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- (57) Claim

1. Silica compatible with products of guanidine type characterised in that it exhibits a surface chemistry such that its acidity function H_0 is greater than 3.3.

38. Procedure for manufacturing a silica compatible with guanidines according to any one of the previous claims, said procedure consisting of a reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica, characterised in that following separation of the silica from the suspension, the resulting cake is washed with water until the conductivity of the filtrate is 200 microsiemens.cm⁻¹ at the most.

54. Toothpaste composition, characterised in that it includes a silica according to one of the claims 1 to 37 or a silica prepared following the procedure according to one of claims 38 to 53.

IMPROVED SILICA

The present invention is related to a silica usable especially in toothpaste compositions, the procedure for its manufacture as well as toothpaste compositions
5 containing this silica.

It is known that silica is currently used in the preparation of toothpaste compositions. In this, it may moreover play several parts.

It acts first of all as an abrasive agent by
10 helping, through its mechanical action, the elimination of dental plaque.

It may also play the role of a thickening agent to confer defined rheological properties upon the toothpaste, and that of an optical agent to give the
15 toothpaste the desired coloring.

Furthermore, it is known that toothpastes contain various agents especially to prevent caries, to decrease the formation of dental plaque or tartar deposition on the teeth. Among these agents fluorides may be
20 particularly mentioned. Other elements are also used, such as phosphates, pyrophosphates, polyphosphates, polyphosphonates, guanidines, particularly bis-biguanides of which chlorhexidine is one of the most employed elements. Toothpaste formulations may also include zinc,
25 aromas, perfumes, etc.

The presence of these agents within the toothpaste raises the problem of their compatibility with silica. Indeed, in view especially of its absorbant properties,



- 1b -

the latter may have a tendency to react with these agents in such a way that they are no longer available to mediate the therapeutic effects described above.

The aim of the invention is therefore to find
5 silicas which are compatible with the agents mentioned above, especially with guanidines, and hence perfectly suited to toothpaste formulations.

Another aim of the invention pertains to a
10 procedure enabling the manufacture of such compatible silicas.

Now, to this end, the applicant has noticed that the properties of compatibility that are sought depended essentially upon the surface chemistry of the silica used. The applicant has thus establish a certain number
15 of conditions with respect to the surface of silicas so that the latter are compatible.

According to one aspect, the present invention provides silica compatible with the products of guanidine type characterised in that it exhibits a surface
20 chemistry such that its acidity function H_0 is greater than 3.3.

According to a second aspect, the present invention provides a procedure for manufacturing a silica compatible with guanidines according to the first aspect,
25 the procedure consisting of a reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica, characterised in that following separation of the silica



- 1c -

from the suspension, the resulting cake is washed with water until the conductivity of the filtrate is 200 microsiemens.cm⁻¹ at the most.

According to a third aspect, the present invention
5 provides a procedure for manufacturing a silica compatible with guanidines according to the first aspect, the procedure consisting of a reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica,
10 characterised in that the cake resulting from this separation is subjected to a first wash with water, then to a second wash or treatment with an acid solution.

The silica according to the invention is characterised in that it is compatible with products of
15 the guanidine type, especially with chlorhexidine with a compatibility typically of at least 65% and more precisely of at least 90%.

Furthermore, the silica according to the invention, compatible especially with products of the guanidine type
20 and particularly with chlorhexidine, is also characterised by the fact that it shows a surface chemistry such that its acidity function H_0 is at least 3.3.-----



On the other hand, the procedure for manufacturing a silica of the type described above encompasses, according to a first variant, the reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica, and it is characterised in that following separation of the silica, the resulting cake is subjected to a wash with water until the conductivity of the filtrate reaches, at the most, a value of 200 microsiemens.cm⁻¹.

According to a second variant, the procedure for preparing a silica according to the invention encompasses the reaction of a silicate with an acid whereby a suspension or gel of silica is obtained, a separation and drying of the silica, and it is characterised in that the cake resulting from this separation is subjected to a first wash with water, then to a second wash or treatment with an acid solution.

Finally, the invention is related to toothpaste compositions characterised in that they contain a silica of the type described above or prepared following the procedure that has just been mentioned.

Other characteristics and advantages of the invention will be better understood upon reading the specification and concrete, but not limiting, examples that will follow.

As mentioned in the introduction, the main characteristics of the silicas of the invention reside in their surface chemistry. More precisely, one of the aspects to be taken into account in this surface chemistry is acidity. In this respect, one of the characteristics of the silicas of the invention is the strength of the surface acid sites.

Acidity is presently taken in the Lewis sense, i.e. it expresses the tendency of a site to accept a pair of electrons from a base following the equilibrium :



In order to characterise the silicas of the invention, the notion of "acidity function" H_0 , developed by Hammett, is used to measure the tendency of the acid, silica in the present case, to accept a pair of electrons from a base.

The function H_0 is thus defined by the conventional relationship :

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

To determine the acid site strength of a silica of the invention according to the method of Hammett, the indicator method, first described by Walling (J. Am. Chem. Soc., 1950, 72, 1164) is used.

The acid site strength is measured by means of colored indicators, the pK_a of the shift between the acid and basic forms of which is known under the conditions of the experiment.

Thus, the lowest is the pK_a of the indicator undergoing a color change, the strongest is the acidity of the site. Below is a list that summarises as an example, without being limiting, Hammett indicators that may possibly be used to frame the value of H_0 by defining under which form two consecutive indicators are adsorbed.

	Indicator	Color		pKa
		basic form	acid form	
5	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
10	Benzenéazodiphenylamine	yellow	red	+ 1,5
	4-Dimethylaminoazo-1-naphtalene	yellow	red	+ 1,2
	Crystal violet	blue	yellow	+ 0,8
15	p-Nitrobenzeneazo-(p'-nitro)diphenylamine	orange	violet	+ 0,43
	Dicinnamalacetone	yellow	red	- 3,0
	benzalacetophenone	colorless	yellow	- 5,6
	Anthraquinone	colorless	yellow	- 8,2

The coloration of the indicators adsorbed onto a silica gives a measure of the strength of its acid sites. When the color is that of the acid form, then the value of the surface function H_o is equal to or less than the pKa of the indicator.

Weak H_o values correspond to high strength of acid sites.

Thus, a silica that turns red with p-Dimethylaminoazobenzene and yellow with 2-amino-5-azotoluene, for example, will have an acidity function H_o lying between 3,3 and 2.

Experimentally, the titration is carried out with 0,2 g of silica placed in a test tube in the presence of an indicator dissolved at 100 mg/l in cyclohexane.

The silica is dried beforehand for 2 hours and kept humidity free in a dessicator.

The adsorption, if it takes place, occurs within a few minutes of agitation, and the color change can be seen with the naked eye, or possibly by examination of the absorption spectra characteristic of the colored indicators adsorbed, in their acid form as well as in their basic form.

The first characteristic of the silicas of the invention is that they show an acidity function such as that defined above, of at least 3,3.

The strength and nature of the surface acid sites may also be measured by means of infra-red spectrophotometry of the pyridine adsorbed onto the silica.

It is known that the quantity of pyridine adsorbed onto a solid allows the determination especially of the nature of the surface acid sites.

Unlike NH_3 ($pK_b = 5$), pyridine is a relatively strong base ($pK_b = 9$) and hence does

not react with weak sites.

The formation of a pyridinium ion (PyH^+) will allow, in addition, the differentiation between sites of Lewis and Bronsted type.

Information relative to the acidity of the surface of a solid may also be obtained by studying the absorption bands of pyridine in the range 1700 cm^{-1} to 1400 cm^{-1} .

Furthermore, the value of the displacement of the bands characteristic of pyridine and its ionised forms before and after adsorption allows the quantification of the strength of the acid sites.

The pyridinium ion gives a band at 1540 cm^{-1} while pyridine bound by H links or coordination links gives bands in the range $1440\text{--}1465\text{ cm}^{-1}$. Moreover, it appears that the pyridine band found at 1583 cm^{-1} is displaced when pyridine is adsorbed. This band indicates the presence of Lewis acid sites. The acid strength of the latter is proportional to the displacement of the band.

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

Experimentally, measurements are performed on silica suspended in carbon tetrachloride in the presence of pyridine.

The silica is dried beforehand at 190°C for 2 hours and kept free from humidity. After cooling, 1 g of silica is dispersed under magnetic stirring then during an ultrasonic dispersion process (10 mn) into 50 ml of CCl_4 . 0,8 mg of pyridine are added per square meter of silica introduced. The mixture is stirred under reflux for 1 hour.

The same protocol is followed to prepare a blank solution containing the same pyridine concentration but without silica and a blank suspension containing the same silica concentration but without pyridine.

The absorption spectrum of the pyridine is determined by infra-red spectrometric examination of the suspension, the pyridine solution without silica and the silica solution without pyridine.

From the spectrum obtained from the suspension are subtracted the spectrum of the blank solution and the spectrum of the blank suspension.

The silica will be characterised by the position of the remaining bands and by the displacement of the absorption bands of the pyridine and the pyridinium ion with respect to the position of the bands of their non adsorbed forms.

In general, the spectrum obtained should not exhibit a pyridinium peak (band at 1540 cm^{-1}), the absence of this peak thus confirming that the silica has an acidity function of at least 3,3.

The magnitude of the displacement of the pyridine and adsorbed pyridine bands permits the estimation of a lesser or greater acidity of the surface acid sites. In general, this displacement $\Delta\nu$ should be 10 cm^{-1} at the most and more precisely 5 cm^{-1} at the most for the 1440 cm^{-1} band.

According to a preferred method of the invention, this (Δv) is null.

Silica as defined above shows a good compatibility with chlorhexidine, this compatibility, measured by means of the test described further, may be of at least 65 %, especially of at least 80 % and preferably of at least 90 %.

Yet, according to a method particular to the invention, the silicas may be compatible, in addition, with fluorine. In this case, their content in anions of type SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} is, at the most, $5 \cdot 10^{-3}$ moles per 100 g of silica.

This compatibility will be as great as this anion content is low. According to preferred variants, this anion content will be $1 \cdot 10^{-3}$ moles at the most, and more particularly $0,2 \cdot 10^{-3}$ moles per 100 g of silica.

When the silicas are prepared with sulfuric acid to start with, this anion content will be more easily expressed as a content in SO_4 , and by weight. In this case this content is at the most 0,5 %.

According to a preferred variant of the invention, this content is at the most 0,1 % and more precisely 0,02 % at the most.

This compatibility can be further improved, especially with respect to certain elements such as zinc, if conditions with regard to the number of surface acid sites are fulfilled. This number may be measured in term of number of OH groups or silanols per nm^2 .

The determination of this number is made as follows:

The number of surface OH sites is compared to the quantity of water released between 190°C and 900°C .

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

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

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

$$\text{NOH} = \frac{66922,2}{A} \times \frac{P_{190} - P_{900}}{P_{190}}$$

where NOH is the number of OH sites per nm^2 of surface area;

A is the specific surface area of the solid (BET) in m^2/g .

In the present case, the silicas of the invention will advantageously show a number of OH/nm^2 less than or equal to 15, more particularly of 12 at the most, and especially between 3 and 12.

The nature of the OH sites of the silicas of the invention, which is also a characteristic of their surface chemistry, may be estimated by the point of null charge.

This point of null charge (PZC) is defined by the pH of a suspension of silica for which the electrical surface charge of the solid is null, and this is so whatever the ionic strength of the medium. This PZC measures the true pH of the surface, in so far as the latter

is free of any impurities of the ionic type.

The electrical charge is determined by potentiometry. The principal of the method is based on the global balance of adsorbed and desorbed protons on the surface of the silica at a given pH.

From the equations describing the total balance of the operation, it is easy to show that the electrical surface charge C , measured with respect to a reference corresponding to a null surface charge, is given by equation :

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

where:

A represents the solid specific surface area (BET) in m^2/g .

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

F is the Faraday constant,

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

The experimental protocol for the determination of PZC is as follows:

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

Silica is washed beforehand with deionised water of high resistivity (10 Mega.Ohm.cm); dried then degasified.

In practice, one prepares a series of solutions of pH_0 : 8,5, by addition of KOH or HNO_3 , containing an indifferent electrolyte (KNO_3) at a concentration varying between 10^{-5} and 10^{-1} Mole/l.

To these solutions is added a given mass of silica, and the pH of the suspensions obtained is let to stabilise under agitation, at $25^\circ C$ and under nitrogen for 24 hours, let pH'_0 be its value.

Standard solutions are made from the supernatant obtained by centrifuging for 30 minutes at 1000 rotations/mn part of these same suspensions. Let pH'_0 be the pH of these supernatants.

The pH of a known volume of these suspensions and corresponding standard solutions is then adjusted to pH_0 by adding the required quantity of KOH, and the suspensions and standard solutions are left to stabilise for 4 hours.

Let $V_{OH}.N_{OH}$ be the number of base equivalents added to bring a known volume (V) of suspension or standard solution from pH'_0 to pH_0 .

Potentiometric titration of the suspensions is carried out from pH_0 by addition of nitric acid to $pH_f = 2,0$.

One preferably proceeds by acid increment corresponding to a pH variation of 0,2 pH unit. After each addition, the pH is stabilised for 1 mn.



Let $V_h.N_h$ be the number of acid equivalents required to reach pH_f .

From pH_0 , the expression $(V_h.N_h - V_{oh}.N_{oh})$ is plotted as a function of pH increments for all suspensions (at least 3 ionic strengths) and for all the corresponding standard solutions.

5 For each pH value (not 0,2 unit), one then calculates the difference in the consumption of H^+ or OH^- between the suspension and the corresponding standard solution. This operation is repeated for each ionic strength.

This gives the expression $(H - OH)$ that corresponds to the surface proton consumption. The surface charge is calculated from the equation above.

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

The concentration of silica is adjusted according to the specific surface area of the latter.

For example, 2 % suspensions are used for silicas of 50 m^2/g at 3 ionic strengths (0,1; 0,01 and 0,001 mole/l).

15 Titration is carried out with 100 ml of suspension by using potassium hydroxide at 0,1 M.

Practically, the value of this PZC is preferably of at least 3, and more particularly between 4 and 6. The best result of compability with zinc is achieved when this value is 6,5 at the most. In the case of fluorine compatibility, a PZC of 7 at the most is preferred.

20 Still in view of improving compatibility, especially with respect to fluorine, it is advantageous if the aluminium content of the silicas of the invention is 500 ppm at the most.

On the other hand, it may be an advantage that the iron content of the silicas of the invention is 200 ppm at the most.

25 Moreover, it is usually preferred that the calcium content should be 500 ppm at the most, and more particularly 300 ppm at the most.

Silicas of the invention also preferably exhibit a carbon content of 50 ppm at the most and more particularly, 10 ppm at the most.

30 The pH of the silicas according to the invention, measured in accordance with the standard NFT 45-007, is usually 8 at the most. It lies more particularly between 6,0 and 7,5.

The above characteristics permit the production of a silica that is compatible at least with guanidines and in particular with chlorhexidine, and depending upon conditions, in addition, with fluorides, phosphates and their derivatives, and especially zinc.

35 Besides the chemical surface characteristics which have just been described above, and that are prerequisite to compatibilities, the silicas of the invention also show physical characteristics which make them perfectly adapted to their application to toothpaste. These characteristics of structural type will be described below.

Usually, the surface area BET of the silicas of the invention is between 40 and 600 m^2/g , more precisely between 40 and 350 m^2/g . Their surface area CTAB usually varies

between 40 and 400 m²/g, more precisely between 40 and 200 m²/g.

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

Surface area CTAB is the external surface area, determined in accordance with the standard ASTM D3765, except that the adsorption of hexadecyltrimethyl ammonium bromide (CTAB) is carried out at pH 9, and the mean projected surface area of the CTAB molecule is taken to be 35 Å².

The silicas of the invention may of course correspond to the three types usually identified in this field of toothpaste.

Thus, the silicas of the invention may be abrasive. They then show a surface area BET between 40 and 300 m²/g. In this case, the surface area CTAB is between 40 and 100 m²/g.

The silicas of the invention may also be of the thickening type. The value for their surface area BET is then between 120 and 450 m²/g, more precisely between 120 and 200 m²/g. They will then possibly show a surface area CTAB between 120 and 400 m²/g, more precisely between 120 and 200 m²/g.



Finally, according to a third type, the silicas of the invention may be bifunctional. In this case, they have a surface area BET between 80 and 200 m²/g. The surface area CTAB is then between 80 and 200 m²/g.

5 The silicas of the invention may also exhibit an oil uptake that varies between 80 and 500 cm³/100 g, determined in accordance with the standard NFT 30-022 (March 53) and using dibutyl phthalate. The standard NFT 30-022 (March 53) refers to a specific Technical French
10 Standard (Norme Francaise Technique) dated March 1953 according to which oil uptake is determined.

 More precisely, this oil uptake will vary between 100 and 140 cm³/100g in the case of the abrasive silicas, 200 and 400 in the case of the thickening
15 silicas and 100 and 300 in the case of the bifunctional silicas.

 Furthermore, still in view of their application to toothpaste, the silicas are preferably of a particle size varying between 1 and 10 µm.

20 This mean particle size is measured by Coulter-Counter.

 In general, the apparent density will vary between 0.01 and 0.3.

 Preferably the silicas are precipitation silicas.
25 Finally, the silicas of the invention show a refractive index that varies between 1.440 and 1.465.

 The procedure for manufacturing the silicas of the invention will now be described more precisely.



- 8b -

As mentioned previously, this procedure typically consists of the reaction of a silicate with an acid whereby there is formation of a suspension of a gel of silica.

- 5 It should be noticed that it is possible to use any known protocol to obtain this suspension or gel (addition of acid into a tank base of silicate, total or partial simultaneous-----



addition of acid and silicate into a tank base of water or silicate solution, etc...), the choice depending mainly upon the physical characteristics of the silica that one wishes to obtain. It should be noted that it may be an advantage to bring the pH of the suspension or gel obtained to a value of 6 at the most, and more precisely between 4 and 6.

5 One then proceeds to the separation of the silica from the reaction medium according to any known method, vacuum filter or press filter, for example.

A cake of silica is then obtained.

Thereafter, the procedure of the invention may be carried out according to two main variants.

10 The first variant concerns the preparation of silicas compatible essentially with guanidines and especially with chlorhexidine.

In this case, the procedure encompasses a washing of the cake. This wash is performed with water, usually deionised water, until a washing filtrate of a conductivity of 200 microsiemens.cm⁻¹ at the most, is obtained.

15 If one wishes to improve further the compatibilities of the silicas obtained with this procedure, the wash will be continued to higher degree.

In particular, according to a preferred method of the invention, the wash will be continued until a conductivity of 100 microsiemens cm⁻¹ is obtained.

20 Once washed according to the method described above, the silica cake or, if sheared, the suspension of its sheared product, is dried according to any known method. Drying may especially be performed by atomisation. The dried product will be ground, if necessary, to obtain the desired particle size.

The second variant of the procedure is related to the preparation of silicas compatible with, besides guanidines, other elements such as fluorine, zinc and phosphates.

25 In this case, the procedure also includes a wash with water, usually deionised water as for the first variant. This wash, however, may be less stringent. It is possible, for example, to proceed until obtaining a filtrate showing a conductivity of 2000 microsiemens cm⁻¹ at the most.

30 At the outcome of this first wash with water, one proceeds, according to this second variant, to a second wash or treatment of the cake with an acid solution or acidified water. This second wash or treatment aims at producing, at the end of the preparation, a silica having a pH of 8 at the most, and more particularly between 6,0 and 7,5, as well as a PZC of at least 3 and more precisely between 4 and 6,0.

35 The wash or treatment may be carried out by passing the acid solution over the cake, or introducing it into the suspension obtained after shearing of the cake.

This acid wash or treatment is performed under conditions such that in order to obtain a silica having the pH mentioned in the previous paragraph, the pH of the suspension or medium prior to drying has to be between 4 and 8, specially 5 and 8 and more precisely 6 and 7.

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

Yet, according to an operational method particular to the invention, this acid solution may also be a solution of an organic acid, especially a complexing acid. This acid will possibly be chosen within the group that includes carboxylic, dicarboxylic, hydroxycarboxylic and amino-carboxylic acids.

As example for such acids one may mention acetic acid, and as examples for complexing acids, tartaric acid, maleic acid, glyceric acid, gluconic acid, citric acid, acetic acid.

It may be an advantage, particularly in the case when a mineral acid is used, to proceed to a last wash with deionised water.

At the outcome of these washes or treatments in accordance with this second variant, a drying step similar to that described above for the first variant is carried out.

According to another particular variant of the invention, following the silicate acid reaction and just prior to the silica separation, a maturation of the suspension or gel is undertaken. This maturation process is usually carried out at a pH of 6 at the most, for example between 4 and 6.

It is also possible to carry out a maturation during the reaction at a pH between 6 and 8. These maturation processes are preferably carried out under hot conditions, for example at a temperature varying between 80 and 100°C, and for a period of time that may vary from fifteen minutes to two hours.

Finally, it has been noticed that it was possible to improve further yet the compatibility of the products of the invention by using another complementary treatment.

The treatment consists of using an alkaline-earth. This element may be introduced either in the suspension or gel of silica, or preferably onto the cake, particularly after the latter has been sheared, in the form of a salt or hydroxide, for example.

One uses more especially an organic salt that complexes alkaline-earths, usually a barium salt, for example barium acetate.

The invention also pertains to toothpaste compositions that contain silicas of the type described above, or obtained in accordance with the procedure that has just been described.

The quantity of silica according to the invention used in toothpaste compositions may vary within large limits, it usually lies between 5 and 35 % by weight.

The silicas of the invention are particularly well suited to toothpaste compositions containing at least one element chosen within the group that includes fluorides, phosphates, guanidines among which chlorhexidine. Indeed, they may show a compatibility, determined in accordance with the following assays, of at least 90 % for each of these elements.

The silicas of the invention are, in addition, compatible with copolymers acid maleic-vinylethylether and therefore, they may also be incorporated into toothpaste compositions

that include these copolymers. Finally, they may exhibit a compatibility with zinc of at least 50 %, preferably of at least 80 %.

With respect to fluorine compounds, the quantity of silica used preferably corresponds to a fluorine concentration in the formulation between 0,01 and 1 % by weight, and more precisely 0,1 % to 0,5 %. Fluorine compounds are in particular the salts of monofluorophosphoric acid and particularly those of sodium, potassium, lithium, calcium, aluminium and ammonium, the mono and the difluorophosphate as well as various fluorides containing fluorine in the form of bound ion, in particular the alkaline fluorides such as those of sodium, lithium, potassium, the ammonium fluoride, stannous fluoride, manganese fluoride, zirconium fluoride, aluminium fluoride as well as products of addition of these fluorides between them or with other fluorides, such as potassium or sodium or manganese fluorides.

Other fluorides may also be used within the present invention such as, for example, zinc fluoride, germanium fluoride, palladium fluoride, titanium fluoride, alkaline fluorozirconates of, for example, sodium or potassium, stannous fluorozirconate, sodium or potassium fluoroborate or fluorosulfates.

Organic fluoride compounds may also be used, preferably those known as the products of addition of long chain amines or amino-acids with hydrogen fluoride, cetylamine fluoride, bis-(hydroxyethyl)aminopropyl N-hydroxyethyl octadecylamine dihydrofluoride, octadecylamine fluoride and N, N', N' tri-(polyoxyethylene) N-hexadecylpropylenediamine dihydrofluoride.

Zinc, on the other hand, is present especially in the form of citrate or sulfate.

Elements suitable as anti-plaque agents of the type polyphosphates or polyphosphonates, guanidines, bis-guanidines are those described in patents US 3.934.002 or 4.110.083, the details of which are incorporated here.

Toothpaste compositions may in addition contain a binding agent.

The main binding agents used are essentially selected among:

- cellulosic derivatives: methylcellulose, hydroxyethylcellulose, sodium carboxymethylcellulose,

- mucilage: carragenates, alginates, agar-agar and geloses,
- gums: gumarabic and gumtragacanth, xanthane, Karaya gum,
- carboxyvinyl and acrylic polymers,
- polyoxyethylene resins.

Toothpaste compositions may also contain, besides the silicas of the invention, one or several other polishing abrasive agents selected especially from:

- the precipitated calcium carbonate,
- magnesium carbonate
- calcium phosphates, di and tricalcium,
- insoluble sodium metaphosphate,



- calcium pyrophosphate,
- titanium oxide (whitening agent),
- silicates,
- aluminas and silico-aluminates,
- oxides of zinc and tin,
- talcum,
- kaolin.

5

Toothpaste compositions may also include detergents, wetting agents, aromatic agents, sweeteners and coloring and preserving agents.

10

The main detergents used are essentially selected among:

- sodium laurylsulfate,
- sodium laurylethersulfate and sodium laurylsulfoacetate,
- sodium dioctylsulfosuccinate,
- sodium laurylsarcosinate,
- sodium ricinoleate,
- sulfated monoglycerides.

15

The main wetting agents used are especially chosen among polyalcohols such as:

- glycerol,
- sorbitol, usually as a water solution at 70 %,
- propylene glycol.

20

The main aromatic agents (perfume) used are essentially chosen among : essences of anise, Chinese anise, mint, juniper berry, cinnamon, clove and rose.

The main sweeteners are especially chosen among orthosulfobenzoic imides and cyclamates.

25

The main colorings used are essentially selected according to the desired coloring among:

- red and pink coloring: amaranth, azorubin, catechou, new coccin (PONCEAU 4R), cochineal, erythrosin,
- green coloring: chlorophyll and chlorophillin,
- yellow coloring: sun yellow (Orange S) and quinolin.

30

The main preserving agents most often used are: parahydroxybenzoates, formalin and its resulting products, hexetidine, quaternary ammonium, hexachlorophene, bromophene and hexamedine.

35

Finally, toothpaste compositions contain therapeutic agents, the most important ones of which are especially chosen among:

- antiseptics and antibiotics,
- enzymes,
- oligo-elements and fluoride compounds that have been described above.

Concrete but not limiting examples will now be given.

Beforehand, the assays used to measure the compatibility of silica with various elements will be described.

Measurement of compatibility with chlorhexidine

4 g of silica are dispersed into 16 g of a chlorhexidine aqueous solution containing 1 % chlorhexidine digluconate.

The suspension is stirred for 24 hours at 37°C.

The suspension is then centrifuged at 20000 r/mn for 30 mn, and the supernatant obtained is filtered on 0,2 µm Millipore filter paper.

0,5 ml of the solution so filtered is then taken and diluted into 100 ml of water in a graduated flask. This solution constitutes the solution of the assay.

A reference solution is made following the same protocol, but omitting the silica. A 1 % chlorhexidine digluconate aqueous solution is stirred for 24 hours at 37°C, then centrifuged at 20000 r/mn, and the supernatant is filtered on 0,2 µm Millipore filter paper. 0,5 ml of the solution so obtained is diluted into 100 ml of water in a graduated flask.

The absorbance of both solutions is then determined at 254 nm by means of a spectrophotometer (Uvikon 810/820).

The quantity of free chlorhexidine, referred to as % compatibility, is defined by the ratio:

$$\% \text{ Compatibility} = \frac{\text{Absorbance of the assay}}{\text{Absorbance of the reference}} \times 100$$

Measurement of compatibility with fluorides

4 g of silica are dispersed into 16 g of a 0,3 % sodium fluoride (NaF) solution. The suspension is stirred for 24 hours at 37°C. After centrifugation of the suspension at 20000 r/mn for 30 mn, the supernatant is filtered on 0,2 µm Millipore filter paper. The solution so obtained constitutes the solution of the assay.

A reference solution is made, following the same protocol but omitting the silica.

Compatibility with fluorides is determined by the % of free fluoride measured with a fluoride sensitive electrode (Orion). It is defined by the following relation.

$$\% \text{ Compatibility} = \frac{\text{Fluoride concentration in the assay (ppm)}}{\text{Fluoride concentration in the reference (ppm)}} \times 100$$

Measurement of compatibility with zinc

4 g of silica are dispersed into 100 ml of a 0,06 % solution of Zn SO₄, 7H₂O. A suspension, the pH of which is stabilised to 7 for 15 minutes by adding NaOH or H₂SO₄, is obtained. The suspension is then stirred for 24 hours at 37°C, then centrifuged at 20000

r/mn for 30 mn.

The supernatant, filtered on 0,2 μ m Millipore filter paper, constitutes the solution of the assay.

A reference solution is made following the same protocol, but omitting the silica.

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

Compatibility is defined by the following relation.

$$\% \text{ compatibility} = \frac{\text{Zn concentration in the assay (ppm)}}{\text{Zn concentration in the reference (ppm)}} \times 100$$

Measurement of compatibility with sodium and potassium pyrophosphates

4 g of silica are dispersed into 16 g of a suspension at 1,5 % of sodium or potassium pyrophosphate. The suspension is stirred for 24 hours at 37°C, then centrifuged at 20000 r/mn for 30 mn.

The supernatant is filtered on 0,2 μ m Millipore filter paper. 0,2 g of the solution, diluted in 100 ml of water in a graduated flask, constitute the solution of the assay.

A reference solution is made following the same protocol, but omitting the silica.

The free pyrophosphate ion ($P_2O_7^{--}$) concentration is determined in both solutions by ion chromatography (DIONEX 2000i system) equipped with an integrator.

Compatibility is determined from the surface areas under the peaks obtained on the chromatograms, and corresponding to the pyrophosphate retention time, of the assay solution and of the reference solution.

$$\% \text{ compatibility} = 100 \times \frac{\text{assay peak surface area}}{\text{reference peak surface area}}$$

EXAMPLE 1

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

In a reactor equipped with a temperature and pH control system and with a turbo powered stirrer are introduced 6 l of deionised water.

After starting the agitation (300 r/mn), the tank base so constituted, is heated to 85°C.

When this temperature is reached, one proceeds to the addition, simultaneously, of 8,5 l of sodium silicate, the silica concentration of which is 120 g/l, the ratio SiO_2/Na_2O equal to 3,5, and the delivery rate 0,34 l/mn, and of 13,5 l of sulfuric acid concentrated at 80 g/l. The acid delivery rate is adjusted so that the pH of the medium remains at a constant value of 8,0.

After 40 mn of addition, the addition of silicate is stopped and the addition of acid

continued until stabilisation of the pH of the reaction medium to 4.

The mixture is then left to mature for 15 mn at this pH and at 85°C.

The mixture is then filtered and the moist cake washed with deionised water until such a time that the conductivity of the filtrate is less than 100 microsiemens.

5 The cake is then washed with water adjusted to pH 4 by the addition of acetic acid.

A final wash is performed with deionised water.

The product is then dried by atomisation and ground in a forplex type grinder to obtain a particle size of 10 microns.

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

10	BET surface area	100 m ² /g
	CTAB surface area	55 m ² /g
	Oil uptake	120 cm ³ /100 g
	pH	6,5

Results from the chemical analysis of the silica are summarised in the table below.

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

Surface chemistry is characterised by the following parameters:

Ho greater than 3,3

PZC = 4

$\Delta Y = 5 \text{ cm}^{-1}$

25 number of OH/nm² : 9

In the table below are summarised the various compatibilities of the silica with the different components of a toothpaste formulation:

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

35

EXAMPLE 2

Example 1 is resumed up to obtaining a silica cake washed with water of pH 4 by addition of acetic acid.

The cake so obtained is sheared in a shearing machine to obtain a fluid suspension.

0,2 g of barium acetate are added while stirring.

The silica is then dried by atomisation, then ground to obtain a mean particle size of 10 μm .

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

5	BET surface area	100 m^2/g
	CTAB surface area	60 m^2/g
	Oil uptake	110 $\text{cm}^3/100 \text{ g}$
	pH	6,5

Results from the chemical analysis of the silica are summarised in the table below.

10

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

15

Surface chemistry is characterised by the following parameters:

H_0 greater than 3,3

PZC = 4,5

$\Delta\gamma = 2 \text{ cm}^{-1}$

number of OH/ nm^2 : 8

20

Compatibilities

Components	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO_4
% Compatibility	95	98	90	70

25

EXAMPLE 3

This example is related to the preparation of a thickening silica gel.

30

In a reactor equipped with a temperature and pH regulation system as well as with a turbo powered stirrer are introduced 14 l of Na silicate, the silica concentration of which is 86 g/l and the ratio $\text{SiO}_2/\text{Na}_2\text{O}$ 3,5.

After starting the agitation (100 r/mn), 1,45 l of 28 % ammonia is added in 2 mn.

0,8 l of sulfuric acid at a concentration of 200 g/l is then added at a rate of 0,2 l/mn.

35

At this stage, the mixture is left to react for 5 mn at a controlled temperature of 20°C.

5,2 l of sulfuric acid at a concentration of 200 g/l is then added at a rate of 0,2 l/mn.

Following appearance of the gel (visual or via examination of the turbidity), the mixture is left to mature for 10 mn.

The gel is then dispersed by stirring the mixture at 400 r/mn for 30 mn.

The pH of the medium is then lowered to a value of 3,5 by addition of sulfuric acid (200 g/l) at a rate of 0,2 l/mn.

The reaction medium is left to stabilise for 1 hour at a temperature of 60°C.

The preparation of the gel is completed by filtering this mixture and by washing the cake obtained twice with 20 l of deionised water of 60°C temperature and with 20 l of water of pH 3.

The treatment specific to the invention is then carried out with a wash performed with deionised water and at 20°C until a conductivity of 200 microsiemens cm^{-1} is obtained.

The cake obtained is sheared to form a homogeneous suspension of silica of 10 % concentration, adjusted by adding water.

The silica is dried by atomisation in an atomiser of type Anhydro. The silica is then ground by means of a JET Pulveriser grinder to obtain a particle size of 1,5 μm .

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

BET surface area	450 m^2/g
CTAB surface area	350 m^2/g
Oil uptake	300 $\text{cm}^3/100 \text{ g}$
pH	6,8
Apparent density	0,270
Refraction index	1,445

Results from the chemical analysis of the silica are summarised in the table below.

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

The surface chemistry is characterised by the following parameters:

H_0 greater than 3,3

PZC = 3,6

No pyridine absorption bands

Compatibilities

Components	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO_4
% Compatibility	90	95	65	50

EXAMPLE 4

This example is related to a thickening silica.

In a reactor equipped with a temperature and pH regulation system are introduced 6 l of water, 150 g of sodium sulfate are then added while stirring.

5 The mixture is heated to 60°C. 10 l of sodium silicate ($R_m = 3,5$ and $SiO_2 = 220$ g/l) and sulfuric acid of concentration 80 g/l are added simultaneously in 40 mn.

The sulfuric acid delivery rate is adjusted so as to maintain the pH of the reaction medium at a constant value of 7,8.

10 The pH of the medium is stabilised at a value of 4,0 by very rapid addition of sulfuric acid. The mixture is left to mature for 15 mn at 60°C.

The reaction mixture is filtered at 60°C, and the silica cake is washed with deionised water so as to obtain a filtrate conductivity of 900 microsiemens.cm⁻¹. The cake is then washed with water of pH 4, adjusted by addition of acetic acid, and a last wash with deionised water is performed.

15 The silica cake so obtained is sheared, then 2 g of calcium acetate are added to it while stirring.

The silica is dried by atomisation, and ground in a Jet Pulveriser to adjust the silica particle size to 1,5 µm.

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

BET surface area	320 m ² /g
CTAB surface area	120 m ² /g
Oil uptake	250 cm ³ /100 g
pH	6,5

Results from the chemical analysis of the silica are summarised in the table below.

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

30

The surface chemistry is characterised by the following parameters:

Ho greater than 3,3

PZC = 4

number of OH/nm² : 11

No pyridine absorption bands

compatibilities

Components	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
% Compatibility	90	95	90	80

EXAMPLE 5

This example is related to the preparation of an abrasive silica.

In a reactor equipped with a temperature and pH regulation system as well as with a turbo powered stirrer are introduced 6 l of deionised water.

After starting the agitation (300 r/mn), the tank base so constituted is heated at 85°C.

Once the temperature is reached, one proceeds to the simultaneous addition of 8,5 l of sodium silicate, the silica concentration of which is 120 g/l, the ratio SiO₂/Na₂O equal to 3,5 and the delivery rate 0,34 l/mn, and 13,5 l of sulfuric acid of concentration 80 g/l. The acid delivery rate is adjusted so as to maintain the pH of the medium at a constant value of 8,0.

After 40 mn of addition, the addition of silicate is stopped and the mixture is left to mature for 15 mn at pH 8.

The addition of acid is continued until the pH of the reaction medium stabilises at 4.

A 15 mn maturation at this pH and at 85°C is then carried out.

The mixture is then filtered, and the moist cake is washed with deionised water until the conductivity of the filtrate reaches a value of 100 microsiemens.cm⁻¹.

The cake is then subjected to two washes with water adjusted to pH 4 by addition of acetic acid.

A final wash is performed with deionised water.

The product is then dried by atomisation and ground in a forplex type grinder to obtain a particle size of 9,0 microns.

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

BET surface area	60 m ² /g
CTAB surface area	50 m ² /g
Oil uptake	120 cm ³ /100 g
pH	6,0

Results from the chemical analysis of the silica are summarised in the table below.

	ions	SO ₄	Al	Fe	Ca	C
5	ppM	100	250	100	200	10

The surface chemistry is characterised by the following parameters:

Ho greater than 3,3

PZC = 4,5

No pyridine absorption bands

Compatibility

Components	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO4-
% Compatibility	95	98	70	80

EXAMPLE 6

This example is related to the preparation of a silica of thickening type. In a reactor equipped with a turbo powered stirrer are introduced 5,07 l of sodium silicate, the silica concentration of which is 120 g/l and the ratio SiO₂/Na₂O = 3,5, and 3,8 l of deionised water.

After starting the agitation (300 r/mn), the tank base so constituted is heated to 68°C.

Once the temperature is reached, one proceeds to the addition of 2,64 l of sulfuric acid of concentration 80,5 g/l. The acid delivery rate is 0,120 l/mn.

After 22 mn of addition, the addition of acid is stopped and the mixture is left to mature for 10 mn (a sudden increase in the turbidity is observed).

4,2 l of sulfuric acid are then added in 35 mn.

The temperature is then raised to 87°C, and sodium silicate, with a delivery rate of 30 ml/mn, and sulfuric acid, with a delivery rate of 52 ml/mn, are simultaneously added for 30 mn.

The temperature is raised to 95°C, and 0,523 l of sulfuric acid is added in 10 mn.

The mixture is then left to mature for 10 mn.

Finally, the pH of the medium is adjusted to 4 by addition of acid.

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

The cake is then washed with water adjusted to pH 4 by the addition of acetic acid.

A final wash is performed with deionised water.

The product is then dried by atomisation and ground in a Jet Pulveriser grinder to obtain a particle size of 1,2 microns.

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

5	BET surface area	180 m ² /g
	CTAB surface area	170 m ² /g
	Oil uptake	350 cm ³ /100 g
	pH	6,8

Results from the chemical analysis of the silica are summarised in the table below.

10

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

15

The surface chemistry is characterised by the following parameters:

H₀ greater than 3,3

PZC = 3,6

No pyridine absorption bands.

Compatibility

20

Components	Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄ -
% Compatibility	90	95	70	60

25

EXAMPLE 7

In this example is described the preparation of a silica cake which will be used as the starting product of the silicas in examples 8 to 12.

30

In a 30 l reactor equipped with a temperature and pH regulation system as well as with a Mixel type agitation system is introduced 1,4 l of sodium silicate, the ratio SiO₂/Na₂O of which is 3,45 and the SiO₂ concentration 135 g/l, preheated to 75°C. After starting the agitation (300 r/mn), the tank base so constituted is heated to 85°C.

35

Once the temperature is reached, this same sodium silicate, with a delivery rate of 0,28 l/mn, and sulfuric acid of concentration 80 g/l, preheated to 75°C and with a delivery rate of 0,16 l/mn, are simultaneously added.

The mean pH of the medium during the simultaneous addition is 9,8.

After 47 mn of simultaneous addition, the addition of silicate is stopped and that of acid is continued, with the same delivery rate, until a pH of 8 is reached. At this stage, the temperature of the reaction medium is raised to 95°C in 10 mn, whilst continuing the addition

of acid to stabilise, within this time, the pH of the reaction medium to 4,2.

A 15 mn maturation is then carried out at this pH and at 95°C.

The mixture is then filtered, and the moist cake is washed with deionised water until conductivity of the filtrate reaches 2000 microsiemens.cm⁻¹.

5 The cake obtained at this stage will be used as a base to elaborate the silicas of controlled surface chemistry of examples 8 to 12.

EXAMPLE 8

The cake obtained in example 7 is used.

10 This cake is dispersed in deionised water to form a silica suspension of 100 g/l, and the suspension is then filtered. The operation is repeated until conductivity of the filtrate reaches 100 microsiemens.cm⁻¹.

The cake is then redispersed in the form of a 150 g/l suspension in deionised water, and the pH of this suspension is adjusted to 6 by addition of acetic acid.

After filtration, a last wash is performed with deionised water.

15 The product is then dried by atomisation and ground in a forplex type grinder to obtain a particle size of 9,0 µm.

EXAMPLE 9

20 A cake, obtained according to the protocol of example 7, is washed with deionised water until conductivity of the filtrate reaches 500 microsiemens.cm⁻¹.

The cake is then washed with 10 l of water adjusted to pH 4 by addition of gluconic acid.

A last wash is then performed with deionised water.

25 The cake is sheared to obtain a homogeneous suspension, and 8,5 g of barium acetate [Ba(C₂H₃O₂)₂·H₂O] are added while stirring. The mixture is left to mature for 30 mn.

The product is then dried by atomisation and ground in a forplex type grinder to obtain a particle size of 9,0 µm.

EXAMPLE 10

30 A cake, obtained according to the protocol of example 7, is washed with deionised water until the conductivity of the filtrate reaches 500 microsiemens.cm⁻¹.

The cake is then redispersed in the form of a 150 g/l suspension in deionised water, and the pH of this suspension is adjusted to 6 by addition of acetic acid.

35 25 g of barium hydroxide [Ba(OH)₂·8 H₂O] are added while stirring, and the mixture is left to mature for 30 mn.

The suspension is filtered and washed with 5 l of water.

The product is then dried by atomisation, and ground in a forplex type grinder to obtain a particle size of 9 microns.

EXAMPLE 11

A cake, obtained according to the protocol of example 7, is washed with deionised water until the conductivity of the filtrate reaches 100 microsiemens.cm⁻¹.

The cake is then redispersed in the form of a 150 g/l suspension in deionised water, and the pH of this suspension is adjusted to 6,3 by addition of acetic acid.

A last wash is then performed with deionised water.

0,1 g of barium acetate [Ba(C₂H₃O₂)₂, H₂O] is added while stirring, and the mixture is left to mature for 30 mn.

The product is then dried by atomisation, and ground in a forplex type grinder to obtain a particle size of 9,0 microns.

EXAMPLE 12

The cake obtained in example 7 is used. This cake is dispersed in deionised water to form a silica suspension of 100 g/l, and the suspension is then filtered. The operation is repeated until conductivity of the filtrate reaches 200 microsiemens.cm⁻¹.

The product is then dried by atomisation, and ground in a forplex type grinder to obtain a particle size of 9,0 microns.

The characteristics of the silicas from examples 8 to 12 are summarised in the following table:

Example	Surface area BET CTAB (m ² /g)	pH	Number OH/nm ²	Oil uptake	PZC	Ho	Refraction index
8	250 50	6,9	12	102	4,5	>3,3	1,460
9	250 45	6,8	10	110	4	>3,3	1,457
10	250 60	7,2	12	105	3,8	>3,3	1,458
11	260 55	7,0	10	105	6	>3,3	1,457
12	250 55	7,5	12	100	3,6	>3,3	1,446

Chemical analysis

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

Compatibilities

		Fluoride NaF	Pyrophosphate Na/K	Chlorhexidine digluconate	Zinc ZnSO ₄
15	Examples				
	8	90	95	75	70
20	9	95	98	80	85
	10	96	95	70	65
	11	95	96	98	80
	12	95	95	70	60

COMPARATIVE EXAMPLE 13

For comparison, below are summarised compatibility measurements obtained from the commercial silicas that are usually used in toothpaste formulations, as well as their physico-chemical characteristics.

Measurements were performed in accordance with the different tests described elsewhere in the text.

5	Silicas Brand Manufacturer	Surface area		Ho	Number OH/nm ²	SO ₄ % by weight	% compatibility			
		CTAB	BET				CHx	F	Zn	Pyr
		(m ² /g)								
	Zeodent 113	50	100	<3	30	0,65	1	95	0	95
	Hubert									
10	Z113	70	175	<3	17	0,50	1	96	0	95
	Zeofinn									
	Syloblanc 81	240	400	<3	17	1,56	0	90	40	95
	Grace									
	Syloid 244		400	<3	17	0,7	4	90	2	90
15	Grace									
	Sipernat 22s	180	190	<3	16	1,0	0	90	20	90
	Degussa									
	Tixosil 53	50	250	<3	30	0,8	0	60	0	90
	Rhone -Poulenc									

CHx = Chlorhexidine, F = Fluorine, Zn = Zinc, Pyr = Pyrophosphate.

It should be noticed that for all the products mentioned in this table, the PZC is less than 3.

25

EXAMPLE 14

This example is related to the formulation of a translucent toothpaste of the gel type with the silicas of the invention.

The formulation is as follows:

% by mass

Sorbitol (70 % aqueous)	65,00
Glycerin	0,00
CMC 7mFD	0,80
Sodium saccharin	0,20
Sodium fluoride	0,24
Sodium benzoate	0,08
Aroma	2,00
Abrasive silica of example 2	15,00
Thickening silica of example 6	8,00
Chlorhexidine digluconate	1,00
Distilled water	7,68.



The toothpaste exhibits satisfactory rheological properties and is suitably extruded, initially and after storage (2 months).

Visual examination of the tooth paste confirms that the behaviour of the extruded material is satisfactory and that it presents in the form of a translucent gel.

5 This toothpaste shows, in addition, the following properties:

Dilution pH at 10 % : 6,8

Abrasive strength to copper standard LNE (mg) : 5,6

Plastic viscosity (Pa.s) : 0,5

Anti-bacterial activity is observed.

10

EXAMPLE 15

This example is related to the formulation of an opaque toothpaste of the paste type:

The formulation is as follows: % by mass

Glycerin 22,00

15

CMC 7mFD 1,00

Sodium saccharin 0,20

Sodium monofluorophosphate 0,76

Sodium fluoride 0,10

Sodium laurylsulfate (30 % aqueous) 4,67

20

Sodium benzoate 0,10

Aroma 0,90

Titanium dioxide 1,00

Abrasive silica of example 5 31,50

ZnSO₄, 7H₂O 0,48

25

Distilled water 37,29.

Rheological and visual examinations of the toothpaste show that the usual properties of the toothpaste are satisfactory.

Of course, the invention is by no means limited to the protocols that have been described, which have been given solely as examples. In particular, the invention encompasses all methods that constitute techniques equivalent to those described, as well as their combinations if the latter are used within the framework of the patent protection as claimed.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Silica compatible with products of guanidine type characterised in that it exhibits a surface chemistry such that its acidity function H_0 is greater than 3.3.
2. Silica according to claim 1, wherein the product of guanidine type is chlorhexidine.
3. Silica according to claim 1 and 2, wherein the silica shows a compatibility with the products of guanidine type of at least 65%.
4. Silica according to claim 3, wherein the silica shows a compatibility with the products of guanidine type of at least 90%.
5. Silica according to any one of claims 1 to 4, wherein the silica shows, in addition, a compatibility with zinc of at least 50%.
6. Silica according to claim 5, wherein the silica shows a compatibility with zinc of at least 90%.
7. Silica according to any one of claims 1 to 6, wherein the silica has a pyridine infra-red adsorption spectrum that exhibits, with respect to the spectrum of pyridine alone, a displacement $\Delta\gamma$ of 10 cm^{-1} at the most.
8. Silica according to claim 7, wherein it has a pyridine infra-red adsorption spectrum that exhibits, with respect to the spectrum of pyridine alone, a displacement $\Delta\gamma$ of 5 cm^{-1} at the most.
9. Silica according to claim 7 or 8, wherein the aforementioned displacement is null.



10. Silica according to any one of the previous claims, wherein its content in anions of the type SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} , CO_3^{2-} is, at the most, 5.10^{-3} moles per 100 g of silica.

11. Silica according to claim 10, wherein its content in the aforementioned anions is 1.10^{-3} at the most per 100 g of silica.

12. Silica according to claim 10 or 11, wherein its content in the aforementioned anions is, at the most, $0.2.10^{-3}$ moles per 100 g of silica.

13. Silica according to any one of claims 10 to 12, wherein its sulfate content, expressed in SO_4 , is 0.5% at the most.

14. Silica according to claim 13, wherein its sulfate content, is 0.1% at the most.

15. Silica according to claim 13 or 14, wherein its sulfate content, is 0.02% at the most.

16. Silica according to any one of the previous claims, wherein it shows a surface chemistry such that the number of OH, expressed as OH/nm^2 , is at the most 15.

17. Silica according to claim 16, wherein the number of OH is 12 at the most.

18. Silica according to any one of the previous claims, wherein its point of null charge (PZC) is at least 3.

19. Silica according to claim 18, wherein its point of null charge is between 4 and 6.

20. Silica according to any one of the previous claims, wherein its aluminium content is 500 ppm at the most.



21. Silica according to any one of the previous claims, wherein its iron content is 200 ppm at the most.

22. Silica according to any one of the previous claims, wherein its calcium content is 500 ppm at the most.

23. Silica according to claim 22, wherein its calcium content is 300 ppm at the most.

24. Silica according to any one of the previous claims, wherein its carbon content is 50 ppm at the most.

25. Silica according to claim 24, wherein its carbon content is 10 ppm at the most.

26. Silica according to any one of the previous claims, wherein its pH is 8 at the most.

27. Silica according to claim 26, wherein its pH is between 6.0 and 7.5.

28. Silica according to any one of the previous claims, wherein its surface area BET is between 40 and 600 m²/g.

29. Silica according to any one of the previous claims, wherein its surface area CTAB is between 40 and 400 m²/g.

30. Silica according to any one of the previous claims, when of abrasive type, wherein its surface area BET is between 40 and 300 m²/g.

31. Silica according to any one of the claims 1 to 29, when of thickening type, wherein its surface area BET is between 120 and 450 m²/g.

32. Silica according to claim 31, wherein its surface area CTAB is between 120 and 400 m²/g.



33. Silica according to any one of the claims 1 to 29, when bifunctional, wherein its surface area BET is between 80 and 200 m²/g.
34. Silica according to any one of the previous claims, wherein it shows an oil uptake of a magnitude between 80 and 500 cm³/100g.
35. Silica according to any one of the previous claims, wherein its mean particle size varies between 1 and 10 µm.
36. Silica according to any one of the previous claims, wherein its apparent density lies between 0.01 and 0.3.
37. Silica according to any one of the previous claims, wherein it is a silica of precipitation.
38. Procedure for manufacturing a silica compatible with guanidines according to any one of the previous claims, said procedure consisting of a reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica, characterised in that following separation of the silica from the suspension, the resulting cake is washed with water until the conductivity of the filtrate is 200 microsiemens.cm⁻¹ at the most.
39. Procedure according to claim 38, wherein the silica is compatible with chlorhexidine.
40. Procedure according to claim 38 or 39, wherein the aforementioned cake is washed with water until the conductivity of the filtrate is 100 microsiemens.cm⁻¹ at the most.



41. Procedure for manufacturing a silica compatible with guanidines according to any one of the previous claims, said procedure consisting of a reaction of a silicate with an acid whereby a suspension or a gel of silica is obtained, a separation and a drying of the silica, characterised in that the cake resulting from this separation is subjected to a first wash with water, then to a second wash or treatment with an acid solution.

42. Procedure according to claim 41, wherein the silica is compatible with chlorhexidine.

43. Procedure according to claim 41 or 42, wherein the first wash is carried out until the conductivity of the filtrate is $2000 \text{ microsiemens.cm}^{-1}$ at the most.

44. Procedure according to any one of claims 41 to 43, wherein the aforementioned acid solution is a solution of organic acid.

45. Procedure according to claim 44, wherein the organic acid is a complexing acid.

46. Procedure according to claim 44 or 45, wherein the aforementioned organic acid is selected within the group of carboxylic acids, dicarboxylic acids, aminocarboxylic acids, hydroxycarboxylic acids.

47. Procedure according to any one of claims 44 to 46, wherein the organic acid is chosen within the group including acetic, gluconic, tartaric, citric, maleic and glyceric acids.

48. Procedure according to any one of claims 38 to 47, wherein aforementioned suspension or gel of silica is



subjected to a maturation process prior to separation.

49. Procedure according to any one of claims 38 to 48, wherein following the reaction of the silicate with acid, the pH of the suspension or gel obtained is adjusted to a value of 6 at the most.

50. Procedure according to claim 49, wherein the pH is adjusted to between 4 and 6.

51. Procedure according to one of claims 38 to 50, wherein an alkaline-earth salt is added either to the suspension or gel, or to the cake following its possible shearing.

52. Procedure according to claim 51, wherein an organic salt is used.

53. Procedure according to claim 52, wherein the organic salt is a complexing alkaline-earth.

54. Toothpaste composition, characterised in that it includes a silica according to one of the claims 1 to 37 or a silica prepared following the procedure according to one of claims 38 to 53.

55. Toothpaste composition according to claim 54 wherein it includes at least one component chosen within the group including fluorine, phosphates, guanidines, zinc, maleic-vinylethylether acid copolymers.

56. A silica compatible with guanidines, substantially as herein described with reference to any one of the Examples but excluding the comparative examples.

57. A procedure for manufacturing a silica compatible with guanidines, said procedure substantially as herein



described with reference to any one of the Examples but excluding the comparative examples.

58. Toothpaste composition, characterised in that it includes a silica according to claim 56 or a silica prepared following the procedure according to claim 57.

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