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(54) Title: STERICALLY STABILISED DISPERSION OF A HYBRID INORGANIC- ORGANIC MATERIAL IN OIL AS A PREPARATION FOR PROTECTION AGAINST UV RAYS AND A PROCESS OF PREPARATION THEREOF

(57) Abstract: The subject of the invention is a sterically stabilised dispersion of a hybrid inorganic-organic material in oil as a preparation for the protection against harmful effects of UV rays. The present invention refers to a new cosmetic material on the basis of composites of hybrid inorganic-organic coatings on TiO₂ nanocrystalline particles or another metallic oxide with increased dispersibility in organic vehicles and decreased formation of free radicals. The basic nanocrystalline particles of TiO₂ and the inorganic coating from the bridged silane are prepared by the sol-gel process. Molecules of an organic steric stabiliser are then covalently bound to the coating of the bridged silane, said stabiliser being selected from one of the following groups of compounds: higher fatty acids, linear polymers, cross-linked polymers, branched polymers and dendritic polymers. The presence of the steric stabiliser prevents the TiO₂ particles to agglomerate, improves dispersibility in organic vehicles, increases water resistance of the preparation and allows the use of high concentrations of oily suspensions that provide for a high factor of protection against harmful effects of UV rays.



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STERICALLY STABILISED DISPERSION OF A HYBRID INORGANIC-ORGANIC MATERIAL IN OIL AS A PREPARATION FOR PROTECTION AGAINST UV RAYS AND A PROCESS OF PREPARATION THEREOF

Field of Invention

The subject of the invention is a sterically stabilised dispersion of a hybrid inorganic-organic material in oil as a preparation for the protection against harmful effects of UV rays and a process of preparation thereof. The present invention belongs to the field of pharmaceutical technology and cosmetology, more precisely to the field of manufacturing of preparations for the protection against harmful effects of UV radiation. It is based on the principles of inorganic and organic chemistry and the chemistry and physics of surfaces. It refers to a new material and process for the preparation thereof on the basis of composites of hybrid inorganic-organic coatings on TiO₂ nanocrystalline particles with increased dispersibility in organic vehicles and decreased formation of free radicals. The process of preparation of said material is based on sol-gel process and subsequent covalent attachment of steric stabilisers. The material so obtained is intended for the manufacture of various sunscreen preparations.

Prior Art

Physical UV filters, of which TiO₂ and ZnO are of most significant importance, were discovered very early, yet their use was not acceptable in cosmetics, since they left white spots on skin due to their non-transparency. Transparency is conditioned by an average size of particles. The TiO₂ particles are transparent, if the average particle size is in the range between 20 to 100 nm, and the ZnO particles are transparent, if the particles have a size from 40 to 100 nm. However, the input particle size is not the only one that is important, the average particle size in the final preparation is of importance as well. Agglomeration of particles in a preparation may occur and the agglomerates thus obtained are no longer transparent.

Apart from scattering, the particles of such size absorb UV light (the nanocrystalline TiO₂ absorbs about 70% of the incoming UV light). Absorption of UV radiation may cause formation of free radicals that directly or through reaction with other ingredients in the sunscreen preparation cause cell damage.

The scope of harmful photocatalytic properties of nanocrystalline physical UV filters may be diminished if the particles are coated with compounds forming hydrated oxides and the latter function as hydroxyl radical catchers. The latter may be prepared e.g. by flame reaction of a nanocrystalline TiO₂ and functionalised silanes [Deller K, Kerner D, Meyer J: Surface-modified titanium dioxide, United States Patent 6663851], with which surface properties may be changed. However, the most often used process for the coating of such materials is the sol-gel process. By using the sol-gel process, coatings based on tetraethyl orthosilicate (TEOS), bis-1,2-triethoxysilylethane (BTSE) and aluminium oxide can be prepared, wherewith a smaller degree of adhesion and a higher degree of mechanical resistance can be achieved and such material is applicable in the coating of kitchen vessels [Shoup R, Rice N, Simes D, Nebo J, Georges GT: Abrasion and impact resistant coating compositions, and articles coated therewith, United States Patent 6905772].

The sol-gel process was also used in the preparation of sunscreen products based on xerogels. Chemical and physical UV filters may be incorporated into the structure of xerogels prepared by the sol-gel process on the basis of starting compounds having a general chemical formula $M(R)_n(P)_m$ (wherein M represents a metal or semi-metal, R represents a hydrolysable substituent, P represents a non-polymerisable substituent, and n may be 2-6, m may assume any value from 0-6) [Sunscreens for protection from sun radiation, WO/1998/031333]. The sol-gel process was also used to prepare SiO₂ coatings on TiO₂ nanoparticles based on silicic acid and TEOS for the application as UV filters [Ishii N, Wada K, Sekiguchi K, Takama M, Ito S, Yano K, Saito Y, Kawasaki K: Cosmetics, silica-coated metal oxide powder and production method therefor, United States Patent 6235270]. Such coatings decrease the scope of free radical formation, yet such composites are not dispersible in oily vehicles due to being strongly hydrophilic but only in water vehicles. In this case they may be subjected to microbiological

contamination and consequently preservatives must be used that can cause oversensitivity reactions like chemical UV filters. Hydrophilic preparations are not water resistant, which is of course desirable. By using oily vehicles a danger of microbiological contamination can be done away with and water resistance of sunscreens may be increased, however, the surfaces of UV filters must be hydrophobic for dispersibility in oily vehicles.

The latter may be achieved by coating the particles with silicic acid or its precursors and by subsequent hydrophobisation of the coating surface with silicone oils, organic alkoxy silanes and salts of high fatty acids [Wada K, Ishii N, Irie M, Sekiguchi K, Takama M: Cosmetic preparation, surface-hydrophobised silica-coated metal oxide particles, sol of silica coated metal oxide, and processes for producing these, United States Patent 6534044]. However, said process comprises many steps and is therefore time consuming and industrially less acceptable. By coating with a wide specter of silanes and siloxanes the photostability of chemical UV filters was improved [Chodorowski S, Xavier Quinn F, Sanchez C: Method for improving UV radiation stability of photosensitive sunscreen filters (United States Patent 6607713)], yet the process of preparation of these composites comprises at least one surfactant, which may additionally irritate skin and cause oversensitivity reactions due to irritability and alergogenity of chemical UV filters. Increased photostability and hydrophoby of a surface and good transparency for visible light of metallic oxides as UV filters may be achieved simultaneously by coating the particles with one or more compounds from the group consisting of silicone oils, alkoxy silanes (e.g. TEOS), silane coupling reagents (as BTSE) or salts of higher fatty acids. Fatty acids in these cases are only adsorbed on particles by a process of spray drying or adsorption from solutions - this may increase hydrophoby, yet desorption may occur in oily vehicles; there is no steric stabilisation and such preparations are thus not stable [Ishii N, Wada K, Takama M: Silica-coated mixed crystal oxide particle, production process thereof and cosmetic material using the same, United States Patent 7347986].

Although the problem of formation of free radicals and dispersibility in oily vehicles

was solved by coating physical UV filters, the suspensions prepared in this way are not entirely resistant against aggregation of particles, because the small size of particles and their large specific surface provide huge interaction potential and the particles may agglomerate. Suspensions of said type are thermodynamically unstable, since the particles irreversibly agglomerate when getting close together. Agglomeration does away with transparency in the visible part of the spectrum and diminishes coverage and consequently protection of skin after application. Due to tendency for aggregation it is not possible to yield high concentrations of suspension and the particles may agglomerate also under the influence of mechanical burdens which may occur during transport of the product.

A problem that has remained unsolved is that the particles are not resistant to irreversible agglomeration and it is therefore not possible to reach high concentrations of suspensions and transparency for the visible light over a long time period. Moreover, known preparations are poorly resistant to water and repeated application is needed after each contact with water.

Solution to the Technical Problem with Embodiments

The problem is solved by the invention by first coating particles of a physical UV filter with a hydrophobic hybrid silane coating, to which a steric stabiliser is then covalently bound, said stabiliser not forming a compact coating. The particles thus obtained, i.e. the particles having one coating and a steric stabiliser, are then dispersed in a suitable oily vehicle. The dispersions thus obtained may then be used for the manufacturing of optional derivatives used in cosmetic industry.

Due to said hybrid silane coating said product is less prone to forming free radicals. Since the coating is hydrophobic, the coated particles are better dispersible in oil. Attachment of a steric stabiliser stabilises dispersed coated particles and they get resistant to agglomeration. Transparency is ensured over a longer period of time and high concentrations of suspensions can be reached. As both the coating and the steric stabiliser are hydrophobic, extremely water resistant oil suspensions can be prepared and consequently there is no need for

repeated application to skin. Owing to improved dispersibility in oil and resistance to the agglomeration of particles such oil suspensions are more efficient than the existing sunscreens based on chemical UV filters even in low concentrations. Efficiency may even be additionally improved by increasing the concentration of particles, which is possible due to the resistance to agglomeration. Efficiency can be evaluated by spectroscopic measurement of the share of penetrated UV light and is represented in Figure 2 in an example of a layer having a thickness of 2 mm with 0.5% by weight of preparation from Embodiment A in olive oil.

The process of preparation of a coating and that of attaching a steric stabiliser are simple and economical and are therefore suited for industrial manufacturing.

The invention will be described by way of embodiments and figures, showing in:

Figure 1: a FTIR spectre of a sample from Embodiment B 2. A peak is marked at 960 cm^{-1} and belongs to a vibration of Ti-O-Si bonds,

Figure 2: Diagram of percentage of penetrated UV-B (280-320 nm) and UV-A (320-400 nm) light of a 2 mm thick layer of dispersion with 0.5 % by weight of preparation from Embodiment A in olive oil.

The subject of the invention is a kinetically stabilised suspension with physical UV filters that is prepared in the suggested solution by a steric stabilisation of particles, which is carried out by covalent attachment of steric stabilisers via -Si-O-C(=O)R, -Si-O-R or a similar bond. R represents long linear or branched conformation changeable compounds with functional groups providing for covalent attachment to silanol groups and do not form a compact coating in any instance, but are attached to the coating of silane with one to ten bonds. Such compounds belong to a group of higher fatty acids, preferably oleic, stearic and/or palmitic acid, linear polymers, preferably polyethyleneglycols, nylon and/or polydimethylsiloxane, cross-linked polymers, preferably various gums, branched polymers, preferably low density polyethylenes, dendritic polymers, preferably dendrones. A steric stabiliser causes reflective interaction that prevents the

particles from getting closer to a distance, at which van der Waals interactions start. The steric reflective interaction thus represents an unsurpassable energetic barrier of agglomeration, due to which the suspension becomes kinetically stabilised.

A further positive effect of a steric stabiliser is improved dispersibility in organic vehicles and improved water resistance of the preparation.

The particles of the physical UV filter in the present invention belong to the group consisting of metallic oxides, preferably to the group of titanium oxide, preferably rutile, anatase, brookite, $\text{TiO}_2\text{-B}$ or a mixture thereof, zinc, cerium, zirconium, iron oxide with a size of 20-100 nm and specific surface from 10-200 m^2/g . The thickness of silane coating, preferably of a bridged, simple or functionalised silane, ranges from 0.5 to 50 nm. A steric stabiliser is covalently bound to the surface of such coating and the coating should therefore be adequately reactive. The reactivity of the coating is adjusted by use of silane, in which a group with a positive inductive effect is coupled to a silicon atom, which increases electron density on the silanol group and thus increases reactivity with electrophilic activated groups of steric stabilisers. The bridged silane represents a compound having a general formula $(\text{R}_1\text{O})_3\text{-Si-R}_2\text{-Si-(OR}_1)_3$, wherein R_1 is a linear or branched alkyl group having 1-15 carbon atoms, and R_2 is a non-hydrolyzable linear, branched or cyclic alkylene or allylene group, which may be substituted or unsubstituted. Preferably bis-1,2-(triethoxysilyl) ethane (BTSE) is used from this group. Simple or functionalised silane is a compound of general chemical formula $(\text{R}_1\text{O})_4\text{-Si}$ or $(\text{R}_1\text{O})_3\text{-Si-X}$; wherein R_1 is a linear or branched alkyl group having 1-15 carbon atoms, X is a non-hydrolyzable hydrophilic, hydrophobic, ionising or non-ionising or single-atom or multiple-atom linear, branched or cyclic, saturated, unsaturated or aromatic functional group. If the metallic oxide is TiO_2 , a covalent bond is formed during the preparation of the coating from bridged, simple or functionalised silane, which is noticed in FTIR specter as a peak with the maximum at $950\text{-}965\text{ cm}^{-1}$, which is shown in Figure 1. The steric stabiliser, which is covalently bound to the coating, represents longer linear or branched

conformation changeable compounds and is attached to the coating of silane only with one or several bonds, wherein said compounds belong to a group of higher fatty acids, preferably oleic, stearic and/or palmitic acid, linear polymers, preferably polyethyleneglycols, nylon and polydimethylsyloxane, cross-linked polymers, preferably various gums, branched polymers, preferably low density polyethylenes or dendritic polymers, preferably dendrons. The oily vehicle, in which coated particles with a covalently bound steric stabiliser are dispersed, is oil or a mixture of oils selected from a group of dermatologically acceptable natural and synthetic oils.

The described coating is prepared following a base catalysed sol-gel process including one or several organic solvents selected from a group of alcohols, ketons, ethers or esters and water, base catalyst, which may be ammonia, ammonia derivative, ammonium salt of an organic or inorganic acid, alkali or earth alkali hydroxide, alkali or earth alkali carbonate or hydrogencarbonate or any other base compound and does not include any surfactant, which might cause oversensitivity reactions.

The steric stabiliser is attached to the coating in the form of an activated derivative, preferably acid halide, anhydride, activated ester, coupled compound preferably obtained by a coupling reagent of dicyclohexylcarbodiimide (DCC) or a similar coupling reagent, wherein the reactions of activation and bonding are carried out in an anhydrous medium in one or several steps. The product obtained by a reaction of attaching a steric stabiliser is isolated, preferably by filtration and dried until the product mass no longer changes. The described dispersion of a sterically stabilised hybrid inorganic-organic material is used in various cosmetic products as a preparation for protection against harmful effects of UV rays, preferably for the manufacturing of creams, lotions, aerosols, gels or sticks or other cosmetic preparations.

Embodiment A:

1. Preparing a coating from a bridged silane:

Prepare a suspension of TiO₂ P25 (Degussa) in a flat-bottom flask in purified water by weighting 600 mg of TiO₂ and suspending it in 300 g of purified water. Close the flask with a closure. Homogenise the suspension for 30 minutes in ultrasound bath at a temperature of 50°C. Further homogenise the suspension for 15 min at room temperature by stirring with a magnetic stirrer at 700 revolutions per minute.

Meanwhile, prepare a reaction mixture in a 100 ml bowl by mixing 46 g of ethanol (Riedel de Haen), 11 g of BTSE (ABCE GmbH) and 6.5 g of water and cover with a parafilm. Simultaneously weight 3 g of 25-percent ammonia solution (Merck) to the 10 ml bowl and close the bowl.

After 15 min of homogenisation of the TiO₂ suspension with the magnetic stirrer, first add the reaction mixture while stirring and then dropwise add the ammonia solution. Re-cover the flask and stir the so prepared mixture with the magnetic stirrer at room temperature for 90 min.

After the completion of reaction filter the product through a membrane filter by suctioning. Discard the filtrate and completely dry the product at normal pressure and 50°C.

2. Attaching a steric stabiliser:

Weight 100 mg of a sample prepared by the process in step 1 (a sample with silanol groups on the surface) to a 100 ml flask, add 100 mg of lauric acid (SAFC). Use a measuring cylinder to measure 50 ml of dichloromethane (Merck). Finally, add 100 mg of dicyclohexylcarbodiimide (DCC) (Aldrich). Pour the measured dichloromethane to the flask with the sample from 1 and lauric acid and add DCC. Cover the flask with closure. Place the so prepared reaction mixture on the magnetic stirrer, add a spatula end of a catalyst (dimethylaminopyridine-DMAP) and set the stirrer to 500 revolutions per minute. After 12 hours of stirring at room temperature, filter the product by suction through a membrane filter and rinse 5-times with dichloromethane and dry the obtained product for 48 hours at 50°C.

3. Dispersing the material from the above process (Step 2) in olive oil

Disperse 20 mg of material obtained by the process in Step 2 in 39.980 g of olive oil (Lex). Then disperse the dispersion for 30 min in ultrasound bath.

Embodiment B:

1. Preparing a coating from a bridged silane:

Prepare a TiO₂ suspension 25 (Degussa) in a flat-bottom flask in purified water by weighting 500 mg of TiO₂ and suspending it in 100 g of purified water. Close the flask with a closure. Homogenise the suspension for 30 minutes in ultrasound bath at a temperature of 50°C. Further homogenise the suspension for 15 min at room temperature by stirring with the magnetic stirrer at 700 revolutions per minute.

Meanwhile, prepare a reaction mixture in a 100 ml bowl by mixing 40 g of ethanol (Riedel de Haen), 30 g of BTSE (ABCE GmbH) and 15 g of water and cover the bowl with a parafilm. Simultaneously weight 3.5 g of 25-percent ammonia solution (Merck) in a 10 ml bowl and close the bowl.

After 15 min of homogenisation of the TiO₂ suspension with the magnetic stirrer, first add the reaction mixture while stirring and then dropwise add the ammonia solution. Re-cover the bowl and stir the so prepared mixture with the magnetic stirrer at room temperature for 90 min.

After the completion of reaction filter the product through a membrane filter by suctioning. Discard the filtrate and completely dry the product at normal pressure and 50°C.

2. Attaching a steric stabiliser:

Weight 100 mg of a sample prepared by the process in step 1 (a sample with silanol groups on the surface) to a 100 ml flask, and suspend it in 50 ml of dichloromethane (Merck). Cover the bowl with a rubber septa. Separately, measure 0.1 ml of stearyl chloride (Aldrich) in a syringe and add it to the suspension through the septa. Place the so prepared reaction mixture on the magnetic stirrer and set the stirrer to 500 revolutions per minute. After 12 hours of stirring at room temperature, filter the product by suction through a membrane filter and rinse 5-times with dichloromethane and dry the obtained product for 48 hours

at 50°C.

3. Dispersing the material from the above process in coconut oil

Disperse 50 mg of material obtained by the process in Step 2 in 30 g of coconut oil (SICTIA). Then disperse the dispersion for 30 min in ultrasound bath.

Embodiment C:

1. Preparing a coating from a bridged silane:

Prepare a TiO₂ suspension P25 (Degussa) in a flat bottom flask in purified water by weighting 1 g of TiO₂ and suspending it in 200 g of purified water. Close the flask with a closure. Homogenise the suspension for 30 minutes in ultrasound bath at a temperature of 50°C. Further homogenise the suspension for 15 min at room temperature by stirring with the magnetic stirrer at 700 revolutions per minute.

Meanwhile, prepare a reaction mixture in a 100 ml bowl by mixing 100 g of ethanol (Riedel de Haen), 50 g of BTSE (ABCE GmbH) and 40 g of water and cover the bowl with a parafilm. Simultaneously weight 5 g of 25-percent ammonia solution (Merck) in a 10 ml bowl and close the bowl.

After 15 min of homogenisation of the TiO₂ suspension with the magnetic stirrer, first add the reaction mixture while stirring and then dropwise add the ammonia solution. Re-cover the bowl and stir the so prepared mixture with the magnetic stirrer at room temperature for 90 min.

After the completion of reaction filter the product through a membrane filter by suctioning. Discard the filtrate and completely dry the product at normal pressure and 50°C.

2. Attaching a steric stabiliser:

Weight 100 mg of a sample prepared by the process in Step 1 (a sample with

silanol groups on the surface) to a 100 ml flask, add 100 mg of palmitic acid anhydride (Aldrich). Use a measuring cylinder to measure 50 ml of dichloromethane (Merck). Pour the measured dichloromethane to the flask with the sample from 1 and the palmitic acid anhydride. Cover the flask with closure. Place the so prepared reaction mixture on the magnetic stirrer and set the stirrer to 500 revolution per minute. After 12 hours of stirring at room temperature filter the product by suction through a membrane filter and rinse 5-times with dichloromethane and dry the obtained product for 48 hours at 50°C.

3. Dispersing the material from the above process in almond oil

Disperse 1 g of the material obtained by the process in Step 2 in 24 g of almond oil (SICTIA). Then disperse the dispersion for 30 min in ultrasound bath.

The embodiments are only explicative and do not limit the patent in its scope.

Claims

1. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil **characterised in that** it comprises a metallic oxide, a coating from a bridged silane and a covalently attached steric stabiliser containing longer linear or branched conformation changeable compounds from the group of higher fatty acids, preferably oleic, stearic and/or palmitic acid, linear polymers, preferably polyethyleneglycols, nylon and/or polydimethylsiloxan, cross-linked polymers, preferably various gums, branched polymers, preferably low density polyethylenes, dendritic polymers, preferably dendrons and provide for covalent attachment to silanol groups with one to ten bonds.
2. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in Claim 1 **characterised in that** the size of particles of a metallic oxide, preferably selected from the group of titanium, zinc, cerium, zirconium, iron oxide ranges from 20-100 nm, with a specific surface from 10-200 m²/g.
3. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any preceding Claims **characterised in that** the metallic oxide in case of a titanium oxide is rutile, anatase, brookite, TiO₂-B or a mixture thereof.
4. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any preceding Claims **characterised in that** the thickness of coating from a bridged silane on the particles of a metallic oxide as claimed in Claims 2 and 3 is between 0.5 in 50 nm.
5. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in Claim 4 **characterised in that** a steric stabiliser is covalently bound to the coating.

6. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in Claims 4 and/or 5 **characterised in that** the coating consists of a bridged silane and the starting material for the coating has the general chemical formula $(R^1O)_3-Si-R^2-Si-(OR^1)_3$, wherein R^1 is a linear or branched alkyl group having 1-15 carbon atoms, R^2 is a non-hydrolysisable linear, branched or cyclic alkylene or allylene group that may be substituted or unsubstituted.

7. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any of Claims 4 to 6 **characterised in that** the starting material for the coating consists of the bridged silane 4-6 bis-1,2-(triethoxysilyl) ethane (BTSE).

8. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any of Claims 1 to 3, 5, 8, **characterised in that** the coating consists of a simple or functionalised silane having a general chemical formula $(R^1O)_4-Si$ or $(R^1O)_3-Si-X$; wherein R^1 is a linear or branched alkyl group having 1-15 carbon atoms, X is a non-hydrolysisable hydrophilic, hydrophobic, ionising or non-ionising, single- or multiple-atom linear, branched or cyclic, saturated, unsaturated or aromatic functional group.

9. Dispersion as claimed in any of Claims 2 to 8 **characterised in that** the metallic oxide with a coating has a typical absorption peak with a maximum at $955-965\text{ cm}^{-1}$ in FT-IR specter, which corresponds to the vibration of the Ti-O-Si bond.

10. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any of Claims 4 to 8 **characterised in that** a steric stabiliser is covalently bound to the coating, said stabiliser comprising longer linear or branched conformation changeable compounds and is attached to the coating of silane with one to ten bonds, wherein said compounds belong to a group of higher fatty acids, preferably oleic, stearic and/or palmitic acid, linear polymers, preferably polyethyleneglycols, nylon and polydimethylsyloxane, cross-linked

polymers, preferably various gums, branched polymers, preferably low density polyethylenes or dendritic polymers, preferably dendrons.

11. Dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any of preceding Claims **characterised in that** the particles coated with a coating, to which a steric stabiliser is covalently bound, are dispersed in an oily vehicle, which is oil or a mixture of oils from the group of dermatologically acceptable natural or synthetic oils.

12. Process for the preparation of a dispersion of a sterically stabilised hybrid inorganic-organic material in oil as claimed in any of Claims 1 to 11 **characterised in that** the coating is prepared by base catalysed sol-gel process including one or several organic solvents from the group of alcohols, ketons, ethers or esters and water, base catalyst, which may be ammonia, ammonia derivative, ammonium salt of an organic or inorganic acid, alkali or earth alkali hydroxide, alkali or earth alkali carbonate or hydrogencarbonate or any other base compound and does not include any surfactant.

13. Process as claimed in Claim 12, **characterised in that** the preparation of the coating comprises the following steps:

- a. suspending 50 mg to 20 g of particles from Claims 2 and 3 in 100 g of water,
- b. homogenising the obtained suspension, preferably by ultrasound or stirring,
- c. separately preparing a reaction mixture prepared by mixing 0.5 to 200 g of starting material as claimed in Claims 6, 7 or 8, and 6.5 to 465 g of organic solvent, 0 to 100 g of water and such quantity of base catalyst to obtain an adequate pH of the mixture (or rather by mixing the quantities of said substances that yield such mass ratios),
- d. adding of reaction mixture from step c to the suspension prepared in steps a and b

- e. gradual adding of the catalyst of Claim 12 to the reaction mixture prepared in step d,
- f. stirring of reaction mixture obtained in step e for 1 to 25 hours at room temperature or at a temperature ranging from 25 to 100°C,
- g. isolating a solid product obtained in step f, preferably by filtration,
- h. drying the isolated solid product obtained in step g at room temperature or at a temperature ranging from 25 to 100°C, until the mass no longer changes.

14. Process as claimed in Claim 12 **characterised in that** said process of covalent attachment of a steric stabiliser to the coating comprises attaching a steric stabiliser in the form of an activated derivative, preferably an acid halide, anhydride, activated ester, coupled compound obtained preferably by the coupling reagent of dicyclohexylcarbodiimide (DCC) or a similar coupling reagent, wherein the reactions of activation and attachment are performed in an anhydrous medium in one to five steps.

15. Process of Claim 14, **characterised in that** the product is isolated after the reaction is completed, preferably by filtration and dried until the mass no longer changes.

16. Use of a dispersion of a sterically stabilised hybrid inorganic-organic material in oil for cosmetic products as a preparation for protection against harmful effects of UV rays, preferably for the preparation of creams, lotions, aerosols, gels or sticks or other cosmetic preparations.

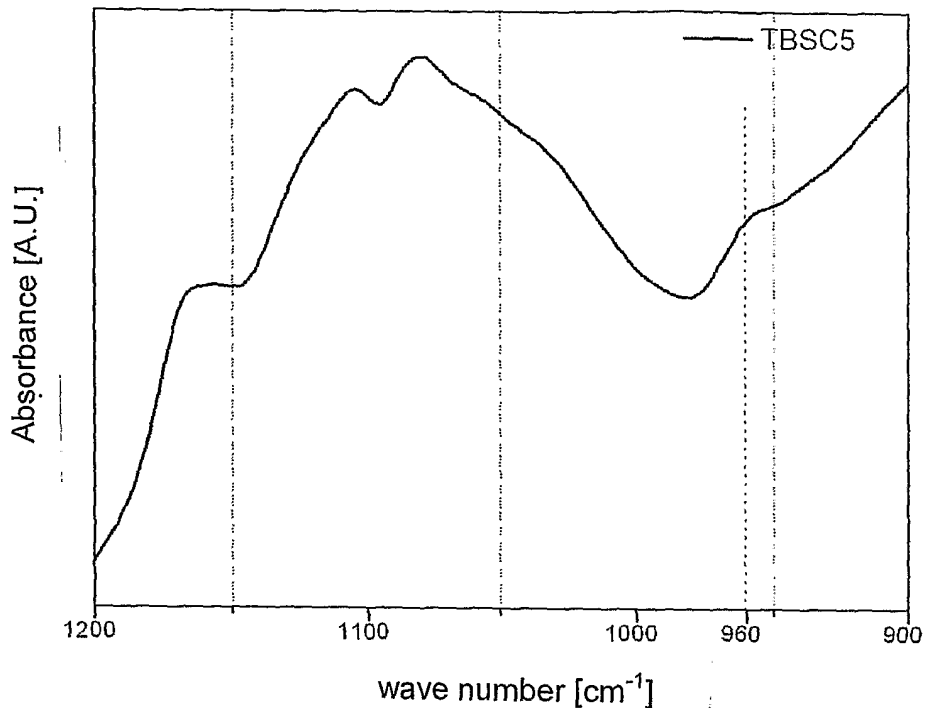


Figure 1

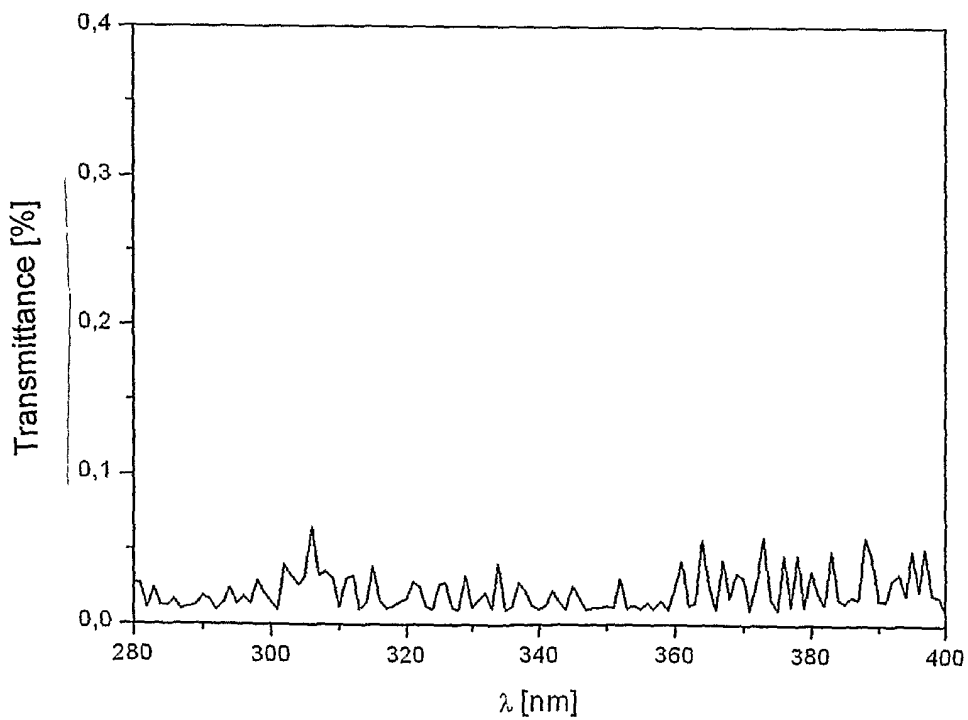


Figure 2