

Cerium oxide powder and cerium oxide dispersion

The invention relates to a powder based on cerium oxide, its preparation and its use. The invention further relates to a dispersion containing this powder.

- 5 Cerium oxide is a significant constituent of catalysts. Furthermore, cerium oxide is an important material for the polishing of glass and electronic components. Particularly in the field of chemomechanical polishing, the journal and patent literature contains numerous treatises improving the
10 properties of cerium oxide powders and of cerium oxide dispersions.

Cerium oxide is usually prepared by calcination of cerium hydroxides or cerium carbonates. The calcined oxides are then milled and sieved.

- 15 Wet-chemical routes and gas-phase processes are also known. Cerium oxide can be prepared by hydrothermal synthesis, as described, for example, in US 5389352. Here, cerium(III) salts are converted oxidatively at elevated temperature and pressure into cerium oxide which crystallizes out in the
20 form of fine particles.

Gas-phase processes such as spray pyrolysis methods in which a cerium oxide precursor, usually in the form of an aerosol, is oxidized in a flame are of particular interest. One such method is described in EP-A-1142830.

- 25 In J. Mater. Res., Vol. 17, pages 1356 - 1362 (2002), Pratsinis et al. describe the preparation of cerium oxide powders of high crystallinity by flame spray pyrolysis of cerium acetate solutions in solvent mixtures comprising acetic acid, isooctane and 2-butanol by oxidation by means
30 of oxygen in an oxygen/methane flame. The solvent mixture is essential to the preparation of a cerium oxide powder which is free of relatively coarse particles.

WO2004/005184A1 claims a process for preparing metal oxides, in which droplets are produced from a solution and these are oxidized in a flame. The solution contains at least one starting material and at least 60%, based on the total solution, of a carboxylic acid as solvent.

A process for preparing cerium oxide comprising coarse and fine material is known from WO01/36332A1. This process discloses the combustion of an aerosol of a cerium oxide precursor in a high-temperature zone of 700-1100 K.

DE-A-10251029 discloses a pyrogenic cerium oxide powder having a coarse fraction comprising crystalline, nonaggregated particles having a mean diameter of from 30 to 200 nm and a fine fraction in the form of aggregates of finely crystalline, grown-together primary particles having a mean aggregate diameter of from 5 to 50 nm and a BET surface area of from 15 to 200 m²/g.

EP-A-1506940 discloses a polycrystalline cerium oxide powder in the form of aggregates of primary particles having a specific surface area of from 70 to 150 m²/g, a mean primary particle diameter of from 5 to 20 nm and a mean, projected aggregate diameter of from 20 to 100 nm and a dispersion containing this cerium oxide powder.

Furthermore, numerous dispersions containing cerium oxide for chemomechanical polishing are described.

EP-A-1203801 discloses an aqueous dispersion containing pyrogenic silicon dioxide doped with cerium oxide, with the cerium oxide being introduced via an aerosol of a cerium salt solution or suspension and the mean particle size in the dispersion being less than 100 nm.

EP-A-133080 discloses an aqueous dispersion which contains particles having a core of doped, pyrogenic low-structured silicon dioxide and a cerium oxide shell and does not exceed a mean secondary particle size of 0.2 µm.

DE-B-10342826 discloses a dispersion of pyrogenic cerium oxide which does not have any particles larger than 1 μm .

US 6827752 claims a cerium oxide dispersion which is stabilized by polyacrylates.

- 5 US 6443811 claims a cerium oxide dispersion in a neutral to weakly basic medium which contains a cationic surface-active agent.

- US 6420269 claims a cerium oxide dispersion which has a pH in the range from 8 to 12 and contains a dispersant,
10 preferably a water-soluble organic polymer, a water-soluble anionic or nonionic surface-active agent or a water-soluble amine.

- A disadvantage of the cerium oxide dispersions according to the prior art is that satisfactory stability in the neutral
15 to weakly alkaline range can be achieved only in the presence of additives.

- It was therefore an object of the present invention to provide a dispersion which is based on cerium oxide and is, without additional additives, sufficiently stable in the
20 neutral to weakly alkaline range to be able to be used for chemomechanical polishing.

- A further object of the invention was to provide a powder based on cerium oxide as a basis for the dispersion. A further object was to provide a process for preparing this
25 powder.

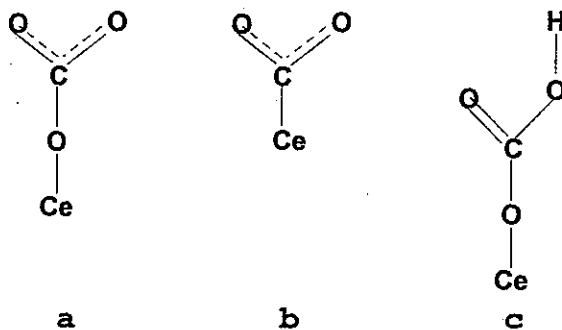
- The invention provides a cerium oxide powder which has carbonate groups and comprises crystalline primary particles which contain cerium oxide and carbonate groups on their surface and in a layer close to the surface,
30 wherein

- the powder has a BET surface area of from 25 to 150 m^2/g ,

- the primary particles have a mean diameter of from 5 to 50 nm,
- the layer close to the surface of the primary particles has a depth of about 5 nm,
- 5 - the carbonate concentration in the layer close to the surface decreases inwards from the surface on which the carbonate concentration is highest,
- the carbon content due to the carbonate groups on the surface is from 5 to 50% by area and that at a depth of about 5 nm in the layer close to the surface is from 0 to 30% by area,
- 10 - the content of cerium oxide, calculated as CeO_2 and based on the powder, is at least 99.5% by weight and
- the content of carbon, encompassing organic and inorganic carbon, is from 0.01 to 0.3% by weight, based on the powder.
- 15

The carbonate groups in the powder of the invention can be detected both on the surface and also at a depth of up to about 5 nm. The carbonate groups are chemically bound and can, for example, be present in the structures a-c.

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The carbonate groups can, for example, be detected by XPS/ESCA analysis. To detect the carbonate groups in the layer close to the surface, part of the surface can be removed by means of argon ion bombardment and the resulting new surface can likewise be analysed by means of XPS/ESCA

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(XPS = X-ray photoelectron spectroscopy; ESCA = electron spectroscopy for chemical analysis).

In the powder of the invention, the primary particles can be present in isolated form or else can be more or less
5 strongly aggregated. The primary particles are preferably very largely in aggregated form.

The powder of the invention can preferably have a proportion of sodium of < 5 ppm and of chlorine of < 20 ppm. The elements mentioned can generally be tolerated
10 only in small amounts in chemomechanical polishing.

Furthermore, a BET surface area of the powder of the invention of from 30 to 100 m²/g can be preferred and a BET surface area of 40-80 m²/g can be particularly preferred for polishing applications.

15 The invention further provides a process for preparing a cerium oxide powder having carbonate groups, in which

- an aerosol is reacted with an oxygen-containing gas at a reaction temperature of from 600°C to 1500°C, preferably from 900°C to 1200°C, in a reaction chamber, the
20 reaction mixture is cooled and the powder is subsequently separated off from the gaseous substances by means of a filter, with
- the aerosol being obtained by atomization of at least one solution containing an organic solvent or solvent
25 mixture and an oxidizable, organic cerium(III) compound dissolved therein by means of at least one atomization gas and
- the volume-based, mean droplet diameter D_{30} of the aerosol being from 30 to 100 μm and the mean residence
30 time in the reaction chamber being from 0.1 s to 5 s, wherein

- the reaction mixture is cooled after leaving the reaction chamber by spraying water droplets into it,
 - the water droplets have a mean, volume-based droplet diameter of less than 100 μm and
- 5 - to generate the water droplets, water is added in an amount according to equation I

$$m_{\text{H}_2\text{O}} = [\text{cp}_{\text{liq}} \cdot (T_b - T_0) + \text{dh}_v + \text{cp}_g \cdot (T_e - T_b)] / 3600 \cdot Q \quad (\text{I})$$

where

- Q = total combustion enthalpy of all starting materials in KW
 - $m_{\text{H}_2\text{O}}$ = amount of H_2O in kg/h required to achieve the end temperature T_e
 - T_0 = inlet temperature of water
 - T_b = boiling point of water at 1 bar
 - T_e = end temperature
 - dh_v = enthalpy of vaporization of water
 - cp_{liq} = heat capacity of water at 50°C
 - cp_g = heat capacity of water vapour at 150°C,
- and
- $T_0 = 5 - 50^\circ\text{C}$, $T_b = 100^\circ\text{C}$, $T_e = 200 - 400^\circ\text{C}$, $\text{dh}_v = 2256.7 \text{ kJ/kg}$, $\text{cp}_{\text{liq}} = 4.181 \text{ kJ/kg}\cdot\text{K}$ and $\text{cp}_g = 1.98 \text{ kJ/kg}\cdot\text{K}$.

25 The oxygen-containing gas is generally air or air enriched with oxygen.

As atomization gas, it is possible to use a reactive gas such as air, air enriched with oxygen and/or an inert gas such as nitrogen in the process of the invention. In general, air is used as atomization gas. The ratio of

30 throughput of the cerium(III) solution/amount of atomization gas is preferably from 0.1 to 25 kg/standard m^3 and particularly preferably from 0.5 to 5 kg/standard m^3 . One or more two-fluid or multifluid nozzles are

particularly suitable for atomization. The atomization pressure is generally from 1 to 100 bar.

In a preferred embodiment of the process of the invention, a fuel gas is additionally added to the reaction mixture.

5 Suitable fuel gases are, in particular, hydrogen, methane, ethane, propane, butane, natural gas. The amount of fuel gas added depends first and foremost on the amount of the solution containing the cerium(III) compound added, its composition and joule value. In general, the ratio of fuel
10 gas/solution is from 0.1 to 2 standard m³/kg.

It can also be advantageous for secondary air to be additionally introduced into the reaction chamber. In general, the amount of secondary air will be such that the ratio of secondary air to primary air is from 0.1 to 10.

15 The process of the invention can preferably be carried out so that the proportion of oxygen in the amount of oxygen-containing gas introduced is greater than that necessary for complete reaction of the cerium(III) compound and the fuel gas. It is particularly advantageous for lambda to be
20 ≥ 1.5 , with lambda being calculated from the sum of oxygen in (air + if appropriate atomization gas)/sum of (cerium(III) compound + fuel gas), in each case in mol/h. Very particular preference is given to $2 < \lambda < 5$.

As organic cerium(III) compounds, it is possible to use, in
25 particular, cerium alkoxides and/or cerium carboxylates. As alkoxides, preference is given to using ethoxides, n-propoxides, isopropoxides, n-butoxides and/or tert-butoxides. As carboxylates, it is possible to use the
30 compounds based on acetic acid, propionic acid, butanoic acid, hexanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, octanoic acid, 2-ethylhexanoic acid, valeric acid, capric acid and/or lauric acid. It can be particularly advantageous to use 2-ethylhexanoates and/or laurates.

As organic solvents or as constituents of organic solvent mixtures, preference is given to using alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol or tert-butanol, diols such as ethanediol, pentanediol,

5 2-methyl-2,4-pentanediol, dialkyl ethers such as diethyl ether, tert-butyl methyl ether or tetrahydrofuran, C₁-C₁₂-carboxylic acids such as acetic acid, propionic acid, butanoic acid, hexanoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, octanoic acid,
10 2-ethylhexanoic acid, valeric acid, capric acid, lauric acid. Furthermore, it is possible to use ethyl acetate, benzene, toluene, naphtha and/or petroleum spirit. Preference is given to using solutions containing C₂-C₁₂-carboxylic acids, in particular 2-ethylhexanoic acid and/or
15 lauric acid.

The invention further provides a cerium oxide powder which has carbonate groups and is obtainable by the process of the invention.

The invention further provides a dispersion containing the
20 cerium oxide powder having carbonate groups according to the invention.

The liquid phase of the dispersion can be water, one or more organic solvents or an aqueous/organic combination, with the phases preferably being miscible. The dispersion
25 can additionally contain pH regulators, surface-active additives and/or preservatives. However, a dispersion containing surface-active additives is not advantageous. Instead, a dispersion which consists of only the cerium oxide powder having carbonate groups, water and optionally
30 a pH regulator is advantageous.

The content of cerium oxide powder containing carbonate groups can preferably be from 0.5 to 60% by weight. Particular preference is given to an aqueous dispersion containing from 20 to 50% by weight, in particular from 35

to 45% by weight, of the powder of the invention.

Furthermore, an aqueous dispersion according to the invention which has a viscosity of < 30 mPas, particularly preferably < 20 mPas, at a concentration of the powder of up to 40% by weight and a temperature of 23°C in a shear rate range from 1 to 1000 s^{-1} can be preferred.

The pH of an aqueous dispersion according to the invention is preferably in the range from 3 to 8. To store the dispersion, a pH of from 3 to 4 is usually set by addition of an acid. Nitric acid is particularly useful for this purpose. The stability of the dispersion is particularly high in this pH range.

When an aqueous dispersion is used as polishing agent, a pH of from 7 to 8 can then be set, for example, by means of ammonia or potassium hydroxide. The dispersion displays satisfactory stability in this range, even without the presence of surface-active additives.

A dispersion whose mean particle size d_{50} determined by means of dynamic light scattering is less than 120 nm, in particular less than 100 nm, is especially suitable for polishing processes.

Furthermore, a dispersion whose mean particle size d_{90} determined by means of dynamic light scattering is less than 200 nm, in particular less than 150 nm, is suitable for this purpose.

The zeta potential of the dispersion of the invention can preferably be at least 20 mV, in particular greater than 30 mV.

The dispersion of the invention can be produced by means of dispersing apparatuses known to those skilled in the art. These can be, for example, rotor-stator machines, high-energy mills in which the particles are milled by collision with one another, planetary kneaders, stirred ball mills,

vibratory ball mills, shaking tables, ultrasonic apparatuses or combinations of the abovementioned apparatuses.

Examples:

The specific surface area is determined in accordance with DIN 66131.

The surface properties are determined by large-area (1 cm²) XPS/ESCA analysis (XPS = X-ray photoelectron spectroscopy; ESCA = electron spectroscopy for chemical analysis).

Evaluation is based on the general recommendations in the DIN specialist report No. 39, DMA(A)97 of the National Physics Laboratory, Teddington, UK, and the previous findings on development-accompanying standardization of the working committee "Oberflächen- und Mikrobereichsanalysen" NMP816(DIN). In addition, the comparative spectra available for the particular case from the specialist literature are taken into account. The values are calculated by background subtraction taking into account the relative sensitivity factors of the electron levels indicated in each case. The results are reported in percent by area. The accuracy is estimated as +/- 5% relative.

The zeta potential is determined in the pH range 3-12 by means of the electrokinetic sound amplitude (ESA). For this purpose, a suspension containing 1% of cerium oxide is prepared. Dispersion is carried out by means of an ultrasonic rod (400 W). The suspension is stirred by means of a magnetic stirrer and pumped by means of a peristaltic pump through the PPL-80 sensor of the ESA-8000 instrument from Matec. From the starting pH value, the potentiometric titration is carried out using 5M NaOH to pH 12. The backtitration to pH 4 is carried out using 5M HNO₃. Evaluation is carried out by means of the instrument software version pcava 5.94.

$$\zeta = \frac{ESA \cdot \eta}{\phi \cdot \Delta \rho \cdot c \cdot |G(\alpha)| \cdot \varepsilon \cdot \varepsilon_0}$$

where ζ zeta potential

ϕ	volume fraction
$\Delta\rho$	density difference between particles and liquid
c	velocity of sound in the suspension
η	viscosity of the liquid
ϵ	dielectric constant of the suspension
$ G(\alpha) $	Inertia correction

The dispersions are produced by ultrasound treatment in water using an ultrasonic finger (Bandelin UW2200/DH13G), setting 8, 100%; 5 minutes). The mean aggregate diameters are determined by means of a particle size analyser LB-500 from Horiba.

Example 1:

An aerosol is produced from 250 kg/h of a solution comprising 50% by weight of cerium(III) ethylhexanoate and 50% by weight of 2-ethylhexanoic acid (joule value of the solution: 29 kJ/kg) and 50 standard m³/h of atomization air by means of a two-fluid nozzle (from Schlick) and is atomized into a reaction chamber. Here, a hydrogen/oxygen flame composed of hydrogen (40 standard m³/h) and primary air (1800 standard m³/h) burns and the aerosol is reacted in this. In addition, secondary air (3200 standard m³/h) is introduced into the reaction chamber. The residence time in the flame is about 20 ms. The temperature 0.5 m below the flame is 1100°C.

An aerosol produced from 900 kg/h of water is subsequently sprayed into the reaction chamber by means of a two-fluid nozzle using 200 standard m³/h of atomization air at an inlet temperature of 20°C. The solid product is separated off from gaseous substances on a filter. The reaction mixture has a temperature of 280°C at this point in time.

The residence time of the reaction mixture in the reaction chamber is 1 s.

Examples 2 to 4 are carried out in a manner analogous to Example 1, with the amounts used and other process parameters being shown in Table 1. The analytical data for the powders obtained are shown in Table 2.

The results of the XPS/ESCA analysis show that very pure surfaces are present. Apart from Ce, C and O, no further elements are detectable. The carbonate C displays a bond energy of about 289 eV.

Furthermore, the d_{50} and d_{90} values of the 1% dispersions of the powders from Examples 1 to 4 are shown in Table 2.

The particle size distribution of a 5% dispersion of the powder from Example 3 in water whose pH has been set to 3.9 by means of HNO_3 gives a d_{50} of 82 nm and a d_{90} of 103 nm.

SiO_2 surfaces can be polished using the dispersion according to the invention and removal rates of > 500 nm/min, preferably up to 1200 nm/min, in particular 1000 nm/min, at a pv of 60 000 N/ms are achieved.

Figure 1 and Figure 2 show polishing results of a 0.5% dispersion of the powder from Example 3 whose pH has been set to 7.6 by means of KOH.

Figure 1 shows the removal rate, in nm/min, as a function of the product of contact pressure and velocity, in N/ms.

In addition, it was found that the motor currents measured in the polishing of SiO_2 and Si_3N_4 differ from one another when the dispersion according to the invention is used. This can be advantageously utilized in STI (shallow trench isolation). The objective of STI is to polish SiO_2 very selectively and to stop the polishing process when the nitride layer is reached. It is known that additives which

increase this selectivity by protecting the nitride can be added to a dispersion for this purpose. Surprisingly, these additives are not necessary in the case of the dispersion of the invention.

- 5 Figure 2 shows the motor current as a function of time in s for SiO_2 and Si_3N_4 .

Table 1: Amounts used and settings

Example		1	2	3	4
Cerium(III) solution	kg/h	250	2.5	12	14
Atomization air*	Standard m^3/h	50	3	20	20
Hydrogen	Standard m^3/h	40	2	4	4.5
Primary air	Standard m^3/h	1800	10	110	110
Secondary air	Standard m^3/h	3200	25	160	160
Total air	Standard m^3/h	5050	28	290	290
Total oxygen	Standard m^3/h	1058	5.86	60	60
Lambda		2.7	3	3	2.6
Temperature**	$^{\circ}\text{C}$	1100	1110	1060	1055
Residence time	s	1	1.4	0.9	0.95
Water	kg/h	900	10	100	110
Atomization air***	Standard m^3/h	200	5	30	50
Temperature T_0	$^{\circ}\text{C}$	20	20	20	20
Temperature T_e	$^{\circ}\text{C}$	280	310	300	290

*) Cerium(III) solution; **) 500 mm under the flame,

***) water

Table 2: Analytical values for the powders according to the invention

Example		1	2	3	4
BET	m ² /g	120	60	58	25
CeO ₂ [*]	% by wt	99.85	99.79	99.82	99.8
C	% by wt	0.12	0.14	0.1	0.15
Zeta potential ^{**}	mV	41	48	52	46
IEP ^{***}	pH	9	9.6	10.6	9.8
C 1s ^{****}	% by area	28.7/26.4	19.0/11.2	15.2/5.9	27.4/11.8
d ₅₀	nm	105	110	114	110
d ₉₀	nm	175	185	198	180

*) in all examples: Na < 5 ppm; Cl < 20 ppm; **) at pH = 4,

) IEP = isoelectric point; *) as

- 5 synthesized/sputtered; sputtered: after removal of the surface by bombardment with argon ions, 5 keV, about 10 min

Claims:

1. Cerium oxide powder which has carbonate groups and comprises crystalline primary particles which contain cerium oxide and carbonate groups on their surface and in a layer close to the surface, wherein

- the powder has a BET surface area of from 25 to 150 m²/g,
- the primary particles have a mean diameter of from 5 to 50 nm,
- the layer close to the surface of the primary particles has a depth of about 5 nm,
- the carbonate concentration in the layer close to the surface decreases inwards from the surface on which the carbonate concentration is highest,
- the carbon content due to the carbonate groups on the surface is from 5 to 50% by area and that at a depth of about 5 nm in the layer close to the surface is from 0 to 30% by area,
- the content of cerium oxide, calculated as CeO₂ and based on the powder, is at least 99.5% by weight and
- the content of carbon, encompassing organic and inorganic carbon, is from 0.01 to 0.3% by weight, based on the powder.

2. Cerium oxide powder having carbonate groups according to Claim 1, characterized in that the primary particles are aggregated.

3. Cerium oxide powder having carbonate groups according to Claim 1 or 2, characterized in that the proportion of sodium is < 5 ppm and that of chlorine is < 20 ppm.

4. Cerium oxide powder having carbonate groups according to any of Claims 1-3, characterized in that the BET surface area is from 30 to 100 m²/g.

5. Process for preparing a cerium oxide powder having carbonate groups, in which

- an aerosol is reacted with an oxygen-containing gas at a reaction temperature of from 600°C to 1500°C, preferably from 900°C to 1200°C, in a reaction chamber, the reaction mixture is cooled and the powder is subsequently separated off from the gaseous substances by means of a filter, with

- the aerosol being obtained by atomization of at least one solution containing an organic solvent or solvent mixture and an oxidizable, organic cerium(III)

compound dissolved therein by means of at least one atomization gas and

- the volume-based, mean droplet diameter D_{30} of the aerosol being from 30 to 100 μm and the mean residence time in the reaction chamber being from 0.1 s to 5 s,

characterized in that

- the reaction mixture is cooled after leaving the reaction chamber by spraying water droplets into it,

- the water droplets have a mean, volume-based droplet diameter of less than 100 μm and

- to generate the water droplets, water is added in an amount according to equation I

$$m_{\text{H}_2\text{O}} = [\text{cp}_{\text{liq}} \cdot (T_b - T_0) + dh_v + \text{cp}_g \cdot (T_e - T_b)] / 3600 \cdot Q \quad (\text{I})$$

where

- Q = total combustion enthalpy of all starting materials in KW

- $m_{\text{H}_2\text{O}}$ = amount of H₂O in kg/h required to achieve the end temperature T_e

- T_0 = inlet temperature of water

- T_b = boiling point of water at 1 bar
- T_e = end temperature
- dh_v = enthalpy of vaporization of water
- cp_{liq} = heat capacity of water at 50°C
- 5 - cp_g = heat capacity of water vapour at 150°C,
where

- $T_0 = 5 - 50^\circ\text{C}$, $T_b = 100^\circ\text{C}$, $T_e = 200 - 400^\circ\text{C}$, $dh_v = 2256.7 \text{ kJ/kg}$, $cp_{liq} = 4.181 \text{ kJ/kg}\cdot\text{K}$ and $cp_g = 1.98 \text{ kJ/kg}\cdot\text{K}$.

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6. Process according to Claim 5, characterized in that a fuel gas is additionally added to the reaction mixture.

7. Process according to Claim 5 or 6, characterized in that λ is ≥ 1.5 , with λ being calculated from the
15 sum of oxygen in (air + if appropriate atomization gas)/sum of (cerium(III) compound + fuel gas), in each case in mol/h.

8. Cerium oxide powder having carbonate groups which is obtainable according to any of Claims 5-7.

20 9. Dispersion containing the cerium oxide powder having carbonate groups according to any of Claims 1-4 and 8.

10. Dispersion according to Claim 9, characterized in that its constituents are the cerium oxide powder having carbonate groups, water and optionally a pH regulator.

25 11. Dispersion according to Claim 9 or 10, characterized in that the content of cerium oxide powder is from 0.5 to 60% by weight.

12. Dispersion according to any of Claims 9-11, characterized in that the pH is from 3 to 8.

30 13. Dispersion according to any of Claims 9-12, characterized in that the mean particle size d_{50}

determined by means of dynamic light scattering is less than 120 nm.

14. Dispersion according to any of Claims 9-13,
characterized in that the mean particle size d_{90}
5 determined by means of dynamic light scattering is less
than 200 nm.

15. Dispersion according to any of Claims 9-14,
characterized in that its zeta potential is at least
20 mV.

- 10 16. Use of the cerium oxide powder having carbonate groups
according to any of Claims 1-4 and 8 or of the
dispersion according to any of Claims 9-15 for
chemomechanical polishing.

- 15 17. Use of the cerium oxide powder having carbonate groups
according to any of Claims 1-4 and 8 as catalyst, as UV
absorber, as toner constituent and as constituent of
fuel cells.