

Silica for dentifrice compositions more particularly compatible with metal cations.

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

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

It firstly serves as an abrasive agent, its mechanical action helping to eliminate dental plaque.

It can also serve as a thickening agent in order to give the dentifrice specific rheological properties and as an optical agent to give it the desired colouring.

It is also known that dentifrices generally contain a fluoride source, usually sodium fluoride or monofluorophosphate used as a caries prophylactic; a binding agent, e.g. an algal colloid such as carrageen, guar gum or xanthan gum; a humectant, which can be a polyalcohol, e.g. glycerine, sorbitol, xylitol and propylene glycol. It also has optional constituents, e.g. surfactants, agents for reducing dental plaque or tartar deposits, taste correcting agents, as well as colouring agents and pigments, etc.

A certain number of metal cations can occur in dentifrice compositions. For example, reference is made to alkaline earth cations, particularly calcium, strontium, barium, cations in group 3a, aluminium, indium, cations of group 4a, germanium, tin, lead and group 8: manganese, iron, nickel, zinc, titanium, zirconium, palladium, etc. The said cations can be in the form of mineral salts, e.g. chloride, fluoride, nitrate, phosphate or sulphate, or in the form of organic salts such as acetate, citrate, etc.

More specific examples are zinc citrate, zinc sulphate, strontium chloride, tin fluoride in the form of the single salt (SnF_2) or the double salt (SnF_2, KF), stannous chlorofluoride SnClF and zinc fluoride (ZnF_2).

The presence of agents containing said metal cations causes a problem of their compatibility with the silica. Thus, particularly due to its absorbent nature, the latter can react with these agents in such a way that they are no longer available for exerting the function imparted to them.

French patent application 87/15276 describes silicas compatible with zinc. However, the silicas described do not have an adequate compatibility with other metal cations such as tin, strontium, etc.

Thus, the object of the present invention is to supply novel silicas compatible with zinc and other metal cations like those referred to hereinbefore.

Another object of the invention is to supply a silica, which is also compatible with the fluoride anion. Thus, the improvement of the compatibility with the cations reduces the compatibility with the fluoride anion. It is therefore important that the proposed silica remains compatible with the fluoride anion occurring in all dentifrice compositions.

Finally, another object of the invention is the process for preparing such compatible silicas.

In this connection, the Applicant has found that the sought compatibility properties were largely dependent on the surface chemistry of the silica used. The Applicant has thus established a certain number of conditions with regards to the surface of silicas in order to make them compatible.

To this end, the silica according to the invention and 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 equal to or below 10, that its zero charge point (ZCP) is between 3 and 6.5 and that it leads to an aqueous suspension, whose pH varies as a function of its electrical conductivity according to the following equation (I):

$$\text{pH} = b - a \log (D) \quad (\text{I})$$

in equation (I):

a is a constant equal to or below 0.6,

b is a constant equal to or below 8.5,

(D) represents the electrical conductivity of the aqueous silica suspension expressed in $\text{microsiemens.cm}^{-1}$.

Another characteristic of the silica according to the invention is that it has a compatibility with at least one divalent and higher valency metal cation chosen from group 2a, 3a, 4a and 8 of the periodic classification of at least 30% and more particularly at least 50% and preferably at least 80%.

The present invention also relates to one of the processes for the preparation of silica according to the invention, which is characterized in that it consists of reacting a silicate with an acid thus leading to a silica gel or suspension, followed by a first aging at a pH equal to or above 6 and equal to or below 8.5, followed by a second aging at a pH equal to or below 5.0, separating the silica, subjecting to hot water washing until it leads to an aqueous suspension, whose pH, measured on a 20% SiO_2 suspension, is in accordance with the following equation:

$$\text{pH} = d - c \log (D) \quad (\text{II})$$

in equation (II):

c is a constant equal to or below 1.0,

d is a constant equal to or below 8.5,

(D) represents the electrical conductivity of the aqueous silica suspension expressed in microsiemens.cm⁻¹

and which is finally dried.

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

Other features and advantages of the invention will be better understood from reading the description and specific, ~~non-limitative~~ examples which follow.

As has been stated, 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 said surface chemistry is the acidity. In this connection, one of the characteristics of the silicas according to the invention is the number of surface acid sites. This number is measured as the number of OH⁻ groups or silanols per nm². In practice, the measurement takes place in the following way. The number of OH⁻ surface sites is likened to the water quantity released by the silica between 190 and 900°C. The silica samples are previously dried at 105°C for 2 hours.

A mass or weight P₀ of silica is placed in a thermobalance and heated to 190°C for 2 hours, i.e. P₁₉₀ is the mass obtained. The silica is then heated to 900°C for 2 hours, i.e. P₉₀₀ is the new mass obtained.

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

$$N_{OH^-} = \frac{66922.2}{A} \times \frac{P_{190} - P_{900}}{P_{190}}$$

in which:

N_{OH^-} is the number of OH^- sites/ nm^2 of surface,

A is the specific surface of the solid measured by BET and expressed in m^2/g .

In the present case, the silicas according to the invention advantageously have a number of OH^-/nm^2 equal to or below 10 and more particularly between 4 and 10.

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 zero charge point. The latter is defined by the pH of a silica suspension for which the electric charge of the surface of the solid is zero, no matter what the ionic force of the medium. This (ZCP) 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 the equations describing the overall balance of the operation, it is easy to show that the electric charge c of the surface, relative to a reference corresponding to a zero surface charge, is given by the equation:

$$c = \frac{F}{A.M.} (H^+) - (OH^-)$$

in which

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

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

F is the Faraday,

(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 (ZCP) is as follows. Use is made of the method described by Berube and de 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, preparation takes place of a series of solutions at $pH_o = 8.5$ by adding KOH or HNO_3 and containing an indifferent electrolyte (KNO_3) at a concentration variable 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, accompanied by stirring, at $25^\circ C$ and under nitrogen for 24 hours, i.e. pH'_o is its value.

Standard solutions are constituted by the supernatant obtained by centrifuging for 30 min at 1000 r.p.m. of part of these suspensions, so that pH'_o is the pH of the supernatants.

The pH is then brought to a known volume of said suspensions and standard solutions corresponding to pH_o by adding the necessary KOH quantity and the suspensions and standard solutions are allowed to stabilize for 4 hours. V_{OH^-} , N_{OH^-} is the number of base equivalents added to pass from pH'_o to pH_o of a known volume (V) of suspension or standard solution.

The potentiometric assay of 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 is the addition of an acid increment corresponding to a pH variation of 0.2 pH unit. After each addition the pH is stabilized for 1 min, so that V_{H^+} , N_{H^+} is the number of acid equivalents to arrive at pH_f .

On the basis of pH_0 , the term $(V_{H^+}, N_{H^+} - V_{OH^-}, N_{OH^-})$ is plotted as a function of the incremented pH for all the suspensions (at least 3 ionic forces) 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 repeated for all the ionic forces. This gives the term $(H^+) - (OH^-)$ corresponding to the surface proton consumption. The surface charge is calculated by the above equation.

This is followed by the plotting of surface charge curves as a function of the pH for all the considered ionic forces. The (ZCP) 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 forces (0.1 ; 0.01 and 0.001 mole/l). The assay is performed on 100 ml of suspension using 0.1 M potassium hydroxide. For the silicas according to the invention, this ZCP must be between 3 and 6.5.

Moreover, in order to improve the compatibility of the silicas according to the invention with respect to other elements and in particular fluorine, it is of interest that the content of divalent and higher valency cations contained in the silica is at the most equal to 1000 ppm. It is in particular desirable for the aluminium content of the silicas according to the invention to be at the most 500 ppm. Moreover, the iron content of the silicas according to the invention is advantageously at the most 200 ppm. In 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 preferably also have a carbon content of at the most 50 ppm and particularly at the most 10 ppm.~~

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

The above characteristics give a silica compatible with divalent and higher valency metal cations and in particular zinc, strontium and tin. This compatibility measured according to the test given hereinafter is at least 30%, more particularly at least 50% and preferably at least 80%. In addition, the silicas according to the invention can have a good compatibility with the anion, fluoride of at least approximately 80% and preferably at least 90%.

Apart from the surface chemistry characteristics which condition the compatibilities, the silicas according to the invention also have physical characteristics making them completely suitable for use in a dentrifice. These structural characteristics will be described hereinafter.

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 method of Brunauer-Emmet-Teller described in the Journal of the American Chemical Society Vol. 60, p.309, February 1938 and standard NF XII-622(3.3).

The CTAB surface is the external surface determined according to standard ASTM D3765, but carrying out the adsorption of hexadecyl trimethyl ammonium bromide (CTAB) at pH 9 and by taking as the projected area of the CTAB molecule 35 Å².

The silicas according to the invention can obviously correspond to the three types normally distinguished in the field of dentifrices. Thus, the silicas according to the invention can be of the abrasive type and then have a BET surface between 40 and 300 m²/g and in this case the CTAB surface is between 40 and 100 m²/g.

The silicas according to the invention can also be of the thickening type and 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 and more particularly between 120 and 200 m^2/g .

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

The silicas according to the invention can also have an oil absorption between 80 and 500 $\text{cm}^3/100\text{g}$ determined according to standard NFT 30-022 (March 1953) using dibutyl phthalate. More specifically, said oil absorption 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 bifunctionals.

Furthermore, for use in dentifrices, the silicas preferably have a particle size between 1 and 10 μm .

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 generally between 1.440 and 1.465.

The preparation process for 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 suspension or a silica gel.

It should be noted that it is possible to use any known operating

procedure in order to arrive 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 a function of the physical characteristics of the silica which it is wished to obtain.

According to a preferred embodiment of the invention the silica gel or suspension is prepared by simultaneously adding the silicate and the acid to a sediment, which can be a water sediment, a colloidal silica dispersion containing 0 to 150 g/l of silica expressed in SiO_2 , a silicate or a mineral or organic salt, preferably alkali metals, such as e.g. sodium sulphate or sodium acetate. The addition of these two reagents takes place simultaneously in such a way that the pH is kept constant between 4 and 10, preferably between 8.5 and 9.5. The temperature is advantageously between 60 and 95°C.

One method of preparing the colloidal silica dispersion preferably having a concentration between 20 and 150 g/l consists of heating an aqueous silicate solution, e.g. at between 60 and 95°C and adding the acid to said aqueous solution until a pH is obtained between 8.0 and 10.0 and preferably close to 9.5.

The concentration of the aqueous silicate solution expressed in SiO_2 is preferably between 20 and 150 g/l. It is possible to use a diluted or concentrated acid and its normality can vary between 0.5 and 36N, preferably between 1 and 2N.

Hereinbefore, silicate has been understood to mean advantageously an alkali metal silicate and preferably a sodium silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ weight ratio between 2 and 4 and preferably equal to 3.5. The acid can be gaseous, such as carbon dioxide gas, or liquid, preferably sulphuric acid.

In a further stage of the inventive process, the suspension or gel undergoes a double aging operation. A first aging is carried out

at a pH of at the most 8.5 and e.g. between 6 and 8.5 and preferably at 8.0. Aging preferably takes place hot, e.g. at between 60 and 100°C and preferably at 95°C for a time between 10 minutes and 2 hours.

Another variant of the invention consists of preparing a silica gel or a suspension progressively adding the acid to a sediment containing the silicate until the desired aging pH is obtained. This operation is carried out at a temperature preferably between 60 and 95°C. The suspension of the silica gel is then aged under the conditions described hereinbefore.

This is followed by a second aging at a pH below 5, preferably between 3 and 5 and in even more preferred manner between 3.5 and 4.0. The temperature and time conditions are the same as for the first aging. Acid is added to bring about the desired aging pH.

It is e.g. also possible to use a mineral acid such as nitric, hydrochloric, sulphuric or phosphoric acid, or even carbonic acid formed by bubbling carbon dioxide gas.

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

The following stage of the process according to the invention involves the washing of the silica cake obtained. Washing takes place under conditions such that the pH of the suspension or medium prior to drying is in accordance with the following equation:

$$\text{pH} = d - e \log.(D) \quad (\text{II})$$

in which:

e is a constant equal to or below 1.0,

d is a constant equal to or below 8.5,

(D) is the electrical conductivity of the aqueous silica suspension expressed in microsiemens.cm⁻¹.

Washing takes place with water preferably at a temperature between 40 and 80°C. As a function of the particular case, one or more and generally two washing operations are carried out with water, preferably deionized water and/or using an acid solution with a pH between 2 and 7. 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 an organic acid solution, particularly a complexing organic acid. This acid can be chosen from carboxylic, dicarboxylic, hydrocarboxylic and amino carboxylic acids.

An example of such an acid is acetic acid and examples of the complexing acids are tartaric, maleic, glyceric, gluconic and citric acid.

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

From a practical standpoint, the washing operations can take place by passing the washing solution onto the cake or by introducing the latter into the suspension obtained, following the crumbling of the cake. Thus, the filter cake, prior to the drying operation, undergoes crumbling, which can be carried out by any known means, e.g. a high speed stirrer.

Thus, before or after washing, the silica cake is crumbled and then dried by any known means. Drying can e.g. take place in a tunnel or muffle furnace or by atomization in a hot air flow, whose intake temperature can vary between approximately 200 and 500°C and whose outlet temperature varies between approximately 80 and 100°C. The residence time is between 10 seconds and 5 minutes.

If necessary, the dried product can be ground to obtain the desired grain size. The operation is performed in a conventional apparatus, such as an impeller mill or an air jet grinder.

The invention also relates to dentifrice compositions containing silicas of the type described hereinbefore, or obtained by the process described.

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

The silicas according to the invention can be used more particularly in dentifrice compositions containing at least one element chosen from the group including fluorides, phosphates and metal cations.

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

Other fluorides are also usable for the present invention, such as e.g. zinc, germanium, palladium and titanium fluoride, e.g. sodium or potassium alkali metal fluozirconates, stannous fluozirconate, potassium or sodium fluosulphates or fluoborate.

The organic fluorine-containing compounds can also be used, preferably

those known as long chain amino acid or amine addition products with hydrogen fluoride, such as cetyl amine hydrofluoride, bis-(hydroxyethyl)-aminopropyl-N-hydroxyethyl octadecyl amine dihydrofluoride, octadecyl amine fluoride, as well as N,N',N'-tri-(polyoxyethylene)-N-hexadecyl propylene diamine dihydrofluoride.

With regards to the components supplying divalent and higher valency metal cations, those which are most frequently used are zinc citrate, zinc sulphate, strontium chloride and tin fluoride.

For elements usable as plaque prophylactics of the polyphosphonate, polyphosphate, guanidine or bis-biguanide type, reference can be made to those referred to in US Patent 3 934 002.

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

cellulose derivatives: methyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl cellulose,

mucilages: carragenates, alginates, agar-agar and geloses,

gums: gum arabic and tragacanth, xanthane gum, karaya gum, carboxyvinyl and acrylic polymers, polyoxyethylene resins.

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

precipitated calcium carbonate,
magnesium carbonate,
dicalcium and tricalcium, calcium phosphates,
insoluble sodium metaphosphate,
calcium pyrophosphate,
titanium dioxide (whitening agent),

silicates,
aluminas and aluminosilicates,
zinc and tin oxides,
talc,
kaolin.

The dentifrice compositions can also comprise surfactants, humectants, aromatizing agents, sweeteners, colouring agents and preservatives.

The surfactants mainly used include sodium lauryl phosphate, lauryl ether sulphate, sodium lauryl sulphoacetate, sodium dioctyl sulphosuccinate, sodium lauryl sarcosinate, sodium ricinoleate and sulphated monoglycerides.

The main humectants used are chosen from among polyalcohols, such as glycerol, sorbitol, generally in 70% solution in water and propylene glycol.

The main aromatizing agents (perfume) are chosen from among aniseed, star anise, mint, juniper, cinnamon, clove and rose oils.

The main sweeteners are chosen from among orthosulphobenzoic imides and cyclamates.

The main colouring agents are chosen as a function of the desired colour:

red and pink colour: amaranth, azorubin, catechu, new coccin (PONCEAU 4 R), cochineal, 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, namely hexetidine, quaternary ammoniums, hexachlorophene, bromophene and hexamedine.

Finally, the dentifrice compositions contain therapeutic agents, the most important being antiseptics, antibiotics, enzymes, oligo-elements and fluorine-containing compounds referred to hereinbefore.

Specific, non-limitative examples of the invention will now be given.

However, before this, the pH measuring protocol as a function of the conductivity and concentration, as well as the tests for measuring the compatibility of the silica with various elements will be described.

pH measurement protocol as a function of the silica concentration and its conductivity.

Silica suspensions with a rising concentration varying from 0 to 25% by weight are formed by dispersing a mass m of silica previously dried at 120°C for 2 hours in a mass 100 m of degassed, deionized water (Millipore quality). The suspensions are stirred for 24 hours at 25°C .

The pH of the suspensions and solutions obtained after centrifuging part of the suspension at 8000 r.p.m. for 40 min. and filtering on a $0.22\text{ }\mu\text{m}$ Millipore filter, are measured at 25°C under a nitrogen atmosphere using a Titroprocessor Metrohm 672-type measuring system.

In the same way, measurement takes place of the conductivity of the suspensions and solutions obtained, as hereinbefore, at 25°C with a Radiometer conductivity meter (CDM83) equipped with a CDC304 cell with a cell constant equal to 1 cm^{-1} . The conductivity is given in $\mu\text{siemens/cm}$.

The suspension effect (SE) is defined by the pH difference between the pH of a 20% silica suspension and the pH of its supernatant solution separated by centrifuging.

Measuring the compatibility with zinc.

4g of silica are dispersed in 100 ml of 0.06% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solution. This gives a suspension, whose pH is stabilized at 7 for 15 minutes by adding NaOH or H_2SO_4 . The suspension is then stirred for 24 hours at 37°C and is then centrifuged at 20,000 r.p.m. for 30 min. The supernatant filtered on the $0.2 \mu\text{m}$ Millipore filter forms the test solution.

A reference solution is obtained by following 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 compatibility is determined by the following relation:

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

Hereinafter, the percent zinc compatibility is designated Zn.

Measuring the compatibility with tin fluoride SnF_2 .

1) An aqueous solution (1) containing 0.40% SnF_2 and 20% glycerine is formed by dissolving 0.40g of SnF_2 and 20g of glycerine in 79.60g of bidistilled water.

2) 4g of silica are dispersed in 16g of the solution obtained in 1). The pH of the suspensions is adjusted to 5 by the addition of 0.1N NaOH. The thus obtained suspension is stirred for 4 weeks at 37°C .

3) The suspension is then centrifuged at 8000 r.p.m. for 30 min. and the supernatant obtained (3) is filtered on a $0.22 \mu\text{m}$ Millipore filter.

4) The free tin concentration is determined by atomic absorption in the solution obtained in 1) and in the supernatant obtained in 3).

5) The compatibility is determined by the following relation:

$$\% \text{ compatibility} = \frac{\text{Sn concentration in the supernatant (3)}}{\text{Sn concentration in the solution (1)}} \times 100$$

Hereinafter the percentage tin compatibility is designated Sn.

Measuring the compatibility with strontium chloride $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

1) An aqueous solution (1) containing 1% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ is formed by dissolving 1g of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in 99g of bidistilled water. The pH of the suspensions is adjusted to 7.0 by adding 0.1N NaOH.

2) 4g of silica are dispersed in 16g of solution obtained in 1). The thus obtained suspension is stirred for 4 weeks at 37°C.

3) The suspension is then centrifuged at 8000 r.p.m. for 30 min. and the supernatant obtained (3) is filtered on the 0.22 μm Millipore filter.

4) The free strontium concentration is determined by atomic absorption in the solution obtained in 1) and in the supernatant obtained in 3).

5) The compatibility is determined by the following relation:

$$\% \text{ compatibility} = \frac{\text{Sr concentration in supernatant (3)}}{\text{Sr concentration in solution (1)}} \times 100$$

Hereinafter, the percent strontium compatibility is designated Sr.

Measuring the compatibility 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 20,000 r.p.m. for 30 min, the supernatant is filtered on the 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 compatibility with fluorides is determined by the free fluoride percentage measured by a selective fluoride electrode (Orion). It is determined by the following relation:

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

Measuring the compatibility with sodium and potassium pyrophosphates.

4g of silica are dispersed in 16g of 1.5% sodium or potassium pyrophosphate. The suspension is stirred for 24 hours at 37°C and is then centrifuged at 20,000 r.p.m. for 30 min.

The supernatant is filtered on a 0.2 µm Millipore filter. 0.2g 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 without silica.

The concentration of the pyrophosphate ion ($\text{P}_2\text{O}_7^{--}$) in the free form of the two solutions is determined by ion chromatography (2000i DIONEX system) equipped with an integrator.

The compatibility is determined by the ratio of the areas of the peaks obtained on the chromatograms and corresponding to the retention

time of the test and reference pyrophosphate.

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

EXAMPLE 1

Into a reactor equipped with a temperature and pH regulating system and a propeller stirring system (Mixel), are introduced 8.32 litres of sodium silicate with a silica concentration of 130 g/l and a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5 and 8.33 litres of soft water with a conductivity of 1 $\mu\text{S}/\text{cm}$. After starting the stirring operation (350 r.p.m.), the thus formed sediment is heated to 90°C .

When the temperature is reached, addition takes place of sulphuric acid with an 80 g/l concentration and a constant flow rate of 0.40 l/min, to bring the pH to 9.5.

This is followed by the simultaneous addition of 45.25 l of sodium silicate with a silica concentration of 130 g/l, a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5 and a flow rate of 0.754 l/min, as well as 29.64 l of 80 g/l sulphuric acid. The sulphuric acid flow rate is adjusted so as to maintain the pH of the reaction medium at a constant value of 9.5.

After 60 min addition, sodium silicate addition is stopped and sulphuric acid addition is continued with a flow rate of 0.494 l/min until the pH of the reaction mixture is stabilized at 8.0. During this phase, the temperature of the medium is raised to 95°C . This is followed by an aging for a time of 30 min at said pH and 95°C . During aging, the pH is kept at 8 by adding acid. At the end of aging, the pH is brought to 3.5 by adding sulphuric acid and this pH value is maintained for 30 min.

After stopping heating, the mixture is filtered and the cake obtained

is washed with 20 l of deionized water and heated to 80°C. The cake obtained after washing is dispersed in the presence of deionized water to form a suspension with a silica concentration equal to 10%.

This is followed by a second filtration with water washing, so as to adjust the conductivity to 500 $\mu\text{S}/\text{cm}$. This is followed by washing with water with a pH adjusted to 5 by citric acid, so as to adjust the pH to a value below 6. This is followed by a final washing with deionized water.

The pH of the aqueous suspension of the crumbled cake and with a 20% SiO_2 content satisfies the following relation:

$$\text{pH} \leq 8.20 - 0.91 \log (D)$$

The silica is dried by atomization. This is followed by a grinding of the silica obtained using an impeller mill to obtain a powder, whose average agglomerate diameter measured on the Coulter counter is 8 μm .

The physicochemical characteristics of the thus obtained silica are given in the following table:

BET surface m^2/g	65
CTAB surface m^2/g	60
DOP absorption $\text{ml}/100\text{g}$ of silica	125
Pore volume $\text{Hg cm}^3/\text{g}$	2.1
pH (5% water)	6.2
Refractive index	1.450
Translucency %	90
SO_4^{2-} ppm	100
Na^+ ppm	60
Al^{3+} ppm	150
Fe^{3+} ppm	100
Ca^{2+} ppm	10
Cl^- ppm	20
C ppm	20

Table I gives the surface chemistry characteristics of the silica according to the invention and Table II the results of the compatibility with the metal cations: zinc, tin, strontium and with the standard components of dentifrice formulations: fluoride and pyrophosphate.

EXAMPLE 2

Into a reactor equipped with a temperature and pH regulating system and a propeller stirring system (Mixel) are introduced 530 l of sodium silicate with a 135 g/l silica concentration and a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5 and 15 l of soft water with a conductivity of 1 $\mu\text{S}/\text{cm}$. After starting up the stirring operation (350 r.p.m.), the thus formed sediment is heated to 90°C. When the temperature is reached, addition takes place of sulphuric acid with a concentration of 80 g/l and a constant flow rate of 0.38 l/min in order to bring the pH to 9.5.

This is followed by the simultaneous addition of 44.70 l of sodium silicate with a silica concentration of 135 g/l, a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5 and a flow rate of 0.745 l/min, as well as 25.30 l of 80 g/l sulphuric acid. The sulphuric acid flow rate is adjusted so as to maintain the pH of the reaction medium at a constant value of 9.5.

After 60 min addition, sodium silicate addition is stopped and sulphuric acid addition is continued with a flow rate of 0.350 l/min until the pH of the reaction mixture is stabilized at 7. During this phase, the temperature of the medium is raised to 95°C. This is followed by aging for 30 min at this pH and at 95°C. During aging, the pH is maintained at 7 by adding acid. At the end of aging, the pH is brought to 4 by adding sulphuric acid and this pH is maintained for 30 min.

After stopping heating, the mixture is filtered and the cake obtained washed with deionized water until a filtrate is obtained with a

conductivity of 2000 $\mu\text{S}/\text{cm}$.

The cake is then crumbled in the presence of water to form a 20% silica suspension.

A final washing stage is carried out with deionized water, so that the pH of the aqueous suspension of the crumbled cake with a 20% SiO_2 content satisfies the following relation:

$$\text{pH} \leq 8.20 - 0.91 \log (D).$$

The silica is dried at 120°C for 24 hours and then ground on an impeller mill to obtain a powder, whose mean agglomerate diameter is $8\mu\text{m}$.

The physicochemical characteristics of the thus obtained silica are given in the following table:

BET surface m^2/g	85
CTAB surface m^2/g	80
DOP absorption $\text{ml}/100\text{g}$ of silica	150
Pore volume $\text{Hg cm}^3/\text{g}$	3.20
pH (5% water)	6.5
Refractive index	1.455
Translucency %	70
SO_4^{2-} %	0.5
Na^+ %	0.05
Al^{3+} ppm	250
Fe^{3+} ppm	120
Ca^{2+} ppm	50
Cl^- ppm	20
C ppm	5

The following Table I gives the surface chemical characteristics of the silicas according to the invention described in Examples 1 and 2. It also gives the results of the compatibility of the silicas according to the invention with the metal cations zinc, tin, strontium

and with the conventional components of dentifrice formulations, namely fluoride and pyrophosphate.

For comparison purposes, Tables I and II give the characteristics and compatibilities of commercially available silicas, whereof the following list constitutes a representative range of standard silicas:

S81 : Syloblanc 81 (GRACE)
Z113 : Zeodent 113 (HUBER)
Sid12 : Sident 12 (DEGUSSA)
Sy115 : Sylox 15 (GRACE)
T73 : Tixosil 73 (RHONE-POULENC)
T83 : Tixosil 83 (RHONE-POULENC)

Table I

Physicochemical characteristics of the silicas according to the invention and conventional silicas.

Physicochemical characteristics of silicas				
Silica	pH log (D)	SE	Ho	ZCP
S81	7.0-0.62z	- 0.17	≤ 2	2.2
Z113	10-1.0z	- 0.70	≤ 3	2.5
Sid12	8.5-0.60z	- 0.20	≤ 3	2.8
Sy115	9.2-0.74z	- 0.94	≤ 3	2.5
T73	10-0.87z	- 0.20	≤ 3	3.0
T83	8.6-0.60z	- 0.18	≤ 3	2.5
Ex 1	8.0-0.50z	- 0.00	≥ 4	4.2
Ex 2	7.4-0.30z	- 0.03	≥ 4	4.0

The meanings of the symbols used in the above table are given below:

pH/log (D) represents the equation $\text{pH} = b - a \log (D)$, in which b and a are two constants and D is the conductivity of the silica

suspension in $\mu\text{Siemens/cm}$,

SE represents the suspension effect measured by the relation

SE = pH suspension - pH supernatant defined elsewhere,

Ho is the Hammett constant,

ZCP represents the pH for which the surface charge of the silica is zero.

Table II

Compatibilities of silicas with active molecules.

Silica	% Compatibilities				
	Zn	Sn	Sr	F	P ₂ O ₇
S81	0	25	20	90	80
Z113	0	15	10	95	90
Sid12	10	25	20	90	80
Syl15	0	10	10	90	80
T73	20	15	10	90	90
R83	10	10	10	95	95
Ex 1	80	60	90	95	95
Ex 2	85	75	95	95	90

The silicas according to the invention differ from conventional silicas as a result of their physicochemical characteristics and their good compatibility with zinc, tin and strontium.



Claims for AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE.

1. Silica, characterized in that it has a surface chemistry such that the number of OH^- expressed in OH^-/nm^2 is equal to or below 10%, its zero charge point (ZCP) is between 3 and 6.5 and leads to an aqueous suspension, whose pH varies as a function of its electrical conductivity according to the following equation (I):

$$\text{pH} = b - a \log (D) \quad (\text{I})$$

in which

a is a constant equal to or below 0.6,

b is a constant equal to or below 8.5,

(D) represents the electrical conductivity of the aqueous silica suspension expressed in $\text{microsiemens.cm}^{-1}$.

2. Silica according to claim 1, characterized in that it has a surface chemistry such that the number of OH^- expressed in OH^-/nm^2 is between 4 and 10.
3. Silica according to one of the claims 1 and 2, characterized in that its ZCP is between 3 and 6.5.
4. Silica according to any one of the claims 1 to 3, characterized in that it has a compatibility with divalent and higher valency metal cations chosen from groups 2a, 3a, 4a and 8 of the periodic classification of at least 30%, preferably at least 50% and more particularly at least 80%.
5. Silica according to claim 4, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium or palladium.
6. Silica according to one of the claims 4 and 5, characterized in that the metal cation is in the form of the mineral salts



chloride, fluoride, nitrate, phosphate or sulphate or in the form of the organic salts acetate and citrate.

7. Silica according to claim 5, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride or tin fluoride.
8. Silica according to claim 1, characterized in that it has a compatibility with the fluoride anion of at least 80% and preferably at least 90%.
9. Silica according to one of the claims 1 to 8, characterized in that it has a content of divalent and higher valency metal cations of at the most 1000 ppm.
10. Silica according to claim 9, characterized in that the aluminium content is at most 500 ppm, the iron content at the most 200 ppm, the calcium content at the most 500 ppm and more particularly at the most 300 ppm.
11. Silica according to one of the claims 1 to 10, characterized in that it has a carbon content of at the most 50 ppm and more particularly at the most 10 ppm.
12. Silica according to one of the claims 1 to 11, characterized in that it has a pH of at the most 7.0 and more particularly between 6.0 and 7.0.
13. Silica according to one of the claims 1 to 12, characterized in that it has a BET surface between 40 and 600 m²/g.
14. Silica according to one of the claims 1 to 13, characterized in that it has a CTAB surface between 40 and 400 m²/g.
15. Silica according to one of the claims 1 to 14, characterized in that it has a BET surface between 40 and 300 m²/g.



16. Silica according to claim 15, characterized in that it has a CTAB surface between 40 and 100 m²/g.
17. Silica according to any one of the claims 1 to 14 of the thickening type, characterized in that it has a BET surface between 120 and 450 m²/g and more particularly between 120 and 200 m²/g.
18. Silica according to claim 17, characterized in that it has a CTAB surface between 120 and 400 m²/g.
19. Silica according to one of the claims 1 to 14 of the bifunctional type, characterized in that it has a BET surface between 80 and 200 m²/g.
20. Silica according to claim 19, characterized in that it has a CTAB surface between 80 and 200 m²/g.
21. Silica according to one of the claims 1 to 20, characterized in that it has an oil absorption between 80 and 500 cm³/100g.
22. Silica according to one of the claims 1 to 21, characterized in that it has a mean particle size between 1 and 10 μm.
23. Silica according to one of the claims 1 to 22, characterized in that it has an apparent density between 0.01 and 0.3.
24. Silica according to one of the claims 1 to 23, characterized in that it is a precipitation silica.
25. Process for the preparation of the silica described in one of the claims 1 to 24, characterized in that it consists of reacting a silicate with an acid, thus leading to a silica gel or a suspension, carrying out a first aging at a pH equal to or above 6 and equal to or below 8.5, then a second aging at a pH equal to or below 5, separating the silica, subjecting it to washing with hot water until it leads to an aqueous



suspension, whose pH, measured on a 20% SiO₂ suspension, is in accordance with the following equation:

$$\text{pH} = d - c \log (D) \quad (\text{II})$$

in which:

c is a constant equal to or below 1.0,

d is a constant equal to or below 8.5,

(D) represents the electrical conductivity of the aqueous silica suspension expressed in microsiemens.cm⁻¹ and finally drying it.

26. Process according to claim 25, characterized in that it consists of preparing the suspension or silica gel by simultaneously adding the silicate and the acid to a sediment, which can be water, a colloidal silica dispersion containing 0 to 150 g/l of silica expressed as SiO₂, a silicate or a mineral or organic salt, preferably an alkali metal salt.
27. Process according to claim 25, characterized in that the addition of two reagents takes place simultaneously in such a way that the pH is kept constant at between 4 and 10 and preferably between 8.5 and 9.5.
28. Process according to any one of the claims 25 and 26, characterized in that the temperature is between 60 and 95°C.
29. Process according to claim 25, characterized in that the colloidal silica dispersion containing 20 to 150 g/l of silica is prepared by heating an aqueous silicate solution at between 60 and 95°C and adding acid to said aqueous solution until a pH between 8.0 and 10.0 and preferably 9.5 is obtained.
30. Process according to one of the claims 25 to 29; characterized in that a first aging of the suspension or silica gel takes



place at a pH between 6 and 8.5 and preferably at 8.0, at a temperature between 60 and 100°C and preferably at 95°C.

31. Process according to claim 25, characterized in that it consists of preparing a suspension or a silica gel by progressively adding acid to a sediment containing the silicate until the desired aging pH is obtained at a temperature between 60 and 95°C.
32. Process according to claim 25, characterized in that washing takes place with water or with the aid of an acid solution with a temperature between 40 and 80°C and preferably between 60 and 80°C.
33. Process according to claim 32, characterized in that the above acid solution is an organic acid solution, particularly a complexing acid.
34. Process according to claim 33, characterized in that the aforementioned organic acid is chosen from among carboxylic, dicarboxylic, aminocarboxylic and hydroxycarboxylic acids.
35. Process according to one of the claims 33 and 34, characterized in that the organic acid is chosen from among acetic, gluconic, tartaric, citric, maleic and glyceric acid.
36. Dentifrice composition, characterized in that it contains a silica according to one of the claims 1 to 24, or a silica prepared by the process according to one of the claims 25 to 35.
37. Dentifrice composition according to claim 36, characterized in that it comprises at least one element chosen from the group including fluorine and phosphates.
38. Dentifrice composition according to claim 36, characterized in that it comprises at least one divalent or higher valency metal cation chosen from group 2a, 3a, 4a and 8 of the periodic classification.



39. Dentifrice composition according to claim 36, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium or palladium.
40. Dentifrice composition according to one of the claims 36 and 37, characterized in that the metal cation is in the form of mineral salts chloride, fluoride, nitrate, phosphate or sulphate, or in the form of organic salts, namely acetate or citrate.
41. Dentifrice composition according to one of the claims 36 to 40, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride or tin fluoride.



Claims for ES.

1. Process for the preparation of a silica having a surface chemistry such that the number of OH^- expressed in OH^-/nm^2 is equal to or below 10%, its zero charge point (ZCP) is between 3 and 6.5 and
5 leads to an aqueous suspension, whose pH varies as a function of its electrical conductivity according to the following equation (I):

$$\text{pH} = b - a \log (D) \quad (\text{I})$$

in which

- a is a constant equal to or below 0.6,
10 b is a constant equal to or below 8.5,
(D) represents the electrical conductivity of the aqueous silica suspension expressed in $\text{microsiemens, cm}^{-1}$,

- characterized in that it consists of reacting a silicate with an acid, thus leading to a silica gel or a suspension, carrying out
15 a first aging at a pH equal to or above 6 and equal to or below 8.5, then a second aging at a pH equal to or below 5, separating the silica, subjecting it to washing with hot water until it leads to an aqueous suspension whose pH, measured on a 20% SiO_2 suspension, is in accordance with the following equation:

20
$$\text{pH} = d - c \log (D) \quad (\text{II})$$

in which

- c is a constant equal to or below 1.0,
d is a constant equal to or below 8.5,
(D) represents the electrical conductivity of the aqueous
25 silica suspension expressed in $\text{microsiemens, cm}^{-1}$ and finally drying it.

2. Process according to claim 1, characterized in that the silica has a surface chemistry such that the number of OH^- expressed in OH^-/nm^2 is between 4 and 10.



3. Process according to one of the claims 1 and 2, characterized in that the silicas ZCP is between 3 and 6.5.
4. Process according to any one of the claims 1 to 3, characterized in that the silica has a compatibility with divalent and higher valency metal cations chosen from groups 2a,3a,4a and 8 of the periodic classification of at least 30%, preferably at least 50% and more particularly at least 80%.
5. Process according to claim 4, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium or palladium.
6. Process according to one of the claims 4 and 5, characterized in that the metal cation is in the form of the mineral salts chloride, fluoride, nitrate, phosphate or sulphate or in the form of the organic salts acetate and citrate.
7. Process according to claim 5, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride or tin fluoride.
8. Process according to claim 1, characterized in that the silica has a compatibility with the fluoride anion of at least 80% and preferably at least 90%.
9. Process according to one of the claims 1 to 8, characterized in that the silica has a content of divalent and higher valency metal cations of at the most 1000 ppm.
10. Process according to claim 9, characterized in that the aluminium content is at most 500 ppm, the iron content at the most 200 ppm, the calcium content at the most 500 ppm and more particularly at the most 300 ppm.



11. Process according to one of the claims 1 to 10, characterized in that the silica has a carbon content of at the most 50 ppm and more particularly at the most 10 ppm.
12. Process according to one of the claims 1 to 11, characterized in that the silica has a pH of at the most 7.0 and more particularly between 6.0 and 7.0.
13. Process according to one of the claims 1 to 12, characterized in that the silica has a BET surface between 40 and 600 m²/g.
14. Process according to one of the claims 1 to 13, characterized in that the silica has a CTAB surface between 40 and 400 m²/g.
15. Process according to one of the claims 1 to 14, characterized in that the silica has a BET surface between 40 and 300 m²/g.
16. Process according to claim 15, characterized in that the silica has a CTAB surface between 40 and 100 m²/g.
17. Process according to any one of the claims 1 to 14 of the thickening type, characterized in that the silica has a BET surface between 120 and 450 m²/g and more particularly between 120 and 200 m²/g.
18. Process according to claim 17, characterized in that the silica has a CTAB surface between 120 and 400 m²/g.
19. Process according to one of the claims 1 to 14 of the bifunctional type, characterized in that the silica has a BET surface between 80 and 200 m²/g.
20. Process according to claim 19, characterized in that the silica has a CTAB surface between 80 and 200 m²/g.



21. Process according to one of the claims 1 to 20, characterized in that the silica has an oil absorption between 80 and 500 cm³/100g.
22. Process according to one of the claims 1 to 21, characterized in that the silica has a mean particle size between 1 and 10 μ m.
- 5 23. Process according to one of the claims 1 to 22, characterized in that the silica has an apparent density between 0.01 and 0.3.
24. Process according to one of the claims 1 to 23, characterized in that the silica is a precipitation silica.
25. Process according to one of the claims 1 to 24, characterized
10 in that it consists of preparing the silica gel or suspension by simultaneously adding the silicate and the acid to a sediment, which can be water, a colloidal silica dispersion containing 0 to 150 g/l of silica, expressed in SiO₂, a silicate, or an organic or mineral salt, preferably alkali metal salt.
- 15 26. Process according to one of the claims 1 to 24, characterized in that the addition of the two reagents takes place simultaneously, so that the pH is kept constant between 4 and 10 and preferably between 8.5 and 9.5.
27. Process according to one of the claims 1 to 25, characterized
20 in that the temperature is between 60 and 95°C.
28. Process according to one of the claims 1 to 24, characterized in that preparation takes place of the colloidal silica dispersion containing 20 to 150 g/l of silica by heating an aqueous silicate solution between 60 and 95°C and adding the acid to said aqueous
25 solution until a pH is obtained between 8.0 and 10.0 and preferably of 9.5.



29. Process according to one of the claims 1 to 28, characterized in that a first aging of the silica gel or suspension takes place at a pH between 6 and 8.5 and preferably of 8.0 and at a temperature between 60 and 100°C and preferably at 95°C.
- 5 30. Process according to one of the claims 1 to 30, characterized in that it consist of preparing a silica gel or suspension by progressively adding the acid to a sediment containing the silicate until the desired aging pH is obtained at a temperature between 60 and 95°C.
- 10 31. Process according to one of the claims 1 to 24, characterized in that washing takes place with water or using an acid solution having a temperature between 40 and 80°C and preferably between 60 and 80°C.
32. Process according to claim 31, characterized in that the afore-
- 15 mentioned acid solution is a solution of an organic acid, particularly a complexing acid.
33. Process according to claim 32, characterized in that the afore-
- 20 mentioned organic acid is chosen from within the group of carboxylic acids, dicarboxylic acids, aminocarboxylic acids and hydroxycarboxylic acids.
34. Process according to one of the claims 32 and 33, characterized in that the organic acid is chosen from within the group including acetic, gluconic, tartaric, citric, maleic and glyceric acids.
35. Dentifrice composition, characterized in that it contains a
- 25 silica prepared by the process according to one of the claims 1 to 34.
36. Dentifrice composition according to claim 35, characterized in that it comprises at least one element chosen from within the



group including fluorine and phosphates.

37. Dentifrice composition according to claim 35, characterized in that it comprises at least one divalent and higher metal cation chosen in group 2a,3a,4a and 8 of the periodic classification.

5 38. Dentifrice composition according to claim 35, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium or palladium.

39. Dentifrice composition according to one of the claims 35 and
10 and 36, characterized in that the metal cation is in the form of mineral salts chloride, fluoride, nitrate, phosphate, sulphate or in the form of organic salts acetate or citrate.

40. Dentifrice composition according to one of the claims 35 to 39,
characterized in that the metal cation is in the form of zinc citrate,
15 zinc sulphate, strontium chloride or tin fluoride.