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GB 2180833 A **GB 1193306 A** **GB 1119784 A**
US 4134746 A

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(54) Abstract Title

Introducing fluoride ions into glass

(57) Aluminosilicate glass is fluoridated by contacting it with a fluoride solution preferably which can evolve ammonia, such as $NH_4.HF_2$.

Aluminosilicate glass particles are fluoridated by stirring them into a solution of $NH_4.HF_2$., can be used in glass ionomer cement compositions with poly(acrylic acid) without tartaric acid or other chelating agent.

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INTRODUCING FLUORIDE IONS INTO GLASS

This invention relates to a method of introducing fluoride ions into glass. Glass so treated may have a variety of uses.

For example, such glass may be used in making a particulate material by reacting to completion such glass (if it is acid-degradable) with an acid polymer, by an acid-base cement-forming reaction, and grinding the product. "Glass" in this specification can include, according to the context, gelatinising minerals such as bentonite or other mixed metal oxides.

The resulting particulate material can be considered as a glass-depleted cement gel, and can be used in a number of distinct light cured dental materials, such as a liner, fissure sealant, bonding agent/adhesive and anterior restorative. It may also be incorporated in existing cement formulations as a fluoride releasing agent, e.g. incorporation in non-resin based cements and also existing resin based cements.

In conventional glass ionomer cements, aluminosilicate glass is reacted with acid. The outer layer of each glass particle is depleted of metal ions and is degraded to a silica gel. The metal ions have been released by the action of the acid to migrate to the surrounding liquid phase, where they are initially soluble but then accumulate to cause gelation and become insoluble. The resulting cement thus has the form of dispersed particles each having an unreacted aluminosilicate glass core surrounded by a metal-depleted silica gel shell, the shell being about ½ micron thick, the particles being dispersed in a gelated matrix of polyacid chains to which the metal ions which were released from the glass are bound. The shell attained this thickness of about ½ micron during the period while the material surrounding it remained liquid and reactive. The shell ceases to thicken when the surrounding material has set.

If using submicron particles, the unreacted aluminosilicate glass cores would no longer remain. The glass particles prior to reaction advantageously not exceeding 2 microns, preferably not exceeding 1½ microns and ideally not exceeding 1 micron, and preferably being spherical, the acid can release all the metal ions throughout the full depth of each particle before the system gels, leaving simply silica gel cores dispersed in a gelated matrix of polyacid chains to which the metal ions which were released from the glass are bound. The more reactive the acid, the larger the size of glass particle that can be wholly reacted, 1.2 - 1.4 μm being conceivable. Such a hydrogel material is levigated for further use. Note that, all the glass having been leached by acid, no unwanted fresh unreacted glass surface can be exposed by such levigation or particularisation, and the hydrogel material is therefore inert in the presence of water and/or cement-forming acids.

An alternative use for glass treated according to the present invention is (when present in stoichiometric excess) as a component of a glass ionomer cement.

According to the present invention, a method of introducing fluoride ions into a glass (including a gelatinising mineral or other mixed metal oxide), comprises contacting the glass in particles optionally not exceeding 2 microns to a fluoride solution and, in such an option, preferably the solvent is added to the glass and fluoride.

Preferably, the fluoride solution is one from which ammonia can evolve, such as ammonium hydrogen difluoride $NH_4.HF_2$, ammonium fluoride, ammonium heptafluorotantalate (V), ammonium hexafluorogermanate (IV), ammonium hexafluoroniobate, ammonium hexafluorophosphate, ammonium hexafluorosilicate, ammonium hexafluorotitanate (IV), ammonium tetrafluoroborate, ammonium trifluoroacetate or ammonium trifluoromethanesulfonate. Low melting point (for ammonium hydrogen difluoride it is 125C) and high acidity of the aqueous solution of these chemicals enhance their fluoride imparting action. Fluoride will substitute into the glass irrespective of particle size, but glasses not exceeding 1½ microns, optionally not exceeding 1 micron, are preferred, increasing the ease with which fluoride ions are introduced throughout the thickness of the glass. Having said this, the F-containing glass made according to the invention and resulting cement could usefully be used as fluoride reservoir in carboxylate systems, even if less effective than sub-micron glasses. Bentonite, for example, would not be reactive enough to participate in an acid-base reaction, but its reactivity can be improved by introducing fluoride as set forth above, typically by reacting the Al_2O_3 to form AlF_3. Thus, the glass may be an aluminosilicate or otherwise acid-degradable.

This method may be used on glass to be made into a particulate material as set forth above, whereby such material becomes suitable for use in a dental cement formulation as a fluoride release reservoir, and can be considered as a "reactive filler" compatible with most if not all dental material curing routes.

The invention makes possible single-paste resin systems, such as a light-curable paste comprising a cross-linkable monomer, a light-activated initiator and a particulate material as set forth above. Such paste may further comprise a zinc-containing glass, a polyalkenoic acid and optionally water so packed as to keep the pH below 4, and optionally contains Ba, Sr or other divalent glass-forming radio-opaque cation from the reacted glass. Another paste may further comprise an aqueous solution of an acid polymer capable of participating in a glass ionomer setting reaction. These two pastes may be presented in a two-paste cement pack, packed out of contact with each other (and preferably in opaque and/or air-tight packaging as appropriate) until the time of use. In such a pack, preferably one or both pastes further comprise a non-zinc acid-degradable glass and/or a polymeric acid and/or water, such that neither paste reacts until it is unpacked and/or mixed with the other paste.

Optionally, the glass is of particles of radius larger than the depth to which fluoride ions have been introduced when, with polyalkenoic acid and water and preferably without chelating agent, it can form a glass ionomer cement. Preferably in this option, the glass to be fluoridated is added to the fluoride solution.

The invention will now be described by way of example.

Examples 1-3	describe a method of fluoridating a glass according to the invention, and
Example 4	describes the use of the resulting glass to make a particulate material being a glass-depleted cement gel,
Example 5	describes another method according to the invention, and.
Example 6	describes the use of the glass resulting from Example 5 to make a glass ionomer cement.

<u>Example 1</u>

1) 2.877 g of ammonium hydrogen difluoride $NH_4.HF_2$ was added to 18.0 g of water in a PTFE beaker and dissolved.

2) To this was added 8.634 g of sub-micron glass (spherical particles) of composition 120.0 g silica; 102.0 g of alumina and 112.0 g of calcium oxide.

3) The resulting slurry was stirred vigorously until the (immediate and strong) evolution of ammonia ceased, about 2 hours.

4) The slurry was calcined in an oven over 24 hours via a progressive increase in temperature from 98°C to 250°C. The resulting fluoridated glass was an off-white powder.

Example 2

Example 1 was repeated, but using 2.158 g of ammonium hydrogen difluoride in step 1) instead of the 2.877 g. At step 4), the slurry was heat-treated for 24 hours at 220°C.

Example 3

Example 1 was repeated, but using 1.439 g of ammonium hydrogen difluoride in step 1) instead of the 2.877 g.

In Examples 1-3, as submicron glass is used, it (in particular the Ca ions in it) becomes fully fluoridated throughout, even if the order of addition of reagents is changed; thus the $NH_4.HF_2$ may equally successfully be mixed dry with the glass, with the water stirred in afterwards. This latter order is preferred if the glass exceeds 1 micron and is intended for the use specified in Example 4. With that latter order of addition of reagents, the evolution of ammonia is noticeably steadier and slower.

Example 4 : The following further steps were performed on the product of each of Examples 1-3:

5) The resulting glass (5 parts) was mixed with 0.4 parts of dry poly(acrylic acid) and 0.15 parts tartaric acid to make 5.55 parts of a powder component.

6) 8.33 parts of a liquid component were made from 4.90 parts of water, 2.45 parts of dry poly(acrylic acid) and 0.98 parts of tartaric acid.

7) The 5.55 parts of the powder component were mixed with the 8.33 parts of the liquid component to degrade or dissolve the glass and form a cement gel. The glass was totally deactivated by the fluoridation and, though gelling in the acid, did not set.

8) The resulting cement gel was dried in an oven at 100-105°C for 24 hours to cure.

9) The cured cement gel was ground and passed through a 45 micron sieve. The sieved lot may be referred to as fluoridated glass-depleted cement, or ground cement, or in other terminology an ionomer gel. It may be used as a fluoride-releasing component in resin-based dental restorative material.

The amount of ammonium hydrogen difluoride used in Example 1 was selected to replace all the oxygen from the calcium oxide of the glass with fluoride ions. The lesser amounts in Examples 2 and 3 were (obviously) meant to achieve less than total replacement. The level of fluoride in the glass would have a bearing on the fluoride release from the resulting resin-modified cement, the reactivity of the glass in cement formation, and the strength of the resulting glass-ionomer cements. In these Examples, no temperature above 220C is required.

Example 5

Examples 1 to 3 were repeated using the stated order of addition of reagents $NH_4.HF_2$ then water then glass. However in Example 5 the glass was of 5-micron spheres. There was the same immediate and strong evolution of ammonia as a vigorous surface reaction took place. The result was glass particles with an outer layer uniformly about ½μm thick rich in crystalline CaF_2 and an inner unaffected core.

Example 6

The samples of Example 5 were mixed in proportions p:l = 2:1 (i.e. glass in stoichiometric excess) with 50% aqueous solutions of poly(acrylic acid) PAA of MW = 50000, in the absence of tartaric acid or other chelating agent. The mixtures remained workable for about 2½ minutes and then set almost instantly. It is conjectured that this method surprisingly yielded a successful snap-set glass ionomer cement because the dissolution of the outer CaF_2-rich layer by the PAA took about 2 minutes (leading to no reaction) and, when the PAA reached the underlying unaffected glass, which it did nearly simultaneously on all particles thanks to their uniformity of fluoridation, the glass ionomer setting reaction was sudden and rapid.

CLAIMS

1. A method of introducing fluoride ions into a glass, comprising contacting the glass with a fluoride solution.

2. A method according to Claim 1, wherein the fluoride solution is one from which ammonia can evolve.

3. A method according to Claim 2, wherein the fluoride solution is ammonium hydrogen difluoride.

4. A method according to any preceding claim, wherein the glass is an acid-degradable glass.

5. A method according to any preceding claim, wherein the glass is an aluminosilicate glass.

6. A method according to any preceding claim, wherein the glass is of particles not exceeding 2 microns.

7. A method according to any preceding claim, wherein the glass is of particles not exceeding 1½ microns.

8. A method according to any preceding claim, wherein the glass is of particles not exceeding 1 micron.

9. A method according to any preceding claim, wherein the solvent is added to the glass and fluoride.

10. A method according to any of Claims 6 to 8, wherein the glass is added to the fluoride solution.

11. A method according to any preceding claim, wherein fluoride ions have been introduced throughout the thickness of the glass.

12. A glass which has had fluoride ions introduced into it by a method according to any preceding claim.

13. A method according to Claim 4 or 5, wherein the glass is of particles of radius larger than the depth to which fluoride ions have been introduced.

14. A method according to Claim 13, wherein the glass is added to the fluoride solution.

15. A glass which has had fluoride ions introduced into it by a method according to Claim 13 or 14.

16. A glass ionomer cement comprising a glass according to Claim 15, a polyalkenoic acid or precursor thereof, and water.

17. A glass ionomer cement according to Claim 16, without chelating agent.

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): C1M (MLA,MLB,MLE,MLF,MLG)
Int Cl (Ed.6): C03C 21/00
Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2180833 A SHIKA KOGYO see whole document	1,5 and 16 at least
X	GB1193306 BROCKWAY see p3 lines 5-95	1 at least
X	GB1119784 BROCKWAY see partic. p5 lines 27-30	1-3 at least
X	US 4134746 LEVENE see claim 1	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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