

The present invention relates to a silica particularly suitable for use in dentifrice compositions, its preparation process and dentifrice compositions incorporating it.

5 It is known that silica, which is widely used in the preparation of dentifrices, can serve several functions. Thus, it can act as an abrasive agent, when its mechanical action assists in eliminating dental plaque. It can also serve as a thickening agent for giving the dentifrice specific rheological properties and as an optical agent for giving it the desired colouring.

10 Moreover, it is known that dentifrices generally contain a fluoride source, usually sodium fluoride or monofluorophosphate used as a caries prophylactic; a binder, e.g. an algal colloid such as carrageen, guar gum or xanthan gum; and a humectant, which can be a polyol, e.g. glycerine, sorbitol, xylitol or propylene glycol.
15 There are also optional constituents, e.g. surfactants, agents for reducing dental plaque or tartar deposits, taste correcting agents, colouring agents and pigments.

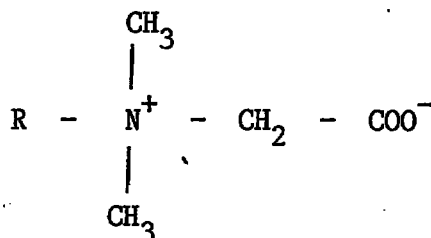
Among the different components of the dentifrice formulation are organic amino compounds, by which is meant compounds having an
20 active molecule containing at least one nitrogen atom. More specific such compounds are fluorine-containing amines used as caries prophylactics and in particular long-chain amino acid or amino addition products with hydrogen fluoride, such as cetylamine hydrofluoride, [bis-(hydroxyethyl)-aminopropyl]-N-hydroxyethyl-octadecylamine dihydrofluoride, octadecylamine hydrofluoride and N,N',N'-tri-(polyoxyethylene)-N-hexadecyl-propylenediamine dihydrofluoride; amine oxides
25 used as nonionic surfactants resulting from the oxidation of tertiary aliphatic amines by hydrogen peroxide, especially alkylamine oxides of formula $R(CH_3)_2 N \rightarrow O$, in which R is a straight or branched-chain C_{10-24} alkyl radical, and amine oxides of formula: $R(CH_2CH_2CH)_2 N \rightarrow O$;
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alkylamines, which can be primary, secondary, tertiary or quaternary amines used as cationic surfactants, e.g. those of formula $R-CH_2NH_2$, dimethyl alkyl amines of formula $R-N(CH_3)_2$, and cetyl trimethyl ammonium bromide; and

- 5 alkyl-betaines, which are N-alkyl derivatives of N,N-dimethylglycine and alkyl-amidoalkyl-betains designated hereinafter as "alkyl betaines".

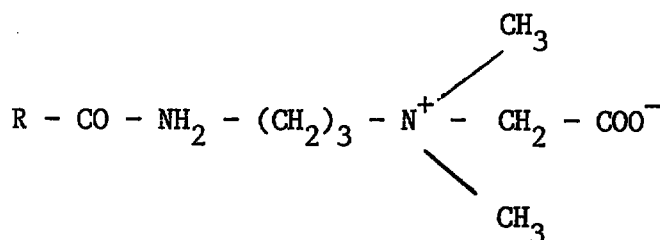
Examples of this class of amphoteric surfactants are:
alkyl betains of formula:

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and alkyl amidopropyl dimethyl betaines of formula:

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R being a straight or branched-chain C_{10-24} alkyl radical.

The presence of organic amino compounds causes the problem of compatibility with silica. Thus, particularly as a result of their absorbing capacities, silica tends to react with such compounds,
20 so that they can no longer fulfil their function.

Therefore the object of the invention is to provide a novel silica more particularly compatible with the aforementioned organic amino compounds and in particular those of the class of fluorine-containing amines and betaines and therefore usable in dentifrice formulations.

Another object of the invention is to supply a silica having a good compatibility with respect to the different cations present in dentifrice formulations, such as e.g. zinc, strontium, tin, etc.

Another object of the invention is to supply a silica which has maximum compatibility with products of the guanidine type and in particular bis-biguanides, whose most representative element is chlorhexidine.

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

15 The Applicant has found in this connection that the sought compatibility properties were essentially dependent on the surface chemistry of the silica used. The Applicant has also established a certain number of conditions with respect to the surface of the silicas in order that they are compatible.

20 The characteristic of the silica of the present invention is that it leads to an aqueous suspension, whose pH varies as a function of its concentration in the area defined by the two inequations:

$$- \text{pH} \leq 7.5 - 0.7 \log (C) \quad (\text{Ia})$$

and

$$- \text{pH} \geq 5.0 - 0.5 \log (C) \quad (\text{Ib})$$

and whose pH varies as a function of its electrical conductivity in the area defined by the two inequations.

$$- \text{pH} \leq 8.5 - 0.4 \log (D) \quad (\text{IIa})$$

and

$$- \text{pH} \geq 7.0 - 0.6 \log (D) \quad (\text{IIb})$$

in the inequations (Ia) and (Ib),

5 (C) represents the weight concentration of the aqueous silica suspension expressed as a % of SiO_2 ,

in the inequations (IIa) and (IIb),

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

10 Another characteristic of the silica according to the invention is that it has an acidity function H_o of at least 4.0.

Another characteristic of the silica according to the invention is that it has a number of OH^- sites per nm^2 equal to or below 12.

15 Another characteristic of the silica according to the invention is that it has a zero charge point (ZCP) of at least 4.

A feature of the silica according to the invention is that it has an at least 30% compatibility with organic amino compounds and more particularly at least 50% and preferably at least 80% with the organic amino compounds chosen from within the group formed by fluor-
20 ine-containing amines, amine oxides, alkyl amines and alkyl betaines.

Another feature of the silica according to the invention is that it has an at least 50% and more particularly at least 70% compatibility with metal cations.

25 Another feature of the silica according to the invention is that it has a compatibility with guanidine-type products and in particular chlorhexidine of at least 30% and more particularly at least 60%.

The present invention is also directed at one of the silica preparation processes, which is characterized in that it consists of reacting a silicate with an acid thus leading to a silica gel or 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 6.0, carrying out a third aging at a pH equal to or below 5.0, separating the silica, washing it with water until it leads to an aqueous suspension, whose pH, measured on a 20% SiO₂ suspension, complies with the following equation:

10 - $\text{pH} = d - e \log (D)$ (III)

in the equation (III)

e is a constant equal to or above 0.6 and equal to or below 1.0,

d is a constant equal to or above 7.0 and equal to or below 8.5,

(D) represents the electrical conductivity of the aqueous silica

15 suspension expressed in microsiemens.cm⁻¹,

followed by the drying thereof.

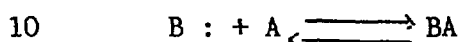
Finally, the invention relates to dentifrice compositions characterized in that they contain silicas as described hereinbefore or prepared in accordance with the process defined hereinbefore.

20 Other features and advantages of the invention will be better understood from reading the following description and specific examples.

The silica according to the invention is characterized in that the pH of its aqueous suspension varies as a function of its concentration and its electrical conductivity, according to the equations
25 given hereinbefore.

The procedure for measuring the pH as a function of the concentration of the aqueous silica suspension and its electrical conductivity is given hereinafter.

As stated hereinbefore, 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 force of their surface acid sites. In this case the acidity is taken in the Lewis sense, i.e. it represents the tendency of a site to accept a pair of electrons of a base in accordance with the equilibrium:



For characterizing the silicas according to the invention, use is made of the notion of "acidity function" H_0 developed by Hammett for measuring the tendency of the acid, the silica in the present case, to accept a pair of electrons from a base.

15 Therefore the function H_0 is defined by the standard relation:

$$pK_a + \log \frac{(B :)}{(B :) (A)} = H_0$$

In order to determine the force of the said acid sites of a silica according to

the invention using the Hammett method, use is made of indicators as initially described by Walling, J. Am. Chem. Soc., 1950, 72, p 1164. The force of the acid sites is determined by colour indicators, whose passage pKa between the acid and basic forms is known under the conditions of use.

Thus, the lower the pKa of the indicator undergoing the colour change the higher the acidity of the site. The following table gives in exemplified manner a non-limitative list of Hammett indicators usable for covering the value of H_0 by determining in which form are adsorbed two successive indicators.

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
Benzene azodiphenylamine	yellow	red	+ 1.5
4-dimethylaminoazo-1-naphthalene	yellow	red	+ 1.2
Crystal violet	blue	yellow	+ 0.8
p-nitrobenzene azo-(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 force of the acid sites. If the colour is that of the acid form of the indicator, then the value of the H_0 function of the surface is equal to or below the pKa of the indicator. Low H_0 values correspond to high force acid sites. Thus, e.g. a silica giving a red colouring with p-dimethylaminoazobenzene and yellow with 2-amino-5-azotoluene will have an acidity function H_0 between 3.3 and 2.

Experimentally, the assay takes place with 0.2 g 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 dessicator. As a result of stirring, adsorption, if it takes place, occurs in a few minutes and the colour change visible with the naked eye is observed or possibly by studying the characteristic adsorption spectra of the adsorbed colour indicators, both in their acid form and in their basic form.

The first characteristic of the silicas according to the invention is that they have an acidity function, as determined hereinbefore, of at least 4.0.

The surface state of the silica according to the invention is such that conditions regarding the number of acid surface sites are fulfilled. The number can be measured in the number of OH⁻ or silanol groups per nm². This number is determined as follows. The number of OH⁻ surface sites is likened to the quantity of water released by the silica between 190 and 900°. The silica samples are previously dried at 105°C for 2 hours. A silica mass P₀ is placed in a thermobalance and heated to 190°C for 2 hours, so that P₁₉₀ is the mass obtained. The silica is then heated to 900°C for 2 hours and P₉₀₀ is the new mass obtained.

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

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

in which:

N_{OH⁻} is the number of OH⁻ sites/nm² of surface,

A is the specific surface of the solid measured by BET and expressed in m²/g.

In the present case, the silicas according to the invention advantageously have a OH⁻/nm² number equal to or below 12 and more particularly at the most 10 and more specifically between 6 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, which 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, provided 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:

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

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,

(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, p 305. The silica is washed beforehand in high resistivity deionized water (10 megaohm.cm), dyed and then pregassed. In practice, a series of solutions at $pH_0 = 8.5$ is prepared 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_0 is its value.

Standard solutions are constituted by the supernatant obtained by centri-

fuging for 30 min at 1000 r.p.m. of part of said same suspensions, i.e. pH'o is the pH of these supernatants.

The pH of a given 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, $V_{OH^-} \cdot N_{OH^-}$ being 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 assay of the suspensions and standard solutions is carried out on the basis of the pH'o by adding nitric acid to pHf = 2.0. Preferably, the procedure involves the addition of an acid increment corresponding to a pH variation of 0.2 pH unit. Following each addition, the pH is stabilized for 1 min, i.e. $V_{H^+} \cdot N_{H^+}$ represents the number of acid equivalents to arrive at pHf.

Starting from pH'o, the term $(V_{H^+} \cdot N_{H^+} - V_{OH^-} \cdot N_{OH^-})$ is plotted as a function of the incremented pH values 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 consumption of H^+ or OH^- for the suspension and for the corresponding standard solution. This operation is repeated for all the ionic forces, which gives the term $(H^+) - (OH^-)$ corresponding to the proton consumption of the surface. The surface charge is calculated by the equation given hereinbefore. The surface charge curves are then plotted 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.

In practice, it is preferable for the ZCP value to be at least 4 and in particular between 4 and 6. In the case of a better compatibility with the metal cations, it is at the most 6.5. For a good compatibility with fluorine, the ZCP is preferably at the most 7.

Still with a view to improving the compatibility, particularly with respect to fluorine, it is of interest that the content of divalent and high valency cations contained in the silica is at the most equal to 1000 ppm. It is desirable for the aluminium content of the silicas according to the invention to be at the most 500 ppm. The iron content of the silicas according to the invention is advantageously at the most 200 ppm. Moreover, 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 more particularly at the most 10 ppm.

The silicas according to the invention, which are compatible with organic amino compounds are also compatible with the different metal cations used in dentifrice compositions. Thus, the latter can inter alia contain metal cations with a valency higher than 1 supplied by active molecules. For example, reference is made to divalent and higher valency metal cations chosen from groups 2a, 3a, 4a and 8 of the periodic classification. More specifically, reference is made to cations of group 2a, namely calcium, strontium and barium, cations of group 3a, namely aluminium and indium, of group 4a, namely germanium, tin and lead and group 8, namely 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, namely 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 in the form of the double salt (SnF_2, KF), stannous chlorofluoride SnClF and zinc fluoride (ZnF_2).

The silicas according to the invention are compatible with the different metal cations. The compatibility of said silicas with the cations defined according to the tests described hereinafter is at least approximately 50%, preferably at least 70% and in more preferred manner at least 80%.

The silicas according to the invention can consequently be used with advantage in dentifrice compositions containing divalent and higher valency

cations and more particularly in compositions incorporating at least one of the following components: zinc citrate, zinc sulphate, strontium chloride and tin fluoride.

According to a special embodiment of the invention, the inventive silicas can also be compatible with guanidines and in particular chlorhexidine. The compatibility measured by the tests described hereinafter is at least approximately 30%. It can be improved and can be at least 60% and preferably at least 90%.

In this case, the silica has a content of anions of the type SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} of at least $5 \cdot 10^{-3}$ mole/100 g of silica. The lower this content, the higher will be this compatibility. According to preferred variants it is at the most $1 \cdot 10^{-3}$ moles and more particularly $0.2 \cdot 10^{-3}$ moles/100 g of silica.

In the case of silicas prepared from sulphuric acid, said anion content is more appropriately expressed by a content in SO_4^{2-} and by weight. In this case, the content is at the most 0.1%. According to a preferred variant of the invention said content is at the most 0.05% and more particularly at the most 0.01%.

Thus, the silicas according to the invention are particularly well suited for use in dentifrice compositions containing guanidines and bisguanides. Reference can be made to those described in US patents 3 934 002 and 4 110 083, whose teaching is incorporated into the present specification.

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

The above characteristics make it possible to have a silica compatible with the aforementioned organic amino compounds, metal cations and, according to the case, also with fluorides and guanidines and in particular chlorhexidine.

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

Generally the BET surface of silicas according to the invention is between 40 and 600 m²/g, more particularly between 40 and 350 m²/g. Their CTAB surface normally varies between 40 and 400 m²/g and more specifically between 40 and 200 m²/g. The BET surface is determined according to the BRUNAUER-EMMET-TELLER method described in the Journal of the American Chemical Society, vol. 60, 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 whilst carrying out the adsorption of hexadecyl trimethyl ammonium bromide (CTAB) at pH 9 and taking 35 Å² as the projected area of the CTAB molecule.

The silicas according to the invention can obviously correspond to the three types normally distinguished in the field of the dentifrice. Thus, the silicas according to the invention can be of the abrasive type. They then have a BET surface between 40 and 300 m²/g. 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. They then have a BET surface between 120 and 450 m²/g and more particularly between 120 and 200 m²/g. They could then have a CTAB surface between 120 and 400 m²/g and more particularly between 120 and 200 m²/g.

Finally, according to a third type, the silicas according to the invention can be bifunctional and then have a BET surface between 80 and 200 m²/g, the CTAB surface then being between 80 and 200 m²/g.

The silicas according to the invention can also have an oil absorption between 80 and 500 cm³/100 g determined according to standard NFT 30-022

(March 53) 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.

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 (d_{50}) is measured by the Coulter counter.

The apparent density will generally vary between 0.01 and 0.3. According to a special embodiment of the invention the silicas are precipitation silicas. Finally, the silicas according to the invention have a refractive index which is generally between 1440 and 1465.

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 reacting 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 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.

A preferred embodiment of the invention 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 SiO_2 , a silicate or a mineral or organic salt, preferably alkali metal, such as e.g. sodium sulphate or sodium acetate. The two reagents are added 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 procedure for preparing the colloidal silica dispersion preferably

having a concentration between 20 and 150 g/l consists of heating an aqueous silicate solution, e.g. to between 60 and 95°C and adding the acid to said aqueous solution until a pH between 8 and 10 and preferably around 9.5 is obtained. The concentration of the aqueous silicate solution expressed as SiO_2 is preferably between 20 and 150 g/l. Use can be made of a dilute or concentrated acid and its normality can vary between 0.5 and 36 N, preferably between 1 and 2 N.

Hereinbefore, the term silicate has been advantageously understood to mean 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 carbonic acid, or liquid, preferably sulphuric acid.

In another stage of the inventive process, the suspension or gel undergoes ageing operations.

A first ageing is carried out at a pH of at the most 8.5 and which is e.g. between 6 and 8.5, preferably at 8. Ageing preferably takes place hot, e.g. at a temperature 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 suspension or a silica gel by progressively adding the acid to a sediment containing the silicate until the desired ageing pH is obtained. This operation is performed at a temperature preferably between 60 and 95°C. The ageing of the suspension or silica gel takes place under the conditions described hereinbefore.

This is followed by a second ageing at a pH below 6, preferably between 5 and 6 and more particularly equal to 5.5. The temperature and time conditions are the same as for the first ageing. For this purpose, the pH is brought to the desired ageing pH by adding acid. Use is e.g. made of a mineral acid, such as nitric, hydrochloric, sulphuric or phosphoric acid, or a carbonic acid formed by carbon dioxide gas bubbling.

A third ageing is carried out at a pH below 5, preferably between 3 and 5

and even more preferably at around 4.

The temperature and time conditions are the same as for the two other ageing operations. The desired ageing pH is obtained by acid addition. This is followed by the separation of the silica from the reaction medium using any known means, such as e.g. a vacuum filter or a filter press. Thus, a silica cake is collected.

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

The first variant relates to the preparation of silicas compatible with the organic amino compounds and the divalent and higher valency metal cations. In this case, the process involves washing the cake under conditions such that the pH of the suspension or the medium before drying must comply with the following equation:

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

in which:

e is a constant equal to or higher than 0.6 and equal to or lower than 1.0,
d is a constant equal to or higher than 7.0 and equal to or lower than 8.5,
(D) represents the electrical conductivity of the aqueous silica suspension expressed in $\mu\text{S cm}^{-1}$.

To this end, it is possible to envisage washing with water, generally deionized water and/or washing with the aid of 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 a solution of an organic acid, particularly an organic complexing acid. This acid can be chosen from among carboxylic, dicarboxylic, hydroxycarboxylic and aminocarboxylic acids. Examples of such acids are acetic acid and examples of complexing acids are 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.

The second variant relates to the preparation of silicas, which are also compatible with guanidines and in particular chlorhexidine.

In similar cases, a more pronounced washing is carried out. It must be continued until a washing filtrate is obtained, whose conductivity is at the most $200 \text{ microsiemens.cm}^{-1}$ and preferably below $100 \text{ microsiemens.cm}^{-1}$. As stated hereinbefore, it is important that the anion concentration is at the most 5.10^{-3} mole/100 g of silica.

As a function of the particular case, it is possible to carry out one or more washing operations, generally two such operations in water and preferably deionized water and/or with the aid of an aqueous solution of an organic acid, particularly those referred to hereinbefore.

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 using any known means, e.g. a high speed rotary stirrer.

The silica cake, before or after washing, is consequently crumbled and dried using any known means. Drying can e.g. take place in a tunnel or muffle furnace or by atomizing in a hot air flow, whose intake temperature can be between approximately 200 and 500°C and whose outlet temperature is 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 carried out 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 in question. The silica quantity according to the invention used in the dentifrice compositions can vary within wide limits and is normally between 5 and 35%.

The silicas according to the invention can be particularly appropriately used in dentifrice compositions containing at least one fluoride, phosphate and/or guanidine (in particular chlorhexidine). Thus, they can have a compatibility, according to the tests described below, of at least 90% for each of these materials.

They are also suitable for dentifrice compositions containing at least one organic amino component and/or components supplying a metal cation of valency 2 or more. They can then have a compatibility, according to the tests described below, of up to 80% for each element.

The silicas according to the invention are particularly suitable for dentifrice formulations simultaneously having at least one single mineral fluoride and/or organic fluoride, at least one alkyl betaine and at least one guanidine, in particular chlorhexidine.

More specific formulations incorporate a sodium fluoride and/or a tin fluoride and/or a fluorine-containing amine, more specifically cetylamine hydrofluoride and/or [bis-(hydroxyethyl)-aminopropyl]-N-hydroxyethyl-octadecylamine dihydrofluoride, an alkyl betaine and chlorhexidine.

The silicas according to the invention are also compatible with copolymers of maleic acid and vinyl ethyl ether and can therefore be incorporated into dentifrice compositions comprising such copolymers. The quantity of the fluorine-containing compounds preferably corresponds to a fluorine concentration in the composition between 0.01 and 1% by weight, more specifically between 0.1 and 0.5%. The fluorine-containing compounds are in particular monofluorophosphoric acid salts and more specifically those of sodium, potassium, lithium, calcium, aluminium, ammonium, monofluorophosphates and difluorophosphates, as well as various fluorides, containing fluorine in bonded ion form and in particular alkali metal fluorides, like those of sodium, lithium and potassium, ammonium fluoride, stannous fluoride, manganese fluoride, zirconium fluoride, and aluminium fluoride, together with addition products of these fluorides with one another or with other fluorides, such as potassium, sodium or manganese fluorides. Other fluorides are also usable for the present invention, e.g. zinc fluoride, germanium fluoride, palladium fluoride, titanium fluoride, alkali metal fluozirconates, e.g. those of sodium and potassium, stannous fluozirconate and sodium or potassium fluosulphates or

fluoborate.

The organic fluorine-compounds referred to at the start of the description can also be used, preferably cetylamine hydrofluoride and [bis-(hydroxyethyl)-aminopropyl]-N-hydroxyethyl-octadecylamine dihydrofluoride.

The most frequently encountered components supplying metal cations of valency 2 or more are zinc citrate, zinc sulphate, strontium chloride and tin fluoride.

Suitable elements usable as plaque prophylactics of the polyphosphate, polyphosphonate, guanidine and bis-biguanide types are disclosed in US patents 3 934 002 or 4 110 083.

The dentifrice compositions can also contain a binder, e.g. cellulose derivatives: methyl cellulose, hydroxyethyl cellulose, and sodium carboxymethyl cellulose;

mucilages: carragenates, alginates, agar-agar and geloses;
gums: gum arabic and tragacanth, xanthan gum and karaya gum;
carboxyvinyl and acrylic polymers; and
polyoxyethylene resins.

Apart from the silicas according to the invention, the dentifrice compositions can also contain one or more polishing abrasive agents, e.g. precipitated calcium carbonate, magnesium carbonate, calcium, dicalcium and tricalcium phosphates, insoluble sodium metaphosphate, calcium pyrophosphate, titanium dioxide (whitening agent), silicates, aluminas,

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aluminosilicates, zinc and tin oxides, talc and kaolin.

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

The most widely used surfactants are sodium lauryl sulphate, sodium lauryl sulphoacetate and lauryl ether sulphate, sodium dioctyl sulphosuccinate, sodium lauryl sarcosinate, sodium ricinoleate and sulphated monoglycerides.

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

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

The main sweetening agents are chosen from among orthosulphobenzoic imides and cyclamates.

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

red and pink colouring: amaranth, azorubin, catechu, new coccin (PONCEAU 4 R), cochineal and erythrosin;

green colouring: chlorophyll and chlorophyllin;

yellow colouring: 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 hexamidine.

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

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

However, before this the measuring protocol for the pH, as a function of

the conductivity and concentration, as well as tests for measuring the compatibility of silica with different elements will be described.

PROTOCOL FOR MEASURING THE pH AS A FUNCTION OF THE SILICA CONCENTRATION AND THE CONDUCTIVITY

Silica suspensions with a rising concentration varying between 0 and 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 deionized, degassed 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 μ m Millipore filter are measured at 25°C under a nitrogen atmosphere with a Metrohm 672 Titroprocessor measuring system.

In the same way, measurement takes place of the conductivity of the suspensions and solutions obtained at 25°C using a Radiometer conductivity meter (CDM83), equipped with a CDC304 cell with a cell constant equal to 1 cm^{-1} . The conductivity is expressed in μ 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 bis-(hydroxyethyl)-aminopropyl-N-hydroxyethyl-octadecyl amine dihydrofluoride

- 1) An aqueous solution (1) containing 1.65% of fluorine-containing amine is formed by adding 5 g of 33% fluorine-containing amine to propane diol in 95 g of bidistilled water.
- 2) 4 g of silica are dispersed in 16 g 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 in (3) is filtered on a 0.22 μ m Millipore filter.

4) The free fluorine-containing amine concentration is determined by nitrogen microanalysis in the solution obtained in 1) and in the supernatant obtained in 3).

5) The compatibility is determined by the following relation:

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

Hereinafter, % fluorine-containing amine compatibility is designated AF.

Measuring the compatibility with cetyl amine hydrofluoride

1) An aqueous solution (1) containing 1.72% of fluorine-containing amine is formed by dissolving 1.72 g of cetyl amine hydrofluoride in 98.28 g of bidistilled water.

2) 4 g of silica are dispersed in 16 g 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 in (3) is filtered on the 0.22 μ m Millipore filter.

4) The free fluorine-containing amine concentration is determined by nitrogen microanalysis in the solution obtained in 1) and in the supernatant obtained in 3).

5) The compatibility is determined by the following relation:

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

Hereinafter, % fluorine-containing amine compatibility is designated AF.

Measuring the compatibility with an alkyl betaine

The alkyl betaine used is a product marketed by AKSO under the trademark

ARMOTERIC LB.

- 1) An aqueous solution (1) containing 2% alkyl betaine is formed by dissolving 6.67 g of 30% alkyl betaine in 93.33 g of bidistilled water.
- 2) 4 g of silica are dispersed in 16 g 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 in (3) is filtered on a 0.22 μ m Millipore filter.
- 4) The free alkyl betaine concentration is determined by organic carbon microanalysis in the solution obtained in 1) and the supernatant obtained in 3).
- 5) The compatibility is determined by the following relation:

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

Hereinafter, % alkyl betaine compatibility is designated aBeta.

Measuring the compatibility with an alkylamidoalkyl betaine

- 1) An aqueous solution (1) containing 2.0% alkylamido alkyl betaine is formed by dissolving 6.67 g of 30% alkylamidoalkyl betaine in 93.33 g of bidistilled water.
- 2) 4 g of silica are dispersed in 16 g 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 in (3) is filtered on a 0.22 μ m Millipore filter.
- 4) the free alkylamidoalkyl betaine concentration is determined by organic carbon microanalysis in the solution obtained in 1) and the supernatant obtained in 3).

5) The compatibility is determined by the following relation:

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

Hereinafter, % alkylamidoalkyl betaine compatibility is designated by beta.

Measuring the compatibility with chlorhexidine

4 g of silica are dispersed in 16 g of an aqueous chlorhexidine solution with a 1% concentration in chlorhexidine digluconate. 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 sampled and diluted in 100 ml of water in a graduated flask. This solution forms the test solution.

A reference solution is formed using the same protocol, but without silica. A 1% chlorhexidine digluconate aqueous solution is stirred for 24 hours at 37°C, centrifuged at 20000 r.p.m. and the supernatant filtered on a 0.2 µm Millipore filter. 0.5 ml of the thus obtained solution is diluted in 100 ml of water in a graduated flask.

The absorptivity of the two solutions is then measured at 254 nm using a spectrophotometer (Uvikon 810/820).

The free chlorhexidine quantity, designated % compatibility is determined by the relation:

$$\% \text{ compatibility} = \frac{\text{Test absorptivity}}{\text{Reference absorptivity}} \times 100$$

Measuring the compatibility with fluorides

4 g of silica are dispersed in 16 g of 0.3% sodium fluoride solution (NaF). 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 the 0.2 μ m Millipore filter. The thus obtained solution forms the test solution. A reference solution is formed using the same protocol, but without silica.

The compatibility with fluorides is determined by the percentage free fluoride measured by the 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 zinc

4 g of silica are dispersed in 100 ml of 0.06% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solution. A suspension is obtained, 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 centrifuged at 20000 r.p.m. for 30 min. The supernatant filtered on the 0.2 μ m Millipore filter forms the test solution. A reference solution is formed by following the same protocol, but without silica. The free zinc concentration of the two solutions is determined by atomic absorption (214 nm).

The compatibility is determined by the following relation:

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

Measuring the compatibility with sodium and potassium pyrophosphates

4 g of silica are dispersed in 16 g of 1.5% sodium or potassium 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 the 0.2 μ m Millipore filter. 0.2 g of the 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 free pyrophosphate ion ($\text{P}_2\text{O}_7^{--}$) of the two solutions

is determined by ion chromatography (DIONEX 2000i 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 pyrophosphate retention time of both the test and the reference.

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

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 130 g/l silica concentration 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 putting stirring into operation (350 r.p.m.), the thus formed sediment is heated at 90°C. When the sought temperature is reached, sulphuric acid with a concentration of 80 g/l is added with a constant flow rate of 0.40 l/min in order 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 and 29.64 l of 80 g/l sulphuric acid. The sulphuric acid rate is adjusted so as to maintain the pH of the reaction medium at a constant value of 9.5.

After adding for 60 min, sodium silicate addition is stopped and sulphuric acid addition continued at a rate of 0.494 l/min until the pH of the reaction mixture is stabilized at 8. During this phase, the temperature of the medium is raised to 95°C. This is followed by ageing for 30 min at said pH and at 95°C. During ageing, the pH is maintained at 8 by adding acid.

At the end of ageing, the pH is brought to 5.5 by adding sulphuric acid at a flow rate of 0.494 l/min and this is followed by ageing for 30 min at said pH and at 95°C. At the end of ageing, the pH is brought to 3.5 by adding sulphuric acid and is maintained at this level for 30 min.

After stopping the heating, the mixture is filtered and the cake obtained washed with deionized water until a filtrate with a conductivity of 2000 $\mu\text{S}/\text{cm}$ is obtained. The cake obtained after washing is dispersed in the presence of deionized water to form a suspension with a silica concentration of 10%. The pH of the suspension is adjusted to 6 by adding acetic acid.

This is followed by a second filtration, and then by water washing, so as to adjust the conductivity to 500 $\mu\text{S}/\text{cm}$ and water washing with a pH adjusted to 5 by acetic acid, so as to adjust the pH to 5.5. A check is then made to establish that the following relation is fulfilled:

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

The cake is then crumbled and the silica dried by atomization. This is followed by grinding of the silica obtained on an impeller mill in order to obtain a powder, whose average agglomerate diameter measured on the COULTER counter is 8 μm .

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

BET surface m^2/g	65
CTAB surface m^2/g	60
DOP oil absorption $\text{ml}/100 \text{ g}$ of silica	125
Pore volume $\text{Hg cm}^3/\text{g}$	1.90
pH (5% water)	6.2
Refractive index	1.450
Translucency %	90
Na^+ ppm	60
SO_4^{2-} ppm	100
Al^{3+} ppm	200
Fe^{3+} ppm	120
Ca^{2+} ppm	30
Cl^- ppm	20
C ppm	5

Table I gives the surface chemistry characteristics of the silica according

to the invention, as well as the results of the compatibility with the organic amino compounds. Table II gives the compatibility results with the conventional components of dentifrice formulations, namely chlorhexidine, fluoride, zinc 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 silica concentration of 135 g/l 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 system (350 r.p.m.), the thus formed sediment is heated to 90°C. When this temperature is reached, sulphuric acid with a concentration of 80 g/l is added with a constant flow rate of 0.38 l/min to bring the pH to 9.5.

This is followed by the simultaneous addition of 44.70 l of sodium silicate with a 135 g/l silica concentration, a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5 and a flow rate of 0.745 l/min and 25.30 l of 80 g/l sulphuric acid. The sulphuric acid 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 at a rate of 0.350 l/min until the pH of the reaction mixture is stabilized at 8. During this phase, the temperature of the medium is raised to 95°C. This is followed by ageing for 30 min at this pH and at 95°C. During ageing the pH is kept at 8 by acid addition. At the end of ageing the pH is brought to 5 by adding sulphuric acid at a rate of 0.400 l/min and subsequently ageing takes place for 30 min at said pH and at 95°C. At the end of ageing the pH is brought to 3.5 by adding sulphuric acid and said pH is maintained at 3.5 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 and the pH is adjusted to 5.1 so as to ensure that

the following relation is proved:

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

The silica is dried by atomization and ground on an impeller mill to obtain a powder, whose mean agglomerate diameter is 8 μm .

The physicochemical characteristics of the thus obtained silica appear below:

BET surface m^2/g	100
CTAB surface m^2/g	80
DOP oil absorption $\text{ml}/100 \text{ g}$ of silica	200
Pore volume $\text{Hg cm}^3/\text{g}$	3.35
pH (5% water)	6.5
Refractive index	1.455
Translucency %	95

SO_4^{2-} %	0.5
Na^+ %	0.25
Al^{3+} ppm	350
Fe^{3+} ppm	120
Ca^{2+} ppm	50
Cl^- ppm	20
C ppm	5

Table I gives the surface chemistry characteristics of the silica according to the invention, as well as the compatibility results with the organic amino compounds. Table II gives the compatibility results with the conventional components of dentifrice formulations, namely chlorhexidine, fluoride, zinc and pyrophosphate.

EXAMPLE 3

Into a reactor equipped with a temperature and pH regulating system and a propeller stirring system (Mixel) are introduced 5.60l of sodium silicate with a silica concentration of 135 g/l and a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 3.5.

After starting up the stirring system (350 r.p.m.), the thus formed sediment is heated to 85°C. When the temperature is reached, sulphuric acid with a concentration of 85 g/l and preheated to 70°C is added at a constant flow rate of 0.50 l/min in order to bring the pH to 9.7.

This is followed by the simultaneous addition of 52.64 l of sodium silicate with a 135 g/l silica concentration, a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 3.5 and at a rate of 0.745 l/min and 30 l of 85 g/l sulphuric acid. The sulphuric acid rate is adjusted so as to maintain the pH of the reaction medium at a constant value of 9.7. The simultaneous addition takes place at 85°C using reagents preheated to 70°C.

After adding for 45 min, sodium silicate addition is stopped and sulphuric acid addition continued at a rate of 0.450 l/min until the pH of the reaction mixture is stabilized at 8. During this phase, the temperature of the medium is raised to 95°C. This is followed by ageing for 10 min at said pH and 95°C. During ageing, the pH is kept at 8 by adding acid. At the end of ageing the pH is brought to 5 by adding sulphuric acid at a rate of 0.750 l/min and this is followed by ageing for 15 min at said pH and 95°C. At the end of ageing the pH is brought to 3.7 by adding sulphuric acid and said pH level is maintained for 60 min.

On stopping heating, the mixture is filtered and the cake obtained washed with deionized water until a filtrate with a conductivity of 2500 $\mu\text{S}/\text{cm}$ is obtained. The cake is then crumbled in the presence of water to form a 20% silica suspension and the pH is adjusted to 5.5 to ensure that the following relation is proved:

$$\text{pH} \leq 7.5 - 0.70 \log (D).$$

The silica is dried by atomization and ground on an impeller mill to obtain a powder having a mean agglomerate diameter of 8 μm .

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

BET surface m^2/g	200
CTAB surface m^2/g	55
DOP oil absorption ml/100 g of silica	110
Pore volume Hg cm^3/g	2.65
pH (5% water)	7.0
Refractive index	1.460
Translucency %	85

SO_4^{2-} %	200
Na %	60
Al^{3+} ppm	150
Fe^{3+} ppm	120
Ca^{2+} ppm	50
Cl^- ppm	20
C ppm	5

The following table I gives the surface chemistry characteristics of the silicas of the invention described in examples 1 to 3. It also gives the compatibility results of the silicas according to the invention with organic amino compounds.

Table II gives the compatibility results with the conventional components used in dentifrice formulations, namely chlorhexidine, fluoride, zinc and pyrophosphate.

For comparison purposes, tables I and II gives the characteristics and different compatibilities of commercially available silicas, the following list constituting a representative range thereof:

S81 : Syloblanc 81 (GRACE)
 Z113 : Zeodent 113 (HUBER)
 Sid12 : Sident 12 (DEGUSSA)
 Syl15 : Sylor 15 (GRACE)
 T73 : Tixosil 73 (RHONE-POULENC)
 T83 : Tixosil 83 (RHONE-POULENC)

TABLE 1

Physicochemical characteristics and compatibility with organic amino compounds of silicas according to the invention and conventional silicas.

Physicochemical characteristics of silicas						% compatibility		
silica	pH/log(C)	pH/log(D)	SE	Ho	ZPC	AF	Beta	CHx
s81	4.7-0.75x	7.0-0.62z	- 0.17	≤ 2	2.2	0	0	0
Z113	8.1-0.94x	10-1.0z	- 0.70	≤ 3	2.5	0	0	0
Sid12	7.6-0.55x	8.5-0.60z	- 0.20	≤ 3	2.8	0	0	0
Syl15	8.1-0.70x	9.2-0.74z	- 0.94	≤ 3	2.5	0	0	0
T73	8.6-0.81x	10-0.87z	- 0.20	≤ 3	3.0	0	0	0
T83	7.5-0.60x	8.6-0.60z	- 0.18	≤ 3	2.5	0	0	0
Ex 1	7.5-0.30x	8.0-0.50z	- 0.00	≥ 4	4.2	85	60	95
Ex 2	6.5-0.80x	8.2-0.90z	- 0.10	≥ 4	4.5	85	50	30
Ex 3	7.0-0.40x	7.4-0.60z	- 0.06	≥ 4	4.0	80	50	90

The symbols used in the above table have the following meanings:

pH/log(C) represents the equation $\text{pH} = b - a \cdot \log(C)$, in which a and b are two constants and C is the weight percentage of silica in the suspension;

pH/log(D) represents the equation $\text{pH} = b' - a' \cdot \log(D)$, 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 $\text{SE} = \text{pH suspension} - \text{pH supernatant}$ defined elsewhere;

Ho is the Hammett constant;

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

AF, AFc, Beta, aBeta and CHx represent the compatibility percentages of fluorine-containing amines, alkyl betaine and chlorhexidine respectively, said quantities being defined elsewhere.

The compatibility percentages obtained with the fluorine-containing amine AFc and the alkyl betaine aBeta are similar to those obtained respectively for AF and Beta.

TABLE II

Compatibility of silicas with the active molecules:

Silica	% Compatibility					
	P207 ⁺	Zn ⁺⁺	F ⁻	AF	Beta	Ctx
s81	80	0	90	0	0	0
Z113	90	0	95	0	0	0
Sid12	80	10	90	0	0	0
Syl15	80	0	90	0	0	0
T73	90	20	90	0	0	0
T83	95	10	95	0	0	0
Ex 1	95	80	95	85	60	95
Ex 2	90	75	95	85	50	30
Ex 3	95	80	95	80	50	90

The results of the table show that the silicas according to the invention and more particularly compatible with organic amino compounds, differ markedly compared with the standard silicas through the following relations:

$$\text{pH} \leq 8.5 - 0.40 \log (D) \text{ and } \text{pH} \geq 7.0 - 0.60 \log (D)$$

$$\text{pH} \leq 7.5 - 0.70 \log (C) \text{ and } \text{pH} \geq 5.0 - 0.50 \log (C)$$



Claims for ES.

1. Process for the preparation of a silica, said silica leading to an aqueous suspension, whose pH varies as a function of its concentration in the area defined by the two inequations:

5 $\text{pH} \leq 7.5 - 0.7 \log (C) \quad (\text{Ia})$

and

$\text{pH} \geq 5.0 - 0.5 \log (C) \quad (\text{Ib})$

and whose pH varies as a function of its electrical conductivity in the area defined by the two inequations:

10 $\text{pH} \leq 8.5 - 0.4 \log (D) \quad (\text{IIa})$

and

$\text{pH} \geq 7.0 - 0.6 \log (D) \quad (\text{IIb})$

in the inequations (Ia) and (Ib),

(C) represents the weight concentration of the aqueous silica sus-
15 pension as a percent of SiO_2 ,

in the inequations (IIa) and (IIb),

(D) represents the electrical conductivity of the aqueous silica suspension in $\text{microsiemens.cm}^{-1}$, characterized in that it consists of reacting a silicate with an acid thus leading to a suspension

20 or silica gel, 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 6.0, a third aging at pH equal to or below 5.0, separating the silica, washing it with water until an aqueous suspension is obtained, whose pH, measured on a 20% SiO_2 suspension, complies with
25 the following equation:

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

in the equation (III)

e is a constant equal to or above 0.6 and equal to or below 1.0,

d is a constant equal to or above 7.0 and equal to or below 8.5,

30 (D) represents the electrical conductivity of the aqueous silica suspension in $\text{microsiemens.cm}^{-1}$, followed by the washing thereof.



2. Process according to claim 1, characterized in that the silica has a surface chemistry such that its acidity function H_0 is at least 4.0.
3. Process according to either of the claims 1 and 2, characterized
5 in that the silica has a surface chemistry such that the OH^- number expressed in OH^-/nm^2 is equal to or below 12 and preferably between 6 and 10.
4. Process according to one of the claims 1 to 3, characterized
10 in that the silica has a zero charge point (ZCP) of at least 4 and preferably between 4 and 6.
5. Process according to one of the claims 1 to 4, characterized in that the silica has a compatibility with the organic amino compounds of at least 30%.
6. Process according to claim 5, characterized in that the silica
15 has a compatibility with the organic amino compounds of at least 50% and more particularly at least 80%.
7. Process according to either of the claims 5 and 6, characterized in that the silica has a compatibility with the organic amino compounds chosen from within the group formed by fluorine-containing
20 amines, amine oxides, alkyl amines and alkyl betaines.
8. Process according to claim 7, characterized in that the organic amino compound is cetylamine hydrofluoride, bis-(hydroxyethyl)-amino propyl-N-hydroxyethyl octadecylamine dihydrofluoride, an amine oxide of formula $R(CH_3)_2N \rightarrow O$, an alkyl betaine of formula $R-N^+(CH_3)_2-CH_2-$
25 COO^- , an alkyl amido alkyl betaine of formula $R-CO-NH_2-(CH_2)_3-N^+(CH_3)_2-CH_2-COO^-$, in said formula R representing a straight or branched-chain alkyl radical with 10 to 24 carbon atoms.



9. Process according to claim 1, characterized in that the silica has a compatibility with the divalent and higher metal cations chosen from within groups 2a,3a,4a and 8 of the periodic classification of at least 50% and more particularly at least 70%.
- 5 10. Process according to claim 9, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium and palladium.
- 10 11. Process according to either of the claims 9 and 10, 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 and citrate.
- 15 12. Process according to claim 11, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride or tin fluoride.
13. Process according to claim 1, characterized in that the silica also has a compatibility with guanadine-type products and in particular chlorhexidine of at least 30% and more particularly at least 60%.
- 20 14. Process according to one of the claims 1 to 13, characterized in that the silica has a content of anions of type SO_4^{2-} , Cl^- , NO_3^- , PO_3^- , CO_3^{2-} of at the most $5 \cdot 10^{-3}$ moles per 100g of silica.
- 25 15. Process according to claim 14, characterized in that the silica has a content of the above anions of at the most $1 \cdot 10^{-3}$, more particularly at the most $0.2 \cdot 10^{-3}$ moles per 100g of silica.
16. Process according to one of the claims 1 to 13, characterized in that the silica has a sulphate content, expressed as SO_4^{2-} of at the most 0.1%, preferably at the most 0.05% and more particularly at the most 0.01%.



17. Process according to one of the claims 1 to 16, characterized in that the silica has a content of divalent and higher metal cations of at the most 1000 ppm.
18. Process according to claim 17, characterized in that the aluminum content is at the 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.
19. Process according to one of the claims 1 to 18, characterized in that the silica has a carbon content of at the most 50 ppm and more particularly at the most 10 ppm.
20. Process according to one of the claims 1 to 19, characterized in that the silica has a pH of at the most 8 and more particularly between 6.0 and 7.5.
21. Process according to one of the claims 1 to 20, characterized in that the silica has a BET surface between 40 and 600 m^2/g .
22. Process according to one of the claims 1 to 21, characterized in that the silica has a CTAB surface between 40 and 400 m^2/g .
23. Process according to one of the claims 1 to 22 of the abrasive type, characterized in that the silica has a BET surface between 40 and 300 m^2/g .
24. Process according to claim 23, characterized in that the silica has a CTAB surface between 40 and 100 m^2/g .
25. Process according to one of the claims 1 to 22 of the thickening type, characterized in that the silica has a BET surface between 120 and 450 m^2/g and more particularly between 120 and 200 m^2/g .



26. Process according to claim 25, characterized in that the silica has a CTAB surface between 120 and 400 m²/g.
27. Process according to one of the claims 1 to 22 of the bifunctional type, characterized in that the silica has a BET surface between
5 80 and 200 m²/g.
28. Process according to claim 27, characterized in that the silica has a CTAB surface between 80 and 200 m²/g.
29. Process according to one of the claims 1 to 28, characterized in that the silica has an oil absorption between 80 and 500 cm³/100g.
- 10 30. Process according to one of the claims 1 to 29, characterized in that the silica has an average particle size between 1 and 10 μm.
31. Process according to one of the claims 1 to 30, characterized in that the silica has an apparent density between 0.01 and 0.3.
- 15 32. Process according to one of the claims 1 to 31, characterized in that the silica is a precipitation silica.
33. Process according to one of the claims 1 to 32, characterized in that it consists of preparing the silica gel or suspension by simultaneously adding the silicate and acid to a sediment, which
20 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 alkali metal salt.
34. Process according to claim 33, characterized in that the addition of the two reagents takes place simultaneously, so that the pH is
25 kept constant between 4 and 10 and preferably between 8.5 and 9.5.



35. Process according to one of the claims 33 and 34, characterized in that the temperature is between 60 and 95°C.
36. Process according to claim 33, characterized in that the colloidal silica dispersion containing 20 to 150 g/l of silica is prepared by heating an aqueous silicate solution between 60 and 95°C and adding acid to said aqueous solution until a pH is obtained which is between 8.0 and 10.0 and preferably is 9.5.
37. Process according to one of the claims 1 to 32, characterized in that it consists 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.
38. Process according to one of the claims 1 to 35, 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 at a temperature between 60 and 100°C and preferably at 95°C.
39. Process according to one of the claims 1 to 38, characterized in that the silica gel or suspension undergoes a second aging at a pH between 5 and 6 and preferably at 5.5 and at a temperature between 60 and 100°C and preferably at 95°C.
40. Process according to one of the claims 1 to 39, characterized in that a third aging of the silica gel or suspension takes place at a pH between 3 and 5 and preferably at 4 and at a temperature between 60 and 100°C and preferably at 95°C.
41. Process according to one of the claims 1 to 32, characterized in that washing takes place with water or using an acid solution.
42. Process according to one of the claims 1 to 32, characterized in that washing takes place until the conductivity of the washing



filtrate is at the most 200 microsiemens,cm⁻¹.

43. Process according to claim 42, characterized in that washing takes place with water or using an acid solution.

44. Process according to one of the claims 41 and 43, characterized
5 in that the aforementioned acid solution is a solution of an organic acid, particularly a complexing acid.

45. Process according to claim 44, characterized in that the afore-
mentioned organic acid is chosen from among the group of carboxylic
acids, dicarboxylic acids, aminocarboxylic acids and hydrocarboxylic
10 acids.

46. Process according to one of the claims 44 and 45, characterized
in that the organic acid is chosen from the group including acetic,
gluconic, tartaric, citric, maleic and glyceric acids.

47. Dentifrice composition, characterized in that it contains a
15 silica prepared by the process according to one of the claims 1 to
46.

48. Dentifrice composition according to claim 47, characterized
in that it comprises at least one element chosen from within the
group including fluorine, phosphates and guanadines.

49. Dentifrice composition according to claim 47, characterized
20 in that it comprises at least one element chosen from within the
group incorporating organic amino compounds and divalent and higher
cations.

50. Dentifrice composition according to claim 47, characterized
25 in that it comprises at least one organic amino compound chosen from
within the group formed by fluorine-containing amines, amine oxides,
alkyl amines and alkyl betaines.



51. Dentifrice composition according to claim 50, characterized in that the organic amino compound is cetyl amine hydrofluoride, bis-(hydroxyethyl)-aminopropyl-N-hydroxyethyl-octadecyl amine dihydrofluoride, an amine oxide of formula $R(\text{CH}_3)_2\text{-N}\rightarrow\text{O}$ an alkyl betaine of formula $\text{R-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, an alkylamidoalkylbetaine of formula $\text{R-CO-NH}_2\text{-(CH}_2)_3\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, in which R represents a straight or branched-chain alkyl radical with 10 to 24 carbon atoms.
52. Dentifrice composition according to claim 47, characterized in that it comprises at least one divalent and higher metal cation chosen from the group 2a,3a,4a and 8 of the periodic classification.
53. Dentifrice composition according to claim 52, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium or palladium.
54. Dentifrice composition according to one of the claims 52 and 53 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 and citrate.
55. Dentifrice composition according to one of the claims 52 to 54, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride or tin fluoride.
56. Dentifrice composition according to claim 47, characterized in that it comprises chlorhexidine.



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

1. Silica, characterized in that it leads to an aqueous suspension, whose pH varies as a function of its concentration in the area defined by the two inequations:

5 $\text{pH} \leq 7.5 - 0.7 \log (C) \quad (\text{Ia})$

and

$\text{pH} \geq 5.0 - 0.5 \log (C) \quad (\text{Ib})$

and whose pH varies as a function of its electrical conductivity in the area defined by the two inequations:

10 $\text{pH} \leq 8.5 - 0.4 \log (D) \quad (\text{IIa})$

and

$\text{pH} \geq 7.0 - 0.6 \log (D) \quad (\text{IIb})$

in the inequations (Ia) and (Ib),

(C) represents the weight concentration of the aqueous silica suspension as a percent of SiO_2 ,

15 in the inequations (IIa) and (IIb),

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

2. Silica according to claim 1, characterized in that it has a
20 surface chemistry such that its acidity function H_0 is at least 4.

3. Silica according to either of the claims 1 and 2, characterized in that it has a surface chemistry such that the OH^- number expressed in OH^-/nm^2 is equal to or below 12 and preferably between 6 and 10.

4. Silica according to one of the claims 1 to 3, characterized
25 in that it has a zero charge point (ZCP) of at least 4 and preferably between 4 and 6.

5. Silica according to one of the claims 1 to 4, characterized in that it has a compatibility with the organic amino compounds of at least 30%.



6. Silica according to claim 5, characterized in that it has a compatibility with the organic amino compounds of at least 50% and more particularly at least 80%.
7. Silica according to either of the claims 5 and 6, characterized in that it has a compatibility with the organic amino compounds chosen from within the group formed by fluorine-containing amines, amine oxides, alkyl amines and alkyl betaines.
8. Silica according to claim 7, characterized in that the organic amino compound is cetylamine hydrofluoride, bis-(hydroxyethyl)-amino propyl-N-hydroxyethyl octadecylamine dihydrofluoride, an amine oxide of formula $R(\text{CH}_3)_2\text{N}\rightarrow\text{O}$, an alkyl betaine of formula $R\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, an alkyl amido alkyl betaine of formula $R\text{-CO-NH}_2\text{-(CH}_2)_3\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, in said formulas R representing a straight or branched-chain alkyl radical with 10 to 24 carbon atoms.
9. Silica according to claim 1, characterized in that it has a compatibility with the divalent and higher metal cations chosen from within groups 2a, 3a, 4a and 8 of the periodic classification of at least 50% and more particularly at least 70%.
10. Silica according to claim 9, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium and palladium.
11. Silica according to either of the claims 9 and 10, 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 and citrate.
12. Silica according to claim 11, characterized in that the metal cation is in the form zinc citrate, zinc sulphate, strontium chloride



or tin fluoride.

13. Silica according to claim 1, characterized in that it also has a compatibility with guanadine-type products and in particular chlorhexidine of at least 30% and more particularly at least 60%.

5 14. Silica according to one of the claims 1 to 13, characterized in that it has a content of anions of type SO_4^{2-} , Cl^- , NO_3^- , PO_3^- , CO_3^{2-} of at the most $5 \cdot 10^{-3}$ moles per 100 g of silica.

10 15. Silica according to claim 14, characterized in that it has a content of the above anions of at the most $1 \cdot 10^{-3}$, more particularly at the most $0.2 \cdot 10^{-3}$ moles per 100g of silica.

16. Silica according to one of the claims 1 to 13, characterized in that it has a sulphate content, expressed as SO_4^{2-} of at the most 0.1%, preferably at the most 0.05% and more particularly at the most 0.01%.

15 17. Silica according to one of the claims 1 to 16, characterized in that it has a content of divalent and higher metal cations of at the most 1000 ppm.

20 18. Silica according to claim 17, characterized in that the aluminium content is at the 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.

19. Silica according to one of the claims 1 to 18, characterized in that it has a carbon content of at the most 50 ppm and more particularly at the most 10 ppm.

25 20. Silica according to one of the claims 1 to 19, characterized in that it has a pH of at the most 8 and more particularly between 6.0 and 7.5.



21. Silica according to one of the claims 1 to 20, characterized in that it has a BET surface between 40 and 600 m²/g.
22. Silica according to one of the claims 1 to 21, characterized in that it has a CTAB surface between 40 and 400 m²/g.
- 5 23. Silica according to one of the claims 1 to 22 of the abrasive type, characterized in that it has a BET surface between 40 and 300 m²/g.
24. Silica according to claim 23, characterized in that it has a CTAB surface between 40 and 100 m²/g.
- 10 25. Silica according to one of the claims 1 to 22 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.
26. Silica according to claim 25, characterized in that it has a CTAB surface between 120 and 400 m²/g.
- 15 27. Silica according to one of the claims 1 to 22 of the bifunctional type, characterized in that it has a BET surface between 80 and 200 m²/g.
28. Silica according to claim 27, characterized in that it has a CTAB surface between 80 and 200 m²/g.
- 20 29. Silica according to one of the claims 1 to 28, characterized in that it has an oil absorption between 80 and 500 cm³/100g.
30. Silica according to one of the claims 1 to 29, characterized in that it has an average particle size between 1 and 10 μm.
31. Silica according to one of the claims 1 to 30, characterized in that it has an apparent density between 0.01 and 0.3.
- 25



32. Silica according to one of the claims 1 to 31, characterized in that it is a precipitation silica.

33. Process for the preparation of a silica as described in one of the claims 1 to 32, characterized in that it consists of reacting a silicate with an acid thus leading to a suspension or silica gel, 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 6.0, a third aging at pH equal to or below 5.0, separating the silica, washing it with water until an aqueous suspension is obtained, whose pH, measured on a 20% SiO₂ suspension, complies with the following equation:

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

in the equation (III)

e is a constant equal to or above 0.6 and equal to or below 1.0,

d is a constant equal to or above 7.0 and equal to or below 8.5,

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

followed by the washing thereof.

34. Process according to claim 33, characterized in that it consists of preparing the suspension or silica gel by simultaneously adding the silicate and acid to a sediment, which can be water, a colloidal dispersion of silica containing 0 to 150 g/l of silica expressed as SiO₂, a silicate or a mineral or organic salt, preferably alkali metal salt.

35. Process according to claim 34, characterized in that the addition of two reagents takes place in simultaneous manner, so that the pH is kept constant at between 4 and 10 and preferably between 8.5 and 9.5.

36. Process according to one of the claims 34 and 35, characterized in that the temperature is between 60 and 95°C.



37. Process according to claim 34, 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 is obtained which
5 is between 8.0 and 10.0 and preferably is 9.5.

38. Process according to claim 33, characterized in that it consists 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 39. Process according to one of the claims 33 to 36, characterized in that the silica gel or suspension undergoes a first aging at a pH between 6 and 8.5 and preferably at 8 at a temperature between 60 and 100°C and preferably 95°C.

15 40. Process according to one of the claims 33 to 39, characterized in that the silica gel or suspension undergoes a second aging at a pH between 5 and 6 and preferably at 5.5 and at a temperature between 60 and 100°C and preferably at 95°C.

20 41. Process according to one of the claims 33 to 40, characterized in that a third aging of the silica gel or suspension is carried out at a pH between 3 and 5 and preferably at 4 and at a temperature between 60 and 100°C and preferably at 95°C.

42. Process according to claim 33, characterized in that washing takes place with water or using an acid solution.

25 43. Process according to claim 33, characterized in that a washing is carried out until the conductivity of the washing filtrate is at the most 200 microsiemens • cm⁻¹.

44. Process according to claim 43, characterized in that washing takes place with water or using an acid solution.



45. Process according to one of the claims 42 and 44, characterized in that the aforementioned acid solution is a solution of an organic acid, particularly a complexing acid.
- 5 46. Process according to claim 45, characterized in that the aforementioned organic acid is chosen from among carboxylic acids, dicarboxylic acids, amino carboxylic acids and hydrocarboxylic acids.
47. Process according to one of the claims 45 and 46, characterized in that the organic acid is chosen from within the group including acetic, gluconic, tartaric, citric, maleic and glyceric acid.
- 10 48. Dentifrice composition, characterized in that it contains a silica according to one of the claims 1 to 32 or a silica prepared by the process according to one of the claims 33 to 47.
- 15 49. Dentifrice composition according to claim 48, characterized in that it comprises at least one element chosen from within the group including fluorine, phosphates and guanadines.
50. Dentifrice composition according to claim 48, characterized in that it comprises at least one element chosen from the group including organic amino compounds and divalent and higher cations.
- 20 51. Dentifrice composition according to claim 48, characterized in that it comprises at least one organic amino compound chosen from within the group formed by fluorine-containing amines, amine oxides, alkyl amines and alkyl betaines.
- 25 52. Dentifrice composition according to claim 51, characterized in that the organic amino compound is cetyl amine hydrofluoride, bis-(hydroxyethyl)-aminopropyl-N-hydroxyethyl-octadecyl amine dihydrofluoride, an amine oxide of formula $R(\text{CH}_3)_2\text{-N}\rightarrow\text{O}$, an alkyl betaine of formula $R\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, an alkylamidoalkylbetaine of formula $R\text{-CO-NH}_2\text{-(CH}_2)_3\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-COO}^-$, in which R represents a straight



or branched-chain alkyl radical with 10 to 24 carbon atoms.

53. Dentifrice composition according to claim 48, characterized in that it comprises at least one divalent and higher metal cation chosen from within the group 2a,3a,4a and 8 of the periodic classification.

54. Dentifrice composition according to claim 53, characterized in that the metal cation is calcium, strontium, barium, aluminium, indium, germanium, tin, lead, manganese, iron, nickel, zinc, titanium, zirconium and palladium.

10 55. Dentifrice composition according to one of the claims 53 and 54, characterized in that the metal cation is in the form of metal salts, chloride, fluoride, nitrate, phosphate, sulphate or in the form of organic salts acetate and citrate.

15 56. Dentifrice composition according to one of the claims 53 to 55, characterized in that the metal cation is in the form of zinc citrate, zinc sulphate, strontium chloride and tin fluoride.

57. Dentifrice composition according to claim 48, characterized in that it comprises chlorhexidine.