

EP 0317378

Description

The present invention is concerned with a silica which can be used more particularly in dentifrice compositions, and also dentifrice compositions incorporating that silica.

It is known that silica is in general use in the preparation of dentifrice compositions where it can also have a number of different functions.

First of all, it acts as an abrasive agent, and helps to remove dental plaque as a result of its mechanical action.

It can also act as a thickener to give specific rheological properties to the dentifrice, and it can also act as an optical agent to give it the desired colour.

Moreover, it is known that dentifrices contain various agents, particularly for the prevention of caries to reduce the formation of dental plaque or the deposition of tartar on the teeth. Of these agents, particular reference may be made to zinc. Other elements are also used, such as phosphate fluorides, pyrophosphates, polyphosphates, polyphosphonates. Dentifrice formulations can also contain flavourings and aromatising agents, etc. . .

The presence of these agents in the dentifrice poses the problem of their compatibility with the silica. As a result, particularly of its absorbing properties, the silica may tend to react with the agents in such a way that they are no longer available to exercise the afore-described therapeutic effects.

The aim of the invention is therefore to find silicas which are compatible with the agents mentioned hereinabove, in particular with zinc, and which can therefore be used in the formulation of dentifrices.

The Applicant has noticed that the compatibility properties sought depended essentially on the surface chemistry of the silica used. It has thus been

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possible to establish a number of conditions regarding the surface of silicas for ensuring their compatibility.

To this end, the silica according to the invention which is able to be used particularly in dentifrice compositions is characterised in that it has a surface chemistry such that the number of OH, expressed as OH/nm², is at the most 15 and that its point zero charge (PZC) is between 3 and 6.5, and that its compatibility with zinc is at least 50%.

The process for the preparation of the silica according to the invention is of the type which comprises reacting the silicate with an acid to obtain a silica suspension or gel, separating and drying the silica, and it is characterised in that after separating the silica from the suspension, a first washing with water takes place of the resulting cake, then a second washing, or a treatment with an acid solution.

The invention is also concerned with dentifrice compositions, characterised in that they contain silicas such as those described hereinabove.

Further characteristics and advantages of the invention will emerge more clearly from reading the following description and concrete examples.

As already mentioned in the introduction, the essential characteristics of the silicas according to the invention reside in their surface chemistry. To be more exact, one of the aspects to be taken into consideration in this surface chemistry is the acidity. In this connection, one of the characteristics of the silicas of the invention is the number of acid sites at the surface.

This number is measured as the number of OH groups or silanols per nm². Usually, the measurement is carried out in the following way.

The number of OH sites at the surface is assimilated to the amount of water released between 190°C and 900°C.

The silica samples are dried initially at 105°C for 2 hours.

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A silica mass Po is placed in a thermobalance and brought to 190°C over 2 hours, i.e. the new mass obtained is P190. The silica is then brought to 900°C over 2 hours, i.e. the new mass obtained is P900.

The number of OH sites is calculated by way of the following equation:

$$NOH = \frac{66922.2}{A} \times (P190 - P900) / 190$$

where NOH is the number of OH sites per nm² of surface, and A is the specific surface of the solid (BET) in m²/g.

In this case, the silicas of the invention have a OH number per nm² of at the most 15. According to a preferred embodiment of the invention, this number of OH is at the most 12, particularly between 3 and 12.

On the other hand, the surface pH is also a characteristic of the silicas of the invention. It is determined by the point zero charge (PZC).

This point zero charge (PZC) is defined by the pH of a silica suspension for which the electric charge of the surface of the solid is zero, irrespective of the ionic strength of the medium. This PZC measures the real pH of the surface, insofar as this latter is free of all impurities of the ionic kind.

The electric charge is determined by potentiometry. The principle of the method is based on the overall balance of the protons adsorbed or desorbed on the surface of the silica at a give pH.

On the basis of equations which describe the overall balance of the operation, it is easy to show that the electric charge C of the surface, taken in relation to a reference corresponding to a zero surface charge, is given by the equation:

$$C = \frac{F}{A.M.} (H - OH)$$

wherein:

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A represents the specific surface of the solid in m^2/g .

M is the amount of solid in the suspension in g,

F is the Faraday constant,

H or OH represents the variation per surface unit of the excess of H^+ or OH^- ions respectively on the solid.

The experimental measurement of the PZC is carried out in the following way.

The method used is that described by Berube and Bruyn (J. Colloid Interface Sc. 1968, 27, 305).

The silica is washed initially in high resistivity deionised water (10 Mega.Ohm.cm); dried and then degassed.

A series of solutions is prepared at pHo 8.5 by adding KOH or HNO_3 and containing an indifferent electrolyte (KNO_3) at a concentration which can vary between 10^{-5} and 10^{-1} Mole/l.

A given silica mass is added to these solutions, and the pH of the suspensions obtained is allowed to stabilise, with agitation, at 25°C and in the presence of nitrogen for 24 hours; that is to say its value is pH'o.

Standard solutions are formed by the supernatant obtained by centrifuging for 30 mins at 10000 revs/min part of said same suspensions, i.e. the pH of these supernatants is pH'o.

The pH of a known volume of these suspensions and corresponding standard solutions is then brought to pHo by adding the necessary amount of KOH, and the suspensions and standard solutions are allowed to stabilise for 4 hours.

The potentiometric dosing of the suspensions is carried out on the basis of pHo by nitric acid addition up to pHf=2.0.

Preferably, the process involves adding an acid increment corresponding to a pH variation of 0.2 units of pH. After each addition, the pH is stabilised for 1 min.

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Let $V_h.NH$ be the number of acid equivalents to arrive at pH_f .

On the basis of pH_o , the term $(V_h.Nh - V_{oh}.N_{oh})$ is plotted as a function of the incremented pH values for all the suspensions (at least 3 ionic strengths) and for all the corresponding standard solutions.

For each pH value (0.2 unit step), the difference is then formed between the H^+ or OH^- consumption for the suspension and for the corresponding standard solution. This operation is renewed for all the ionic strengths.

This gives the term $(H - OH)$ which corresponds to the consumption in protons of the surface. The surface charge is calculated by the above equation.

The surface charge curves are then plotted as a function of the pH for all the ionic strengths under consideration. The PZC is defined by the intersection of the curves.

The silica concentration is adjusted as a function of its specific surface..

By way of example, 2% suspensions are used for silicas of $50 \text{ m}^2/\text{g}$ with 3 ionic strengths (0.1; 0.01 and 0.001 mole/l).

The dosing is carried out on 100 ml of suspension, using 0.1 M potassium hydroxide.

For the silicas according to the invention, this PZC must be between 3 and 6.5.

Moreover, in order to improve the compatibility of these silicas according to the invention with elements other than zinc, particularly fluorine, it is advantageous if the aluminium content is at the most 500 ppm.

On the other hand, the iron content of the silicas according to the invention can advantageously be at the most 200 ppm.

Moreover, it is preferable if the calcium content can be at the most 500 ppm, and more particularly at the most 330 ppm.

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The silicas according to the invention also usually have a carbon content of at the most 50 ppm, and more particularly of at the most 10 ppm.

Finally, the pH of the silicas according to the invention, measured according to NFT Standard 45-007, is usually at the most 7. It is more particularly between 5.5 and 7, and particularly 6 and 7.

The above characteristics make it possible to obtain a silica which is at least compatible with zinc. This compatibility, measured in accordance with the test given below, is of at least 50%, more particularly of at least 80%, and preferably of at least 90%. Depending on the case, the silica according to the invention can also be compatible with fluorides, phosphates and their derivatives.

In addition to the surface chemistry characteristics which will be described hereinafter and which condition the compatibilities, the silicas according to the invention also have physical characteristics which make them perfectly suitable for use in dentifrice. These characteristics of a structural type will be described hereinafter.

Usually, the BET surface of the silicas according to the invention is between 40 and 600 m²/g, more particularly between 40 and 350 m²/g. Their CTAB surface usually varies between 40 and 400 m²/g, more particularly between 40 and 200 m²/g.

The BET surface is determined according to the BRUNAUER-EMMET-TELLER method, described in the Journal of the American Chemical Society vol. 60, page 309, February 1938 and in accordance with the standard NF X11-622(3.3).

The CTAB surface is the outer surface, determined in accordance with the ASTM Standard D 3765, but whilst carrying out the adsorption of ammonium hexadecyltrimethyl bromide (CTAB) at pH 9 and taking as the mean projected area of the CTAB molecule 35 Å².

The silicas of the invention can, of course, correspond to the three types usually distinguished between in the domain of dentifrices.

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Thus, the silicas of the invention can be of the abrasive type. They thus have a BET surface of between 40 and 300 m²/g. In this case, the CTAB surface is between 40 and 100 m²/g.

The silicas of the invention can also be of the thickening type. They then have a BET surface of between 120 and 450 m²/g, more particularly between 120 and 200 m²/g. They can thus have a CTAB surface of between 120 and 400 m²/g, more particularly of between 120 and 200 m²/g.

Finally, in accordance with a third type, the silicas of the invention can be bifunctional. They here have a BET surface of between 80 and 200 m²/g. The CTAB surface is thus between 80 and 200 m²/g.

The silicas of the invention can also have an oil sample of between 80 and 500 cm³/100 g, determined in accordance with NFT Standard 30-022 (March 1953) by using dibutyl phthalate.

To be more exact, the oil sample will be between 100 and 140 cm³/100 g for abrasive silicas, between 200 and 400 for thickening silicas, and between 100 and 300 for bifunctional silicas.

Moreover, still with a view to their use in dentifrice, the silicas preferably have a particle size of between 1 and 10 µm. This mean particle size is measured with the Coulter counter.

The apparent density will usually vary between 0.01 and 0.3.

According to one particular embodiment of the invention, the silicas are precipitation silicas.

Finally, the silicas of the invention have a refractive index of between 1.440 and 1.465.

The process for the preparation of silicas according to the invention will now be described in greater detail.

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As stated hereinabove, the process is of the type comprising reacting a silicate with an acid to result in the formation of a silica suspension or gel.

It should be noted that it is possible to use any known operating procedure to obtain this suspension or gel (adding acid to a silicate sediment, simultaneous total or partial addition of acid and silicate to a water sediment or silicate suspension, etc. . .), the selection essentially being made as a function of the physical characteristics of the silica which is to be obtained. It will be noted that it can be advantageous to bring the pH of the suspension or gel obtained to a value of at the most 6, and more particularly of between 4 and 6.

The silica is then separated from the reaction medium using any known means, e.g. a vacuum filter or a filter press.

Thus, a silica cake is collected.

In accordance with the main feature of the process, a first washing of the cake is then carried out.

The first washing is carried out in water, usually in deionised water.

The process then comprises a second washing or treatment with an acid solution.

The purpose of this second washing or treatment is to obtain at the end of the preparation a silica with a pH of at the most 7, and more particularly of between 5.5 and 7, and particularly 6 and 7, and also a PZC of between 3 and 6.5.

This acid solution can be a solution of a mineral acid such as nitric acid, for example.

According to another embodiment, this acid solution can also be a solution of an organic acid, particularly a complexing acid. This acid can be selected

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from the group of carboxylic, dicarboxylic, hydrocarboxylic and aminocarboxylic acids.

Examples of such acids are acetic acid, and examples of complexing acids are tartaric, maleic, glyceric, gluconic, citric and acetic acids.

The second washing or treatment can be carried out by passing the acid solution over the cake, or by introducing the acid solution into the suspension obtained after disintegration of the cake. The washing or acid treatment is carried out under conditions such that in order to obtain a silica with the final pH stated hereinabove, the pH of the suspension or medium before drying must be between 4 and 6, and more particularly 5 and 6.

It can be advantageous, particularly in instances where a solution is used of a mineral acid, to carry out a final washing in deionised water.

According to another particular variant, after the silicate acid reaction and just prior to separating the silica, the suspension or gel undergoes ageing. This ageing usually takes place at a pH of at the most 6, e.g. of between 4 and 6. It is also possible to carry out an ageing process during the reaction with a pH of between 6 and 8. These ageing processes are preferably carried out under hot conditions, e.g. at a temperature of between 80 and 100°C, and over a period of time which can vary between fifteen minutes and two hours.

Once the silica cake has been washed or treated according to the aforementioned operating procedures, the cake, or, if it has been disintegrated, the disintegration suspension, is dried by any known means. Drying can, in particular, take place by atomization. The dried product will be ground, if necessary, to give the desired grain size distribution.

The invention is also concerned with dentifrice compositions containing the silicas of the afore-described type.

The amount of silica according to the invention used in dentifrice compositions can vary greatly, usually being between 5 and 35% by weight.

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The silicas of the invention are particularly well suited to dentifrice compositions containing at least one element selected from the group including fluorides, phosphates, zinc.

As far as fluorine-containing compounds are concerned, their quantity preferably corresponds to a fluorine concentration in the composition of between 0.01 and 1% by weight, and more particularly 0.1% to 0.5%. The fluorine-containing compounds are, in particular, the salts of monofluorophosphoric acid and especially those of sodium, potassium, lithium, calcium, aluminium and ammonium, monofluorophosphate and difluorophosphate, as well as the various fluorides containing fluorine in the form of the ion more particularly linked with the alkaline fluorides, such as those of sodium, lithium, potassium, ammonium fluoride, stannous fluoride, manganese fluoride, zirconium fluoride, aluminium fluoride, as well as the addition products of said fluorides with one another or with other fluorides, such as potassium, sodium or manganese fluorides.

Other fluorides are also able to be used for the present invention, such as zinc fluoride, germanium fluoride, palladium fluoride, titanium fluoride, alkaline fluozirconates, e.g. of sodium or potassium, stannous fluozirconate, fluoborate or fluosulphates of sodium and potassium.

Organic fluorine-containing compounds can also be used, preferably those known as long chain amine or amino acid addition products with hydrogen fluoride, cetylamine fluoride, bis-(hydroxyethyl)-aminopropyl-N-hydroxyethyl-octadecylamine dihydrofluoride, octadecylamine fluoride and N,N'-tri-(polyoxyethylene)-N-hexadecylpropylenediamine dihydrofluoride.

As far as zinc is concerned, it is present more particularly in the form of citrate or sulphate.

With regard to the elements which can be used as anti-plaque agents of the polyphosphate or polyphosphonate, guanidine and bis-biguanide type, reference can be made to those mentioned in the patents US 3 934 002 or US 4 110 083 whose teaching is incorporated here.

Dentifrice compositions can also contain a binder.

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The main binders used are selected, in particular, from:

- cellulose derivatives: methyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl cellulose,
- mucilages: carraghenates, alginates, agar-agar and geloses,
- gums: gum Arabic, gum tragacanth, gum xanthane and gum Karaya,
- carboxyvinyl and acrylic polymers,
- polyoxyethylene resins.

In addition to the silicas of the invention, dentifrice compositions can also contain one or more other polishing abrasive agents, selected in particular from:

- the afore-mentioned calcium carbonate,
- magnesium carbonate,
- calcium, dicalcium and tricalcium phosphates,
- insoluble sodium metaphosphate,
- calcium pyrophosphate,
- titanium oxide (whitening agent),
- silicates,
- aluminas and silico aluminates,
- zinc and tin oxides,
- talc,
- kaolin.

Dentifrice compositions can also contain detergents, humectants, aromatizing agents, sweeteners, colourants and preservatives.

The main detergents used are selected, in particular, from:

- sodium laurylsulphate,
- sodium laurylsulfoacetate and laurylether sulphate,
- sodium dioctylsulfosuccinate,
- sodium laurylsarcosinate,
- sodium ricinoleate,
- sulphated monoglycerides.

The main humectants used are selected, in particular, from polyalcohols, such as:

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- glycerol,
- sorbitol, usually in 70% solution in water,
- propylene glycol.

The main aromatizing agents (flavourings) are selected, in particular, from: anise, Chinese anise, mint, bay, juniper, star anise, cinnamon, clove and rose oils.

The main sweeteners are selected, in particular, from among orthosulfobenzoic imides and cyclamates.

The main colourants used are selected, in particular, depending on the desired colour from:

- red and pink colour: amaranth, azorubin, catechu, new coccin (PONCEAU 4R), cochineal and erythrosin,
- green colour: chlorophyll and chlorophyllin,
- yellow colour: sun yellow (Orange S) and quinoline yellow.

The most widely used preservatives are parahydroxybenzoates, formol and products giving off same, hexetidine, quaternary ammoniums, hexachlorophene, bromophene and hexamedine.

Finally, dentifrice compositions contain therapeutic agents, the most important of these being selected from:

- antiseptics and antibiotics,
- enzymes,
- oligo-elements and fluorine-containing compounds which have been described hereinabove.

Specific, but non-limitative examples will now be given, and, before this, tests for measuring the compatibility of silica with various elements.

Measuring Compatibility with Fluorides

4 g of silica is dispersed in 16 g of 0.3% sodium fluoride (NaF) solution. The suspension is agitated for 24 hours at 37°C. After centrifuging the suspension at 20000 revs/min for 30 mins, the supernatant is filtered on a

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0.2 μ m Millipore filter. The solution thus obtained constitutes the test solution.

A reference solution is formed by using the same protocol, but in the absence of silica.

Compatibility with fluorides is determined by the percentage of free fluoride measured by a fluoride-selective electrode (Orion). It is determined by the following equation.

$$\% \text{ compatibility} = \frac{\text{F concentration of test (ppm)}}{\text{F concentration of reference (ppm)}} \times 100$$

Measuring Compatibility with Zinc

4 g of silica is dispersed in 100 ml of 0.06% Zn SO₄ · 7H₂O solution. A suspension is obtained whose pH is stabilised at 7 for 15 minutes by adding NaOH or H₂SO₄. The suspension is then agitated for 24 hours at 37°C, and then centrifuged at 20000 revs/min for 30 mins.

The supernatant filtered on the 0.2 μ m Millipore filter forms the test solution.

A reference solution is formed using the same protocol, but in the absence of silica.

The concentration of free zinc of the two solutions is determined by atomic absorption (214 nm).

The compatibility is determined by the following equation:

$$\% \text{ compatibility} = \frac{\text{Zn concentration of test (ppm)}}{\text{Zn concentration of reference (ppm)}} \times 100$$

Measuring Compatibility with Potassium and Sodium Pyrophosphates

4 g silica is dispersed in 16 g of 1.5% potassium or sodium pyrophosphate suspension. The suspension is agitated for 24 hours at 37°C, then centrifuged at 20000 revs/min for 30 mins.

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The supernatant is filtered on a 0.2 μm Millipore filter. 0.2 g of solution diluted in 100 ml of water in a graduated flask forms the test solution.

A reference solution is formed by following the same protocol, but in the absence of silica.

The concentration of free pyrophosphate ion (P_2O_7^-) of the two solutions is determined by ionic chromatography (DIONEX 2000i system) provided with an integrator.

The compatibility is determined by the relationship of the areas of the peaks obtained on the chromatograms and corresponding to the pyrophosphate retention time with respect to the test and reference.

$$\% \text{ compatibility} = 100 \times \frac{\text{area of peak of test}}{\text{area of peak of reference}}$$

EXAMPLE 1

6 litres of deionised water is introduced into a reactor equipped with a temperature and pH regulating system and with a turbine agitation system.

After agitation commences (300 revs/min), the sediment thus formed is heated to 85°C.

When the temperature is reached, 8.5 l of sodium silicate with a silica concentration of 120 g/l, a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 3.5 and a flow rate of 0.34 l/min is added simultaneously with 13.5 l of sulphuric acid of concentration 80 g/l. The acid flow rate is adjusted in such a way as to keep the pH of the medium at a constant value of 8.0.

Following a 40 minute addition, the mixture is allowed to age for 10 mins at that pH and at that temperature.

The addition of silicate is stopped, and the addition of acid continues until the pH of the reaction mixture is stabilised at 4.

Ageing then takes place for 15 mins at that pH and at 85°C.

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The mixture is then filtered, and the wet cake is washed in deionised water.

The cake is then dispersed in the deionised water to form a homogeneous suspension with a silica concentration of 50 g/l. The pH of this suspension is adjusted to 5.8 by adding nitric acid, and the mixture is allowed to stabilise at that pH for 15 mins.

The suspension is filtered.

The product is then dried by atomization and ground on a forplex type grinder in order to give a grain size of 9 microns.

The physico-chemical characteristics of the silica thus obtained are as follows:

BET surface.....	90 m ² /g
CTAB surface.....	60 m ² /g
Oil sample.....	105 cm ³ /100 g
pH.....	6.8
Number of OH/nm ²	8.

The chemical analyses of the silica are given in the following table.

ions	Al	Fe	Ca	C
ppm	350	110	300	10

The PZC of the silica is 4.5.

The following table gives the different compatibilities of the silica thus obtained with the ingredients of a dentifrice formulation and measured with the aid of the various tests described elsewhere:

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Zinc ZnSO ₄
% compatibility	90	98	90

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COMPARATIVE EXAMPLE 2

By way of comparison, compatibility measurements are given hereinbelow with commercial silicas generally used in dentifrice formulations, and also their physico-chemical characteristics.

Silica Brand Manufacturer	CTAB BET Surface m^2/g	Number OH/nm ²	Zn	F	Compatibility Pyrophosphate
Zeodent 113 Hubert	50 100	30	0	95	95
Tixosil 53 Rhône-Poulenc	50 250	30	0	60	90
Z 119 Rhône-Poulenc	50 60	25	20	95	95

The PZC for the silicas in this table is less than 3.

EXAMPLE 3

This example is concerned with the formulation of an opaque, paste-type dentifrice:

The formula is as follows:

Glycerin.....	22.00
7mFD CMC.....	1.00
Sodium saccharinate.....	0.20
Sodium monofluorophosphate.....	0.76
Sodium fluoride.....	0.10
Sodium laurylsulphate (30% aqueous).....	4.67
Sodium benzoate.....	0.10
Aromatizing Agents.....	0.90
Titanium dioxide.....	1.00
Silica of Example 1.....	31.50
ZnSO ₄ , 7 H ₂ O.....	0.48
Distilled water.....	37.29

Rheological and visual experiments on the dentifrice paste obtained show that the usual dentifrice properties are good.

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Claims

1. A silica, characterised in that it has a surface chemistry such that the number of OH expressed in OH/nm^2 is at the most 15 and that its point zero charge (PZC) is between 3 and 6.5 and its compatibility with zinc is at least 50%.
2. A silica according to Claim 1, characterised in that the number of OH is at the most 12, in particular between 3 and 12.
3. A silica according to one of the preceding claims, characterised in that it has an aluminium content of at the most 500 ppm.
4. A silica according to one of the preceding claims, characterised in that it has an iron content of at the most 200 ppm.
5. A silica according to one of the preceding claims, characterised in that it has a calcium content of at the most 500 ppm, in particular of at the most 300 ppm.
6. A silica according to one of the preceding claims, characterised in that it has a carbon content of at the most 50 ppm, and more particularly of at the most 10 ppm.
7. A silica according to one of the preceding claims, characterised in that it has a pH of at the most 7, and more particularly of between 5.5 and 7.
8. A silica according to one of the preceding claims, characterised in that it has a BET surface of between 40 and 600 m^2/g .
9. A silica according to one of the preceding claims, characterised in that it has a CTAB surface of between 40 and 400 m^2/g .
10. A silica according to one of the preceding claims, of the abrasive type, characterised in that it has a BET surface of between 40 and 300 m^2/g .

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11. A silica according to Claim 10, characterised in that it has a CTAB surface of between 40 and 100 m²/g.

12. A silica according to any one of Claims 1 to 9, of the thickening type, characterised in that it has a BET surface of between 120 and 450 m²/g, more particularly of between 120 and 200 m²/g.

13. A silica according to Claim 12, characterised in that it has a CTAB surface of between 120 and 400 m²/g.

14. A silica according to any one of Claims 1 to 9, of the bifunctional type, characterised in that it has a BET surface of between 80 and 200 m²/g.

15. A silica according to Claim 14, characterised in that it has a CTAB surface of between 80 and 200 m²/g.

16. A silica according to one of the preceding claims, characterised in that it has an oil sample of between 80 and 500 cm³/100 g.

17. A silica according to one of the preceding claims, characterised in that it has a mean particle size of between 1 and 10 µm.

18. A silica according to one of the preceding claims, characterised in that it is a precipitation silica.

19. A dentifrice composition, characterised in that it contains a silica according to one of Claims 1 to 18.

20. A dentifrice composition according to Claim 19, characterised in that it contains at least one element selected from the group including fluorine, phosphates, zinc.

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