

A COLLOIDAL DISPERSION AND REDISPERSIBLE COMPOSITION
IN THE FORM OF A COLLOIDAL DISPERSION, BASED ON CERIUM OXIDE

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The present invention is concerned with a colloidal dispersion and a redispersible composition in the form of a colloidal dispersion with a cerium oxide base.

Dispersions of cerium compounds are used in numerous applications. Particular mention may be made of heterogeneous catalysis, and, in particular, catalysis for the treatment of exhaust gases from internal combustion engines (catalysis for automotive post-combustion). These dispersions can also be used as anti-corrosion coating agents or in cosmetics.

However, the use of these dispersions is restricted because of a certain instability over time which results in sedimentation. Furthermore, the cost of transporting these dispersions is further increased because in addition to the active element it is necessary to transport the liquid phase in which the active element is in suspension.

It is therefore particularly worthwhile to be able to have available either stable dispersions or solid products capable of being re-dispersed in order to give a colloidal suspension.

Furthermore, the known processes for the preparation of these dispersions only enable suspensions to be obtained which have a very acid pH, i.e. usually of less than 5.

Now, in the applications mentioned hereinabove, and, in particular, in the case of cosmetics, it is important to be able to have available colloidal dispersions with less acid pH values.

A first object of the invention is therefore the preparation of a stable colloidal dispersion of cerium oxide which has, in particular, a high pH value.

A second object of the invention is therefore the obtaining of a solid composition with a cerium oxide base which is redispersible in the form of a colloidal dispersion.

To this end, the colloidal dispersion of cerium oxide in a liquid phase according to the invention is characterised in that it further comprises at least one additive selected from:

- β -diketones;
- monocarboxylic acids comprising a hydroxy function in the α - or β -position;
- diols.

The invention is also concerned with a redispersible composition in the form of a colloidal dispersion, characterised in that it comprises a cerium oxide and at least one additive selected from:

- β -diketones;
- monocarboxylic acids comprising a hydroxy function in the α - or β -position;
- diols

The invention is also concerned with a process for the preparation of a colloidal dispersion of cerium oxide, characterised in that at least one additive selected from:

- the β -diketones;
- monocarboxylic acids comprising a hydroxy function in the α - or β -position;
- diols

is added to a colloidal dispersion of cerium oxide as the starting material.

The dispersions according to the invention are particularly advantageous in that they are stable for several months at least up to pH values in the order of 7.5.

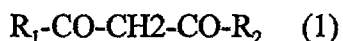
Further features, details and advantages of the invention will emerge more fully from reading the following description, as well as the various concrete but non-limitative examples intended to illustrate it.

Throughout the description, the term, "colloidal dispersion of a cerium compound" denotes any system which is constituted by fine solid particles of colloidal dimensions based on

cerium oxide and/or hydrated cerium oxide (cerium hydroxide) in suspension in a liquid phase, said species furthermore possibly containing residual quantities of bonded or adsorbed ions, e.g. nitrate, acetate, citrate or ammonium ions. It will be noted in dispersions of this kind that cerium is to be found either completely in the form of colloids, or both in the form of ions and in the form of colloids.

Furthermore, it shall be stated here that the mean diameter of the colloids must be understood as denoting the mean hydrodynamic diameter of these latter, as determined by quasi-elastic diffusion of light in accordance with the method described by Michael L. Mc CONNELL in the review, "Analytical Chemistry 53, No. 8, 1007 A, (1981).

As stated hereinabove, the colloidal dispersion of the invention is characterised by the presence of an additive which can first of all be selected from the β -diketones. These are, in particular, compounds of the formula (1)



wherein R_1 and R_2 can be the same or different and represent a substituted or unsubstituted alkyl, alkoxy, aryl, aryloxy, aralkyl, arylalkyloxy group. At least one of R_1 and R_2 can also represent a polyalkylene ether alcohol residue.

Mention can be made, most particularly, of the compounds of formula (1) in which R_1 is an alkyl group, preferably methyl and R_2 represents an alkyl group, more particularly identical to R_1 or an aryl group, in particular a phenyl group.

Compounds which may be mentioned by way of example are those of the formula $CH_3-CO-CH_2-CO-CH_3$ (acetylacetone), $CH_3-CO-CH_2-CO-C_6H_5$ (benzoylacetone) or $C_6H_5-CO-CH_2-CO-C_6H_5$. By way of example of a polyalkylene ether alcohol residue, R_1 or R_2 can be a group of the formula $BuO(CH_2-CH_2O)_n$.

According to another embodiment of the invention, the afore-mentioned additive can be selected from monocarboxylic acids comprising a hydroxy function in the α - or β -position.

More particularly, phenol acids, e.g. salicylic acid, can be used.

According to a third embodiment of the invention, the afore-mentioned additive can be selected from diols.

The afore-mentioned additive is selected as a function of its hydrophobic or hydrophilic nature, depending on the type of dispersion which is to be obtained, in an aqueous or solvent medium.

The afore-mentioned additive is usually present in a quantity such that the additive/cerium oxide molar ratio varies between 0 (this value being excluded) and 5, and, preferably, between 0 and 1.

The mean diameter of the colloids of the dispersion is usually at the most 500 nm, and, preferably, at the most 10 nm.

Furthermore, the dispersion of the invention has a pH value of between 1 and 7.5, more particularly of between 5 and 7.5. This is understood as meaning that the dispersion of the invention remains stable in that pH range. Outside that range, destabilization thereof may occur. However, it should be noted that this possible destabilization is not irreversible. In fact, on returning to a pH within the range given above, a stable dispersion is once again obtained.

The colloidal dispersion of the invention can be a dispersion which is either in aqueous phase or in organic phase. In this latter case, the organic phase is selected from that which solubilises the afore-mentioned additive.

In the case of a dispersion in organic phase, the organic solvent used can be an inert aliphatic or cycloaliphatic hydrocarbon, or a mixture of the two, e.g. mineral oil or petroleum spirit, or mineral ether or petroleum ether, which may also contain aromatic components. Examples which can be given are hexane, heptane, octane, nonane, decane, cyclohexane, cyclopentane, cycloheptane and liquid naphthenes. Aromatic solvents such as benzene, toluene, ethylbenzene and xylenes are also suitable, as well as petroleum cuts of the Solvesso type (trade mark filed by the company EXXON), particularly Solvesso 100 which contains mainly

a mixture of methylethyl and trimethylbenzene and Solvesso 150 which contains a mixture of alkylbenzenes, in particular dimethylethylbenzene and tetramethylbenzene.

It is also possible to use chlorinated hydrocarbons such as chloro- or dichlorobenzene and chlorotoluene, as well as aliphatic ethers and cycloaliphatic ethers, such as diisopropyl ether and dibutyl ether, aliphatic ketones and cycloaliphatic ketones, such as methyl isobutyl ketone, diisobutyl ketone, mesityl oxide, and phenol ketones, such as acetophenone.

Esters can be envisaged. Esters capable of being used can be cited as those obtained from C1 to C8 alcohols, and, in particular, the palmitates of a secondary alcohol, such as isopropanol.

In the case of dispersions in organic phase, the liquid phase can further comprise an acid or a mixture of acids, the acid(s) being able to be selected from those comprising from 11 to 50 carbon atoms, and, preferably from 15 to 25 carbon atoms, and having at least one branch in the alpha-, beta-, gamma- or delta-position of the atom which carries the acid hydrogen.

It is advantageous if the pKa of at least one of the acids is at the most equal to 5, preferably equal to 4.5.

It is also advantageous if the side chain(s) of the branched acids comprises/comprise at least two carbon atoms, preferably three carbon atoms.

By way of example, it is possible to cite acids containing phosphorus, such as phosphoric acids, in particular diesters of phosphoric acid, phosphonic acids and their monoesters, and phosphinic acids.

It is also possible to cite the acids which make up the mixture of acids known by the name, isostearic acid.

It can be advantageous to add to the organic phase a promoter agent whose function is, during preparation of the dispersion in organic phase, to accelerate transfer of the colloids from the aqueous phase to the organic phase and to improve the stability of the organic dispersions obtained. The promoter agents used may be compounds having an alcohol function, and, most particularly, linear or branched aliphatic alcohols with 6 to 12 carbon atoms.

Specific examples can be cited as 2-ethylhexanol, decanol, dodecanol, or a mixture thereof.

The proportion of said agent in the organic phase is not critical and can vary greatly.

However, a proportion of between 2 and 15% by weight is usually particularly suitable.

There will now follow a description of the process for the preparation of the dispersion of the invention.

The starting material is a colloidal dispersion which could have been obtained by any known means. Reference may be made, in particular, to the processes described in European Patent Applications EP 206906, EP 208581, EP 316205. Most particularly, colloidal dispersions may be used which have been obtained by the thermohydrolysis of an aqueous solution of a cerium (IV) salt, such as nitrate, in particular in acid medium. A process of this kind is described in European Patent Application EP 239477 or EP 208580.

At least one additive of the type described hereinabove is added to this dispersion, in the afore-described quantities. After the additive has been added, it is possible to heat the dispersion to accelerate the reaction.

If necessary, it is possible to increase the pH of the dispersion thus obtained by various methods.

A first method consists in adding to the dispersion a base, e.g. sodium carbonate.

Another method consists in subjecting the dispersion to a dialysis treatment. In this case, the dialysis is carried out between a solution at the desired pH by using a dialysis membrane which is resistant to the pH of the dispersion and which has an exclusion diameter which is impermeable to the colloids. This can be, for example, a cellulosic membrane with a thin wall. One advantage of this method is to enable dispersions to be obtained which have a low anion content, and, more particularly, a low nitrate content. In this way, by way of example, for nitrates the NO_3/Ce molar ratio in the dispersion is less than 0.7 and can be, more particularly, between 0.01 and 0.7, and, still more particularly, between 0.15 and 0.3.

The description of the process given here relates to the preparation of the dispersion in aqueous phase. To prepare a dispersion in organic phase, a dispersion is first of all prepared in aqueous phase in the way stated, and that aqueous dispersion is then contacted with an organic phase of the composition disclosed hereinabove.

It is also possible to remove the water by drying the aqueous dispersion, and to then return the product obtained to the organic phase.

The dispersion of the invention also makes it possible to obtain a redispersible composition in the form of a colloidal dispersion.

To obtain a composition of this kind, said dispersion is subjected to evaporation, centrifugation, ultra-filtration, or osmotic compression.

The evaporation, centrifugation and ultra-filtration can be carried out using any suitable device.

Osmotic compression is a known method, the principle of which consists in equilibrating the chemical potential of the water through a membrane.

The procedure is carried out by placing the colloidal dispersion in a dialysis bag, e.g. of cellulosic material, this bag being placed in an aqueous solution whereof the chemical potential of the water differs from that of the aqueous phase of the dispersion. This can be

done, for example, by using an aqueous solution of polyethylene glycol (PEG), or of dextran. The concentration of PEG or of dextran fixes the osmotic pressure and therefore the final concentration of the colloidal dispersion of cerium compound.

The treatments which have just been mentioned are carried out by themselves or in combination, and they allow a colloidal dispersion to be converted continuously into a gel or a paste and then a powder. This paste or powder can possibly be dried at a temperature such that there is no evaporation of the additive described hereinabove. The concentration of cerium can range from a value of 2 to 200 g/l in the colloidal dispersion up to a value of 700g/kg, that is to say 1750 g/l in the powder or gel.

In this way, a redispersible composition in the form of a colloidal dispersion is obtained which is characterised in that it comprises a cerium oxide and at least one additive selected from the β -diketones, monocarboxylic acids comprising a hydroxy function in the α - or β -position, and diols.

This composition can be re-dispersed in a liquid medium, and in this way a colloidal dispersion is obtained which is identical to the colloidal dispersion of the invention described hereinabove.

The colloidal dispersions of the invention, such as those described hereinabove, or those of the type obtained by re-dispersing a redispersible composition, can be used in numerous applications. Particular mention may be made of catalysis, particularly for automotive post-combustion, lubrication, ceramics and cosmetics, and, in this case, they can be used in the preparation of cosmetics compositions, particularly in the preparation of anti-UV creams. They can be used on a substrate such as an anti-corrosion agent.

Some examples will now be given.

EXAMPLE 1

The starting material is a colloidal dispersion of CeO_2 with a pH of 2. The size of the colloids is 5nm. The concentration is 200g/l.

Acetylacetone is then added to the dispersion in a quantity such that the acetylacetone/cerium molar ratio is 1. A dispersion according to the invention is immediately obtained. A 10% solution of NaOH is then added in order to obtain a pH value of 6.5. This dispersion remains stable, and the particle size defined by the afore-mentioned method remains the same as that of the initial sol.

This dispersion is concentrated by osmotic compression. The solution used to concentrate the dispersion is constituted by a 45% solution of dextran in water containing a concentration of acetylacetone in the order of 10 g/l.

When osmotic equilibrium has been reached, the product is in the form of a paste having a concentration of 300 g/kg, that is to say 400 g/l.

Part of this paste is taken, and deionised water is added. It disperses spontaneously in order to give a dispersion identical to the initial dispersion.

The other part of this paste is dried more completely in air in the presence of silica gel to a concentration of 1400 g/l, that is to say 650 g/kg.

It is then re-dispersed in water, and it gives the initial dispersion.

EXAMPLE 2

0.07 g of salicylic acid is added to 100 ml of a CeO_2 dispersion with an oxide concentration of 20 g/l and a size of the colloids of 5 nm.

This stable dispersion has a pH value of 2. Part of this dispersion is concentrated by osmotic compression, as before. The powder obtained is dispersed in a solution of nitric acid with a pH value of 2.

In this way, a dispersion is obtained containing particles of cerium oxide identical to the initial particles.

The other part of the dispersion is dialysed against a solution of water containing 0.7 g/l of salicylic acid whereof the pH value can be fixed between 2 and 6 by means of NaOH or HNO₃. In this way, a stable dispersion is obtained whereof the pH value is that of the dialysis solution.

The concentration of this dispersion is 20 g/l. It can be increased by evaporating the water. In this way, a powder having a concentration of 300 g/kg, that is to say 400 g/l, is prepared, which is partly re-dispersed in water to obtain a dispersion of cerium oxide with a pH value of between 2 and 6 as a function of the initial pH value of the dispersion prior to drying.

EXAMPLE 3

The initial dispersion of cerium oxide of Example 2 is used.

20 ml thereof is mixed with 0.4 g of Rhodiastab 50® (C₆H₅-CO-CH₂-CO-C₆H₅). The mixture is placed in a closed bottle in a furnace at 50°C for 48 hours. In this way, a stable sol is obtained.

The water can be removed by evaporation in a furnace at 80°C. In this way, a powder is obtained which is dispersed in 20 ml of acetophenone.

In this way a stable dispersion in organic medium is obtained.

EXAMPLE 4

The same procedure is followed as in Example 3, but using 0.4 g of Rhodiastab 83® (C₆H₅-CO-CH₂-CO-CH₃).

EXAMPLE 5

This example reveals the benefit of having a dispersion according to the invention for use in cosmetics.

1 g acetylacetone is added to 100 ml of a 20g/l dispersion of CeO_2 whereof the size of the colloids is 5 nm. The pH value of the dispersion is then brought to 6 by dialysis against an aqueous solution at pH 6.

The range of absorption of the ultraviolet radiation is measured using a spectrometer. In the case of the initial dispersion, this range stops at 380 nm. In the case of the dispersion according to the invention, this range is extended up to 460 nm.



CLAIMS

1. - A colloidal dispersion of a cerium oxide in a liquid phase, characterised in that it also comprises at least one additive selected from:
 - β -diketones;
 - monocarboxylic acids comprising a hydroxy function in the α - or β -position;
 - diols.
2. - A dispersion according to claim 1, characterised in that the additive is selected from:
 - the compounds of formula (1)
$$R_1-CO-CH_2-CO-R_2 \quad (1)$$
in which R_1 and R_2 can be the same or different and represent a substituted or unsubstituted alkyl, alkoxy, aryl, aryloxy, aralkyl, arylalkyloxy group, or a polyalkylene-ether-alcohol residue;
 - from phenol acids.
3. - A dispersion according to claim 1 or claim 2, characterised in that it has a pH of between 1 and 7.5, and, more particularly, of between 5 and 7.5.
4. - A dispersion according to one of the preceding claims, characterised in that the liquid phase is water.
5. - A dispersion according to one of the preceding claims, characterised in that the liquid phase is an organic solvent.
6. - A dispersion according to one of the preceding claims, characterised in that it comprises the afore-mentioned additive in a quantity such that the molar ratio of additive / cerium oxide varies between 0 (this value being excluded) and 5, and, preferably, between 0 and 1.



7. - A process for the preparation of a colloidal dispersion of a cerium oxide, characterised in that added to a colloidal dispersion of the initial cerium oxide is at least one additive selected from:
- β -diketones;
 - monocarboxylic acids comprising a hydroxy function in the α or β position;
 - diols.
8. - A process according to claim 7, characterised in that after adding at least one afore-mentioned additive, a base is added to the dispersion.
9. - A process according to claim 7 or claim 8, characterised in that after adding at least one afore-mentioned additive, the dispersion is subjected to a dialysis treatment.
10. - A redispersible composition in the form of a colloidal dispersion, characterised in that it comprises a cerium oxide and at least one additive selected from:
- β -diketones;
 - monocarboxylic acids comprising a hydroxy function in the α - or β -position;
 - diols.
11. - A process for the preparation of a redispersible composition according to the preceding claim, characterised in that the starting material used is a dispersion of the type according to one of claims 1 to 6, or of the type obtained by way of the process according to one of claims 7 to 9, and said dispersion is subjected to evaporation, centrifugation, ultra-filtration or osmotic compression.
12. - Use of a dispersion of the type according to one of claims 1 to 6, or of the type obtained by way of the process according to one of claims 7 to 9, or of the type obtained by re-dispersing a redispersible composition according to claim 10 on a substrate such as an anti-corrosion agent, in a cosmetics composition, in catalysis, in particular for automotive post-combustion, in lubrication, or in ceramics.

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(54) Title: COLLOIDAL DISPERSION AND REDISPERSIBLE COMPOSITION IN THE FORM OF A CERIUM OXIDE BASED COLLOIDAL DISPERSION		
(57) Abstract: The invention relates to a colloidal dispersion, characterised in that it comprises a cerium oxide and at least one additive selected amongst β diketones, the monocarboxylic acids comprising an α- or β-hydroxy function and diols. It also relates to a redispersible composition in the form of a cerium oxide based colloidal dispersion and the same said additives. The colloidal dispersion of the invention may be obtained by a process which is characterised in that at least one above mentioned additive is added to a starting cerium oxide colloidal dispersion. Finally, the invention relates to the use of a dispersion of the above type or of the type obtained by redispersing a redispersible composition, on a substrate as anticorrosion agent, in a cosmetic composition, for catalytic purposes particularly in motor vehicle post combustion, for lubrication or in ceramics.		