PROCESS FOR MELTING AND REFINING SILICA-BASED GLASS


(12) Title: PROCESS FOR MELTING AND REFINING SILICA-BASED GLASS

Abstract: A process for making silica-based glass includes; (a) forming a glass precursor melt that includes glass network formers and glass network modifiers, the glass precursor melt being at a temperature in the range of 900°C to 1700°C and having a viscosity of not more than 30 Pa·s, and (b) refining the glass precursor melt. Either or both steps (a) (b) can include stirring and/or be carried out under reduced pressure to enhance refining. The refined glass precursor melt preferably is mixed with additional materials including silica (SiO2) to form a silica-based glass melt.

Figure 1: Diagram of the process for melting and refining silica-based glass melt.

- **Raw Materials:** Soda Ash (Na2CO3), Silica Sand (SiO2), Limestone (CaCO3).
- **Stage 1:** Melting, Reacting & Refining
  - xCaO3 + yNa2CO3 + ySiO2 → xNa20.ySiO2.xCaO + yCO2
  - Vacuum optional to increase reaction kinetics. Low viscosity melt under vacuum to rapidly remove bubbles.
- **Stage 2:** Mixing, Dissolution, Homogenization
  - Reduced pressure to eliminate residual bubbles.
  - Mixing, stirring or agitation to enhance dissolution rates.

[Continued on next page]
before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
PROCESS FOR MELTING AND REFINING SILICA-BASED GLASS

The present disclosure relates to a process for melting and refining silica-based glass, and particularly to such a process that employs sodium-calcium-silicate glass as an intermediate or precursor product.

Background and Summary of the Disclosure

Silica-based glass, such as soda-lime glass, is prevalent in the manufacture of glass containers and other products. Formation of the glass melt typically involves mixing the various glass-forming components at elevated temperature. The glass typically has a residence time in a furnace on the order of twenty-four hours to fully dissolve the raw materials of the batch composition and to refine the glass by driving off gases. The gases must be driven off ultimately to produce a solidified glass product without entrained gas bubbles. (The process of removing bubbles in molten glass is called "refining," sometimes referred to as "fining.") In addition to being undesirably slow, this in-furnace process involves a large amount of space and high energy input.

A general object of the present disclosure is to provide a process for making silica-based glass, which is more rapid and requires less energy input than conventional processes.

The present disclosure embodies a number of aspects that can be implemented separately from or in combination with each other.
A process for making a silica-based glass, in accordance with one aspect of the present disclosure, includes: (a) reacting at least one glass network former and at least one glass network modifier to form a glass precursor melt, the glass precursor melt being at a temperature in the range of 900°C to 1700°C and having a viscosity of not more than 30 Pa·s, and (b) refining the glass precursor melt. Target viscosity preferably is less than 15 Pa·s, more preferably less than 8 Pa·s and most preferably not more than 3 Pa·s. Target viscosity can be in the range of 1 to 3Pa·s, with a value of 2Pa·s being a preferred target. Glass viscosity can be measured at a temperature of 1300°C by an Orton RSV-1600 viscometer using an Orton part number 13-1500 spindle. Other viscosity measuring techniques can be employed.

The term "glass network former" is employed in its usual sense in the art as referring to oxides and non-oxides capable of forming and being incorporated into a random glass network or lattice. Silica (SiO2), alumina (Al2O3) and boric oxide (B2O3) are three examples of glass network formers. The term "glass network modifier" likewise is employed in its usual sense to refer to oxides within the glass that do not participate in forming the glass network structure and force the glass network to form around the modifier. Examples include the oxides of the alkali metals (sodium, lithium and potassium) and oxides of the alkaline earth metals (calcium, magnesium and barium).

Either or both steps (a) and (b) can be carried out under reduced pressure to enhance refining. The refined glass precursor melt preferably is mixed with additional glass network former materials, including silica (SiO2) and/or non-gas releasing network modifiers, to reach the desired glass melt composition. Cullet and/or minor ingredients such as colorants can be added at this stage. Step (b) can include stirring.
The term "gas releasing" is used to describe chemical forms of an element that evolve gases upon decomposition, including the carbonate, bicarbonate, sulfate, hydrate, hydroxide, nitrate, chloride or acid form(s) of a given element. The term "non-gas releasing" is used to describe chemical forms of an element that do not evolve gases upon decomposition, including the oxide, sulfide and elemental forms of a given element.

A process for making a silica-based glass in accordance with another aspect of the present disclosure includes: (a) forming a low-viscosity sodium-calcium-silicate solution in liquid phase while releasing gaseous reaction products, and (b) mixing the sodium-calcium-silicate solution with additional material including silica to form a soda-lime glass melt. Step (a) is carried out by (a1) melting, reacting and refining calcium carbonate, soda ash and silica, or (a2) by melting, reacting and refining salt and silica in the presence of water followed by addition of calcium carbonate. The sodium-calcium-silicate liquid solution intermediate phase product of step (a) preferably has a viscosity of not more than 30 Pa-s to promote release of gaseous reaction products such as carbon dioxide in step (a1) or hydrogen chloride in step (a2).

Step (a) and/or step (b) can be carried out under reduced pressure further to promote release of gaseous reaction products. Step (b) can include stirring.

A process for making a glass precursor melt in accordance with a third aspect of the disclosure includes mixing at least one glass network former with at least one glass network modifier, and refining the glass precursor melt by performing at least part of the mixing step at elevated temperature and under reduced pressure to promote release of gases. Preferably, all of the gas releasing glass network modifiers and gas releasing glass network formers that are required to achieve the desired glass product melt composition are added to the precursor melt
for refining in step (a). Additional non-gas releasing glass network formers and non-gas releasing glass network modifiers are mixed with the glass precursor melt to form the desired glass product melt composition. Cullet and/or minor ingredients such as colorants can be added.

**Brief Description of the Drawings**

The disclosure, together with additional objects, features, advantages and aspects thereof, will best be understood from the following description, the appended claims and the accompanying drawings, in which:

- FIG. 1 is a block diagram of a process for reacting, melting and refining silica-based glass in accordance with one exemplary embodiment of the disclosure; and

- FIG. 2 is a block diagram of a process for reacting, melting and refining silica-based glass in accordance with a second exemplary embodiment of the disclosure.

**Detailed Description of Preferred Embodiments**

The ASTM defines glass as "an inorganic product of fusion which has been cooled to a rigid condition without crystalizing." Traditional glasses are composed of glass forming oxides (oxides that can form glasses by themselves), intermediate oxides (oxides that can form glasses if mixed with a small amount of other selected oxides), and glass network modifiers (oxides that are difficult to vitrify but are used to modify the structure and properties of a glass composed of glass forming and/or intermediate oxides).

One particular classification (Varshneya) places elements and their oxides into the following categories:

- Glass formers: B, Si, Ge, Al, P, V, As, Sb, Zr
- Intermediates: Ti, Zn, Al, Th, Be, Zr, Cd
Among the list given above, the elements most often used as modifiers in commercial glass manufacture are alkalis. The container glass industry traditionally has used silica (SiO₂) as the glass forming oxide with varying amounts of sodium and calcium oxides as glass modifiers, and small amounts of intermediates such as aluminum oxides. An appropriately chosen glass composition typically is prepared by the following three steps—(a) batch melting, (b) homogenization (primarily sand dissolution), and (c) refining or bubble removal. The process of refining or removing bubbles, either by dissolving them in the melt or by allowing them to rise to the top of the melt, often is the most time consuming step in the melting operation.

Preferred glass network formers are compounds of Si, Al and B. Glass network formers preferably are in an oxide form. Preferred glass network modifiers are compounds of sodium, lithium and/or potassium, and/or compounds of calcium, magnesium and/or barium. Glass network modifiers and intermediates can be selected from the group consisting of oxide, carbonate, bicarbonate, sulfate, sulfide, hydride, hydroxide, nitrate and/or chloride forms of the recited elements.

In the past, various methods have been explored in an effort to reduce glass refining time; these methods typically required a great deal of energy and were very time consuming. Most methods involve heating the glass melt to temperatures well above the raw material batch melting point, introducing refining agents that either help dissolve the bubbles or increase the size of the bubbles which causes the bubbles to rise to the top of melt quicker, reducing the height (thickness) of the glass melt (during the refining step), and/or increasing the...
residence time of the glass melt to achieve more thorough refining. Other refining methods have employed vacuum, ultrasonic waves and centrifugal acceleration to assist in bubble removal with limited commercial success.

The present disclosure recognizes that most bubbles in a glass melt are CO₂ or SO₂ that is released during the dissolution of the raw batch materials and that the refining, or removal of bubbles from a glass melt, is more easily accomplished if the melt has a low viscosity. Network modifiers reduce the viscosity of a glass melt so that the bubbles can rise to the top of the melt more quickly. Therefore, in this disclosure, most, if not all, of the raw materials that evolve gasses preferably are added to the low viscosity glass precursor melt to achieve more thorough and faster refining, prior to adding the remaining glass network forming materials to produce the final glass melt composition. The glass precursor melt preferably is a melt formulated to have a viscosity less than 30 Pa·s. Traditional raw materials such as soda ash (Na₂CO₃) and calcium carbonate (CaCO₃) release primarily carbon dioxide, and should be for the most part added prior to refining of the precursor melt. In addition, it should be noted that a wide variety of gas releasing raw materials may be advantageously added into the precursor melt. These compounds may include sulfates, sulfides, hydrates, hydroxides, chlorides, nitrates and nitride compounds of desired metals.

FIG. 1 illustrates a process for making silica-based glass in accordance with one exemplary embodiment of the present disclosure. A first stage of the process involves melting, reacting and refining input materials and production of a low-viscosity sodium-calcium-silicate (Na₂O.SiO₂.CaO) solution in liquid phase by melting, reacting and refining silica (SiO₂) and substantially all of the desired gas releasing glass network modifiers. This reaction produces
a silicate solution in liquid phase and having a relatively low viscosity to promote release of gas reaction products. The term "low-viscosity" in accordance with the present disclosure means having a viscosity of not more than 30 Pa·s, preferably less than 15 Pa·s, more preferably less than 8 Pa·s, yet more preferably not more than 3 Pa·s. Target viscosity can be in the range of 1 to 3 Pa·s, with a value of 2 Pa·s being a preferred target. Glass viscosity can be measured at a temperature of 1300°C by an Orton RSV-1600 viscometer using an Orton part number 13-1500 spindle. Other viscosity measuring techniques can be employed. This first stage 20 preferably is carried out under reduced pressure (vacuum) further to promote release of gaseous reaction products. The silicate solution precursor melt or intermediate product of this first stage typically has a silica molar content on the order of 40-60%.

The silicate solution precursor melt or intermediate product of the first stage 20 is fed to the second stage 30, which involves mixing, dissolution and homogenization of the glass precursor melt with additional raw materials 40, including the shortfall of glass network formers silica (SiO2) or alumina (Al2O3) or boric oxide (B2O3) and/or additional non-gas releasing network modifier materials needed to reach the desired composition of the final glass melt. Cullet and/or minor ingredients such as colorants 40 can be added in this second stage 30. Additional silica is added at the second stage 30 to reach the desired final glass composition with a silica content typically on the order of 65-80% by weight. The second stage 30 can include stirring and/or other mixing to promote dissolution and homogenization of the final silica-based glass melt.

FIG. 2 illustrates a second embodiment of the process in accordance with the present disclosure. In this process, the first stage 20a involves melting, reacting and refining salt
(NaCl) and silica (SiO2) in the presence of water (H2O, preferably steam) to produce sodium silicate (Na20.SiO2) and release hydrogen chloride (HCl) gas. This step is immediately followed by addition of calcium carbonate (CaCO3) such as limestone. The calcium carbonate is rapidly melted, again to produce a low-viscosity sodium-calcium-silicate solution in liquid phase to promote release of gaseous reaction products. Again, the first stage 20a can be carried out under vacuum further to promote release of gaseous reaction products. The second stage 30, which involves mixing, dissolution and homogenization of the precursor melt with additional raw materials 40 in FIG. 2 is the same as the second stage in FIG. 1. The result of either process is a silica-based glass melt.

The first stage 20 in FIG. 1 or 20a in FIG. 2 preferably is carried out at a temperature in the range of about 900C to about 1700C. The second stage 30 in FIGS. 1 and 2 preferably is carried out at a temperature greater than about 900C. Most preferably, the first stage 20 or 20a is carried out at a temperature of about 1250C for not more than 2 hours. The glass network modifiers within the precursor melt 20 or 20a preferably have an alkali metal to alkaline metal molar ratio of 1:3 to 3:1. The glass precursor melt preferably has a glass network former to glass network modifier molar ratio of 2:1.5 to 1:2. The sodium-calcium-silicate solution glass precursor melt of the first stage 20 or 20a preferably has a sodium:calcium:silica molar ratio of about 1:1:1.5 to 1:1:4.

In summary, the glass precursor melt composition at the first stage 20 or 20a is designed to minimize the viscosity at reasonable processing temperatures to facilitate refining. Therefore, all glass network modifiers that are in a chemical form that releases gases upon decomposition preferably are added in the first stage (20 or 20a). And, all glass network formers
that are added in chemical form that releases gases upon decomposition are added in the first stage. Additionally, any glass network former or glass network modifier that is added in a chemical form that does not release gases upon decomposition may be added in the first stage at appropriate chemical ratios to minimize the viscosity of the glass precursor melt. All materials added in the second stage (30) are to be in a chemical form that does not release a significant quantity of gases upon decomposition.

There thus has been disclosed a process for making silica-based glass that fully achieves all of the objects and aims previously set forth. The disclosure has been presented in conjunction with presently referred embodiments, and alternatives and modifications have been discussed. Other alternatives and modifications readily will suggest themselves to persons of ordinary skill in the art in view of the foregoing description. The disclosure is intended to embrace all such modifications and variations as fall within the spirit and broad scope of the appended claims.
Claims

1. A process for making a silica-based glass composition, which includes the steps of:

(a) forming a glass precursor melt that includes glass network formers and glass network modifiers, said glass precursor melt having a temperature in the range of 900°C to 1700°C and having a viscosity of not more than 30 Pa*s, and:

(b) refining said glass precursor melt.

2. The process set forth in claim 1 wherein said step (b) includes performing said step (a) under reduced pressure.

3. The process set forth in claim 1 wherein said glass network formers are selected from the group consisting of Si, Al, Ge, P, V, Sb and Zr.

4. The process set forth in claim 3 in which the glass network formers are in an oxide or a sulfide compound form.
5.

The process set forth in claim 3 wherein said glass network formers are selected from the group consisting of the oxide, sulfide or acid forms of the recited elements.

6.

The process set forth in claim 1 in which substantially all gas releasing glass network modifiers required for said silica-based glass composition are added into the precursor melt in said step (a).

7.

The process set forth in claim 1 wherein said glass network modifiers are selected from the group consisting of Sc, La, Y, Sn, Ga, In, Th, Pb, Mg, Li, Zn, Ba, Ca, Sr, Cd, Na, Cc, K, Rb, Hg, and Cs.

8.

The process set forth in claim 1 wherein said glass network modifiers are selected from the groups consisting of the alkali metals (sodium, lithium and potassium) and the alkaline earth metals (calcium, magnesium and barium).
9. The process set forth in claim 8 wherein said glass network modifiers are selected from the group consisting of the carbonate, bicarbonate, sulfate, hydrate, hydroxide, nitrate, chloride or acid forms of the recited elements.

10. The process set forth in claim 1 which includes the step of:

(c) adding to the refined glass precursor melt following said step (b) additional non-gas releasing network formers and non-gas releasing network modifiers to form said silica-based glass composition.

11. The process set forth in claim 10 wherein said step (c) includes stirring.

12. The process set forth in claim 10 including adding cullet and/or minor ingredients such as colorants during said step (c).

13. The process set forth in claim 10 wherein said step (c) is carried out at a temperature greater than about 900C.
The process set forth in claim 10 wherein said step (c) is carried out at a temperature of between 1250°C and 1450°C.

A process for making a silica-based glass, which includes the steps of:

(a) forming a low-viscosity sodium-calcium-silica (Na2O.CaO.SiO2) precursor melt solution in liquid phase by:

(a1) melting, reacting and refining calcium carbonate (CaCO3), soda ash (Na2O3) and silica (SiO2), or

(a2) melting, reacting and refining salt (NaCl) and silica (SiO2) in the presence of water (H2O) followed by addition of calcium carbonate (CaCO3),

and then

(b) mixing the sodium-calcium-silica precursor melt solution of step (a) in liquid phase with additional materials including silica (SiO2) to form a silica-based glass melt.

The process set forth in claim 8 or 15 wherein said precursor melt has an alkali metal oxide to alkaline earth metal oxide molar ratio of 1:3 to 3:1.
17. The process set forth in claim 1 or 15 wherein said precursor melt has a network modifier to network former molar ratio of 2:1.5 to 1:2.

18. The process set forth in claim 15 wherein said sodium-calcium-silica precursor melt solution of step (a) has a viscosity of not more than 30 Pa s.

19. The process set forth in claim 10 or 15 wherein said step (a) is carried out at a temperature in range of about 900°C to about 1700°C.

20. The process set forth in claim 10 or 15 wherein said step (a) is carried out at a temperature of about 1250°C to 1450°C.

21. The process set forth in claim 10 or 15 wherein said step (b) is carried out at a temperature greater than about 900°C.
22.

The process set forth in claim 15 wherein said step (a) and/or said step (b) is carried out under reduced pressure to promote release of gases.

23.

The process set forth in claim 22 wherein said step (b) includes stirring.

24.

A process for making a glass precursor melt, which includes the steps of:

(a) mixing at least one glass network former with at least one glass network modifier, and

(b) refining the glass precursor melt by performing at least part of said step (a) at elevated temperature and under reduced pressure to promote release of gases produced by said precursor melt.

25.

The process set forth in claim 24 wherein said step (a) is performed at a molar ratio of said at least one glass network former to said at least one glass network modifier such that said precursor melt during said step (b) has a viscosity of not more than 30 Pa-s.

26.

The process set forth in claim 24 including:
(c) mixing additional materials with the glass precursor melt of said step (b) to form a glass product melt composition.

27.

5 The process set forth in claim 26 including:
(d) stirring the glass precursor melt during said step (c) to promote decomposition of said additional materials and homogenization of said glass product melt.

28.

10 The process set forth in claim 25 wherein all gas releasing glass network modifiers that are required for the glass product melt composition are added in step (a).

29.

The process set forth in claim 1, 18 or 25 wherein said viscosity is less than 15 Pa*s.

30.

The process set forth in claim 29 wherein said viscosity is less than 8 Pa*s.

31.

The process set forth in claim 30 wherein said viscosity is not more than 3 Pa*s.
32.

The process set forth in claim 31 wherein said viscosity is in the range of 1 to 2 Pa*s.
Additional Raw Materials:
- Shortfall in Silica Sand (SiO₂) and other non-gas releasing network formers or non-gas releasing network modifiers
- Cullet
- Other Additives

Stage 1: Melting, Reacting & Refining
\[
z\text{CaCO}_3 + x\text{Na}_2\text{CO}_3 + y\text{SiO}_2 \rightarrow x\text{Na}_2\text{O}_y\text{SiO}_2.z\text{CaO} + x\text{CO}_2
\]
Vacuum optional to increase reaction kinetics. Low viscosity melt under vacuum to rapidly remove bubbles.

Stage 2: Mixing, Dissolution, Homogenization
- Reduced pressure to eliminate residual bubbles.
- Mixing, stirring or agitation to enhance dissolution rates.

FIG. 1

Soda-Lime Glass Melt
Additional Raw Materials:
Shortfall in Silica Sand (SiO2) and other non-gas releasing network formers or non-gas releasing network modifiers
Cullet
Other Additives

Raw Materials:
Salt (NaCl)
Water (H2O)
Silica Sand (SiO2)
Limestone (CaCO3)

Stage 1: Melting, Reacting & Refining
\[ x\text{NaCl} + y\text{H}_2\text{O} + z\text{SiO}_2 \rightarrow x/2\text{Na}_2\text{O} \cdot z\text{SiO}_2 + 2y\text{HCl} \] followed by addition of CaCO3
Vacuum optional to increase reaction kinetics.
Low viscosity melt under vacuum to rapidly remove bubbles.

Stage 2: Mixing, Dissolution, Homogenization
Reduced pressure to eliminate residual bubbles.
Mixing, stirring or agitation to enhance dissolution rates.

FIG. 2
Soda-Lime Glass Melt
INTERNATIONAL SEARCH REPORT

INTERNATIONAL SEARCH REPORT

PCT/US2012/062978

A. CLASSIFICATION OF SUBJECT MATTER

I N V. C93B5/225 C03C3/087 CQ3B3/Q2 C03C1/02

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-I nternal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X See patent family annex.

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Date of the actual completion of the international search: 11 February 2013

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

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**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/US2012/062978

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