visible light, especially UV light. However, visible light alone may also suffice in an embodiment.
The invention provides in a further aspect an object comprising a titania coating obtainable by the production method as described herein. In a preferred embodiment, the titania coating has a porosity of at least 40%, such as at least 50%, like at 75%. In a further preferred embodiment, the titania coating is free of organic material (see also above). In yet a further preferred embodiment, at least 80 wt.%, such as 90-100 wt.% of the metal elements in the titania coating consists of Ti. In a specific embodiment, the object further comprises a liquid collection unit and/or a water distribution unit. Such water distribution unit may be arranged to provide water, such as rain water, to at least part of the titania coating on the surface of the object.

The coating may be coated to part of the surface of the object or to the entire surface of the object.

Therefore, the invention also provides in an aspect the use of electro spraying a titanium comprising liquid to a surface of an object to provide a titanium comprising layer and subsequent heating of the titanium comprising layer thus obtained to provide an titania coating on the surface of the object. More especially, the invention provides the use of electro spraying, the object is further used to abate the nitrogen oxide content in a nitrogen oxide comprising fluid.

The technique of electro spraying per se is known in the art. For instance, US2005139156 describes an apparatus and method for manufacturing ultra-fine particles using an electro spray device is disclosed. One or more capillary provided at its tip with a nozzle is positioned within a guide duct and precursors such as metal organic materials and metal halogen compounds, or non-volatile substances or volatile substances are supplied to the capillary. Voltages are applied to the capillary and the guide duct, respectively, so that a voltage difference is generated there between and the highly charged liquid droplets from the capillary are sprayed. The sprayed liquid droplets are carried along the guide duct together with carrier gas injected into the guide duct. When heat energy is applied to the liquid droplets, chemical reactions of the liquid droplets occur. A collecting plate positioned in front of the guide duct collects ultra-fine particles formed by the chemical reactions.
Brief description of the drawings

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Figures 1a-1c schematically depict an embodiment of an electro spray apparatus and the process of providing the titania layer;

Figures 2a-2d schematically depict a number of embodiments wherein the titania coated object is used;

Figures 3a-3b depict SEM figures of tiles with a titania coating according to the invention.

The figures are not necessarily on scale.

Description of preferred embodiments

Figure 1a schematically depicts an embodiment and variations thereon of the method for the production of a titania coating on a surface 101 of an object 100. The object 100 may be any object 100, such as an object 100 selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element. The titania coating is provided by electro spraying a titanium comprising liquid 15 (herein also indicated as “liquid 15”) to the surface 101 of the object 100 to provide a titanium comprising layer 85. To this end, an electro spray apparatus 1 (also indicated as “apparatus 1”) is provided, which comprises a nozzle 10 (which may include a plurality of nozzles) with nozzle opening(s) 11. Through this nozzle opening 11, the liquid 15 is ejected and a spray 50 is formed. Liquid 15 may be obtained from a liquid reservoir 5.

Between the nozzle 10 and another object, an electric field is applied. Due this electric field, which may be in the range of about 1-25 kV, such as about 2-20 kV, the shape of the pending droplet (at nozzle opening 11) changes into a conical shape. By electrostatic, surface tension forces and hydrodynamic forces, at the tip a cone, also called “Taylor cone” is created, from the apex of which a (small) jet emerges which breaks up into droplets. The droplets, indicated with reference 55, may be in the range of about 1 nm to about 50 μm. During the flight of the droplets 55, at least part of the solvent (see below) may evaporate. At least part of the total amount of moles titanium compounds dissolved in the solvent may react to titania that impinges on the surface
101 of the object 100. The surface 101 to be coated is arranged opposite (downstream) of the nozzle opening 11. The surface 101 is at least arranged that during use of the electro spray apparatus 1, the spray 50 may reach the surface 101 of the object 100.

The other object, between which and the nozzle 10 an electric field is applied, may be the object 100 with surface 101 or may be a counter of shielding electrode 30. This counter electrode 30 is especially arranged to allow the spray pass by. For instance, a hollow round counter electrode 30 may be used. Optionally, instead of the counter electrode 30, the object 100 is used as counter electrode. Further optionally, an electric field is applied between the nozzle 10 and the counter electrode 30, and electric field is applied between the counter electrode 30 and the object 100. Characteristic distances between the nozzle opening 11 and the counter electrode are in the range of 1-10 cm and between the counter electrode 30 and the surface 101 in the range of about 2-20 cm. The technique of electro spraying is known in the art, and is for instance described in the Proceedings of the International Workshop on the Synthesis and measurements of Ultrafine Particles, Delft, May 28-29, 1993, pages 71-78 (Vercoulen et al); A.A. van Zomeren et al in J. Aerosol. Sc. Vol. 25 (6) 1994, 1229-1235; J.P. Borra et al in J. Aerosol. Sc. Vol. 30 (7) 1999, 945-958, which are herein incorporated by reference.

Hence, in general there are a number of preferred options to apply the electric field(s).

Preferably, an electric field is applied between the nozzle 10 and counter electrode 30, preferably a ring-shaped counter electrode 30. Preferably, the object 100 is grounded (when present as existing road or building object, such object 100 is in general grounded per se). Hence, a power source 42 may be arranged to apply the electric field between nozzle 10 and counter electrode 30.

Optionally, in addition thereto, an electric field may be applied between the ring-shaped counter electrode 30 and the object 100, which electric field has preferably the same direction as the field between the nozzle 10 and the counter electrode 30. Hence, a power source 43 may be arranged to apply the electric field between the counter electrode 30 and the object 100.

Alternatively, an electric field may be applied between the nozzle 10 and the object 100. Hence, a power source 41 may be arranged to apply the electric field between the nozzle 10 and the object 100.
The layer formed, indicated with reference 85 (see figure 1b) may be a mixture of titaniam, hydrolyzed titaniam, titanium compounds from the liquid 15 (such as titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra methoxide, and/or titanium tetra chloride) and optionally some solvent. This layer is indicated as titanium comprising layer 85 and can be seen as precursor layer of the titaniam coating 80. Hence, the method further especially comprises heating the titanium comprising layer 85 thus obtained to provide the titaniam coating 80. Further, by heating the adhesion of the titaniam layer 80 to the surface 101 is improved. Heating may be performed at for instance a temperature in the range of about 500-1500°C, preferably above about 700 °C. Further, especially the anatase type of titaniam is comprised by the layer 80.

To promote titaniam formation, while electro spraying the titaniam comprising liquid 15 further fluid 65 comprising water vapour may be provided to a space between the nozzle opening 11 of the electro spray apparatus 1 and the surface 101 of the object 100. To this end, further a fluid supply 60 with fluid supply opening 61 may be provided, which is arranged to provide the fluid 65 in the space between the object 100 and the nozzle opening 11. Especially this fluid may comprise water vapour, such as steam, or air with water droplets, which further promotes reaction of the titanium compounds from the liquid into hydrolyzed titaniam, and optionally also titaniam. Hence, the fluid 65 may especially comprise a water spray or a water vapour (such as steam).

Further to promote titaniam formation, while spraying or after spraying or while spraying and after spraying a fluid 65 comprising H₂O₂ is provided to the titanium comprising layer 85. Hence, fluid 65 may comprise water vapour and/or H₂O₂ (vapour).

Hence, during the above described process, and especially while heating, the titaniam layer 80 is provided, see figure 1c.

An advantage of the method is that the method may be applied to an object of an existing road or building object, such as tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element.

Figures 2a-2d by way of example show a non-limiting number of possible embodiments, wherein figure 2a schematically shows a tunnel 300 (as road or building object), figure 2b schematically shows a sound barrier 400 (as road object) and a pavement 500 (as road object), and figures 2c and 2d schematically shows variations on the sound barrier 400 (as road object), especially in relation to a water distribution unit 140.
Referring to figure 2a, the tunnel 400 encloses part of a road 200. The tunnel is at least partly composed of tunnel elements or tunnel wall elements 301. In this embodiment, the tunnel wall elements 301 may be the objects 100 with titania coating 80. In this figure, a number of tunnel wall elements 301 is shown, but it may also be possible that the tunnel wall can be considered as one single (concrete) wall, substantially consisting of only one tunnel wall element 301 (i.e. here the tunnel wall). The tunnel 300 further comprises tunnel lighting units 70, which may be arranged to (further) provide light 71, such as UV light and/or visible light. Preferably, the lighting units 70 are arranged top provide light 71 substantially only to the titania coated objects 100 (i.e. here tunnel wall elements 301), thereby substantially avoiding illuminating the road with (UV) light 71 (i.e. thereby substantially preventing (UV) light 71 illumination of traffic). Optionally, a liquid collection unit 110 is arranged to collect liquid dripping from the objects 100.

Air, as nitrogen oxide comprising fluid, within the tunnel 300, is indicated with reference 600. Nitrogen oxides within the tunnel comprised in air 600 may be abated due to the presence of the titania layer 80 on the objects 100 and the UV light 71.

Figure 2b schematically depicts again a part of road 200, along which on the left side pavement 500 and on the right side sound barrier 400 are shown. Right from the sound barrier 500, again pavement 500 is shown. The pavement 500 may comprise pavement elements 501, such as tiles or plates, for instance from concrete or stone, etc. Here, the pavement elements 501 may be the objects 100, i.e. at least part of the pavement 500 may comprise objects 100. Further, the sound barrier 400 may consists of elements 401, like plates or bricks, etc. In this embodiment, the sound barrier elements 401 may be the objects 100.

Air 600, as nitrogen oxide comprising fluid, over road 200, pavement 500 and sound barrier 400, is indicated with reference 600. Nitrogen oxides comprised in air 600 may be abated due to the presence of the titania layer 80 on the objects 100 and the UV light 71. The sound barrier 400 may comprise a water distribution unit 140, arranged to provide water to at least part of the titania coating 80 on the object(s) comprised by the sound barrier 400. Such water distribution unit 140 may for instance be a kind of sprinkler arrangement, especially arranged to collect rain water and/or arranged to collect groundwater and/or surface water (such as from a ditch) and/or tap water, and especially arranged to distribute this rain water over the coating 80. In this
way the titania coating 80 may be washed with a liquid (especially rain water). Further, the sound barrier 400 may comprise liquid collection unit 110, arranged to collect the liquid from the coating, which may comprise acid rain water (such as rain water comprising HNO₃ and HNO₂).

Figure 2c schematically depicts a cross section of an embodiment of the object 100 with water distribution unit 140 and liquid collection unit 110, wherein the object 100 may for instance be integrated in sound barrier 400. In this schematically depicted embodiment, the water distribution unit 140 comprises one or more spray nozzle 141, arranged to distribute water over the coating 80 of object 100.

Finally, figure 2d schematically depicts again a cross section of an embodiment of the object 100 with water distribution unit 140 and liquid collection unit 110, wherein the object 100 may for instance be integrated in sound barrier 400. In this schematically depicted embodiment, the water distribution unit 140 in this embodiment comprises a surface 142, arranged to receive rain water and arranged to distribute the rain water over the coating 80 of the object 100. In this embodiment, the surface 142 is simply a slanted surface, having an angle α relative to a horizontal larger than 0° and smaller than 90°, being substantially adjacent to part of the coating 80, such that rain water flows from the surface 142 down on the coating 80.

In these and other ways, objects 100 may be integrated in road and building objects such as street furniture (like sound barriers), which allows application of the method for the removal of a nitrogen oxide in the nitrogen oxide comprising fluid 600, wherein the nitrogen oxide comprising fluid 600 is exposed to object 100 comprising titania coating 80, which coating 80 is obtainable by the above described and herein claimed method for the production of the titania coating 80 on surface 101) of the object 100.

Therefore, it appears that electro spraying of a titanium comprising liquid 15 to the surface 101 of object 100 to provide titanium comprising layer 85 and subsequent heating of the titanium comprising layer 85 thus obtained to provide titania coating 80 on the surface 101 of the object 100, provides the object 100 that may advantageously be used to abate the nitrogen oxide content in a nitrogen oxide comprising fluid 600, such as air.

Thus, the invention provides a method for the production of a titania coating 80 on a surface 101 of an object 100 comprising electro spraying a titanium comprising
liquid 15 to the surface 101 of the object 100 to provide a titanium comprising layer 85; and heating the titanium comprising layer 85 thus obtained to provide the titania coating 80, wherein the object 100 is an object selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element. Such object 100 may especially be used to abate the nitrogen oxide content in a nitrogen oxide comprising fluid 600.

Example

A tile was coated according to the invention (E1), having a high porosity, see also exemplary SEM figures 3a-3b (Figure 3a shows in detail the titania coating and Figure 3b shows part of the tile, and on top thereof the titania coating).

Further, a porous material was coated with a titania paint (PA1) and a non-porous material is coated with a titania containing paint (PA2).

Both were arranged in a reactor and measured on the removal of nitrogen oxides in the reactor, in the presence of absence of UV light.

It is found that the abatement with E1 is high. Also PA1 reduces the amount of nitrogen oxides, also in the absence of light. It appears that the removal capacity of PA1 of nitrogen oxides reduces with time. It is concluded that PA1 substantially only reduces the amount of nitrogen oxides due to adsorption, such as by the porous substrate. PA2 has hardly any activity.

The term “substantially” herein, such as in “substantially all emission” or in “substantially consists”, will be understood by the person skilled in the art. The term “substantially” may also include embodiments with “entirely”, “completely”, “all”, etc. Hence, in embodiments the adjective substantially may also be removed. Where applicable, the term “substantially” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. The term “comprise” includes also embodiments wherein the term “comprises” means “consists of”.

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of
the invention described herein are capable of operation in other sequences than described or illustrated herein.

The devices herein are amongst others described during operation. As will be clear to the person skilled in the art, the invention is not limited to methods of operation or devices in operation.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. Use of the verb "to comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The invention may be implemented by means of hardware comprising several distinct elements, and by means of a suitably programmed computer. In the device claim enumerating several means, several of these means may be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.
Claims

1. Use of a road or a building object (100) having an electro sprayed titania coating (80), for the abatement, under influence of light, of a nitrogen oxide in a nitrogen oxide comprising fluid, wherein the road or building object is selected from the group consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element, wherein the titania coating (80) has a porosity of at least 75%.

2. Use according to claim 1, wherein the titania coating (80) is free of organic material and wherein 95-100 wt.% (relative to the total weight of the titania coating) of the metal elements in the titania coating (80) consists of Ti.

3. Use according to any one of the preceding claims, wherein the titania coating comprises ≤ 0.5 wt.% (relative to the total weight of the titania coating) organic material.

4. Use according to any one of the preceding claims, wherein the light comprises UV light.

5. Use according to any one of the preceding claims, wherein the light comprises visible light.

6. Use according to any one of the preceding claims, wherein the nitrogen oxide is selected from the group consisting of N₂O, NO, N₂O₃ and N₃O₄.

7. Use according to any one of the preceding claims, wherein the electro sprayed road or a building object (100) has been obtained by electro spraying a road or building object after arranging at its predetermined position as road or building object.

8. A method for the production of a titania coating (80) on a surface (101) of an object (100) comprising
   a. electro spraying a titanium comprising liquid (15) to the surface (101) of the object (100) to provide a titanium comprising layer (85); and
   b. heating the titanium comprising layer (85) thus obtained to provide the titania coating (80),

wherein the object (100) is an object selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element.
9. The method according to claim 8, wherein the titanium comprising liquid (15) comprises one or more titanium compounds selected from the group consisting of titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra methoxide, and titanium tetra chloride.

10. The method according to any one of claims 8-9, wherein while electro spraying the titanium comprising liquid (15) further fluid (65) comprising water vapour is provided to a space between a nozzle opening (11) of an electro spray apparatus (1) and the surface (101) of the object (100).

11. The method according to any one of claims 8-10, wherein while spraying or after spraying or while spraying and after spraying a fluid (65) comprising H₂O₂ is provided to the titanium comprising layer (85).

12. The method according to any one of claims 8-11, wherein heating the titanium comprising layer (85) comprises heating at a temperature in the range of 500-1500°C.

13. The method according to any one of claims 8-12, wherein the method is applied to an object of an existing road or building object.

14. The method according to any one of claims 8-13, wherein the titania coating (80) obtained is free of organic material and wherein 90-100 wt.% (relative to the total weight of the titania coating) of the metal elements in the titania coating (80) consists of Ti.

15. A method for the removal of a nitrogen oxide in a nitrogen oxide comprising fluid (600), the method comprising exposing the nitrogen oxide comprising fluid (600) in the presence of light to an object (100) comprising a titania coating (80) obtainable by a method for the production of the titania coating (80) on a surface (1010) of an object (100) comprising

a. electro spraying a titanium comprising liquid (15) to the surface (101) of the object (100) to provide a titanium comprising layer (85); and

b. heating the titanium comprising layer (85) thus obtained to provide the titania coating (80),

wherein the titania coating (80) has a porosity of at least 75%, wherein the titania coating (80) is free of organic material, and wherein 90-100 wt.% (relative to the total weight of the titania coating) of the metal elements in the titania coating (80) consists of Ti.
16. The method according to claim 14, wherein the nitrogen oxide is selected from the group consisting of N₂O, NO, N₂O₃ and N₃O₄.

17. The method according to any one of the claims 15-16, wherein the object (100) is an object (100) selected from the group of road or building objects consisting of a tile, a tunnel wall element, a road element, a runway element, a quay element, and a sound barrier element.

18. The method according to any one of the claims 15-17, further comprising providing artificial light (71) to the titania coating (80).

19. The method according to claim 18, wherein the object (100) is a tunnel wall element.

20. The method according to any one of the claims 15-19, further comprising washing the titania coating (80) with a liquid and collecting the liquid after washing.

21. An object (100) comprising a titania coating (80) obtainable by the method according to any one of the claims 8-14.

22. The object according to claim 21, wherein the titania coating (80) has a porosity of at least 75%, wherein the titania coating (80) is free of organic material, and wherein 90-100 wt.% (relative to the total weight of the titania coating) of the metal elements in the titania coating (80) consists of Ti.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. CO4B41/50
B01J35/00

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)
CO4B

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

Electronic database consulted during the international search (name of database and, where practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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31 July 2008 (2008-07-31)
abstract | 21,22 |

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Further documents are listed in the continuation of Box C.

See patent family annex.

**Date of the actual completion of the international search**

30 November 2009

**Date of mailing of the international search report**

28/12/2009

**Name and mailing address of the ISA/European Patent Office, P.B. 5318 Patentlaan 2 NL-2300 HJ Rijswijk, Tel. (+31-70) 940-3040, Fax (+31-70) 940-3010**

Authorized officer
Rosenberger, Jürgen
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### INTERNATIONAL SEARCH REPORT

**Information on patent family members**

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<td>WO 2008010196 A</td>
<td>24-01-2008</td>
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