

DESCRIPTION

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

It is known that silica is widely used in the preparation of dentifrice compositions, where it can have a number of different functions.

It firstly acts as an abrasive agent and helps, as a result of its mechanical action, to eliminate dental plaque. It can also act as a thickening agent to give predetermined rheological properties to the dentifrice, as well as an optical agent for giving it the desired colour.

Moreover, it is known that dentifrices contain various agents, particularly for the prevention of caries, for reducing dental plaque formation or the deposition of tartar on teeth. Particular reference is made to zinc from among these agents. Other elements are also used such as fluorides, phosphates, pyrophosphates, polyphosphates, polyphosphonates, etc. The dentifrice formulations can also contain flavours, perfumes, etc.

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

Therefore the object of the invention is to provide silicas which are compatible with the aforementioned agents and in particular zinc and which can therefore be 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 compatibility properties are essentially dependent on the surface chemistry of the silica used. Therefore a certain number of conditions regarding the surface of silicas for ensuring their compatibility has been established.



To this end, the silica according to the invention and which is more particularly usable in dentifrice compositions is 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 that its point zero charge (PZC) is between 3 and 6.5 and has a compatibility with zinc of at least 50%.

In addition, the silica preparation process according to the invention is of the type involving a reaction of a silicate with an acid in order to obtain a silica gel or suspension, a separation and a drying of the silica and it is characterized in that following the separation of 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.

Finally, the invention relates to dentifrice compositions characterized in that they contain silicas like those described hereinbefore or prepared according to the aforementioned process.

Other features and advantages of the invention can be better gathered from the study of the following description and specific examples which follow.

As has been stated in the introduction, the essential characteristics of the silicas according to the invention are their surface chemistry. More specifically, one of the aspects to be taken into account in this surface chemistry is the acidity. One of the characteristics of the silicas according to the invention is consequently the number of surface acid sites. This number is measured as the number of OH groups or silanols per nm^2 and in practice the measurement takes place in the following way.



The number of OH surface sites is likened to the quantity of water released 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. the new mass obtained is P_{900} .

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

$$NOH = \frac{66922.2}{A} \times (P_{190} - P_{900}) / 190$$

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 inventive silicas have at the most 15 OH/ nm^2 . According to a preferred embodiment of the invention said OH number is at the most 12 and is in particular between 3 and 12.

Moreover, the surface pH is also one of the characteristics of the silicas according to the invention and it is determined 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, this applying no matter what the ionic strength of the medium. This PZC measures the real pH of the surface, to the extent that it frees 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, taken with respect to a reference corresponding to a zero surface



charge, is given by the equation:

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

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 measurement of the PZC takes place in the following way. Use is made of the method described by Berube et Bruyn (J. Colloid Interface Sc. 1968, 27, 305). The silica is washed beforehand in high resistivity deionized water (10 megaohm.cm), followed by drying and degassing.

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 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 constituted by the supernatant obtained by centrifuging for 30 min at 10000 r.p.m. of 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 pHo by adding the necessary KOH quantity and the suspensions and standard solutions are allowed to stabilize for 4 hours.

The potentiometric dosing of the suspensions is carried out on the basis



of pH_o by nitric acid addition up to $pH_f=2.0$.

The preferred procedure is adding an acid increment corresponding to a pH variation of 0.2 unit, the pH being stabilized for 1 min after each solution, $V_h.N_h$ being the number of acid equivalents for arriving at pH_f .

On the basis of pH_o , the term $(V_h.N_h - V_{oh}.N_{oh})$ 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, said operation being repeated for all the ionic strengths. This gives the term $(H - OH)$ corresponding 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 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, use is made of 2% suspensions for silicas of $50 \text{ m}^2/\text{g}$ with 3 ionic strengths (0.1 ; 0.01 and 0.001 mole/l). Dosing takes place 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.

In order to improve the compatability of the silicas according to the invention with elements other than zinc and in particular fluorine, it is of interest that their aluminium content is 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 preferred manner, the calcium content can be at the most 500 ppm and more particularly at the most 300 ppm.



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

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

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

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

Generally the BET surface of the silicas according to the invention is between 40 and 600 m²/g. Their CTAB surface normally varies between 40 and 400 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, p.309, February 1938 and according to Standard NF XII-622(3.3).

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

The silicas according to the invention can obviously correspond to the



three types conventionally differentiated 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 and 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 and more particularly between 120 and 200 m^2/g . They could then have a CTAB surface between 120 and 400 m^2/g .

Finally, according to a third type, the silicas according to the invention can be bifunctional. In this case they have a BET surface between 80 and 200 m^2/g , whilst the CTAB surface is between 80 and 200 m^2/g .

The silicas according to the invention can have an oil sample between 80 and 500 $\text{cm}^3/100\text{g}$ determined according to NFT Standard 30-022 (March 1953), whilst using dibutyl phthalate. 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, 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 an embodiment of the invention the silicas are precipitation silicas.

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

The preparation process of the inventive silicas will now be described. 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 suspension.

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

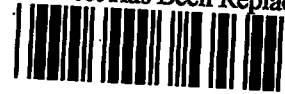
This is followed by the separation of the silica from the reaction medium adopting any known means, such as e.g. a vacuum filter or a filter press. Thus, a silica cake is collected.

According to the main feature of the inventive process, said cake then undergoes a first washing. The first washing takes place with water, generally deionized water. The process then involves a second washing or treatment with an acid solution. The object 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 especially 6 and 7, as well as a PZC between 3 and 6.5.

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

According to another embodiment of the invention, this acid solution can also be a solution of an organic acid, particularly a complexing acid. This acid could be chosen from carboxylic, dicarboxylic, hydrocarboxylic and aminocarboxylic acids.

Examples of such acids are acetic acid, whilst for the complexing acids reference is made to tartaric, maleic, glyceric, gluconic, citric and acetic acid.



This second washing or treatment can take place by the passage of the acid solution over the cake or the introduction of the latter into the suspension obtained after the disintegration of the cake.

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

According to another variant of the invention following the silicate acid 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 ageing during the reaction at a pH between 6 and 8. These ageing operations preferably take place hot, e.g. at a temperature between 80 and 100°C and for between 15 minutes and 2 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 in order to obtain the desired grain size distribution.

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

The silica quantity according to the invention used in the dentifrice compositions can vary widely and is conventionally between 5 and 35% by weight.

The silicas according to the invention are particularly suitable for



dentifrice compositions containing at least one element chosen from the group including fluorides, phosphates and zinc.

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,
aluminas 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 compatability of the silica with the various elements will be described.



Measuring the compatability with fluorides

4 g of silica are dispersed in 16 g 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

4 g of silica are dispersed in 100 ml of 0.06% Zn SO₄, 7H₂O solution, which gives a suspension, whose pH is stabilized to 7 for 15 minutes by the addition of NaOH or H₂SO₄. 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

4 g of silica are dispersed in 16 g 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 ($\text{P}_2\text{O}_7^{--}$) 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

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

When the temperature is reached, simultaneously 8.5l of sodium silicate with a silica concentration of 120 g/l of $\text{SiO}_2/\text{Na}_2\text{O}$ ratio equal to 3.5 and flow rate 0.34 l/min and 13.5l of sulphuric acid of concentration



80 g/l are added. 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, the mixture is aged for 10 min at the indicated pH and temperature values. The silicate addition is stopped and the acid addition is continued until the pH of the reaction mixture is stabilized at 4. Ageing then takes place for 15 min at this pH value 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 2000 microsiemens.

The cake is then dispersed in deionized water to form a homogeneous suspension with a 50 g/l silica concentration. The pH of this suspension is adjusted to 5.8 by adding nitric acid and the mixture is allowed to stabilize at this pH for 15 min. The suspension is filtered. The product is then dried by atomization and ground on a Forplex grinder to obtain a grain size of 9 microns.

The physicochemical characteristics of the thus obtained silica 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 silica compatibilities obtained in this way 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
% Compatible	90	98	90

COMPARATIVE EXAMPLE 2

For comparison purposes, we give below compatability measurements with the commercially available silicas generally used in dentifrice formulations, as well as their physicochemical characteristics.

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

The PZC for the silicas of this table is below 3.

EXAMPLE 3

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



- 17 -

Glycerin	22.00
7mFd CMC	1.00
Sodium saccharinate	0.20
Sodium monofluorophosphate	0.76
Sodium fluoride	0.10
Sodium lauryl sulphate (30% aqueous)	4.67
Sodium benzoate	0.10
Aroma	0.90
Titanium dioxide	1.00
Silica of Example 1	31.50
$\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$	0.48
Distilled water	37.29

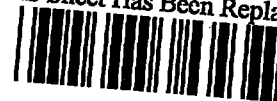
The rheological and visual experiments on the dentifrice paste obtained reveals that the usual dentifrice properties are good.



CLAIMS



1. Silica 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 that its point zero charge (PZC) is between 3 and 6.5 and its compatibility with zinc is at least 50%.
2. Silica according to claim 1, characterized in that the number of OH is at the most 12 and in particular between 3 and 12.
3. Silica according to any one of the preceding claims, characterized in that it has an aluminium content of at the most 500 ppm.
4. Silica according to any one of the preceding claims, characterized in that it has an iron content of at the most 200 ppm.
5. Silica according to any one of the preceding claims, characterized in that it has a calcium content of at the most 500 ppm and in particular at the most 300 ppm.
6. Silica according to any 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.
7. Silica according to any one of the preceding claims, characterized in that it has a pH of at the most 7 and more particularly between 6 and 7.
8. Silica according to any one of the preceding claims, characterized in that it has a BET surface between 40 and $600 \text{ m}^2/\text{g}$.
9. Silica according to any one of the preceding claims, characterized in that it has a CTAB surface between 40 and $400 \text{ m}^2/\text{g}$.
10. Silica according to any one of the preceding claims, of the abrasive



type, characterized in that it has a BET surface between 40 and $300 \text{ m}^2/\text{g}$.

11. Silica according to claim 10, characterized in that it has a CTAB surface between 40 and $100 \text{ m}^2/\text{g}$.
12. Silica according to any one of the claims 1 to 9, of the thickening type, characterized in that it has a BET surface between 120 and $450 \text{ m}^2/\text{g}$ and more particularly between 120 and $200 \text{ m}^2/\text{g}$.
13. Silica according to claim 12, characterized in that it has a CTAB surface between 120 and $400 \text{ m}^2/\text{g}$.
14. Silica according to any one of the claims 1 to 9, of the bifunctional type, characterized in that it has a BET surface between 80 and $200 \text{ m}^2/\text{g}$.
15. Silica according to claim 14, characterized in that it has a CTAB surface between 80 and $200 \text{ m}^2/\text{g}$.
16. Silica according to any one of the preceding claims, characterized in that it has an oil sample between 80 and $500 \text{ cm}^3/100 \text{ g}$.
17. Silica according to any one of the preceding claims, characterized in that it has an average particle size between 1 and $10 \mu\text{m}$.
18. Silica according to any one of the preceding claims, characterized in that it is a precipitation silica.
19. Process for the preparation of a silica according to any one of the preceding claims of the type involving a reaction of a silicate with an acid which leads to a silica gel or a suspension, a separation and a drying of the silica, characterized in that following the separation of the silica from the suspension a first washing with water takes place of the resulting cake, followed by a second washing or a treatment with an acid solution.





20. Process according to claim 19, characterized in that the aforementioned acid solution is a solution of an organic and in particular complexing acid, more especially chosen from among carboxylic, dicarboxylic, amino carboxylic and hydrocarboxylic acids.
21. Process according to claim 20, characterized in that the organic acid is chosen from among acetic, gluconic, tartaric, citric, maleic and glyceric acid.
22. Process according to any one of the claims 19 to 21, characterized in that following the reaction of the silicate with an acid, the pH of the suspension obtained is brought to a value of at the most 6 and in particular between 4 and 6.
23. Process according to any one of the claims 19 to 22, characterized in that the silica gel or suspension undergoes ageing prior to separation.
24. Dentifrice composition, characterized in that it contains a silica according to one of the claims 1 to 18 or a silica prepared by the process according to one of the claims 19 to 23.
25. Dentifrice composition according to claim 24, characterized in that it contains at least one element chosen from the group including fluorine, phosphates and zinc.



* C L M S *