

Surface-modified titanium dioxide

The invention relates to a surface-modified, pyrogenically produced titanium dioxide, a process for its production as well as its use.

- 5 It is known that highly-disperse pyrogenic titanium dioxide (for example, titanium dioxide P 25 S from Degussa-Hüls AG), on account of its low average primary particle size (21 nm) and of the structure of the aggregates and agglomerates resulting from the pyrogenic production process, has advantageous properties as a UV-A and UV-B blocker in cosmetic sunblock preparations. In addition, it is known that an increasing degree of dispersion of the titanium dioxide has a favourable effect on the UV-blocking action.
- 15 The hydrophilic surface of the pyrogenically produced titanium dioxide necessitates the use of high shear forces in order to achieve a high degree of dispersion, above all in oleophilic preparations. Consequently, pyrogenically produced titanium dioxides already surface-modified with
- 20 alkylsilyl groups are known (titanium dioxide T 805 from Degussa-Hüls Aktiengesellschaft) which, in addition to the improved dispersibility in oleophilic preparations even at low shear energies, also bring about an improved UV-blocking and a decreased photochemical activity in the
- 25 pyrogenic titanium dioxide. (Technical Information TI 1176 "Highly dispersed Titanium Dioxide for sunblock preparations").

A disadvantage of the known surface-modified pyrogenic titanium dioxides is the low interaction with hydrophilic

30 constituents of the cosmetic sunblock preparations, which is due to the exclusively oleophilic character of the surface.

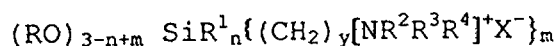
The object of the invention is the development of a pyrogenically produced titanium dioxide, the surface modification of which imparts to it an oleophilic as well as a hydrophilic character, and which exhibits a good
5 dispersibility in hydrophilic and in oleophilic media.

The invention provides surface-modified, pyrogenically produced titanium dioxide, which is characterised in that it is treated with at least one ammonium-functional silane.

In one embodiment of the invention, the surface-modified,
10 pyrogenically produced titanium dioxide can be characterised by the following physicochemical data:

BET surface area:	15 to 100 m ² /g
Bulk density:	150 to 700 g/l
pH value:	2.5 to 8.5
15 Loss on drying:	0.1 to 2.0 wt. %
Loss on ignition:	0.3 to 13.0 wt. %
Carbon content:	0.3 to 12.0 wt. %
Methanol wettability:	0 to 50 wt. %

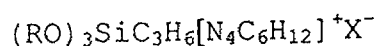
In one embodiment of the invention, the invention can
20 provide a surface-modified, pyrogenically produced titanium dioxide, which is characterised in that an ammonium-functional silane corresponding to the general formula



$n = 0-2$; $m = 1-2$ with $n+m < 3$; $y = 1-5$; $X = F, Cl, Br, I$
25 $R = \text{alkyl (C1-C5)}$; $R^1 = \text{alkyl (C1-C18), aryl}$; $R^2 = H, \text{alkyl, aryl, benzyl}$;

$R^4 = H, \text{alkyl, aryl, } -C_2H_4NR^5_2 \text{ with } R^5 = \text{alkyl}$

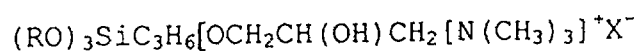
or one of the silanes listed below



30 $R = \text{alkyl (C1-C5)}$; $X = Cl, Br, I$

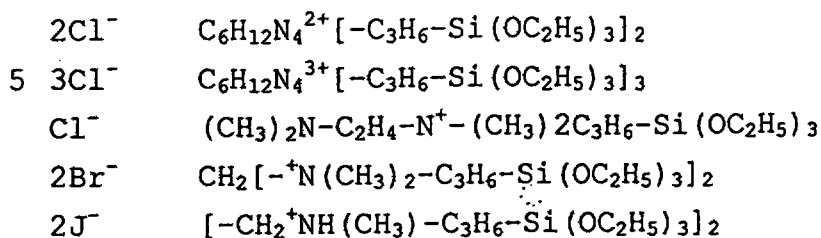


$R = \text{alkyl (C1-C5)}$; $X = Cl, Br, I$



R = alkyl (C1-C5); X = Cl, Br, I

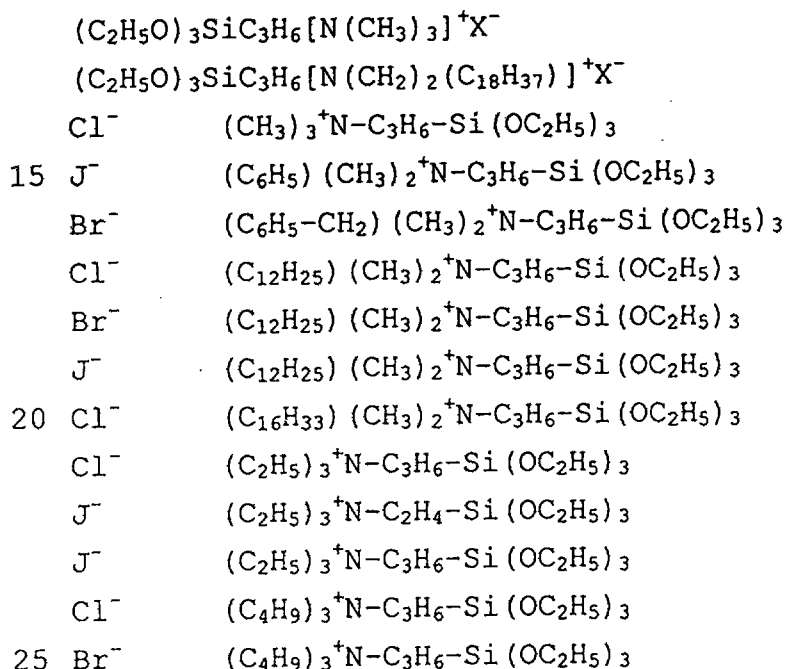
or one of the following silanes



or a mixture of two or more of the above-mentioned silanes

10 is used for the surface modification.

Examples of silanes which could be used are:



The invention also provides a process for the production of the surface-modified, pyrogenically produced titanium dioxide, which is characterised in that the pyrogenically produced titanium dioxide, in a mixing unit with intensive
 30 mixing, optionally in the presence of water or dilute acid, is sprayed with the silane, with the silane mixture or with a solution of the silane or silane mixture in ethanol, and then further stirred for approximately 10 to 30 minutes and
 35 subsequently tempered for between 0.5 and 6 hours at a temperature of 100 to 400°C. The tempering can be carried out in an atmosphere of protective gas, for example, N₂.

The pyrogenically produced titanium dioxide used can be a titanium dioxide of the type described in Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 21 (1982) pages 464 - 465.

- 5 The surface-modified, pyrogenically produced titanium dioxide according to the invention can be used in the field of cosmetics, in particular as a sunblock, also in toner powders, paints and varnishes, in silicone rubber, as abrasives and polishes, for example, in the field of CMP.
- 10 In the field of cosmetics, in particular in sunblock preparations, the surface-modified pyrogenically produced titanium dioxide according to the invention exhibits the following advantages:
- improved absorption of radiation in the range of 300-500
15 nm
 - good dispersibility in oleophilic and hydrophilic preparations

Examples

The titanium dioxide used was the pyrogenically produced
20 titanium dioxide P 25. Titanium dioxide P 25 is known from the series of publications Pigmente No. 56 "Hochdisperse Metalloxide nach dem Aerosilverfahren", 4th Edition, February 1989, Degussa AG.

The physicochemical data for titanium dioxide P 25 is as
25 follows:

		Titanium dioxide P 25
CAS Reg. Number		13463-67-7
Behaviour towards water		hydrophilic
Appearance		loose white powder
BET surface area ¹⁾	m ² /g	50 ± 15
Average size of primary particles	nm	21
Tamped density ²⁾	g/l	ca. 100
Specific weight ¹⁰⁾	g/ml	ca. 3.7
Loss on drying ³⁾ on leaving the supplier's premises (2 hours at 105°C)	%	< 1.5
Loss on ignition ⁴⁾ ¹⁾ (2 hours at 1000°C)		< 2
pH value ⁵⁾ (in 4% aqueous dispersion)		3-4
SiO ₂ ⁸⁾		< 0.2
Al ₂ O ₃ ⁸⁾		< 0.3
Fe ₂ O ₃ ⁸⁾		< 0.01
TiO ₂ ⁸⁾		> 99.5
ZrO ₂ ⁸⁾		-
HfO ₂ ⁸⁾		-
HCl ⁸⁾⁹⁾		< 0.3
Screen oversize ⁶⁾ (after Mocker, 45 µm)	%	< 0.05

1) in accordance with DIN 66131

2) in accordance with DIN ISO 787/XI, JIS K 5101/18 (not screened)

3) in accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21

5 4) in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23

5) in accordance with DIN ISO 787/IX; ASTM D 1208, JIS K 5101/24

6) in accordance with DIN ISO 787/XVIII; JIS K 5101/20

7) based on the substance dried for 2 hours at 105°C

- 8) based on the substance calcined for 2 hours at 1000°C
 9) HCl content is a constituent of the loss on ignition
 10) determined by means of a pycnometer with reference to air

Preparation - general procedure

- 5 TiO₂ P25 is placed in a mixer and sprayed with the silane, with mixing. The silane can be dissolved in a solvent, for example, ethanol. On conclusion of the spraying, mixing is continued for a further 10 to 30 minutes, followed by tempering for a period of 0.5 to 6 hours at a temperature of 100 to 400°C. The spraying and/or the tempering can be carried out in an atmosphere of protective gas, for example, under nitrogen.

Preparation of the described Examples

Example	Silane	Quantity of silane [g/100g P25]	Quantity of ethanol [g/100g P25]	Tempering time [h]	Temperature [°C]
1	Si 270/75	5	10	2	120
2	Si 270/75	7.5	0	2	120
3	Si 270/75	10	20	2	120
4	Si 275/75	5	10	2	120
5	Si 275/75	7.5	0	2	120
6	Si 275/75	10	20	2	120

15 Silanes used

Si 270/75 = $\text{Cl}^-(\text{CH}_3)_3\text{N}^+ - \text{C}_3\text{H}_6 - \text{Si}(\text{OC}_2\text{H}_5)_3$ (75% solution in ethanol)

Si 275/75 = $\text{Cl}^-(\text{C}_{18}\text{H}_{37})(\text{CH}_3)_2\text{N}^+ - \text{C}_3\text{H}_6 - \text{Si}(\text{OC}_2\text{H}_5)_3$ (75% solution in ethanol)

1. Physicochemical data

Example	Silane	Tamped density (g/l)	Carbon content (%)	pH value	Loss on drying (%)	Loss on ignition (%)	CH ₃ OH wettability wt. %
1	Si 270/75	225	1.3	3.7	0.5	2.9	0 %
2	Si 270/75	282	1.6	3.5	0.8	3.6	0 %
3	Si 270/75	397	2.1	3.6	0.4	4.6	0 %
4	Si 275/70	215	2.1	3.6	0.8	3.4	0 %
5	Si 275/70	368	3.2	3.3	1.0	4.9	20 %
6	Si 275/70	384	3.5	3.3	0.8	5.2	10 %

The products exhibit a hydrophilic and oleophilic character and can be used with advantage in cosmetic preparations.

Results of the tests of applicability

The measured UV/VIS spectra of prepared sunblock pastes exhibited good absorptions in the UV-A and UV-B region.

The comparison with the known product T 805 is shown in
5 Figure 1.

These results show that the titanium dioxides according to the invention can be used very effectively in sunblock preparations.

Thus a better absorption of the radiation is achieved
10 primarily in the 300 to 500 nm range.

The product T 805 is a pyrogenically produced titanium dioxide which has been treated with a trialkoxyoctylsilane.

Claims

1. Surface-modified, pyrogenically produced titanium dioxide, characterised in that it is treated with at least one ammonium-functional silane.
- 5 2. Surface-modified, pyrogenically produced titanium dioxide according to claim 1, characterised by the following physicochemical data:

	BET surface area:	15 to 100 m ² /g
10	Bulk density:	150 to 700 g/l
	pH value:	2.5 to 8.5
	Loss on drying:	0.1 to 2.0 wt. %
	Loss on ignition:	0.3 to 13.0 wt. %
	Carbon content:	0.3 to 12.0 wt. %
15	Methanol wettability:	0 to 50 wt. %
3. Process for the production of the surface-modified, pyrogenically produced titanium dioxides according to claim 1 or claim 2, characterised in that the pyrogenically produced titanium dioxide, in a mixing unit
 - 20 with intensive mixing, optionally in the presence of water or dilute acid, is sprayed with the silane, with the silane mixture or with a solution of the silane or silane mixture in ethanol, and then further stirred for approximately 10 to 30 minutes and subsequently tempered
 - 25 for between 0,5 and 6 hours at a temperature of 100 to 400°C.
4. Use of the surface-modified, pyrogenically produced titanium dioxide according to claim 1 in cosmetics, in sunblocks, in toner powders, in paints and varnishes, in
 - 30 silicone rubber, as abrasives and polishes, for example, in the field of CMP.



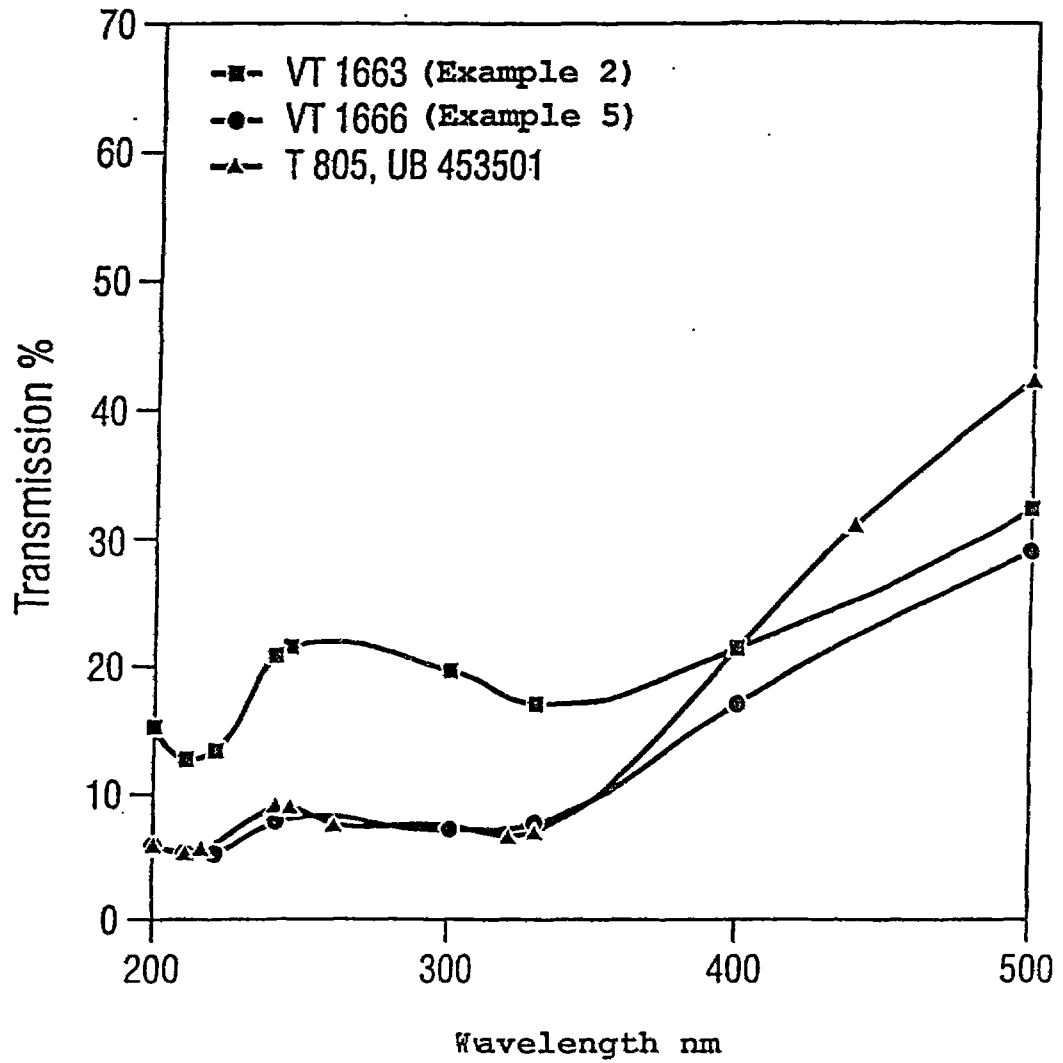
Abstract

Surface-modified titanium dioxide

Pyrogenically produced titanium dioxide surface-modified
with ammoniumfunctional silanes is produced by spraying the
5 pyrogenically produced titanium dioxide with the silane,
with the silane mixture or with a solution of the silane or
silane mixture in ethanol, and tempering.

It can be used in the field of cosmetics in sunblocks, in
toner powders, in paints and varnishes, in silicone rubber,
as abrasives and polishes, for example, in the field of
CMP.

Fig.1

Fig. 1UV Transmission of highly-disperse
titanium dioxide

3% in IPP with 7% - 10% Aerosil 200

Film thickness 10 μm