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(54) Titre : COMPOSITIONS POUR LA FORMATION DE VERRE HYDROSOLUBLE
(54) Title: COMPOSITIONS OF WATER SOLUBLE GLASS

(57) **Abrégé/Abstract:**

A composition for a water soluble glass is described. The composition is unusual in that it contains no or very small quantities (up to 5 mole %) of alkali metal compounds. The composition typically comprises: P_2O_5 : 30 to 60 mole %; CaO: 20 to 35 mole %; MgO: 15 to 25 mole %; ZnO: 0 to 10 mole %; and optionally may contain: Ag_2O or Ag_2O_3 : 0 to 5 mole %; and/or total alkali metal compounds (e.g. Na_2O and/or K_2O): 0 to 5 mole %. The composition is especially suitable for processing into water soluble glass fibres or wool.



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(21) International Application Number: PCT/GB99/01677 (22) International Filing Date: 27 May 1999 (27.05.99) (30) Priority Data: 9811661.9 1 June 1998 (01.06.98) GB (71) Applicant (for all designated States except US): GILTECH LIMITED [GB/GB]; 9/12 North Harbour Estate, Ayr KA8 8AA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): HEALY, David, Michael [IE/GB]; Midton House, By Alloway, Ayr KA7 4EG (GB). (74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITIONS OF WATER SOLUBLE GLASS (57) Abstract A composition for a water soluble glass is described. The composition is unusual in that it contains no or very small quantities (up to 5 mole %) of alkali metal compounds. The composition typically comprises: P ₂ O ₅ : 30 to 60 mole %; CaO: 20 to 35 mole %; MgO: 15 to 25 mole %; ZnO: 0 to 10 mole %; and optionally may contain: Ag ₂ O or Ag ₂ O ₃ : 0 to 5 mole %; and/or total alkali metal compounds (e.g. Na ₂ O and/or K ₂ O): 0 to 5 mole %. The composition is especially suitable for processing into water soluble glass fibres or wool.		

1 COMPOSITIONS OF WATER SOLUBLE GLASS

2

3 The present invention relates to a composition for a
4 water-soluble glass, especially for a glass adapted for
5 fibre production.

6

7 It is known that certain glasses in which the usual
8 glass former, silicon dioxide, is replaced with
9 phosphorous pentoxide are soluble in water and body
10 fluids. The rate of dissolution is controlled largely
11 by the addition of glass modifiers such as calcium
12 oxide. In simple terms, the greater the concentration
13 of the modifier the slower the rate of dissolution.
14 The rate of dissolution may range from minutes through
15 to several years.

16

17 Soluble phosphate based glasses which have demonstrated
18 good biocompatibility can incorporate inorganic metals
19 such that a sustained release of the metals can be
20 provided at the wound site. Such materials can also
21 find use in mechanical applications where, for example,
22 slow release of an anti-corrosion agent may be
23 beneficial.

24

25 Certain applications require that the glass is in the

1 form of wool or fibres for mechanical applications such
2 as insulation wool and packaging. Thus, for example,
3 Mohr et al in "Fibre Glass" (Van Norstrand, Reinhold
4 Company, New York 1978) and Jaray in "A New Method of
5 Spinning Glass Fibres" (28th Annual SPI RP/C Institute
6 proceedings 1973, Section 3-A) describe the production
7 of wool and fibres, respectively, from molten glass.
8 The glass fibres can be used for insulation,
9 construction or even communication purposes. Glass
10 wool also finds uses in packaging and insulation
11 applications.

12
13 Normally, glass fibres are produced from molten glass
14 using traditional fibre pulling techniques; whereby
15 filaments of high temperature molten glass (850°-
16 1300°C) are formed into strands and stretched over pull
17 rolls before being collected onto a reel.

18
19 Glass wool formation is similar in that the glass is
20 initially melted in a crucible. The crucible has
21 suitable apertures to allow filaments of glass to flow
22 downwards, which are then "blown" into wool using jets
23 of either steam or compressed air. Alternatively,
24 glass wool can be formed using a flame attenuation
25 process, developed by Owens-Corning Fibreglass
26 Corporation circa 1940. In this process molten glass
27 passes through a bushing stage where primary filaments
28 approximately 1 mm wide are formed. The fibres are
29 then aligned into an exact uniformly juxtaposed array,
30 using a fibre guide, into a jet flame issuing from an
31 internal combustion burner. The jet flame causes
32 thinning and lengthening of the fibres before they are
33 collected on a steel mesh belt.

34
35 In both cases, the glass is either supplied in molten
36 form direct from a crucible or from a temperature-

1 gradient furnace.

2

3 Generally, water soluble glasses do not lend themselves
4 to these traditional fibre and wool forming techniques.

5 As an example, US Patent 4,604,097 of Graves et al.

6 discloses a water soluble drawn fibre, composed

7 primarily of calcium oxide and phosphorous pentoxide.

8 The fibre produced has a very low tensile strength,

9 compared to fibres spun from non-soluble glass

10 compositions.

11

12 Further, water soluble glasses can also be chemically

13 aggressive when molten, unlike traditional glasses

14 where silicon dioxide is used as the glass former.

15 Additionally, the fibres produced are prone to thermal

16 shock and can suffer from devitrification or

17 crystallisation.

18

19 To combat problems of devitrification and

20 crystallisation, water soluble glass fibres have been

21 previously produced in exacting conditions. Thus, for

22 example, Zimmer et al. in WO-A-92/07801 discloses

23 drawing fibres from a water soluble glass composed

24 primarily of phosphorus pentoxide, calcium oxide and

25 iron oxide. In order to keep the viscosity of the

26 glass suitable for drawing, the fibres were drawn at

27 1200°C. Also as a result of the chemically aggressive

28 nature of the glass at that temperature the glass was

29 pulled in an oxygen rich atmosphere (as high as 80%

30 oxygen by volume). Obviously the commercial production

31 of glass fibres under these high temperature controlled

32 atmospheric conditions is expensive.

33

34 The problems of working with water soluble glass are

35 compounded by the very nature of the glass. Metal

36 oxides of elements such as lead and tellurium have

previously been used in glass as additives to affect qualities of the glass; crystallisation temperature, viscosity and density, for example. As a result of environmental concerns and particularly when the glasses are to be used in a biological application these additives must be avoided and replaced by more acceptable alternatives.

Our copending Application, No. WO-A-98/54104, describes a method of producing water soluble glass fibres. We have now found a particular type of composition which is especially suited to this method. In the prior art compositions described therein a mixture of Group I and Group II compounds are present, and a typical phosphorus pentoxide based glass composition comprises approximately 30 mole % Na_2O and approximately 15 mole % CaO .

The composition of the present invention comprises a glass former (which is typically phosphorus pentoxide) and an alkali earth metal compound. Preferably no alkali metal (Group I) elements or compounds containing such elements are present, although very low quantities (eg 1-2 mole % up to as much as 5 mole %) may be useful to adjust the rate of dissolution of the glass. This low level or absence of alkali metal compounds forms a distinction over the water soluble glass compositions currently available. The reference to alkali metal compounds herein refers to compounds of Group Ia (Li, Na, K, Rb, Cs and Fr) and the reference to alkali earth metal compounds herein refers to compounds of Group IIa (Be, Mg, Ca, Sr, Ba, Ra).

The present invention thus provides a water soluble glass fiber comprising P_2O_5 : 45 to 55 mole %; CaO : 25 to 30 mole %; MgO : 18 to 22 mole %; ZnO : 0 to 10 mole

%; and up to a total of 5 mole % of alkali metal compounds or other additive compounds.

Desirably the glass former will preferably be mainly P_2O_5 . Solution rate control and stability can be affected by the addition of other glass formers such as boron, silica, alumina, sulphur, germanium, arsenic etc. Generally the mole percentage of phosphorous pentoxide in the glass composition is less than 85 mole %, preferably less than 60 mole % and especially between 30-60 mole %.

Alkali earth metals and lanthanide oxides or carbonates are preferably used as glass modifiers. Generally, the mole percentage of alkali earth metals and lanthanide oxides or carbonates is less than 60 mole %, preferably between 40-60 mole %.

Boron containing compounds (eg B_2O_3) are preferably used as glass additives. Generally, the mole percentage of boron containing compounds is 15 mole % or less, preferably 10 mole % or less, especially 5 mole % or less.

As indicated above, other compounds may also be added to the glass to modify its properties, for example SiO_2 , Al_2O_3 , SO_3 , sulphate ions (SO_4^{2-}) or transition metal compounds (eg. first row transition metal compounds), but these will be present only in very low quantities, for example up to a total amount of 5 mole % or less of the glass composition.

Typically the soluble glasses used in this invention comprise phosphorous pentoxide (P_2O_5) as the principal glass-former, together with any one or more

1 glass-modifying non-toxic materials such as magnesium
2 oxide (MgO), zinc oxide (ZnO) and calcium oxide (CaO).
3 The rate at which the glass dissolves in fluids is
4 determined by the glass composition, generally by the
5 ratio of glass-modifier to glass-former and by the
6 relative proportions of the glass-modifiers in the
7 glass. By suitable adjustment of the glass
8 composition, the dissolution rates in water at 38°C
9 ranging from substantially zero to 25mg/cm²/hour or more
10 can be designed. However, the most desirable
11 dissolution rate R of the glass is between 0.01 and
12 2.0mg/cm²/hour.

13
14 The water-soluble glass is thus preferably a phosphate
15 glass, and preferably comprises a source of silver ions
16 which may advantageously be introduced during
17 manufacture as silver orthophosphate (Ag₃PO₄). The
18 glass preferably enables controlled release of silver
19 and other constituents in the glass and the content of
20 these additives can vary in accordance with conditions
21 of use and desired rates of release, the content of
22 silver generally being up to 5 mole %. While we are
23 following convention in describing the composition of
24 the glass in terms of the mole % of oxides, of halides
25 and of sulphate ions, this is not intended to imply
26 that such chemical species are present in the glass nor
27 that they are used for the batch for the preparation of
28 the glass.

29
30 The optimum rate of release of silver ions into an
31 aqueous environment may be selected by circumstances
32 and particularly by the specific function of the
33 released silver. The invention provides a means of
34 delivering silver ions to an aqueous medium at a rate
35 which will maintain a concentration of silver ions in
36 said aqueous medium of not less than 0.01 parts per

1 million and not greater than 10 parts per million. In
2 some cases, the required rate of release may be such
3 that all of the silver added to the system is released
4 in a short period of hours or days and in other
5 applications it may be that the total silver be
6 released slowly at a substantially uniform rate over a
7 period extending to months or even years. In
8 particular cases there may be additional requirements,
9 for example it may be desirable that no residue remains
10 after the source of the silver ions is exhausted or, in
11 other cases, where the silver is made available it will
12 be desirable that any materials, other than the silver
13 itself, which are simultaneously released should be
14 physiologically harmless. In yet other cases, it may
15 be necessary to ensure that the pH of the resulting
16 solution does not fall outside defined limits.

17

18 An exemplary composition contains:

19 P_2O_5 : 30 to 60 mole %;

20 CaO : 20 to 35 mole %;

21 MgO : 15 to 25 mole %;

22 ZnO : 0 to 10 mole %;

23 and optionally may contain:

24 Ag_2O or Ag_2O_3 : 0 to 5 mole %; and/or

25 total alkali metal compounds (e.g. Na_2O and/or

26 K_2O): 0 to 5 mole %.

27

28 A preferred composition contains:

29 P_2O_5 : 45 to 55 mole %;

30 CaO : 25 to 30 mole %;

31 MgO : 18 to 22 mole %;

32 ZnO : 0 to 10 mole %; and

33 up to a total of 5 mole % of other additive

34 compounds such as Ag_2O , Na_2O , K_2O etc.

35

36

1 These glasses are characterised by having a melting
2 point of approximately 550°C and being of high tensile
3 strength.

4

5 According to a further aspect of the present invention
6 the composition described above processed into glass
7 fibres and/or wool.

8

9 In the method described in our copending Application
10 WO-A-98/54104 a composition for water-soluble glass is
11 heated above its melting point and then cooled to a
12 working temperature at which fibre formation occurs.

13

14 Generally, the glass is initially heated to a melting
15 temperature of 800°-1200°C, preferably 1000°-1200°C.
16 The temperature is then slowly lowered to the working
17 temperature at which fibre formation occurs.

18

19 Generally, the working temperature of the glass will be
20 at least 200°C lower than the temperature at which the
21 glass is initially heated. Suitable working
22 temperatures may fall within the following ranges 500°-
23 1000°C, more preferably 600°-850°C, especially 650°-
24 750°C. The working temperature selected will depend
25 upon the glass composition, but an approximate
26 indication of a suitable working temperature can be
27 established as hereinafter described. Depending upon
28 the glass composition used, the working temperature may
29 be a range of suitable temperatures. The range of
30 working temperatures may be narrow, for example of only
31 10°C, so that fibre formation may occur only between
32 the temperature of N°C to (N+10)°C. Other glass
33 compositions may have a wider temperature range for the
34 working temperature in which glass formation is
35 possible.

36

1 Alternatively, the working temperature of the glass may
2 be defined as 150-300°C above the Tg of the glass.

3
4 In order to obtain an approximate indication of the
5 working temperature for any particular glass
6 composition, the glass composition should be slowly
7 heated to its melting point. As soon as the glass is
8 molten, frequent attempts to pull the composition
9 upwardly to form a fibre should be made, with the
10 temperature of the composition being very gradually
11 increased between attempts. The temperature range of
12 the composition during which fibre formation is
13 possible should be noted and used as a preliminary
14 working temperature in the process of the invention.

15
16 It will be clear to those skilled in the art that the
17 pulling speed at which the fibre is drawn off can
18 affect the choice of working temperature and the
19 diameter of the fibre required. Where a fibre of
20 relatively large diameter is required, the fibre tends
21 to be pulled more slowly and the working temperature
22 may need to be decreased slightly. Where a fibre of
23 relatively small diameter is required (eg a glass
24 wool), the fibres may be drawn at the much higher
25 pulling speed and the working temperature may need to
26 be increased (thus lowering the viscosity of the
27 composition to accommodate the increased pulling
28 speed). Selection of the exact working temperature in
29 respect of any particular fibre size and composition
30 will be a simple matter of routine evaluation of
31 optimal process conditions.

32
33 With reference to the "working temperature" of the
34 glass, the skilled person will appreciate that the
35 furnace temperature may differ considerably from the
36 temperature of the glass itself and indeed there may be

1 a significant temperature gradient in the glass.
2 Ideally the "working temperature" will be the
3 temperature of the glass as fibre formation (ie.
4 pulling) takes place. In many compositions however, it
5 may not be practical to measure the temperature at the
6 surface of the glass where pulling occurs by insertion
7 of a temperature probe as the introduction of the probe
8 may precipitate crystallisation of the glass. One
9 alternative is to place a temperature probe into the
10 bushing and to monitor the bushing temperature which
11 will be a good indicator of the glass temperature at
12 the moment of fibre formation. Alternatively an Infra
13 Red pyrometer may be focused onto the appropriate area
14 of the glass and used to monitor the temperature.
15

16 The glass to be formed into fibres will generally be
17 heated until molten, optionally clarified, and then
18 cooled slowly and controllably until the appropriate
19 working temperature is reached and fibre formation can
20 commence. The initial heating of the glass above its
21 melting point and the subsequent fibre formation may be
22 carried out in a single vessel or, alternatively, the
23 molten glass may be transferred to a vessel designed
24 specifically for fibre formation. One way of holding
25 the molten glass in a vessel having a bushing within
26 its lower surface until the temperature drops to the
27 required working temperature is to coat or fill the
28 holes of the bushing with a material that gradually
29 melts over the period of time taken for the glass to
30 reach the temperature required.
31

32 The most important aspect of the present invention is
33 the manner in which the working temperature is reached.
34 We have found that the molten glass, which may
35 preferably be heated significantly above its melting
36 point, should be allowed to cool in a highly controlled

1 manner, the temperature being only gradually reduced
2 until the working temperature is reached. A stirrer
3 may be present to ensure that the temperature of the
4 whole of the molten glass is kept as uniform as
5 possible.

6
7 The glass is cooled to a temperature at which the glass
8 will not crystallise for at least the period of time
9 needed to convert the melt to fibre. This temperature
10 is termed a "holding temperature". The rate of cooling
11 from this holding temperature is determined by the rate
12 at which the melt is consumed at the bushing and the
13 difference in temperature between the bushing
14 temperature (the working temperature) and the melt
15 holding temperature.

16
17 Due to low viscosity and narrow temperature band for
18 many of these compositions, control of the balance
19 between melt temperature, bushing temperature and glass
20 throughput rate is critical.

21
22 The glass composition produces good stable strong
23 consistent fibres.

24
25 The present invention will now be described by
26 reference to the following, non-limiting, examples:

27

WO 99/62835

12

PCT/GB99/01677

1 **Example 1**

2 CaO 30 mole %

3 MgO 20 mole %

4 P₂O₅ 50 mole %

5

6 Furnace at 1050°C.

7 Bushing 5.5mm holes.

8 Bushing temperature 700°C - 720°C.

9 Speed up to 80kmph.

10 Very strong fibre.

11

12 **Example 2**13 (K₂O 5 mole % trace to alter dissolution rate)

14 CaO 25 mole %

15 MgO 20 mole %

16 P₂O₅ 50 mole %

17

18 Furnace 1000°C.

19 Bushing 5.5mm.

20 Bushing temperature 560°C - 620°C.

21 Speed up to 70kmph.

22 Very strong fibre.

23 Anti-microbial.

24

25 **Example 3**

26 CaO 28.5 mole %

27 MgO 18.5 mole %

28 Ag₂O 3 mole %29 P₂O₅ 50 mole %

30

31 Furnace temperature 1050°C - 1150°C.

32 Bushing 4 x 5.5mm.

33 Bushing temperature 700°C.

34 Speed 50kmph.

35 Very good, strong fibre.

36 Anti-microbial.

1 **Example 4**

2 CaO 30 mole %

3 MgO 20 mole %

4 P₂O₅ 50 mole %

5

6 As Example 3 (without silver).

7

8 **Example 5**

9 CaO 25 mole %

10 MgO 20 mole %

11 ZnO 10 mole %

12 P₂O₅ 45 mole %

13

14 The fibres show excellent tensile strength, flexibility
15 and shock resistance. These fibres are suitable for
16 applications requiring slower release and greater
17 tensile strength plus biodegradability. The fibres are
18 suitable for orthopaedic implants and tissue
19 engineering applications.

WE CLAIM:

1. A water soluble glass fiber comprising:

P₂O₅: 45 to 55 mole %;
CaO: 25 to 30 mole %;
MgO: 18 to 22 mole %;
ZnO: 0 to 10 mole %; and
up to a total of 5 mole % of alkali metal compounds
or other additive compounds.
2. A water soluble glass fiber as claimed in claim 1
which comprises a maximum of 2 mole % of alkali metal
compounds.
3. A water soluble glass fiber as claimed in claim 1
which comprises 4 mole % or less of Na₂O and/or K₂O as the
only alkali metal compound(s).
4. A water soluble glass fiber as claimed in claim 3
which comprises 2 mole % or less of Na₂O and/or K₂O as the
only alkali metal compound(s).
5. A water soluble glass fiber as claimed in claim 1
which comprises no alkali metal compounds.
6. A water soluble glass fiber as claimed in claim 1
which further comprises up to 5 mole % of a silver ion
releasing metal compounds.

7. A water soluble glass fiber as claimed in claim 1 which has a melting point of approximately 550° C.

8. A water soluble glass fiber as claimed in claim 1 in the form of glass wool

9. A water soluble glass fiber as claimed in claim 1 which further comprises up to 5 mole % of Ag_2O or Ag_2O_3 .