
COATING COMPOSITION

The invention relates to a composition for coating walls, façades or the like.

Such compositions are used, for example, for the manufacture of paints and plaster systems for interior and exterior applications. A special area of application of such compositions is the manufacture of thermal insulation composite systems. In these applications, these compositions can especially be used for the manufacture of a top coating for thermal insulation composite systems. Here, in some cases, an algae and fungus infestation of the top coating can occur following the completion of the respective thermal insulation composite systems, especially on the northern side of buildings.

In view of these problems in the state of the art, the invention is based on the problem of providing a composition of the kind described above, allowing the effective blocking of such algae and fungus growth, and a method for producing such compositions.

In accordance with the invention, this problem is solved by means of a further development of the known compositions, which is essentially characterized in that the composition exhibits a photocatalytically active substance with a significant light absorption at at least one absorption wavelength in the range of 380 to 500 nm.

This invention is based on the insight that photocatalytically active substances can be used not only for the degradation of pollutants, as set forth in DE 100 64 317 A1, but also for the blocking of the cell growth of algae and fungi. In this process, the special properties of the photocatalytically active substance, which is used in accordance with the invention, enable the utilization of normal sunlight which hits interior spaces and also the northern side of buildings via reflection and dispersion, while at the same time ensuring that the photocatalysis on the photocatalytically active substance takes place due to the use of the binders with the properties described. Overall, this makes it possible to effectively reduce the algae and fungus growth even without the use of the traditionally employed biocides to inhibit algae and fungus growth.

In an especially preferred composition within the framework of the invention, the ratio of absorbance (Kubelka-Munk function $F(R_{00})$) of the photocatalytically active substance to the absorbance (Kubelka-Munk function $F(R_{00})$) of the binder is greater than 6.25×10^{-3} , preferably greater than 1×10^{-2} at at least one absorption wavelength in the range of 380 and 500 nm. In this composition, the binder can exhibit an absorbance of less than 0.8, specifically less than 0.5, at at least one absorption wavelength in the range of 380 to 500 nm, specifically in the range of 400 to 450 nm, if the photocatalytically active substance exhibits an absorbance of more than 0.005, specifically more than 0.01, and especially preferably 0.02 or more, under the same measuring conditions at the absorption wavelength.

Binders used within the context of the invention may exhibit organic and / or inorganic constituent parts. The use of binders which exhibit, as the case may be, exclusively inorganic constituent parts has proven expedient with respect to the prevention of a photocatalytically induced decomposition of the binder.

In an especially preferred embodiment of the invention, the binder may exhibit at least one organic component and at least one inorganic component. By carefully selecting the binder, it is possible to ensure that radicals produced by the photocatalytic substances do not result in the decomposition of the binder and a respective chalking of the wall or façade coating. In accordance with an especially preferred embodiment of the invention, the photocatalytically active substance exhibits a semiconductor, specifically TiO_2 . With semiconductors, the photocatalytic action is generated by the production of electron hole pairs at the incidence of light, which produce highly reactive free radicals at the surface of the material which can contribute to the blocking of the cell growth. Titanium dioxide is such a semiconductor. By using titanium dioxide, it is possible to achieve a photocatalytic action in the wavelength range of 400 to 450 nm when a mixing, especially doping with a foreign substance, such as e. g. S, N and/or C takes place.

In this context, it has proven to be especially advantageous in view of the desired photocatalytic action in the wavelength range of 400 to 450 nm if the sulfur and/or carbon content of the titanium dioxide used as photocatalytically active substance is 0.05 to 4 percent by weight, preferably 0.05 to 2 percent by weight and especially preferably 0.4 to 1.5 percent by weight. It has been shown that the desired effect manifests especially noticeably if the titanium dioxide, as the case may be mixed with sulfur and/or carbon, is present in the anatase phase. It has furthermore proven to be advantageous if the sulfur and/or carbon is incorporated only in a surface layer of the titanium dioxide particles of the composition in accordance with the invention.

The photocatalytically active substance shows a particularly good action if it exhibits a specific surface pursuant to BET of 100 to 250 m^2/g , preferably 130 to 170 m^2/g , and/or does not show carbonate bands either in the X-ray photo electron spectrum or in the infrared spectrum. In view of a particularly high absorbance of the photocatalytically active substance in the range of 400 to 450 nm, it has proven to be advantageous if the photocatalytically active substance is at least partially prepared by mixing a titanium-containing compound, preferably dissolved in a solvent, with an organic carbon compound and by thermal treatment of this mixture at a temperature of 500 °C or less, preferably 400 °C or less, and especially preferably 350 °C or less, and over 150 °C, especially over 200 °C or more.

The photocatalytically active substance thus obtained may exhibit especially strong absorption bands given a bond energy of 285.6 eV in the X-ray photo electron spectrum (XPS) relative to the O1s band at 530 eV.

To obtain a composition that suppresses the cell growth particularly effectively, it has proven to be expedient to use an amorphous, partially crystalline or crystalline titanium oxide or hydrous titanium oxide or a titanium hydrate or a titanium oxyhydrate to produce the photocatalytically active compound, with the titanium-containing compound possibly being a titanium hydrate from a sulphate process. The titanium hydrate can be neutralized and washed beforehand, so that the SO_3 content of the solid substance after drying is less than 1 percent by weight. The carbon compound employed for the production of the photocatalytically active substance used in the composition in accordance with the invention expediently has a decomposition temperature of max. 400 °C, especially preferably 350 °C or less, specifically 300 °C or less. In this context, the carbon compound can comprise at least one functional group, such as e. g. an OH-, CHO-, COOH- and NH_x and/or SH_x group. The use of ethylene glycol, glycerin, carbohydrates, ammonium hydroxides or mixtures thereof has proven to be especially expedient. In addition or as an alternative, carbon black or activated charcoal can be used as carbon compound. In the production of the photocatalytically active substances to be used in a composition in accordance with the invention, the thermal treatment can take place in a calcination unit, preferably a rotary furnace, to be operated continuously, whereby a titanium dioxide commercially available in powder or sludge form is used for the preparation of a suspension in a solvent and a small amount of the carbon disulphide compound is added to and mixed with this suspension, the solvent is removed, the residue is dried at a drying temperature and then calcinated at a calcination temperature. E. g. water can be used as solvent.

In view of the achievement of an especially strong photocatalytic action, it has proven to be expedient to heat the dried residue in a closed container to 300 °C within one hour and then to maintain it for another three hours at this temperature. The calcination of the powdery residue by heating expediently takes place until, following a color change from white to dark brown, another color change to beige takes place.

In addition to the at least one binder and the photocatalytically active substances, the composition according to the invention can also comprise a dispersing agent, such as e. g. sodium polyphosphate and/or a solution of polyacrylate, sodium salt, at least one thickening agent, such as e. g. modified methyl hydroxy ethyl cellulose, hydrophobic polyurethane, cellulose ether, and/or a polysaccharide, an anti-foaming agent, such as e. g. a mixture of paraffin oil, hydrophobic silicic acid and emulsifying agents, and/or polysiloxane copolymer with hydrophobic silicic acid, emulsified in water, at least one pigment, such as e. g. titanium dioxide, at least one filler, such as e. g. a silicate, kaolin or the like, at least one hydrophobization agent, such as e. g. a potassium methyl siliconate in aqueous solution and/or at least one microbiocide or in-can preservative, such as e. g. isothiazolinone. The coating obtained with a composition in accordance with the invention can exhibit a structure with a grain size of up to 6 mm. In addition or as an alternative, the compositions according to the invention can also comprise adsorbing agents, such as activated charcoal, silicic acid and micro silica. In this case, the substances adsorbed on the adsorbing agent can be effectively decomposed using the photocatalytically active substance of the composition.

It has proven to be especially advantageous if the composition in accordance with the invention is a supercritical composition in which the solid fraction is adjusted to the liquid fraction or the binder fraction such that no complete wetting of the solids takes place. In this case, a porous coating is formed, allowing to ensure a reliable contact between the pollutants to be eliminated and the photocatalytically active substance.

The composition in accordance with the invention preferably comprises an adsorbing agent, such as e. g. activated charcoal, silicic acid, micro silicas, silica gels, zeolites, bentonites, diatomaceous earth, foamed glass or the like.

It has been shown that the photocatalytically active substances that are used in accordance with the invention, especially on the basis of sulfur and/or carbon-containing titanium dioxide, exhibit an electron spin resonance spectrum with a significantly increased light absorption, as compared to pure titanium dioxide, in the wavelength range of over 400 nm (vlp-TiO₂), which, when measured at a temperature of 5 K, exhibits a significant signal only in the g value range of 1.97 to 2.05.

In the context of the production of the compositions in accordance with the invention, it has proven to be especially advantageous to produce, in a first step, an intermediate product by dispersing the photocatalytically active substance in an inorganic binder and to mix this intermediate product in a second step with an organic binder. In this process, coagulates are produced in the first step from the photocatalytically active substance and the inorganic binder generally inert with respect to the radicals capable of being produced with the photocatalytically active substance, with these coagulates being capable of being bonded to each other in the second steps via the organic binder. Preferred embodiments of the invention are listed in the following tables, with the numerical data referring to weight percentages of the respective components of the compositions.

Example 1 – Silicone resin paint for interior applications

Water	--	35.7
Isothiazolinones	Microbiocide	0.4
Salts of polyacrylic acid or phosphate esters and tetra potassium pyrophosphate	Dispersing agent	0.9
Mineral oil	Anti-foaming agent	0.4
Cellulose thickening agent	Thickening agent	0.6
Polysiloxane	Hydrophobization	1.0
Silicone resin emulsion	Binder	4.0
Titanium dioxide	White pigment	13.0
Photocatalytic titanium dioxide	Pigment	10.0
Silicates	Filler	10.0
Kaolin	Filler	9.0

Styrene / acrylate	Binder	15.0
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Example 2 – Silicate paint for interior applications

Water	-	26.6
Cellulose ether and polysaccharides	Thickening agent	0.4
Tetra alkyl alkylene diamine	Stabilizer for water glass	0.2
Polyacrylate with sodium salt	Dispersing agent	0.1
Potassium water glass	Binder	14.0
Potassium methyl silicate	Hydrophobization	1.0
Photocatalytic titanium dioxide	Pigment	10.0
Titanium dioxide	White pigment	22.0
Kaolin	Filler	10.0
Silicates	Filler	7.0
Polysiloxane copolymer	Anti-foaming agent	0.2
Styrene / acrylate	Binder	8.5

Example 3 – Silicate / Silicone paint for interior applications

Water	-	26.5
Cellulose ether and polysaccharides	Thickening agent	0.4
Tetra alkyl alkylene diamine	Stabilizer for water glass	0.2
Polyacrylate with sodium salt	Dispersing agent	0.1
Silicone resin emulsion	Binder	4.3
Potassium water glass	Binder	14.0
Potassium methyl silicate	Hydrophobization	1.0
Photocatalytic titanium dioxide	Pigment	10.0
Titanium dioxide	White pigment	22.0
Kaolin	Filler	10.0
Silicates	Filler	7.0

Polysiloxane copolymer	Anti-foaming agent	0.2
Styrene / Acrylate	Binder	4.3

Example 4 – Silicone plaster for interior applications

Water	-	13.8
Polysaccharide and cellulose	Thickening agent	0.5
Salt of polyacrylic acid	Dispersing agent	0.1
Silicone resin emulsion	Binder	3.0
Titanium dioxide	White pigment	0.8
Photocatalytic titanium dioxide	Pigment	10.0
Vinyl acetate ethylene copolymerizate	Binder	3.0
Silicates	Filler	1.4
Calcium carbonate	Filler	25.9
Diatomaceous earth	Filler	2.9
Isothiazonlinone	Microbiocide	0.2
Wax dispersion	Hydrophobization	0.4
Calcium carbonate	Structural sand	38.0

Example 5 – Silicate plaster for interior applications

Water	-	24.5
Cellulose ether	Thickening agent	0.2
Potassium hydroxide	pH regulator	0.1
Silicic acid	Anti-foaming agent	0.1
Sodium salt	Dispersing agent	0.4
Calcium hydroxide	Binder	8.0
Photocatalytic titanium dioxide	Pigment	10.0
Titanium dioxide	White pigment	3.0
Cellulose	Filler	1.0

Ethylene vinyl ester terpolymer	Binder	2.9
Linseed oil stand oil	Binder	0.4
Silicon dioxide	Filler	9.4
Calcium carbonate	Structural sand	40.0

Example 6 – Silicone resin paint for exterior applications

Water	-	31.0
Salts of polyacrylic acid and sodium polyphosphate	Dispersing agent	0.4
Isothiazolinones	Microbiocide	1.2
Cellulose	Thickening agent	0.3
Siloxanes	Anti-foaming agent	0.3
Dicarboxylic acid ester	Film formation agent	1.0
Silicone resin emulsion	Binder	9.3
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	12.0
Calcium carbonate	Filler	17.7
Magnesium aluminum silicate	Filler	12.0
Caustic soda	pH regulator	0.1
Styrene / acrylate	Binder	9.5
Polyurethane	Thickening agent	0.2

Example 7 – Silicate paint for exterior applications

Water	-	18.0
Cellulose ether, saccharides and acrylates	Thickening agent	0.7
Tetra alkyl alkylene diamine	Stabilizer for water glass	0.3
Polycarboxylic acid and ammonium derivative	Dispersing agent	0.2
Potassium methyl siliconate and polysiloxane	Hydrophobization	1.0

Potassium water glass	Binder	20.0
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	12.0
Kaolin	Filler	1.0
Diatomaceous earth, silicates and silicon dioxide	Filler	12.0
Barium sulphate	Filler	20.0
Solvent	Film formation agent	0.6
Styrene / acrylate	Binder	9.0
Siloxanes	Anti-foaming agent	0.2

Example 8 – Silicate / silicone paint for exterior applications

Water	-	18.0
Cellulose ether, saccharides and acrylates	Thickening agent	0.7
Tetra alkyl alkylene diamine	Stabilizer for water glass	0.3
Polycarboxylic acid and ammonium derivative	Dispersing agent	0.2
Silicone resin emulsion	Binder	5.0
Potassium methyl silicate and polysiloxane	Hydrophobization	1.0
Potassium water glass	Binder	20.0
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	12.0
Kaolin	Filler	1.0
Diatomaceous earth, silicates and silicon dioxide	Filler	12.0
Barium sulphate	Filler	20.0
Solvent	Film formation agent	0.6
Styrene / acrylate	Binder	4.0
Siloxane	Anti-foaming agent	0.2

Example 9 – Silicone plaster for exterior applications

Water	-	11.8
Isothiazoninones	Microbiocide	0.8
Saccharide	Thickening agent	0.1
Sodium salt	Dispersing agent	0.1
Silicone resin emulsion	Binder	2.0
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	1.6
Diatomaceous earth, silicates and silicon dioxide	Filler	3.8
Aluminum hydroxide	Filler	8.8
Cellulose	Filler	0.7
Calcium carbonate	Filler	10.6
Solvent	Film formation agent	0.8
Styrene / acrylate	Binder	6.0
Ethylene vinyl ester terpolymer	Binder	5.5
Tetra potassium pyrophosphate	Dispersing agent	0.3
Mineral oil	Anti-foaming agent	0.1
Calcium carbonate	Structure sand	42.0

Example 10 – Silicate plaster for exterior applications

Water	-	7.2
Polysaccharide	Thickening agent	0.1
Tetra alkyl alkylene diamine	Stabilizer for water glass	0.3
Potassium water glass	Binder	4.1
Potassium methyl siliconate	Hydrophobization	0.3
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	1.8
Diatomaceous earth and silicates	Filler	2.8
Calcium carbonate	Filler	32.0
Polyacryl nitrile	Filler	0.3

Mineral fiber	Filler	0.5
Styrene / acrylate	Binder	8.3
Solvent	Film formation agent	0.2
Isothiazolinones	Microbiocide	0.3
Fatty alcohol suspension	Drying retarder	0.5
Silicic acid	Delustering agent	1.3
Calcium carbonate	Structural sand	35.0

Example 11 – Dispersion varnish for exterior applications

Water	-	14.0
Anionic salts	Dispersing agent	0.2
Mineral oil	Anti-foaming agent	0.3
Solvent	Film formation agent	5.0
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	20.0
Silicates	Filler	3.0
Pure acrylate	Binder	50.0
Potassium hydroxide	pH regulator	0.2
Acrylic acid	Thickening agent	2.0
Isothiazolinones	Microbiocide	0.3

Example 12 – Concrete glaze for exterior applications

Water	-	23.0
Anionic salts	Dispersing agent	0.5
Cellulose ether	Thickening agent	0.2
Mineral oil	Anti-foaming agent	0.3
Photocatalytic titanium dioxide	Pigment	5.0
Titanium dioxide	White pigment	1.5
Diatomaceous earth	Filler	2.0

Calcium carbonate	Filler	27.0
Solvent	Film formation agent	4.0
Styrene / acrylate	Binder	35.0
Acrylic acid	Thickening agent	1.0
Isothiazolinones	Microbiocide	0.5

Example 13 – Lime plaster for exterior applications

Water	-	23.50
Cellulose ether	Thickening agent	0.20
Caustic potash	pH regulator	0.10
Mineral oil	Anti-foaming agent	0.10
Salt of polyacrylic acid	Dispersing agent	0.40
Cellulose fiber	Filler	1.00
Titanium dioxide	White pigment	3.00
Calcium hydroxide (lime)	Binder	8.00
Vinyl chloride ethylene vinyl ester	Binder	2.90
Photocatalytic titanium dioxide	Pigment	5.00
Linseed oil stand oil	Binder	0.40
Silicates	Filler	2.00
Silica sand	Filler	13.40
Calcium carbonate	Structural sand	40.00

Example 14 - Lime plaster for interior applications

Water	-	23.50
Cellulose ether	Thickening agent	0.2
Caustic potash	pH regulator	0.1
Mineral oil	Anti-foaming agent	0.1

Salt of polyacrylic acid	Dispersing agent	0.4
Cellulose fiber	Filler	1.0
Titanium dioxide	White pigment	3.0
Calcium hydroxide (lime)	Binder	8.0
Vinyl chloride ethylene vinyl ester	Binder	2.9
Photocatalytic titanium dioxide	Pigment	10.0
Linseed oil stand oil	Binder	0.4
Silicates	Filler	2.0
Silica sand	Filler	13.4
Calcium carbonate	Structural sand	35.0

Example 15 – Cement plaster for exterior applications

Marble powder	Filler	24.0
Calcium carbonate	Structural sand	33.0
Calcium carbonate	Filler	4.0
Silica sand	Filler	12.0
Fiber	Filler	0.5
Cellulose ether	Thickening agent	0.3
Silicates	Filler	0.5
Calcium sulphate	Filler	0.2
Photocatalytic titanium dioxide	Pigment	5.0
Oleate	Hydrophobization	0.3
White cement	Binder	13.2
Calcium hydroxide	Binder	7.0

Example 16 – Cement plaster for interior applications

Marble powder	Filler	24.0
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Calcium carbonate	Structural sand	28.0
Calcium carbonate	Filler	4.0
Silica sand	Filler	12.0
Fiber	Filler	0.5
Cellulose ether	Thickening agent	0.3
Silicates	Filler	0.5
Calcium sulphate	Filler	0.2
Photocatalytic titanium dioxide	Pigment	10.0
Oleate	Hydrophobization	0.3
White cement	Binder	13.2
Calcium hydroxide	Binder	7.0

Example 17 – Gypsum plaster for interior applications

Gypsum (calcium sulphate)	Binder	24.0
Rock powder (e. g. marble powder)	Filler	29.6
Cellulose / starch - ether	Thickening agent	0.3
Photocatalytic titanium dioxide	Pigment	10.0
Calcium carbonate	Structural sand	35.0
Styrene / acrylate	Binder	1.0
Tartaric acid	Retarder	0.1

Example 18 – Gypsum / lime plaster for interior applications

Gypsum (calcium sulphate)	Binder	4.0
White lime hydrate	Binder	10.0
Rock powder (e. g. marble powder)	Filler	28.7
Cellulose / starch - ether	Thickening agent	0.7
Photocatalytic titanium dioxide	Pigment	10.0
Calcium carbonate	Structural sand	45.0

Styrene / acrylate	Binder	1.5
Tartaric acid	Retarder	0.1

The composition in accordance with the invention may be used in all types of coatings, such as e. g. paints, plasters, varnishes and glazes. It can be used on new and old construction subsurfaces in interior and exterior applications, such as e. g. masonry, plaster surfaces, paintwork, wallpaper; wood, metal, glass and ceramic surfaces, thermal insulation composite systems, installed façade elements and the like.

In the following, the photocatalytically active substance suitable for use, especially advantageously, in the production of compositions in accordance with the invention, is explained in detail based on a vlp-TiO₂ :

The vlp-TiO₂ that is especially advantageously suitable for use within the framework of the invention shows a higher photocatalytical effectiveness than the types described in the state of the art. The degradation of 4-chlorophenol by a defined amount of vlp-TiO₂ given exposure for 120 minutes to light having a wavelength ≥ 455 nm serves as the measure of photocatalytic effectiveness (referred to as "photoactivity" in the following). The measuring method is described in detail below. Under the above-mentioned measuring conditions, the photoactivity of the vlp-TiO₂ in accordance with the invention is at least 20 %, preferably at least 40 %, and especially preferably at least 50 %.

The sulfur and/or carbon content is in the range of 0.05 to 4 percent by weight in relation to TiO₂, preferably 0.05 to 2.0 percent by weight and especially preferably 0.3 to 1.5 percent by weight. Optimal results are obtained with carbon contents of 0.4 to 0.8 percent by weight.

The titanium dioxide particles contain carbon only in a surface layer and are therefore referred to as "carbon-modified" in the following – in contrast to the volume-doped titanium dioxide prepared as per Sakthivel & Kisch (2003). The carbon or the carbon compounds of the vlp-TiO₂ in accordance with the invention presumably are bonded primarily covalently via oxygen on the TiO₂ surface and are capable of being leached with alkalines.

The photocatalyzer can additionally or alternatively contain nitrogen and / or sulfur.

In contrast to unmodified TiO_2 , the vlp- TiO_2 suitable for use in the production of compositions in accordance with the invention absorbs visible light having a wavelength $\lambda \geq 400$ nm. The Kubelka-Munk function $F(R_{00})$ proportional to the absorbance is approximately 50 % of the value at 500 nm and approx. 20 % of the value at 400 nm.

The electron spin resonance spectrum (ESR) of the vlp- TiO_2 suitable for use in accordance with the invention, measured at a temperature of 5 K, is characterized by a strong signal with a g value of 2.002 to 2.004, especially 2.003. In the g value range of 1.97 to 2.05, no further signals are observed. The intensity of the signal at g = approx. 2.003 increases by exposure to light having a wavelength of $\lambda \geq 380$ nm (UV-free 100 W halogen lamp, cold light filter KG5) as opposed to measurement in the dark.

The X-ray photoelectron spectrum (XPS) of the vlp- TiO_2 in accordance with the invention is characterized by the occurrence of a strong absorption band given a bond energy of 285.6 eV relative to the O1s band at 530 eV.

It is furthermore characteristic that, in contrast to the photocatalyzer based on Sakthivel & Kisch (2003), the vlp- TiO_2 does not show carbonate bands either in the X-ray photoelectron spectrum (XPS) or the infrared spectrum.

Under exposure to visible light, the vlp- TiO_2 shows a water contact angle of ca. 8 °; unmodified TiO_2 , on the other hand, shows a contact angle of ca. 21 °.

The photocatalyzer suitable for use in accordance with the invention enables the degradation of pollutants not only by artificial visible light, but also by diffuse daylight in interior spaces. It can be used to decompose contaminants in the air which come into contact with the composition in accordance with the invention.

The photocatalyzer can be used in coatings in interior and exterior applications, such as e. g. paints, plasters, varnishes and glazes for the application on masonry, plaster surfaces, paintwork, wallpaper and wood, metal, glass and ceramic surfaces, or on building components such as e. g. thermal insulation composite systems and installed façade elements, as well as in street pavings and in plastics, plastic foils, fibers and paper.

The photocatalyzer can, in addition, be used in the production of prefabricated concrete parts, concrete paving stones, roof tiles, ceramic, tiles, wallpaper, fabrics, panels and facing elements for ceilings and walls in interior and exterior applications.

Further applications in the construction industry result from the light-induced increase in hydrophilia of the TiO_2 surface.

The invention is explained in more detail below in reference to the Figures 1 to 12.

Figure 1 shows the Kubelka-Munk function $F(R_{00})$ (arbitrary units) proportional to the relative absorbance for unmodified TiO_2 and for TiO_2 modified with C (vlp- TiO_2) as a function of the wavelength and reveals that the vlp- TiO_2 absorbs in the visible spectral area, in contrast to unmodified titanium dioxide. $F(R_{00})$ is approx. 50 % at 500 nm and approx. 20 % at 600 nm of the value at 400 nm.

Figure 2 shows the electron resonance spectra (ESR) of the vlp- TiO_2 (spectrum A) suitable for use in accordance with the invention and the TiO_2 (spectrum B) produced as per Sakthivel & Kisch, captured in the dark and at a temperature of 5 K. Spectrum A shows only a significant signal with a g value of 2.000. Spectrum B shows, in addition to a primary signal, three further signals in the range of the g values 1.97 to 2.05 at g approx. 2.003 .

Figure 3 contains the X-ray photoelectron spectra (XPS) of the vlp- TiO_2 (spectrum A) in accordance with the invention and the already known TiO_2 precipitated from titanium tetrachloride with tetrabutyl ammonium hydroxide as per Sakthivel & Kisch (spectrum B). The spectrum of the vlp- TiO_2 exhibits a pronounced C1s signal at a bond energy of 285.6 eV relative to the O1s absorption band at 530 eV, which is an indication of elementary carbon. Spectrum B, on the other hand, shows C1s signals for elementary carbon at a bond energy of 284.5 eV as well as, additionally, bands at 289.4 eV and 294.8 eV, which are an indication of carbonate. The respective IR spectra also exhibit typical carbonate bands at 1738, 1096 and 798 cm^{-1} .

Figure 4 illustrates the photocatalytical effectiveness of vlp-TiO₂ in contrast to unmodified TiO₂ in the degradation of 4-chlorophenol (as 2.5 x 10⁻⁴ molar aqueous solution) by artificial visible light ($\lambda \geq 455$ nm). The figure shows the decrease in total content of organic carbon (TOC_t) in the solution in relation to the starting value (TOC₀). With the vlp-TiO₂, the complete degradation takes place after three hours.

Figure 5 illustrates the photocatalytical effectiveness of vlp-TiO₂ in contrast to unmodified TiO₂ in the degradation of 4-chlorophenol (as 2.5 x 10⁻⁴ molar aqueous solution) by the diffuse daylight of an interior space. The figure shows the decrease in total content of organic carbon (TOC_t) in the solution in relation to the starting value (TOC₀). Even under low-intensity diffuse daylight (7 to 10 W/m² in the range of 400 to 1200 nm), the vlp-TiO₂ effects a degradation of 80 % within 6 hours. Even under very low-intensity diffuse daylight lighting (1.6 to < 1 W/m²), the vlp-TiO₂ still shows significant photoactivity in contrast to the commercially available TiO₂ photocatalyzers (Degussa P25, Kemira UV Titan [titanium], Sachtleben Hombikat, Tayca MT-100SA). The measurement of the degradation rate of 2.5 x 10⁻⁴ molar 4-chlorophenol solution was performed as described above.

a) Light intensity: 1.6 W/m²; duration: 12 h

<u>Catalyzer</u>	<u>BET Surface</u>	<u>Degradation Rate</u>
vlp-TiO ₂	170 m ² /g	16 %
P25	50 m ² /g	4 %
UV Titan	20 m ² /g	5 %
Hombikat	240 m ² /g	9 %
MT-100SA	50 m ² /g	5 %

b) Light intensity: < W/m²; duration: 24 h

<u>Catalyzer</u>	<u>BET Surface</u>	<u>Degradation Rate</u>
vlp-TiO ₂	170 m ² /g	18 %
Hombikat	240 m ² /g	3 %

Figure 6 illustrates the photocatalytical effectiveness of vlp-TiO₂ as opposed to unmodified TiO₂ in the degradation of benzene (5 percent by volume), acetaldehyde (2 percent by volume) and carbon monoxide (5 percent by volume) by the diffuse daylight of an interior space. The reaction container is a 1 liter round bottomed flask, equipped with a paper round filter coated with 12 mg titanium dioxide (d = 15 cm). The decrease in total content of organic carbon (TOC_i) in the atmosphere in relation to the starting value (TOC₀) is shown. The curves show the degradation of benzene, acetaldehyde or carbon monoxide by the vlp-TiO₂ in accordance with the invention as well as the degradation of acetaldehyde by unmodified titanium dioxide.

Figure 7 shows an X-ray powder diffractogram of the vlp-TiO₂, which only exhibits anatas reflexes. The crystallite size calculated according to the Scherrer method is 10 nm.

Figure 8 shows an image produced via high-resolution transmission electron microscopy (HTEM) with the grid lines of the crystallites. The crystallite size can be estimated to the order of 10 nm.

Figure 9 shows a carbon depth profile of the vlp-TiO₂, represented as C/Ti ratio. It was determined using ion bombardment (Ar⁺) and ESCA analysis. The indicated bombardment time of 5×10^3 seconds is equivalent to a depth of approx. 5 nm.

Figure 12 shows the Kubelka-Munk functions of compositions in accordance with the invention with different binders in comparison to the Kubelka-Munk function of the photocatalytically active substance.

A method for the manufacture of photocatalytically active substances suitable for use in accordance with the invention is based on a titanium compound which is available in the form of an amorphous, partially crystalline or crystalline titanium oxide or aqueous titanium oxide and/or a titanium hydrate and/or titanium oxyhydrate and which is referred to in the following as starting titanium compound.

In the titanium dioxide production, the starting titanium compound can, for example, be produced using either the sulphate method or the chloride method. Titanium hydrate or titanium oxyhydrate or metatitanic acid is precipitated e. g. in the hydrolysis of titanyl sulphate or titanyl chloride.

The starting titanium compound may be available as a finely grained solid or in suspension with a respective solid fraction of at least 15 weight by percent, with the specific surface of the solid measuring at least 50 m²/g as per BET, preferably ca. 150 to 350 m²/g as per BET, and specifically 150 to 250 m²/g as per BET.

For the industrial implementation of the process, titanium hydrate from the sulphate process is preferred as the starting titanium compound for economic reasons. Any adhering sulfuric acid is advantageously first removed from this titanium hydrate, using neutralization and washing, so that the sulphate fraction of the solid is < 1 percent by weight, calculated as SO₃, after drying.

A carbon-containing substance especially advantageously suitable for use in the production of photocatalytically active substances that can be used according to the invention has a degradation temperature of max. 400 °C, preferably < 300 °C. Carbon-containing substances such as e. g. wood, carbon black or activated charcoal and especially organic carbon compounds such as hydrocarbons having at least one functional group have proven to be suitable. The functional group may be: OH; CHO; COOH; NH_x; SH_x; COOR, wherein R is an alkyl or aryl residue. For example, succinic acid, glycerin or ethylene glycol are possible. Sugar and other carbohydrates as well as organoammonium hydroxide, especially tetra alkyl ammonium, may also be used. Also suitable are mixtures of the above-mentioned compounds. Preferably, water-soluble polyalcohols having a carbon-oxygen ratio of ca. 0.7 to 1.5, preferably ca. 1, are used, specifically pentaerythrite. The carbon compound may be used as solid, solution or suspension.

The organic carbon compound should have a maximally high affinity towards the surface of the starting titanium compound in order to be capable of forming a close bond with it.

The starting titanium compound is intimately mixed with the organic carbon compound in such a way that a surface coating of the starting titanium compound with the carbon compound takes place. The organic carbon compound can be present in physisorbed or chemisorbed form on the surface of the starting titanium compound. The coating of the surface of the starting titanium compound may be effected by dissolution of the carbon compound in the suspension of the starting titanium compound or by mixing the suspension of the carbon compound with the suspension of the starting titanium compound.

Intensive mixing of the carbon compound with a previously dried starting titanium compound in powder form is also possible. Alternatively, in the event titanium hydrate is used, the carbon compound can also be admixed to the solution to be hydrolyzed as early as in the production step of the titanium hydrate. In the finished mixture of starting titanium compound and carbon compound, the amount of the carbon compound relative to the starting titanium compound (as solid) is 1 to 40 percent by weight.

If the finished mixture is available as a suspension, it can be dried to form a powdery solid prior to the further processing. For this purpose, known processes such as spray drying or fluid bed drying are suitable.

The finished and, as the case may be, predried mixture is thermally treated at temperatures of max. 400 °C. The thermal treatment is performed in an oxidizing atmosphere, preferably air or an oxygen-air mixture. In this process, the organic carbon compound is degraded on the surface of the starting titanium compound and the H₂O, CO₂ and CO is released. Although the thermal treatment may also take place in the – discontinuous – batch mode, for example in a commercially available lab oven, a continuous process, allowing for a specific temperature profile to be run, is preferred for economic reasons. All processes allowing the implementation of a respective temperature profile and the necessary retention time are possible as continuous processes. Indirectly and directly heated rotary ovens are especially suited units. But it is also possible to use continuously operated fluidized bed reactors, fluid bed driers and heated ploughshare mixers. The three last-mentioned units can also be operated in discontinuous mode.

The thermal treatment is preferably performed such that a product (vlp-TiO₂) with a carbon content of 0.05 to 4.0 percent by weight, preferably 0.05 to 2.0 percent by weight, especially preferably 0.3 to 1.5 percent by weight and specifically 0.4 to 0.8 percent by weight is obtained. In the course of the thermal treatment, a color change from white to brown and finally beige takes place. The end product is characterized by a beige to slightly yellowish-brownish coloration. It is characterized in that the carbon is detectable in amorphous and polycrystalline areas of the surface of the surface layer as well as on the surface itself. The product is photoactive in visible light.

Following the thermal treatment, the product is deagglomerized using known processes, for example in a pin mill, jet mill or counter jet mill. In the case of predried mixtures in powder form, the thermal treatment for the most part results in agglomerate-free products which do not require further milling. The grain fineness to be achieved is dependent on the grain size of the starting titanium compound. The grain fineness or specific surface of the product is only slightly lower, but is in the same order of magnitude as that of the educt. The desired grain fineness of the photocatalyzer is dependent on the field of use of the photocatalyzer. It is usually in a similar range as that of the TiO_2 pigments, but can also be above or below it. The specific surface as per BET is 100 to 250 m^2/g , preferably 130 to 200 m^2/g , and specifically 130 to 170 m^2/g .

Photocatalytically active substances suitable for use within the context of the invention will be described in more detail using the following examples. It is not intended for these to restrict the scope of the invention.

Example 1

An aqueous titanium oxyhydrate paste (35 percent by weight solid), prepared using the sulphate method, is diluted with distilled water at room temperature to such a degree that a stirrable suspension is obtained. The solid fraction is 20 to 25 %. A sufficient amount of NaOH solution (36 percent by weight) is added until a pH value in the range of 6.0 to 7.0 is obtained. Then the suspension is filtered and washed with distilled water until the SO_3 content, measured on the dried residue, is under 1 percent by weight.

The titanium oxyhydrate neutralized and washed in this way is then diluted again with distilled water to form a stirrable suspension (25 % solid) and 12 percent by weight succinic acid, relative to the solid, is added. The succinic acid is added to the suspension as a solid and the suspension is stirred until the succinic acid is completely dissolved. The suspension is heated to approx. 60 °C to improve the solubility of the succinic acid .

The suspension prepared in this way is dried under a surface evaporator (IR radiator), while being stirred, until the suspension turns into a pasty mass. The pasty mass is then dried in a lab drying cabinet at 150 °C until the solid fraction is > 98 %.

300 g of the dried mixture of titanium oxyhydrate / succinic acid are finely ground (e. g. by mortaring or sifting) and the powder thus obtained is placed, in a quartz dish with cover, in a lab oven at 290 °C. Every 1 to 2 hours, the quartz dish is removed and the powder is again mixed. After 13 to 15 hours in the lab oven, the color of the powder has changed from initially yellowish to grey-black to yellowish-brown. The thermal treatment resulting in the vlp-TiO₂ is completed when the carbon content has decreased from initially 5 to 5.5 percent by weight to approx. 0.65 to 0.80 percent by weight.

Subsequently, the photocatalyzer is deagglomerized and analyzed for carbon content, optical properties, BET surface and photoactivity.

Example 2

Analogous procedure as in example 1, with the difference that 12 percent by weight pentaerythrite is added to the titanium oxyhydrate suspension as a solid.

Example 3

Analogous procedure as in example 2, with the difference that 5 percent by weight pentaerythrite is added to the titanium oxyhydrate suspension as a solid.

Example 4

A titanium oxyhydrate / pentaerythrite suspension is prepared, using 5 percent by weight pentaerythrite, as described in example 1. In variation from example 1, the thermal treatment of the thus obtained suspension is performed in a continuously operated rotary oven as follows:

The rotary oven is operated in the reverse flow mode and heated directly via a gas burner. The open flame of the gas burner is protected by a flue, which prevents direct contact with the product (vlp-TiO₂). The heated oven length is 7 m and the clear diameter is 0.3 m. The suspension is finely sprayed into the feeder of the oven. The feed quantity of the suspension is 40 kg/h. Chain fixtures in the feeder of the oven serve to ensure good swirling and hence rapid drying and subsequent crushing of the dried material. The processing time in the continuously operated rotary oven is 1 hour. The oven temperature in the discharge area is controlled via the amount of gas on the burner to 260 °C. At the oven discharge, the vlp-TiO₂ presents as a fine powder with a yellowish-brown color. Then the vlp-TiO₂ is deagglomerized in a lab mixer (Braun, MX 2050) and analyzed for carbon content, optical properties, BET surface and photoactivity.

Example 5

Analogous procedure as in Example 4, with the difference that the oven temperature in the discharge area is controlled via the amount of gas on the burner to 280 °C.

Example 6

A suspension of titanium oxyhydrate and pentaerythrite is prepared, using 5 percent by weight pentaerythrite, as described in Example 1. In variation from Example 1, the suspension is predried in an electrically heated oven to form a solid in powder form with a residual moisture content of 22 %. The thermal treatment of the predried fed material in powder form is performed in a continuously operated, indirectly heated rotary oven as follows:

The rotary oven is operated in the cocurrent flow mode and electrically heated in three zones. The entire heated oven length is 2700 mm and the clear diameter is 390 mm. The solid in powder form is conveyed over a dosing screw feeder into the feeder of the oven.

Chain fixtures over the entire length of the rotating cylinder ensure a homogeneous distribution in the oven and prevent caking to the oven wall. The amount fed is 25 kg solid per hour. The processing time through the continuously operated rotary oven is 0.5 hours. The oven temperature is electrically controlled in three heating zones. The temperature of each of the three heating zones is individually controllable. At the oven discharge, the vlp-TiO₂ presents as beige-colored fine powder. Then the vlp-TiO₂ is deagglomerized in a lab mixer (Braun, MX 2050) and analyzed for carbon content, optical properties, BET surface and photoactivity.

Example for comparison

In analogy to Example 2, a TiO₂ pigment (anatase) with a BET surface of approx. 10 m²/g (commercial product Kronos 1000) is mixed with 12 % pentaerythrite and is then thermally treated.

Example	Organics	Thermal °C	Treatment Time (h)	Analytics C content (%)	of PLV - L *	the Test B *	vlp A *	TiO ₂ BET m ² /g	Photoactivity Degradation of 4-CP in 120 min. (%)
1	Succinic acid	290	13	0.79	85.4	9.85	1.63	164	48
2	Pentaerythrite	290	28	0.75	86.9	10.08	1.53	158	50
3	Pentaerythrite	290	10	0.76	83.7	10.03	1.59	140	63
4	Pentaerythrite	260 *	1 **	0.92	85.1	11.7	1.2	152	58
5	Pentaerythrite	280 *	1 **	0.50	85.8	9.4	2.2	160	68
6	Pentaerythrite	300 ***	0.5 **	0.78	83.0	11.0	2.6	167	86
Counter-example	Pentaerythrite	290	42	0.82	74.7	9.12	2.50	11.6	< 5

* Max. temperature, measured at the discharge of the rotary oven

** Processing time of the material fed through the rotary oven

*** Temperature of the three heating zones, measured in the area of the heating elements

The table provides a summary of the analytics and photoactivity of the vlp-TiO₂ that is suitable for use within the framework of the invention.

vlp-TiO₂, prepared from titanium hydrate (Examples 1 to 6) shows an excellent photocatalytic effectiveness in the visible spectral range with good optical values (PLV test). The use of anatase pigment instead of titanium hydrate results in a product without appreciable photoactivity (example for comparison).

Example 7

5 g titanium dioxide (commercial product TRONOX Titanhydrat-0 [titanium hydrate] of the company of Kerr-McGee Pigments GmbH) is suspended at room temperature in 20 ml distilled water; 5 ml ethylene glycol (commercial product of the company of FLUKA AG) is added to the suspension and the suspension is treated in the ultrasound bath (Sonorex Super RK 106 of the company of Bandelin Electronic, Berlin; 35 kHz, 120 W eff. Hf power). Following magnetic stirring over night, the solvent is removed, preferably in the vacuum; the residue is dried at 100 to 200 °C, preferably ca. 200 °C, for at least 12 hours; subsequently, it is heated to 300 °C in a closed vessel within one hour and then maintained at this temperature for another three hours. In this process, a color change of the powder from white to dark brown to beige is observed. Longer heating results in colorless, inactive powders. The elementary analysis of the product yields 2.58 percent by weight carbon, 0.02 percent by weight nitrogen and 0.40 percent by weight hydrogen. Unmodified TiO₂ contains 0.07 percent by weight [carbon] and 0.0 percent by N and 0.0 percent by weight H.

Example 8

To strip the superficial carbon compound, 5 g vlp-TiO₂ is stirred over [night] into 100 ml of 2 M sodium hydroxide (pH 12). Centrifuging yields a brown-yellow extract and a barely colored white residue; the latter is dried at 100 °C. The powder thus obtained shows no activity during the degradation of 4-chlorophenol in the visible light. When the powder is reunited with the extract and slightly heated, preferably to ca. 200 °C, it exhibits the same activity as the untreated (unleached) vlp-TiO₂ in the degradation reaction.

Example 9

To coat a plastic foil, a powder prepared as shown in Example 6 is suspended in the ultrasound bath in a liquid such as methanol or ethanol and the resulting suspension is applied to the sheet as thinly as possible using a spray bottle. Following drying at 343 K, the coating can be repeated up until the desired layer thickness is obtained.

Instead of the plastic foil, a different carrier, such as e. g. paper (cf. experiment as per Figure 6) or aluminum (cf. under test methods h), "dip coating") may be used.

Methods of measurement

a) Determination of the optical values (PLV test)

The method serves to determine the optical values for brightness L^* , coloring a^* and coloring b^* of the vlp-TiO₂. A powder compact is prepared from the vlp-TiO₂ to be tested under defined conditions using a hydraulic small press of the company of MATRA, Frankfurt. Then the remission values are determined on the powder compact using the HUNTERLAB Tristimulus Colorimeter.

The vlp-TiO₂ is ground prior to the preparation of the compact. To do this, 100 g of the vlp-TiO₂ obtained is placed in a commercially available mixer (manufacturer: Braun, model: MX 2050) and is mixed 12 times for 5 seconds. Between each grinding step, the mixer is opened and the powder is mixed again. A white sheet of paper, matte on both sides, is placed on the base plate having a circular depression, and then a metal ring (height 4 cm, diameter 2.4 cm) is pressed into the depression using the press. Ca. 25 g of the ground vlp-TiO₂ is fed into the metal ring under slight shaking and tapping. Using a pressure of 2 - 3 kN, the powder is compressed.

The pressing process is repeated a second time until the target operating pressure of 15 kN is reached. By carefully turning and pulling it, the metal ring is separated from the base plate. The paper between the base plate and the ring is removed. The compact is now in the ring and is used for the measuring procedure using the HUNTERLAB colorimeter. The measured values L^* , a^* , b^* are read off directly on the colorimeter.

b) Determination of Photoactivity (degradation of pollutants)

In artificial visible light:

15 mg of the vlp-TiO₂ is dispersed in 15 ml of a 2.5×10^{-4} molar solution of 4-chlorophenol for 10 minutes in the ultrasound bath and then exposed to light on an optical bench in a water-cooled round cuvette. The exposures to light for the determination of the photoactivity are performed using an Osram XBO 150 W Xenon short arc lamp installed in a focusing lamp case (AMKO Mod. A1020, focal length: 30 cm). The spectrum of this lamp is shown in Figure 10. The reactions are performed in a water-cooled round cuvette with 15 ml capacity and an inner diameter of 30 mm and a layer thickness of 20 mm. The reaction suspension may be stirred using a stirring motor and stirring magnet attached on the side. The round cuvette is depicted in Figure 11. The cuvette is retained in the focal point of the lamp. The light is focused in such a way that only the reaction space of the cuvette is exposed. All components are firmly mounted on an optical bench. To eliminate UV light, a Kantfilter (Fa. Schott) with a transmittance of $\lambda \geq 455$ is introduced into the path of the rays. In order to prevent possible heating of the reaction space from the light exposure, an IR filter is additionally mounted in the path of the rays. This is a cylinder filled with water (diameter 6 cm, length 10 cm).

The decrease in concentration of 4-chlorophenol is monitored using UV spectroscopy ($\lambda = 224$) or, in the case of degradation (oxygen), via measurement of the total content of organic carbon (TOC value).

In the diffuse daylight of an interior space:

50 mg of the vlp-TiO₂ is dispersed in 50 ml of a 2.5×10^{-4} molar solution of 4-chlorophenol for 10 minutes in the ultrasound bath and then exposed to the daylight of an interior space in an Erlenmeyer flask (100 ml) while stirring.

Degradation of acetaldehyde gas, benzene vapor and carbon monoxide:

In a round flask (1 l) filled with air-saturated acetaldehyde gas (2 percent by volume) or benzene vapor (5 percent by volume) or carbon monoxide, two round filters (paper, d = 15 cm, 2 mg catalyzer per filter), coated on both sides with vlp-TiO₂, are introduced. Then the flask is exposed to the daylight in the lab and the decrease in pollutants and the formation of carbon monoxide is monitored using IR spectroscopy.

c) Determination of the carbon content

The determination is performed in terms of total organic carbon content (TOC) using the LECO C-200 carbon analyzer. The measuring method is based on the combustion of the organic substance contained in the vlp-TiO₂ in the induction oven under oxygen gas and the subsequent determination of the carbon dioxide formed using IR detection. The weighed-in quantity is ca. 0.4 g.

d) Determination of the specific surface according to BET (Brunauer-Emmett-Teller)

The BET surface is measured using a Tristar 3000 of the company of Micromeritics based on the static volumetric principle.

e) XPS measurements

The Phi 5600 ESCA spectrometer instrument (pass energy of 23.50 eV; Al standard; 300.0 W; 45.0 °C) was used to measure the bond energies.

f) ESR measurements

To measure the electron resonance spectra, a Bruker Elexys 580 spectrometer X-band (9.5 GHz) was used. The sample was evacuated up to 10^{-5} Torr, filled with helium up to a pressure of 10^{-2} Torr and then melted. The measurements were performed under the following conditions:

Magnetic field modulated with 100 Hz. RF power: 0.0002 – 1 mW. Field: 3340 – 3500 G. Sweep width: 100 – 500 G. Conversion time: 81.92 ms. Time constant: 40.96 ms. Modified amplitude: 0.2 – 13 G temperature: 5 K. The g value is determined using a Hall probe.

g) Measurement of the diffuse reflection spectra (Kubelka-Munk function)

The diffuse reflection spectra of the powders were measured with a Shimadzu UV 2401PC UV/Vis spectrometer, which was equipped with an Ulbricht sphere. Barium sulphate was used as white standard and was used to grind the powders in a mortar prior to the measurement. The Kubelka-Munk function is proportional to the absorbance.

h) Superhydrophilic properties

For the measurement of the contact angle of water, vlp-TiO₂ and unmodified TiO₂ were respectively suspended in distilled water, applied to a 5 x 5 cm aluminum plate using "dip coating" and calcinated for 1 hour at 400 °C. Following storage in daylight, a contact angle of 21 ° was measured for unmodified titanium dioxide, and a contact angle of only 8 ° was measured for vlp-TiO₂. The contact angle for the uncoated aluminum plate was 91 °.

Figure 12 shows the Kubelka-Munk function of compositions according to the invention in comparison with the Kubelka-Munk function of the photocatalytically active substance used for the manufacture of these compositions. In the figure, a) shows the Kubelka-Munk function of the photocatalytically active substance. b) shows the Kubelka-Munk function of a composition with styrene acrylate (Alberdingk AS 6002) as a binder.

c) indicates the Kubelka-Munk function of a composition in accordance with the invention with a silicone resin as a binder. d) shows the Kubelka-Munk function of a composition in accordance with the invention with vinyl acetate ethylene (Mowilith LDM 1871) as a binder. e) shows the Kubelka-Munk function of a composition with a copolymer of a styrene/butyl acrylate (Dilexo AS 151) as a binder.

The binder fraction of the composition in accordance with the invention is 2 to 60 percent by weight, preferably 3 to 50 percent by weight, specifically 9 to 35 percent by weight. The fraction of the photocatalytically active substance in the composition is expediently 2 to 40 percent by weight, preferably 2 to 20 percent by weight, especially preferably 4 to 15 percent by weight, specifically 5 to 10 percent by weight. It has been shown that the targeted photocatalytic effect can already be obtained to an especially satisfactory extent if the fraction of the photocatalytically active substance is 5 percent by weight or more. It has furthermore been shown that the effects of the photocatalytically active substance on the remaining properties of compositions according to the invention remain virtually negligible if the fraction of the photocatalytically active substance is 10 percent by weight or less.

The invention is not limited to the examples of embodiments explained in reference to the drawing. Instead, the use of compositions with different types of binders is also contemplated. In addition, not only carbon-doped photocatalytically active substances may be used within the context of the invention. It has proven to be especially advantageous to use sulfur-doped photocatalytically active substances as well.

CLAIMS

1. Composition for coating walls, façades or the like comprising at least one binder, characterized by at least one photocatalytically active substance with a significant light absorption at at least one absorption wavelength in the range of 380 to 500 nm.
2. Composition in accordance with claim 1, characterized in that the ratio of the absorbance (Kubelka-Munk function $F(R_{00})$) of the photocatalytically active substance and the absorbance (Kubelka-Munk function $F(R_{00})$) of the binder at at least one absorption wavelength in the range of 380 nm and 500 is greater than 6.25×10^{-3} , preferably 1×10^{-2} .
3. Composition in accordance with claim 1 or 2, characterized by a binder which exhibits an absorbance (Kubelka-Munk function $F(R_{00})$) of less than 0.8, specifically less than 0.5, at at least one absorption wavelength in the range of 380 to 500 nm, specifically in the range of 400 to 450 nm, if the photocatalytically active substance exhibits an absorbance (Kubelka-Munk function $F(R_{00})$) of over 0.005, specifically over 0.01, and especially preferably 0.02 or more, at the absorption wavelength under the same measurement conditions.
4. Composition for coating walls, façades and the like, especially according to claim 1, comprising at least one binder and at least one photocatalytically active substance, characterized in that the binder exhibits at least one organic component and/or at least one inorganic component.
5. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance exhibits a semiconductor, specifically TiO_2 .
6. Composition in accordance with claim 5, characterized in that the semiconductor is mixed, specifically doped, at least in parts, with a foreign substance, such as e. g. S, N and/or C.

7. Composition in accordance with claim 5 or 6, characterized in that the titanium dioxide is essentially present in an anatas phase.
8. Composition in accordance with any of the preceding claims, characterized in that the sulfur and/or carbon content of the photocatalytically active substance is 0.05 to 4 percent by weight, preferably 0.05 to 2 percent by weight, and especially preferably 0.4 to 1.5 percent by weight.
9. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance is at least partially prepared by mixing a titanium-containing compound, preferably dissolved in a solvent, such as e. g. water, with an organic carbon compound and thermal treatment of this mixture at a temperature of 500 °C or less, preferably 400 °C or less, and especially preferably 300 °C or less, and exceeding 150 °C, especially 200 °C or more.
10. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance exhibits a strong absorption band at a bond energy of 285.6 eV in the X-ray photo electron spectrum (XPS) relative to the O1s band at 530 eV.
11. Composition in accordance with any of the preceding claims, characterized by at least one dispersing agent, at least one thickening agent, at least one anti-foaming agent, at least one pigment, at least one filler, at least one hydrophobization agent and/or at least one microbiocide.
12. Composition in accordance with any of the preceding claims, characterized by a supercritical composition, in which the solid fraction is adjusted to the liquid fraction such that no complete wetting of the solids takes place.
13. Composition in accordance with any of the preceding claims, characterized by at least one adsorption agent, such as e. g. activated charcoal, silicic acid, microsilica, silica gels, zeolites, bentonites, diatomaceous earth, foamed glass or the like.

14. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance exhibits an electron spin resonance spectrum (ESR), measured at a temperature of 5 K, which displays only one significant signal in the range of the g value of 1.97 to 2.05.
15. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance exhibits at least one signal in the ESR spectrum at a g value of 2.002 to 2.004.
16. Composition in accordance with any of the preceding claims, characterized in that the Kubelka-Munk function $F(R_{00})$ proportional to the absorbance for the photocatalytically active substance at 500 nm is approx. 50 % and at 600 nm approx. 20 % of the value at 400 nm.
17. Composition in accordance with any of the preceding claims, characterized by a photoactivity of at least 20 %, preferably at least 40 % and specifically at least 50 %.
18. Composition in accordance with any of the preceding claims, characterized in that the sulfur and/or carbon content of the photocatalytically active substance is in the range of 0.4 to 0.8 percent by weight.
19. Composition in accordance with any of the preceding claims, characterized in that the carbon and/or sulfur of the photocatalytically active substance is for the most part integrated only in a surface layer of the titanium dioxide particles.
20. Composition in accordance with any of the preceding claims, characterized in that the photocatalytically active substance shows no carbonate bands either in the X-ray photo electron spectrum (XPS) or in the infrared spectrum.
21. Composition in accordance with any of the preceding claims, characterized in that the specific surface of the photocatalytically active substance pursuant to BET is 100 to 250 m²/g, preferably 130 to 200 m²/g and especially preferably 130 to 170 m²/g.

22. Method for the production of a composition in accordance with any of the preceding claims, characterized in that, in a first step, an intermediate product is produced by dispersion of the photocatalytically active substance in an inorganic binder and that, in a second step, this intermediate product is mixed with an organic binder.

23. Use of a composition in accordance with any of the claims 1 to 21 in paints, plasters, varnishes and/or glazes for application on masonry, plaster surfaces, paintwork, wallpaper; wood, metal, glass and ceramic surfaces and/or thermal insulation composite systems and/or installed façade elements in interior and/or exterior applications.