

The present invention relates to a silica more particularly usable in dentifrice compositions, its preparation process and to dentifrice compositions containing said silica.

It is known that silica is widely used in the preparation of dentifrice compositions, where it can fulfil several functions.

It firstly acts as an abrasive agent by aiding the elimination of dental plaque through its mechanical action.

It can also have a thickening agent function for giving predetermined rheological properties to the dentifrice and can serve as an optical agent to give it the desired colouring.

Moreover, it is known that dentifrices contain various agents particularly for the prevention of caries, for reducing the formation of dental plaque or tartar deposits on teeth. Among these agents particular reference is made to fluorides. Other elements are also used, such as phosphates, pyrophosphates, polyphosphates, polyphosphonates, guanidines, especially bis-biguanides, whereof one of the most widely used elements is chlorohexidine. The dentifrice formulations can also contain zinc, flavours, perfumes, etc.

The presence of these agents in the dentifrice leads to the problem of their compatibility with silica. Particularly as a result of its absorbing characteristics, silica tends to react with these agents in such a way that they are no longer available for exerting the aforementioned therapeutic effects.

The object of the invention is therefore to find silicas which are compatible with the aforementioned agents and in particular guanidine and which can be readily used in the formulation of dentifrices. Another

object of the invention is a process permitting the preparation of such compatible silicas.

The Applicant has found that the sought compatability properties were essentially dependent on the surface chemistry of the silica used. Thus, the Applicant has established a certain number of conditions regarding the surface of the silicas in such a way that they are compatible.

The silica according to the invention is characterized in that it has a compatability with guanidine type products and in particular chlorhexidine of at least 65% and more particularly at least 90%.

Moreover, the silica according to the invention, which is compatible with products of the guanidine type and especially chlorhexidine, is also characterized in that it has a surface chemistry such that its acidity function H_0 is at least 3.3.

According to a first variant, the inventive process for the preparation of silica of the above type, comprises a reaction of a silicate with an acid, with a view to obtaining a silica gel or suspension, followed by the separation and drying of the silica and is characterized in that following the separation of the silica, the cake resulting from this separation is washed with water until the conductivity of the filtrate is at the most 200 microsiemens cm^{-1} .

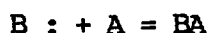
According to a second variant, the inventive silica preparation process comprises a reaction of a silicate with an acid, with a view to obtaining a silica gel or a suspension, followed by the separation and drying of the silica and is characterized in that the cake resulting from this separation undergoes a first washing with water and then a second washing or treatment with an acid solution.

Finally, the invention relates to dentifrice compositions containing a silica of the type described hereinbefore or prepared by the aforementioned process.

Other features and advantages of the invention will become more apparent from reading the following description relative to specific examples.

As has been stated in the introduction, the essential characteristics of the silicas according to the invention are based on their surface chemistry. More specifically, one of the aspects to be taken into account in said surface chemistry is the acidity. In this connection one of the characteristics of the silicas according to the invention is the strength of their surface acid sites.

Acidity here is understood in the Lewis sense, i.e. it translates the tendency of a site to accept a pair of electrons from a base in accordance with the equilibrium:



In order to characterize the silicas according to the invention, use is made of the "acidity function" H_o developed by Hammett for measuring the tendency of the acid, silica in the present case, to accept a pair of electrons from a base. Thus, the H_o function is defined by the standard relation:

$$\frac{pK_a + \log (B :)}{(B :)(A)} = |H_o$$

For determining the strength of the acid sites of a silica according to the invention using the Hammett method, use is made of the indicators initially described by Walling (J. Am. Chem. Soc. 1950, 72, 1164). The strength of the acid sites is determined by the colour indicators whereof, under the conditions of use, the passage pK_a between the acid and basic forms is known.

Thus, the lower the pK_a of the indicator undergoing the colour change, the stronger the acidity of the site. The following table gives in

an exemplified manner a list of Hammett indicators which can be used for surrounding the H_o value by determining in which form two successive indicators are adsorbed.

Indicator	Colour		pKa
	basic form	acid form	
Neutral red	yellow	red	+ 6.8
Methyl red	yellow	red	+ 4.8
Phenylazonaphthylamine	yellow	red	+ 4.0
p-Dimethylaminoazobenzene	yellow	red	+ 3.3
2-Amino-5-azotoluene	yellow	red	+ 2.0
Benzeneazodiphenylamine	yellow	red	+ 1.5
4-Dimethylaminoazo-1-naphthalene	yellow	red	+ 1.2
Crystal violet	blue	yellow	+ 0.8
p-Nitrobenzeneazo-(p'-nitro) diphenylamine	orange	violet	+ 0.43
Dicinnamalacetone	yellow	red	- 3.0
Benzalacetophenone	colourless	yellow	- 5.6
Anthraquinone	colourless	yellow	- 8.2

The colour of the indicators adsorbed on a silica is a measure of the strength of the acid sites. If the colour is that of the acid form of the indicator then the value of the H_o function of the surface is equal to or below the pKa of the indicator. Low H_o values correspond to high strength acid sites.

Thus, for example, a silica giving a red colouring with p-Dimethylaminoazobenzene and a yellow colouring with 2-Amino-5-azotoluene will have an acidity function H_o between 3.3 and 2.

Experimentally, dosing takes place with 0.2g of silica placed in a test tube in the presence of a 100 mg/l indicator solution in cyclohexane. The silica is previously dried at 190°C for 2 hours and kept protected

from moisture in a desiccator. As a result of stirring, the adsorption, if it takes place, occurs within a few minutes and note is taken of the colour change which is visible with the naked eye or possibly by studying the absorption spectra characterizing adsorbed colour indicators, both in their acid form and in their basic form.

The first feature of the silicas according to the invention is that they have an acidity function, as determined hereinbefore, of at least 3.3.

The strength and nature of the acid surface sites can also be measured by the infrared spectrometry of the pyridine adsorbed on the silica. It is known that the pyridine quantity adsorbed on a solid makes it possible to determine the nature of the acid surface sites. Pyridine is a relatively strong base ($pK_b = 9$) and unlike NH_3 ($pK_b = 5$) does not react with weak sites. The formation of a pyridinium ion (PyH^+) will also make it possible to differentiate Lewis and Bronsted sites.

Information on the acidity of the surface of a solid can also be obtained by studying the absorption bands of pyridine in the range 1700 to 1400 cm^{-1} . Moreover, quantification of the strength of the acid sites is made possible through the value of the displacement of the bands characteristic of pyridine and its ionized form, before and after adsorption.

The pyridinium ion gives a band at 1540 cm^{-1} , whilst the pyridine bonded by H bonds or coordination gives bands in the range 1440 to 1465 cm^{-1} . Moreover, it would appear that the pyridine band at 1583 cm^{-1} is displaced when the pyridine is adsorbed. This band indicates the presence of Lewis acid sites. The acid strength of the latter is proportional to the displacement of the band.

In summarizing, it is possible to use bands at 1540, 1640 and 1485 cm^{-1} for defining the acidity of the Bronsted type and bands in the range 1440 to 1465 cm^{-1} for the Lewis acidity.

Experimentally measurements were carried out on a silica suspension in carbon tetrachloride in the presence of pyridine.

The silica is dried beforehand at 190°C for 2 hours and kept protected from moisture. After cooling, 1g of silica is dispersed in 50 ml of CCl_4 by magnetic stirring, followed by ultrasonic dispersion (10 min). 0.8 mg of pyridine is added per m^2 of silica introduced. Refluxing accompanied by stirring is carried out for 1 hour.

The same protocol is used for preparing a control solution with the same pyridine concentration, but without silica and a control suspension of the same silica concentration, but without pyridine.

The adsorption spectrum of pyridine is obtained by infrared spectroscopy on the suspension, the silica-free pyridine solution and the pyridine-free silica suspension. From the spectrum obtained on the basis of the suspension is removed the spectrum corresponding to the control solution and the spectrum corresponding to the control suspension.

The silica is characterized by the position of the remaining bands and the displacement of the absorption bands of the pyridine and the pyridinium ion compared with the position of the bands of their non-adsorbed forms. In general terms, the spectrum obtained must not have a pyridinium peak (band at 1540 cm^{-1}), the absence of said peak indicating that the silica present has an acid function H_0 of at least 3.3.

The importance of the displacement of the pyridine and adsorbed pyridine bands makes it possible to evaluate the varying acidity of the acid surface sites. In general terms, for the 1440 cm^{-1} band, said displacement () must be at the most 10 cm^{-1} and more particularly at the most 5 cm^{-1} . According to the preferred embodiment of the invention, it is zero.

The silica, as defined hereinbefore, has a good compatibility with chlorhexidine. When measured by the test described hereinafter, said

compatibility can be at least 65%, particularly at least 80% and preferably at least 90%.

However, according to a particular embodiment of the invention, the silicas can also be compatible with fluorine. In this case, they have a content of anions of the type SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} of at the most $5 \cdot 10^{-3}$ moles per 100g of silica.

The lower the said content, the greater said compatibility. According to preferred variants, it will be at the most $1 \cdot 10^{-3}$ moles and more especially $0.2 \cdot 10^{-3}$ moles per 100g of silica.

In the case of silicas prepared from sulphuric acid, said anion content is more conveniently expressed by a content in SO_4 and by weight. In this case, the content is at the most 0.5%.

According to a preferred variant of the invention, said content is at the most 0.1% and more especially at the most 0.02%.

This compatibility can be further improved, particularly relative to certain elements like zinc, on observing the conditions on the number of acid surface sites. This number can be measured as a number of OH groups or silanols per nm^2 . This number is determined in the following way. The number of surface OH sites is likened to the quantity of water freed by the silica between 190 and 900°C. The silica samples are previously dried at 105°C for 2 hours.

A silica mass P_0 is placed in a thermobalance and heated to 190°C for 2 hours, i.e. the mass obtained is P_{190} . The silica is then heated to 900°C for 2 hours, i.e. P_{900} is the new mass obtained.

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

$$\text{NOH} = \frac{66922.2}{A} \times \frac{P_{190} - P_{900}}{P_{190}}$$

in which NOH is the number of OH sites per nm^2 of surface and A is the specific surface of the solid (BET) in m^2/g .

In the present case, the silicas according to the invention advantageously have an OH number/ nm^2 equal to or below 15, more particularly at the most 12 and especially between 3 and 12.

The nature of the OH sites of the silicas according to the invention, which also constitutes a characterization of their surface chemistry, can also be evaluated by the point zero charge (PZC). The latter is defined by the pH of a silica suspension for which the electric charge of the surface of the solid is zero and this applies no matter what the ionic strength of the medium. This PZC measures the real pH of the surface, to the extent that the latter is free from all ionic impurities.

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 given pH.

On the basis of equations describing the overall balance of the operation, it is easy to demonstrate that the electric charge C of the surface relative to a reference corresponding to a zero surface charge is given by the equation:

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

in which:

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

M is the solid quantity 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 protocol for determining the PZC is as follows. Use is made of the method described by Berube and Bruyn (J. Colloid Interface Sc. 1968, 27, 305). The silica is washed beforehand in high resistivity deionized water (10 megaohm.cm), dried and then degassed.

In practice, a series of solutions is prepared at $pH_o:8.5$ by adding KOH or HNO_3 and containing an indifferent electrolyte (KNO_3) at a concentration varying between 10^{-5} and 10^{-1} mole/l. To these solutions is added a given silica mass and the pH of the suspensions obtained is allowed to stabilize under stirring at $25^\circ C$ and under nitrogen for 24 hours, i.e. its value is $pH'o$.

Standard solutions are formed by the supernatant obtained by centrifuging for 30 min at 1000 r.p.m. of a part of said same suspensions, i.e. $pH'o$ is the pH of these supernatants. The pH of a known volume of these suspensions and the corresponding standard solutions is then brought to pH_o by adding the necessary KOH quantity and the suspensions and standard solutions are allowed to stabilize for 4 hours. Thus $Voh.Noh$ is the number of base equivalents added to pass from $pH'o$ to pH_o a known volume (V) of suspension or standard solution.

The potentiometric dosing of the suspensions and standard solutions is carried out on the basis of pH_o by adding nitric acid up to $pH_f=2.0$. The preferred procedure involves the addition of an acid increment corresponding to a pH variation of 0.2 unit and after each addition the pH is stabilized for 1 minute. Thus, $Vh.Nh$ is the number of acid equivalents required to obtain pH_f .

On the basis of pH_o , the term $(Vh.Nh - Voh.Noh)$ 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 the corresponding standard solution. This operation is repeated for all the ionic strengths. This gives the term $(H - OH)$ corresponding to the consumption of protons by the surface. The surface charge is calculated by the above equation.

This is followed by the plotting of the surface charge curves as a function of the pH for all the considered ionic strengths. The PZC is defined by the intersection of the curves.

The silica concentration is adjusted as a function of its specific surface. For example, 2% suspensions are used for $50 \text{ m}^2/\text{g}$ silicas with 3 ionic strengths (0.1; 0.01 and 0.001 mole/L). Dosing is carried out on 100 ml of suspension using 0.1 M potassium hydroxide.

In practice, it is preferable for the value of said PZC to be at least 3 and more particularly between 4 and 6. In the case of a better compatibility with zinc, it is at the most 6.5. For fluorine compatibility, it is preferable to have a PZC of at the most 7.

For improving the compatibility, particularly with respect to fluorine, it is of interest for the aluminium content of the silicas according to the invention to be at the most 500 ppm. In addition, the iron content of the silicas according to the invention is advantageously at the most 200 ppm. In a preferred manner, the calcium content is at the most 500 ppm and more particularly at the most 300 ppm.

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

The pH of the silicas according to the invention measured according to NFT Standard 45-007 is generally at the most 8 and more particularly between 6.0 and 7.5.

The above characteristics make it possible to obtain a silica which is compatible with at least guanidines and in particular chlorhexidine and, as a function of the particular case, also with fluorides, phosphates and their derivatives and in particular zinc.

Apart from the surface chemistry characteristics described hereinbefore and which condition the compatibilities, the silicas according to the invention also have physical characteristics making them perfectly suitable for their use in dentifrices. These structural characteristics will be described hereinafter.

Generally the BET surface of the silicas according to the invention is between 40 and 600 m^2/g and more especially between 40 and 350 m^2/g . Their CTAB surface normally varies between 40 and 400 m^2/g , more particularly between 40 and 200 m^2/g .

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

The CTAB surface is the outer surface determined according to ASTM Standard D3765, but whilst carrying out the adsorption of cetrimonium bromide (CTAB) at pH 9 and taking as the projected area of the CTAB molecule 35 $\text{\AA}^2$.

The silicas according to the invention can obviously correspond to the three standard types in the dentifrice field.

Thus, the silicas according to the invention can be of the abrasive type. They then have a BET surface between 40 and 300 m^2/g . In this case, the CTAB surface is between 40 and 100 m^2/g .

The silicas according to the invention can also be of the thickening type. They then have a BET surface between 120 and 450 m^2/g , more especially 120 and 200 m^2/g . They could then have a CTAB surface between

120 and 400 m^2/g , more especially between 120 and 200 m^2/g .

Finally, according to a third type, the silicas according to the invention can be bifunctional. They then have a BET surface between 80 and 200 m^2/g . The CTAB surface is then between 80 and 200 m^2/g .

The silicas according to the invention can also have an oil sample between 80 and 500 $\text{cm}^3/100\text{g}$ determined according to NFT Standard 30-022 (March 1953) using dibutylphthalate.

More specifically, said oil sample is between 100 and 140 $\text{cm}^3/100\text{g}$ for abrasive silicas, 200 and 400 for thickening silicas and 100 and 300 for bifunctional silicas.

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

The apparent density generally varies between 0.01 and 0.3. According to a particular embodiment of the invention, the silicas are precipitation silicas.

Finally, the silicas according to the invention have a refractive index which is generally between 1.440 and 1.465.

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

As stated hereinbefore, this process is of the type involving the reaction of a silicate with an acid, which gives rise to the formation of a silica gel or a suspension. It should be noted that it is possible to use any known operating procedure for arriving at said suspension or gel (addition of acid to a silicate sediment, simultaneous total or partial addition of acid and silicate to a water sediment or silicate solution, etc.), the choice essentially being made as a function of

the desired physical characteristics of the silica. It can be advantageous to bring the pH of the solution or gel obtained to a value of at the most 6 and in particular between 4 and 6.

This is followed by the separation of the silica from the reaction medium by any known means, such as e.g. a vacuum filter or filter press. Thus, a silica cake is collected.

The process according to the invention can then be realized according to two main variants.

The first variant relates to the preparation of silicas essentially compatible with guanidines and particular chlorhexidine. In this case, the process involves the washing of the cake. This washing takes place with water, generally deionized water, until a washing filtrate is obtained, whose conductivity is at the most 200 microsiemens cm^{-1} . If it is desired to further improve the compatibility of the silicas obtained by the process, said washing can be continued to a greater extent. In particular, according to a preferred embodiment of the invention, said washing is continued to a conductivity of at the most 100 microsiemens cm^{-1} .

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

The second variant of the process relates to the preparation of silicas which are compatible with elements such as fluorine, zinc and phosphates, as well as guanidines.

In this case, the process also involves a washing with water, generally deionized water, as in the first variant. However, this washing can be less marked. For example, it can be carried out until a filtrate

is obtained with a conductivity of at the most 200 microsiemens cm^{-1} .

Following onto said first washing with water, according to the second variant a second washing or treatment of the cake is carried out with an acid solution or acidulated water. This second washing or treatment aims at obtaining, at the end of the preparation, a silica with a pH of at the most 8 and more particularly between 6.0 and 7.5 and also a PZC of at least 3 and more particularly between 4 and 6.

The washing or treatment can take place by passing the acid solution onto the cake, or introducing the latter into the suspension obtained following the disintegration of the cake.

This acid solution can e.g. be a solution of a mineral acid, such as nitric acid

However, according to a special embodiment of the invention, said acid solution can also be a solution of an organic acid, particularly a complexing organic acid. This acid can be chosen from carboxylic, dicarboxylic, hydrocarboxylic and aminocarboxylic acids.

An example of such acids is acetic acid and in the case of the complexing acids tartaric, maleic, glyceric, gluconic and citric acids.

Particularly when using a solution of a mineral acid, it can be advantageous to carry out a final washing with deionized water.

Following the washing or treatment operations according to said second variant, drying is carried out in the same way as described hereinbefore for the first variant.

According to another variant of the invention, following the acid-silicate reaction and just prior to the separation of the silica, the suspension or gel is aged. This ageing generally takes place at a pH of at the most 6 and e.g. between 4 and 6.

It is also possible to carry out an ageing during the reaction, e.g. at a pH between 6 and 8. Said ageing operations are preferably carried out hot, e.g. at a temperature between 80 and 100°C and over a period of between 15 minutes and 2 hours.

Finally, it has been found that it was possible to further improve the compatibility of the inventive products by another complimentary treatment. This treatment consists of using an alkaline-earth product, which can be introduced either into the suspension or the silica gel, or, preferably, onto the cake, especially following the crumbling of the latter, e.g. in the form of a salt or hydroxide.

In particular, use is made of an organic salt and in particular an alkaline-earth complexing agent, generally a barium salt, e.g. barium acetate.

The invention also relates to dentifrice compositions containing the silicas of the type described hereinbefore or obtained by the process which has been discussed.

The silica quantity according to the invention used in the dentifrice compositions can vary within wide limits and it is generally between 5 and 35%.

The silicas according to the invention can be more particularly used in dentifrice compositions containing at least one element chosen from the group including fluorides, phosphates, guanidines and in particular chlorhexidine. According to the following tests, they can have a compatibility of at least 90% for each of these elements.

The silicas according to the invention are also compatible with maleic

acid-vinylethyl ether copolymers and can also be incorporated into dentifrice compositions containing these copolymers. Finally, they can have a compatability with zinc of at least 50% and preferably at least 80%.

With regards to the fluorine-containing compounds, their quantity preferably corresponds to a fluorine concentration in the composition between 0.01 and 1 and more particularly 0.1 and 0.5% by weight. The fluorine-containing compounds are in particular the salts of monofluorophosphoric acid and especially those of sodium, potassium, lithium, calcium, aluminium and ammonium, the 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 and with other fluorides, such as potassium, sodium or manganese fluorides.

Other fluorides are also usable for the present invention, such as e.g. 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 and 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',N'-tri-(polyoxyethylene)-N-hexadecylpropylenediamine dihydrofluoride.

The zinc is more particularly present in the citrate or sulphate form.

With regards to the elements usable as plaque-preventing agents of the polyphosphate, polyphosphonate, guanidine and bis-biguanide type, reference can be made to those described in US Patent 3 934 002.

The dentifrice compositions can also contain a binder. The main binders used are in particular those chosen from among:

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.

Apart from the silicas according to the invention, the dentifrice compositions can also contain one or more other abrasive polishing agents chosen from among:

precipitated calcium carbonate,
magnesium carbonate,
calcium, dicalcium and tricalcium phosphates,
insoluble sodium metaphosphate,
calcium pyrophosphate,
titanium oxide (whitening agent),
silicates,
aluminers and silico aluminates,
zinc and tin oxides,
talc,
kaolin.

The dentifrice compositions can also contain detergents, humectants, aromatizing agents, sweeteners, dyes and preservatives.

The main detergents used are in particular chosen from among:

sodium laurylsulphate,
sodium laurylsulfoacetate and laurylether sulphate,
sodium dioctylsulfosuccinate,
sodium laurylsarcosinate,
sodium ricinoleate,

sulphated monoglycerides.

The main humectants used are in particular chosen from among polyalcohols such as:

glycerol,
sorbitol, generally in 70% solution in water,
propylene glycol.

The main aromatizing agents (perfumes) used are in particular chosen from among aniseed, mint, bay, juniper, star anise, cinnamon, clove and rose oils.

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

The main dyes are chosen as a function of the desired colour from among:

red and pink colour: amaranth, azoruby, 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 the same, hexetidine, quaternary ammoniums, hexachlorophene, bromophene and hexamedine.

Finally, the dentifrice compositions contain therapeutic agents, the most important of these being selected from among antiseptics and antibiotics, enzymes, oligo-elements and fluorine-containing compounds described hereinbefore.

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

Measurement of the compatability with chlorhexidine

4g of silica are dispersed in 16g of an aqueous chlorhexidine solution with a 1% chlorhexidine digluconate concentration. The suspension is stirred for 24 hours at 37°C. The suspension is then centrifuged at 20000 r.p.m. for 30 min and the supernatant obtained is filtered on a 0.2 µm Millipore filter.

0.5 ml of the thus filtered solution is then removed and diluted in 100 ml of water in a graduated flask. This solution constitutes the test solution.

A reference solution is formed in accordance with the same protocol, but in the absence of silica. A 1% aqueous chlorhexidine digluconate solution is stirred for 24 hours at 37°C, then centrifuged at 20000 r.p.m. and the supernatant is filtered on the 0.2 µm Millipore filter. 0.5 ml of the thus obtained solution is diluted in 100 ml of water in a graduated flask.

This is followed by the measurement of the absorbance of the two solutions at 254 nm with the aid of a spectrophotometer (Uvikon 810/820). The free chlorhexidine quantity designated % compatability is determined by the relation:

$$\% \text{ compatability} = \frac{\text{Absorbance of the test}}{\text{Absorbance of the reference}} \times 100$$

Measuring the compatability with fluorides

4g of silica are dispersed in 16g of 0.3% sodium fluoride (NaF) solution. The suspension is stirred for 24 hours at 37°C. After centrifuging the suspension at 20000 r.p.m. for 30 min, the supernatant is filtered on a 0.2 µm Millipore filter. The thus obtained solution constitutes the test solution.

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

The compatability with the fluorides is determined by the free fluoride percentage measured by a fluoride-selective electrode (Orion). It is determined by the following relation:

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

Measurement of the compatability with zinc

4g of silica are dispersed in 100 ml of 0.06% $\text{Zn SO}_4 \cdot 7\text{H}_2\text{O}$ solution, which gives a suspension, whose pH is stabilized to 7 for 15 minutes by the addition of NaOH or H_2SO_4 . The suspension is then stirred for 24 hours at 37°C , followed by centrifuging at 20000 r.p.m. for 30 min.

The supernatant filtered on the 0.2 μm Millipore filter constitutes the test solution. A reference solution is then formed by using the same protocol, but in the absence of silica.

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

The compatability is determined by the following relation:

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

Measuring the compatability with potassium and sodium pyrophosphates

4g of silica are dispersed in 16g of 1.5% potassium or sodium pyrophosphate suspension. The suspension is stirred for 24 hours at 37°C and then centrifuged at 20000 r.p.m. for 30 min. 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 free pyrophosphate ion ($P_2O_7^{--}$) concentration of the two solutions is determined by ion chromatography (DIONEX 2000i system) equipped with an integrator.

The compatability 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.

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

EXAMPLE 1

This example relates to the preparation of a compatible silica of the abrasive type.

6 litres of deionized water are introduced into a reactor equipped with a temperature and pH regulating system and a turbine stirring system. After starting up the stirring operation (300 r.p.m.), the thus formed sediment is heated at 85°C.

When the temperature is reached, there is a simultaneous addition of 8.5L of sodium silicate with a 120 g/L silica concentration with a SiO_2/NaO_2 ratio equal to 3.5 and a flow rate of 0.34 L/min, and 13.5L of sulphuric acid of concentration 80 g/L. The acid flow rate is adjusted in such a way as to maintain the pH of the medium at a constant value of 8.0.

Following an addition over a period of 40 minutes, the silicate addition is stopped and the acid addition is continued until the pH of the reaction mixture is stabilized at 4. This is followed by a 15 minute ageing at said pH and at 85°C.

The mixture is then filtered and the moist cake washed with deionized water, until the conductivity of the filtrate is below 100 microsiemens.

This is followed by a washing of the cake with water brought to pH 4 by the addition of acetic acid. A final washing operation is carried out with deionized water.

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 10 microns.

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	100 m ² /g
CTAB surface	55 m ² /g
Oil sample	120 cm ³ /100 g
pH	6.5

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

ions	SO ₄	Al	Fe	Ca	C
ppM	100	250	130	300	10

The surface chemistry is quantified by the following parameters:

Ho above 3.3
PZC = 4
 $\Delta V = 5 \text{ cm}^{-1}$
number of OH/nm²: 9

The following table gives the compatibilities of the silica with the different ingredients of a dentifrice formulation.

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
% Compatibility	95	98	75	70

EXAMPLE 2

Example 1 is repeated to obtain a silica cake washed with water at pH 4 through the addition of acetic acid. The thus obtained cake is disintegrated in a disintegrator to obtain a fluid suspension. 0.2 g of barium acetate is added, accompanied by stirring. The silica is then dried by atomization and ground to obtain an average particle size of 10 μm .

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	100 m^2/g
CTAB surface	60 m^2/g
Oil sample	110 $\text{cm}^3/100 \text{ g}$
pH	6.5

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

ions	SO_4	Al	Fe	Ca	C
ppM	100	250	130	400	40

The surface chemistry is quantified by the following parameters:

Ho above 3.3
PZC = 4.5
 $\Delta\psi = 2 \text{ cm}^{-1}$
number of $\text{OH}/\text{nm}^2 = 8$

Compatibilities

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc Zn SO ₄
% Compatibility	95	98	90	70

EXAMPLE 3

This example relates to the preparation of a thickening silica gel.

14 litres of sodium silicate with a 86 g/l silica concentration and a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 3.5 are introduced into a reactor equipped with a temperature and pH regulating system and a turbine stirring system. After starting up stirring (100 r.p.m.), 1.45l of 28% ammonia is added in 2 min. This is followed by the addition of 0.8l of sulphuric acid with a concentration of 200 g/l and a flow rate of 0.2 l/min. The mixture is then reacted for 5 min at a temperature controlled to 20°C.

This is followed by the addition of 5.2l of sulphuric acid with a concentration of 200 g/l and a flow rate of 0.2 l/min.

After the appearance of the gel (visual or by turbidity measurement), the mixture is allowed to age for 10 minutes. The gel is then dispersed by stirring the mixture at 400 r.p.m. for 30 min.

The pH of the medium is then lowered to 3.5 by adding sulphuric acid (200 g/l) with a flow rate of 0.2 l/min. The reaction mixture is allowed to stabilize for 1 hour at 60°C.

The preparation of the gel is completed by filtering said mixture and by washing the cake obtained using twice 20l of deionized water at 60°C and 20l of water at pH 3.

The treatment according to the invention is then carried out by washing with deionized water and at 20°C until a conductivity of 200 micro-siemens cm^{-1} is obtained. The cake obtained is crumbled to form a

homogeneous silica suspension of concentration 10% adjusted by the addition of water.

The silica is dried by atomization on an Anhydro atomizer. The silica is then micronized on a JET Pulverizer grinder to have a grain size of 1.5 μm .

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	450 m^2/g
CTAB surface	350 m^2/g
Oil sample	300 $\text{cm}^3/100\text{g}$
pH	6.8
Apparent density	0.270
Refractive index	1.445

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

ions	SO_4	Al	Fe	Ca	C
ppM	500	200	120	300	10

The surface chemistry is quantified by the following parameters:

Ho above 3.3

PZC = 3.6

No pyridine adsorption bands.

Compatibilities

Ingredients	Fluoride	Pyrophosphate	Chlorhexidine	Zinc
	NaF	NaK	digluconate	Zn SO_4
% Compatibility	90	95	65	50

EXAMPLE 4

This example relates to a thickening silica.

6 litres of water are introduced into a reactor equipped with a pH and temperature regulating system, followed by the addition of 150 g of sodium sulphate accompanied by stirring.

The mixture is heated to 60°C and there is a simultaneous addition of 10l of sodium silicate ($R_m = 3.5$ and $SiO_2 = 220 \text{ g/l}$) and sulphuric acid with a concentration of 80 g/l in 40 min.

The sulphuric acid flow rate is adjusted in such a way as to keep the pH of the reaction medium at a constant value of 7.8. The pH of the medium is stabilized at the value 4.0 by the very rapid addition of sulphuric acid and ageing takes place for 15 min at 60°C.

The reaction mixture is filtered at 60°C and the silica cake is washed with deionized water so as to have a conductivity of the filtrate of 900 microsiemens.cm⁻¹. The cake is then washed with water at pH=4, adjusted by the addition of acetic acid and a final washing with deionized water takes place. The thus obtained silica cake is crumbled and then 2g of calcium acetate are added thereto, accompanied by stirring.

The silica is dried by atomization and micronization takes place on a Jet Pulverizer grinder to adjust the silica particle size to 1.5 µm.

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	320 m ² /g
CTAB surface	120 m ² /g
Oil sample	250 cm ³ /100g
pH	6.5

The chemical analyses of the silica appear in the following table.

ions	SO ₄	Al	Fe	Ca	C
ppM	100	200	120	300	20

The surface chemistry is quantified by the following parameters:

Ho above 3.3

PZC = 4

number of OH/nm² = 11

No pyridine adsorption bands.

Compatibilities

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
% compatible	90	95	90	80

EXAMPLE 5

This example relates to the preparation of an abrasive silica.

6 litres of deionized water are introduced into a reactor equipped with a temperature and pH regulating system and a turbine stirring system. After starting up stirring (300 r.p.m.), the thus formed sediment is heated at 85°C.

When the temperature is reached there is a simultaneous addition of 8.5l of sodium silicate with a 120 g/l silica concentration and ratio of SiO₂ to Na₂O of 3.5 and at a flow rate of 0.34 l/min, and 13.5l of sulphuric acid with a concentration of 80 g/l. The acid flow rate is adjusted so as to maintain the pH of the medium at a constant value of 8.0.

Following 40 min addition, silicate addition is stopped and the mixture is allowed to age for 15 min at 85°C and pH 8. The acid addition is continued until the pH of the reaction mixture is stabilized at 4. Ageing then takes place for 15 min at said pH and 85°C.

The mixture is then filtered and the moist cake washed with deionized water until the conductivity of the filtrate is 100 microsiemens.cm⁻¹. The cake is then washed twice with water brought to pH 4 by the addition of acetic acid. A final washing takes place with deionized water.

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 microns.

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	60 m ² /g
CTAB surface	50 m ² /g
Oil sample	120 cm ³ /100g
pH	6.0

The chemical analyses of the silica are given below.

Ions	SO ₄	Al	Fe	Ca	C
ppM	100	250	100	200	10

The surface chemistry is quantified by the following parameters:

Ho above 3.3

PZC = 4.5

No pyridine adsorption bands.

Compatability

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
% Compatible	95	98	70	80

EXAMPLE 6

This example relates to the preparation of a thickening silica in a reactor equipped with a turbine stirring system, into which are introduced 5.07l of sodium silicate of silica concentration 120 g/l and SiO₂/Na₂O ratio of 3.5 and 3.8l of deionized water. After starting the stirring operation (300 r.p.m.), the thus formed sediment is heated at 68°C. When the temperature is reached, 2.6l of sulphuric acid of concentration 80.5 g/l are added, the acid flow rate is 0.120 l/min.

After 22 min addition, the acid addition is stopped and the mixture is allowed to age for 10 min (a sudden turbidity increase is observed). This is followed by the addition of 4.2l of sulphuric acid in 35 min.

The temperature is then raised to 87°C and there is a simultaneous addition of sodium silicate at a rate of 30 ml/min and sulphuric acid at a rate of 52 ml/min for 30 min.

The temperature is raised to 95°C and 0.523l of sulphuric acid is added in 10 min. The mixture is then allowed to age for 10 min. Finally, the pH of the medium is brought to 4 by adding acid.

The mixture is then filtered and the moist cake washed with deionized water until the conductivity of the filtrate is 100 microsiemens cm⁻¹.

The cake is then washed with water brought to pH 5 by the addition of acetic acid. A final washing takes place with deionized water.

The product is then dried by atomization and micronized on a Jet Pulverizer grinder to obtain a grain size of 1.2 microns.

The physicochemical characteristics of the thus obtained silica are as follows:

BET surface	180 m ² /g
CTAB surface	170 m ² /g
Oil sample	350 cm ³ /100g
pH	6.8

The chemical analyses of the silica appear in the following table.

ions	SO ₄	AL	Fe	Ca	C
ppM	500	200	120	300	10

The surface chemistry is quantified by the following parameters:

Ho above 3.3

PZC = 3.6

No pyridine adsorption bands.

Compatability

Ingredients	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
% compatible	90	95	70	60

EXAMPLE 7

This example describes the preparation of a silica cake, which will serve as the starting product for the silicas of examples 8 to 12.

Into a 30L reactor equipped with a temperature and pH regulating system and a Mixel type stirring system are introduced 1.4L of sodium silicate of SiO₂/Na₂O ratio of 3.5 and an SiO₂ concentration of 135 g/L, preheated to 75°C. After starting up the stirring (300 r.p.m.), the thus formed sediment is heated to 85°C. When the temperature is reached, there

is a simultaneous addition of said same sodium silicate at a flow rate of 0.28 l/min and a sulphuric acid of concentration 80 g/l preheated to 75°C and at a flow rate of 0.16 l/min.

The average pH of the medium during the simultaneous addition is 9.8. Following 47 min of simultaneous addition, silicate addition is stopped and acid addition continued at the same rate until a pH of 8 is reached. The temperature of the reaction mixture is then raised to 95°C in 10 min, whilst continuing the acid addition in order to stabilize the pH of the reaction mixture at 4.2 in this same time.

This is followed by ageing for 15 min at this pH and at 95°C.

The mixture is then filtered and the moist cake washed with deionized water until the conductivity of the filtrate is 2000 microsiemens cm^{-1} . The cake obtained will be used as a base for producing the silicas of controlled surface chemistry of examples 8 to 12.

EXAMPLE 8

The cake of example 7 is used and dispersed in deionized water to form a 100 g/l silica suspension, which is then filtered. The operation is repeated until a filtrate conductivity of 100 microsiemens cm^{-1} is obtained.

The cake is then redispersed in the form of a 150 g/l suspension in deionized water and the pH of the latter is brought to 6 by adding acetic acid. After filtering, a final washing takes place with deionized water. The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 μm .

EXAMPLE 9

A cake obtained according to the operating procedure of example 7 is washed with deionized water until a filtrate conductivity of 500 microsiemens cm^{-1} is obtained. The cake is then washed with 10L of water

brought to pH 4 by gluconic acid addition. A final washing then takes place with deionized water.

The cake is disintegrated to obtain a homogeneous suspension and, accompanied by stirring, 8.5 g of barium acetate are added ($\text{Ba C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$). The mixture is aged for 30 min.

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 μm .

EXAMPLE 10

A cake obtained according to the operating procedure of example 7 is washed with deionized water until a filtrate conductivity of 500 microsiemens. cm^{-1} is obtained.

The cake is then redispersed in the form of a 150 g/l suspension in deionized water and the pH of the latter is brought to 6 by the addition of acetic acid.

Accompanied by stirring, 25g of barium hydroxide $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ are added and the mixture is allowed to age for 30 min. The suspension is then filtered and washed with 5l of water.

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 microns.

EXAMPLE 11

A cake obtained according to the operating procedure of example 7 is washed with deionized water until a conductivity of the filtrate of 100 microsiemens. cm^{-1} is obtained.

The cake is then redispersed in the form of a 150 g/l suspension in deionized water and the pH of the latter is brought to 6.3 by acetic acid addition. A final washing then takes place with deionized water.

Accompanied by stirring, 0.1 g of barium acetate $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, H_2O is then added and the mixture is allowed to age for 30 min.

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 microns.

EXAMPLE 12

The cake of example 7 is used, which is dispersed in deionized water to form a 100 g/l silica suspension, which is then filtered. The operation is repeated until the filtrate conductivity is 200 microsiemens. cm^{-1} .

The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9.0 microns.

The characteristics of the silicas of examples 8 to 12 are given in the following tables:

Example	BET Surfaces m^2/g	CTAB	pH	Oil sample	PZC	Ho refractive index
			OH/nm^2			
8	250	50	6.9 12	102	4.5 >3.3	1.460
9	250	45	6.8 10	110	4 >3.3	1.457
10	250	60	7.2 12	105	3.8 >3.3	1.458
11	260	55	7.0 10	105	6 >3.3	1.457
12	250	55	7.5 12	100	3.6 >3.3	1.446

Chemical Analysis

Examples	Ions (ppM)				
	SO ₄	Al	Fe	Ca	C
8	70	300	150	300	20
9	150	350	200	350	20
10	200	400	200	350	50
11	50	230	120	120	20
12	200	415	200	355	20

Compatibilities

Examples	Fluoride	Pyrophosphate	Chlorhexidine	Zinc
	NaF	Na/K	digluconate	ZnSO ₄
8	90	95	75	70
9	95	98	80	85
10	96	95	70	65
11	95	96	98	80
12	95	95	70	60

COMPARATIVE EXAMPLE 13

For comparison, the following table gives the compatibility measurements of commercially available silicas generally used in dentifrice formulations, as well as their physicochemical characteristics. The measurements are carried out in accordance with the tests described elsewhere.

Silicas Brand Manufacturer	CTAB	BET	Ho	OH/nm ²	SO ₄	% compatability			
	Surface	m ² /g			% by weight	CHx	F	Zn	PYR
Zeodent 113 Hubert	50	100	<3	30	0.65	1	95	0	95
Z113 Zeofinn	70	175	<3	17	0.50	1	96	0	95
Syloblanc 81 Grace	240	400	<3	17	1.56	0	90	40	95
Syloid 244 Grace		400	<3	17	0.7	4	90	2	90
Sipernat 22s Degussa	180	190	<3	16	1.0	0	90	20	90
Tixosil 53 Rhône Poulenc	50	250	<3	30	0.8	0	60	0	90

CHx=chlorhexidine, F = fluorine, Zn = zinc, Pyr = pyrophosphate.

It should be noted that the PZC is below 3 for all the products given in the table.

EXAMPLE 14

This example relates to the formulation of a translucent dentifrice paste of the gel type using silicas according to the invention. The formula is as follows:

Sorbitol (70% aqueous)	65.00
Glycerin	0.00
7mFD CMC	0.80
Sodium saccharinate	0.20
Sodium fluoride	0.24
Sodium benzoate	0.08
Aroma	2.00
Abrasive silica, example 2	15.00

Thickening silica, example 6	8.00
Chlorhexidine digluconate	1.00
Distilled water	7.68

The dentifrice has satisfactory rheological properties and is extruded in an appropriate manner initially and after storage (2 months).

Visual examination of the dentifrice confirms that the behaviour of the extrudate is correct and that it is in the form of a translucent gel. This dentifrice also has the following properties:

pH, 10% dilution	: 6.8
Abrasive power on copper LNE Standard (mg)	: 5.6
Plastic viscosity (Pa.s)	: 0.5

There is an anti-bacterial activity.

EXAMPLE 15

This example relates to the formulation of an opaque dentifrice of the paste type. The formula is as follows:

Glycerin	: 22.00
7mFD CMC	: 1.0
Sodium saccharinate	: 0.20
Sodium monofluorophosphate	: 0.76
Sodium fluoride	: 0.10
Sodium laurylsulphate (30% aqueous)	: 4.67
Sodium benzoate	: 0.10
Aroma	: 0.90
Titanium dioxide	: 1.00
Abrasive silica, example 5	: 31.50
ZnSO ₄ , 7 H ₂ O	: 0.48
Distilled water	: 37.29

The rheological and visual examination of the dentifrice paste obtained reveals that the usual properties of the dentifrice are good.



CLAIMS

1. Silica, characterized in that it has compatability with products of the guanidine type and in particular chlorhexidine of at least 65% and more particularly at least 90%.
2. Silica according to claim 1, characterized in that it also has a compatability with zinc of at least 50% and preferably 80%.
3. Silica more particularly compatible with products of the guanidine type and especially chlorhexidine, characterized in that it has a surface chemistry such that its acidity function H_0 exceeds 3.3.
4. Silica according to claim 3, characterized in that it has an infra-red pyridine adsorption spectrum having compared with the pyridine spectrum alone a displacement $\Delta\nu$ of at the most 10 cm^{-1} and in particular at the most 5 cm^{-1} .
5. Silica according to claim 4, characterized in that the aforementioned displacement is zero.
6. Silica according to any one of the preceding claims, characterized in that it has an anion content of the type SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} and CO_3^{2-} of at the most $5 \cdot 10^{-3}$ moles for 100g of silica.
7. Silica according to claim 6, characterized in that it has a content of the aforementioned anions of at the most $1 \cdot 10^{-3}$, more particularly at the most $0.2 \cdot 10^{-3}$ moles per 100 g of silica.
8. Silica according to claims 6 or 7, characterized in that it has a sulphate content, expressed in SO_4 , of at the most 0.5%, preferably at the most 0.1% and more especially at the most 0.02%.
9. Silica according to any one of the preceding claims, characterized in that it has a surface chemistry such that the number of OH,



expressed in OH/nm^2 , is at the most 15 and more particularly at the most 12.

10. Silica according to one of the preceding claims, characterized in that it has a point zero charge (PZC) of at least 3 and more particularly between 4 and 6.
11. Silica according to one of the preceding claims, characterized in that it has an aluminium content of at the most 500 ppm.
12. Silica according to one of the preceding claims, characterized in that it has an iron content of at the most 200 ppm.
13. Silica according to one of the preceding claims, characterized in that it has a calcium content of at the most 500 ppm, in particular at the most 300 ppm.
14. Silica according to one of the preceding claims, characterized in that it has a carbon content of at the most 50 ppm and more particularly at the most 10 ppm.
15. Silica according to one of the preceding claims, characterized in that it has a pH of at the most 8 and more particularly between 6.0 and 7.5.
16. Silica according to one of the preceding claims, characterized in that it has a BET surface between 40 and $600 \text{ m}^2/\text{g}$.
17. Silica according to one of the preceding claims, characterized in that it has a CTAB surface between 40 and $400 \text{ m}^2/\text{g}$.
18. Silica according to one of the preceding claims, of the abrasive type, characterized in that it has a BET surface between 40 and $300 \text{ m}^2/\text{g}$.



19. Silica according to claim 18, characterized in that it has a CTAB surface between 40 and 100 m²/g.
20. Silica according to one of the claims 1 to 17, of the thickening type, characterized in that it has a BET surface between 120 and 450 m²/g, more particularly between 120 and 200 m²/g.
21. Silica according to claim 20, characterized in that it has a CTAB surface between 120 and 400 m²/g.
22. Silica according to any one of the claims 1 to 17, of the bifunctional type, characterized in that it has a BET surface between 80 and 200 m²/g.
23. Silica according to claim 22, characterized in that it has a CTAB surface between 80 and 200 m²/g.
24. Silica according to one of the preceding claims, characterized in that it has an oil sample between 80 and 500 cm³/100 g.
25. Silica according to one of the preceding claims, characterized in that it has an average particle size between 1 and 10 μm.
26. Silica according to one of the preceding claims, characterized in that it has an apparent density between 0.01 and 0.3
27. Silica according to one of the preceding claims, characterized in that it is a precipitation silica.
28. Process for the preparation of a silica compatible with guanidines, more particularly chlorhexidine, according to one of the preceding claims of the type involving reacting a silicate with an acid to obtain a silica gel or suspension, separating and drying the silica, characterized in that following the separation of the silica, the cake resulting from this separation is washed with water until



the conductivity of the filtrate is at the most 200 microsiemens.cm⁻¹.

29. Process according to claim 28, characterized in that the aforementioned cake is washed with water until the conductivity of the filtrate is at the most 100 microsiemens.cm⁻¹.
30. Process for the preparation of a silica compatible with guanidine and in particular chlorhexidine, according to one of the preceding claims, of the type involving reacting a silicate with an acid, so as to obtain a suspension or a silica gel, characterized in that the cake resulting from said separation undergoes a first washing with water and then a second washing or treatment with an acid solution.
31. Process according to claim 30, characterized in that the first washing is carried out until the conductivity of the filtrate is at the most 2000 microsiemens.cm⁻¹.
32. Process according to claims 30 or 31, characterized in that the aforementioned acid solution is a solution of an organic acid, particularly a complexing acid.
33. Process according to claim 32, characterized in that the aforementioned organic acid is chosen from among carboxylic, dicarboxylic, amino carboxylic and hydroxycarboxylic acids.
34. Process according to claims 32 or 33, characterized in that the organic acid is chosen from among acetic, gluconic, tartaric, citric, maleic and glyceric acids.
35. Process according to any one of the claims 28 to 34, characterized in that the precipitated silica gel or suspension undergoes ageing prior to separation.



36. Process according to any one of the claims 28 to 35, characterized in that following the reaction of the silicate with an acid, the pH of the suspension or gel obtained is adjusted to a value of at the most 6 and in particular between 4 and 6.
37. Process according to one of the claims 28 to 36, characterized in that addition takes place to either the suspension or gel, or to the cake, possibly following the disintegration of the latter, of an alkaline-earth salt.
38. Process according to claim 37, characterized in that use is made of an organic salt, particularly an alkaline-earth complexing agent.
39. Dentifrice composition, characterized in that it contains a silica according to one of the claims 1 to 27, or a silica prepared by the process according to one of the claims 28 to 38.
40. Dentifrice composition according to claim 39, characterized in that it contains at least one element chosen from the group including fluorine, phosphates, guanidines, zinc and maleic acid-vinyl-ethyl ether copolymers.