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(54) Title: HIGH ALKALI GLASS COMPOSITION

(57) Abrégé/Abstract:
A glass composition useful in preparing fiberglass comprises 12 to 25 weight% CaO; 12 to 16 weight% Al_2O_3; 52 to 62 weight% SiO_2; 0.05 to 0.8 Fe_2O_3; and greater than 2 up to about 8 weight% alkali metal oxide.

Abstract

A glass composition useful in preparing fiberglass comprises 12 to 25 weight% CaO; 12 to 16 weight% Al_2O_3; 52 to 62 weight% SiO_2; 0.05 to 0.8 Fe_2O_3; and greater than 2 up to about 8 weight% alkali metal oxide.

HIGH ALKALI GLASS COMPOSITION

Background

The majority of all continuous filament fiberglass is made from E-glass and used in applications such as fiber reinforced plastics and non-woven mat for roofing reinforcement. Historically, E-glass was developed as a low electrical conductivity glass, giving it the "E" designation for "electrical". To achieve low conductivity, the total alkali content, commonly designated as R_2O (Na_2O, K_2O, and Li_2O), had to be very low. The lack of R_2O, which is a good flux, was compensated by a large percentage of alkaline earth oxide (CaO, MgO), which is a weaker flux. The composition was developed around a eutectic in the SiO_2-Al_2O_3-CaO system. Some of the CaO was replaced by MgO, and B_2O_3 was added to help lower the viscosity. The resulting composition space, known as E-glass, has an ASTM specification, D-578-05, to designate the standard composition ranges, shown in Table 1. Early patents in this composition range were relatively high in B_2O_3 and include U.S. Patent Nos. 2,334,961 and 2,571,074.

TABLE 1

Printed Circuit Boards and Aerospace	Weight%
B_2O_3	5 to 10
CaO	16 to 25
Al_2O_3	12 to 16
SiO_2	52 to 56
MgO	0 to 5
$Na_2O + K_2O$	0 to 2
TiO_2	0 to 0.8
Fe_2O_3	0.05 to 0.4
F_2	0 to 1.0

General	Weight%
B_2O_3	0 to 10
CaO	16 to 25
Al_2O_3	12 to 16
SiO_2	52 to 62
MgO	0 to 5
Total Alkali	0 to 2
TiO_2	0 to 1.5
Fe_2O_3	0.05 to 0.8
F_2	0 to 1.0

Because of the very good water durability and fiberizability of E-glass, it became the composition of choice for general-purpose continuous filament glass fiber. The ASTM composition ranges, especially for general applications, are relatively wide, except for alkali (R_2O), and can consist of glasses with a wide range of properties.

For E-glass, the most expensive raw materials are those that supply boron (such as borax, boric acid, Ulexite, and Colemanite) and these materials can comprise one-third or more of the total raw material cost even though the B_2O_3 content in the glass is below 10%. One factor adding to the cost of boron in E-glass is the very low alkali (R_2O) content, which necessitates replacement of borax with higher cost boric acid unless colemanite is a viable alternative. The trend over the last several decades has been to reduce the B_2O_3 content in E-glass for raw material cost savings but the trade off typically comes in the form of higher melting temperatures and higher melt viscosity. Higher melt viscosity results in higher fiberization temperatures, represented by the temperature at which the viscosity of the melt is equal to 1000 poise and designated by T_{log3}. An example of a low boron E-glass patent is U.S. Patent No. 7,022,634 and an example of an essentially "boron-free" E-glass patent is U.S. Patent No. 5,789,329.

The use of recycled glass, known as cullet, is common practice in glasses melted for production of insulation wool and glass containers, but not for E-glass. Cullet can be broken down into two categories: pre-consumer and post-consumer. The most common grade of pre-consumer cullet available is known as plate cullet, while the most common grade of post-consumer cullet is a mixture of green, amber, and flint (clear) crushed bottles, referred to as "three-mix". The majority of commercially available pre-consumer and post-consumer cullet has 12-16% R_2O, limiting the amount that could be used as a raw material for E-glass, due to the low total alkali metal oxides content of 0 to 2 weight% in E-glass formulations.

With the limit of 2% total alkali, E-glass produced with a three-mix cullet containing 13.9% R_2O could only consist of a maximum of 11 weight% recycled content from the cullet. Glass recycling not only uses less energy than manufacturing glass from sand, limestone, and other processed minerals, but also saves emissions of carbon dioxide, a greenhouse gas.

Table 2 below sets forth example compositions of plate cullet and three-mix cullet.

TABLE 2

Glass Oxides (weight%)	Plate Cullet	Three-mix
SiO_2	72.4	72
Al_2O_3	0.3	2.0
Fe_2O_3	0.2	0.25
B_2O_3	0	0
Na_2O	13.8	13.2
K_2O	0.08	0.7
CaO	9.3	10.7
MgO	3.6	0.8
F_2	0	0

It is an object of the present application to provide a glass composition which gives technologists greater flexibility in designing glass compositions for a wide range of glass properties and low cost production. More particularly, it is an object of the present application to provide a glass composition which allows for increased amounts of recycled glass, resulting in less greenhouse gas emissions and a decrease in the amount of material going to landfills.

Summary

In accordance with the foregoing objectives, provided is a glass composition useful in preparing fiberglass comprising:

12 to 25 weight% CaO, for example, 16 to 25 weight% CaO;

12 to 16 weight% Al_2O_3;

52 to 62 weight% SiO_2;

0.05 to 0.8 Fe_2O_3; and

greater than 2 up to about 8 weight% alkali metal oxide.

The total alkali metal oxides content of greater than 2 up to about 8 weight% allows for incorporation of up to 55 weight% recycled content in the glass composition in the form of cullet.

Detailed Description

The presently disclosed glass composition useful in preparing fiberglass comprises:

12 to 25 weight% CaO, for example, 16 to 25 weight% CaO;

12 to 16 weight% Al_2O_3;

52 to 62 weight% SiO_2;

0.05 to 0.8 Fe_2O_3; and

greater than 2 up to about 8 weight% alkali metal oxide.

In comparison to the ASTM specification for E-glass having a CaO content of 16 to 25 weight%, the addition of alkali metal oxide above 2 weight% can be accompanied by a reduction in CaO, and therefore, the CaO content of the presently disclosed glass composition can be as low as 12 weight%. The presently disclosed glass composition can further comprise:

B_2O_3 in an amount up to 10 weight%;

MgO in an amount up to 5 weight%;

TiO_2 in an amount up to 1.5 weight%; and/or

fluoride in an amount up to 1.0 weight%.

The alkali metal oxide of the presently disclosed glass composition can comprise one or more alkali metal oxides selected from the group consisting of Na_2O, K_2O, and Li_2O. The presently disclosed glass composition can comprise Li_2O in an amount up to 5 weight%.

Advantages of the presently disclosed high alkali content glass compositions include more effective electrical melting; higher usage of recycled glass (cullet); lower precious metal usage for fiberization, possibly non-precious metal bushings; longer bushing life; more flexibility in batch materials (borax to replace boric acid, feldspar to replace clay); and reduction in boron content without increasing T_{log3}. With higher alkali content there is a need to balance water durability with T_{log3} but for many applications E-glass is over-designed for water durability.

In particular, the total alkali metal oxides content of greater than 2 up to about 8 weight% allows for incorporation of larger amounts of recycled glass, for example, commercially available cullet product, as compared to E-glass compositions. While a glass composition limited to 2 weight% alkali metal oxides content can consist of up to 11 weight% recycled content, a glass having up to about 8 weight% alkali metal oxides content can consist of up to 55 weight% recycled content. Accordingly, the presently disclosed glass composition provides greater flexibility in designing glass compositions for a wide range of glass properties and low cost

production, and results in less greenhouse gas emissions and a decrease in the amount of material going to landfills.

The presently disclosed glass composition allows for a wide range of B_2O_3 content, which gives a wide range of fiberization properties. In particular, reduced B_2O_3 content permits one to realize cost savings associated with lower batch costs and abatement requirements. At the same time, employing the presently disclosed glass composition allows one to also achieve the cost savings without significantly increasing the energy required for melting the glass, reducing fiberization efficiency, or requiring a development of new bushing technology.

Two glass properties that are of importance to manufacturing are the T_{log3} and liquidus (crystallization) temperature. The T_{log3} is the temperature at which the glass melt viscosity is equal to 1000 poise, corresponding to the temperature of fiberization, and in part is correlated to the energy required for melting and fiberization. The liquidus temperature represents the upper temperature limit for crystallization to occur.

In the production of fiberglass, the molten glass in the bushing is typically maintained at or above the T_{log3} for optimum fiberization efficiency. A glass composition with a higher T_{log3} requires more energy to achieve this viscosity and therefore, incurs higher energy costs. In fiberglass production, it is preferred that the glass melt be maintained at a temperature at least 100°F above the liquidus to avoid crystallization problems (in bushings or forehearth) and consequently, lower fiberization efficiencies. It has been found that in the commercial production of E-glass fibers, fiberization efficiency is significantly reduced as the difference between T_{log3} and liquidus (referred to as "Delta T") falls below approximately 100°F and certainly when the difference falls below 50°F.

In an embodiment, the T_{log3} of the presently disclosed glass composition is less than 2300°F, for example, less that 2250°F, less than 2220°F, less than 2200°F, or less than 2160°F. In an embodiment, the liquidus temperature of the glass composition is at least 100°F less than that of the T_{log3} temperature (for example, at least 140°F less than the T_{log3} temperature, at least 150°F less than the T_{log3} temperature, or at least 160°F less than the T_{log3} temperature), to therefore provide a Delta T of at least 100°F. Thus, the liquidus temperature is generally at least below 2150°F, for example, less than 2100°F or less than 2000°F.

The presently disclosed glass composition allows one to take advantage of the cost benefits associated with relatively lower B_2O_3 content, but avoid the disadvantages of crystallization and fiberization problems. In particular, the presently disclosed glass composition yields a glass with a suitable T_{log3} and maintains a Delta T of at least 100°F, while utilizing a relatively lower B_2O_3 content. In an embodiment, the presently disclosed glass composition comprises about 3.5 to about 5.5 weight% B_2O_3.

The presently disclosed glass composition allows for increased glass conductivity for increased electrical boost usage in melting providing for more efficient energy utilization in the melting process. In particular, increased amounts of recycled glass in the presently disclosed glass composition provides for higher glass conductivity for more efficient use of electric boost in glass melting furnaces.

Increased amounts of recycled glass in the presently disclosed glass composition also decreases melt energy and results in less green house gas emission from the process. There are three main mechanisms by which the combination of cullet use and greater R_2O can decrease green house gas emissions. In the presently disclosed glass composition, the additional R_2O allows the amount of CaO in the glass to be decreased. A common source of CaO in a glass batch is limestone, which can consist of greater than 40% CO_2. By reducing the amount of CaO required in the glass, the amount of limestone used is reduced, along with its associated CO_2 emissions.

By increasing R_2O, additional cullet can be used in the glass batch. Since cullet is a source of CaO but contains no CO_2, it supplants some of the limestone used to create the glass, further reducing the CO_2 emitted during production.

By increasing the use of cullet, the energy required to melt the glass batch is reduced. If the energy source is natural gas or electricity produced by the burning of natural gas and/or coal, then reducing the energy usage will also result in CO_2 reductions.

E-glass is typically melted in gas-fired glass furnaces. In these furnaces, the burning of natural gas provides the majority of the energy to melt the glass while electricity can be used to

supplement the natural gas. The use of electricity to melt E-glass is currently limited by the low electrical conductivity of the glass. By increasing the amount of R_2O in the glass, the electrical conductivity of the glass will improve which will increase the proportion of energy which can be supplied by electricity. Since electricity can be created without creating CO_2 via nuclear, wind, solar, and geo-thermal methods, increasing the amount of melt energy supplied by electrical could result in additional CO_2 reductions. Furthermore, since electrical boost is more efficient at delivering energy for glass melting, less total energy is required when the proportion of electrical energy to natural gas energy is increased.

Fiberization is typically accomplished by drawing fibers though a multi-orifice bushing plate made from precious metals such as platinum and rhodium. These metals tie up a significant dollar value and are subject to large market price fluctuations. The amount of precious metal required for a given throughput is dependent on the T_{log3} of the glass with higher T_{log3} glasses requiring thicker bushings and/or shorter bushing service life. Reducing the T_{log3} can result in significant savings by reducing the amount of precious metal in service and/or increasing bushing service life. Reducing T_{log3} also opens up the possibility of utilizing non-precious metals for bushings.

In an embodiment, the presently disclosed glass composition has a viscosity and fiberization temperature that is sufficiently low to realize reasonable fiberization rates and efficiencies in without the use of expensive precious metal alloys (typically Pt-Rh alloy) as the bushing material. Thus, in a method of preparing fiberglass using the presently disclosed glass composition, a non-Pt/Rh bushing is employed.

The following examples are intended to be exemplary and non-limiting.

Examples

Table 3 below sets forth examples of the presently disclosed glass composition.

TABLE 3

Glass Oxides (weight%)	Comparative Example 1	Comparative Example 2	Example A	Example B	Example C	Example D	Example E
SiO_2	55.0	60.0	55.5	57.6	56.7	54.7	54.4
Al_2O_3	13.6	13.2	13.7	13.8	13.7	13.6	13.6
Fe_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TiO_2	0.5	0.5	0.5	0.5	0.5	0.5	0.5
B_2O_3	4.9	0.0	4.9	4.2	4.1	6.7	8.4
Na_2O	1.8	0.6	5.1	5.1	5.1	3.0	3.0
K_2O	0.1	0.1	0.1	0.1	0.1	0.1	0.1
R_2O	1.9	0.7	5.2	5.2	5.2	3.1	3.1
CaO	22.0	22.3	17.9	17.0	17.9	18.7	17.3
MgO	1.8	3.1	1.9	1.5	1.5	2.3	2.4
T_{log3} (°F)	2168	2298	2170	2235	2207	2155	2147
Liquidus (°F)	2027	2159	2030	2058	2078	2004	1942
Delta T (°F)	141	139	140	177	129	151	205

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The glasses of Table 3 were prepared by melting in lab scale quantities and physical properties were measured. Comparative Examples 1 and 2 are examples of E-glass from U.S. Patent Nos. 7,022,634 and 5,789,329, respectively. Examples A through C are glasses of the presently disclosed glass composition that contain approximately 5% R_2O and fall within the desirable range for T_{log3}, liquidus, and Delta T. Examples D and E are glasses of the presently disclosed glass composition that contain approximately 3% R_2O and fall within the desirable range for T_{log3}, liquidus, and Delta T. In addition, experimentation has shown the trend that increases in alkali content can be effectively accompanied by decreases in CaO content. Therefore, at the high end of the alkali range for the present invention it would be reasonable to have CaO levels below 16%. It would also be reasonable to have CaO levels as low as 12%, especially in formulations with higher amounts of B_2O_3 content.

While various embodiments have been described, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

CLAIMS:

1. A glass composition useful in preparing fiberglass comprising:

a combination of recycled glass cullet and minerals, wherein the minerals include borax, and wherein the combination comprises:

i) 12 to 25 weight% CaO;

ii) 12 to 16 weight % Al_2O_3;

iii) 52 to 62 weight % SiO_2;

iv) 0.05 to 0.8 weight % Fe_2O_3;

v) 3 to 8 weight % alkali metal oxide wherein the alkali metal oxide comprises at least 3 weight percent sodium oxide; and

vi) up to 10 weight% B_2O_3, wherein the B_2O_3 is provided by the borax.

2. The glass composition of claim 1, comprising 16 to 25 weight % CaO.

3. The glass composition of claim 1, further comprising MgO in an amount up to 5 weight %.

4. The glass composition of claim 1, further comprising TiO_2 in an amount up to 1.5 weight %.

5. The glass composition of claim 1, further comprising fluorine in an amount up to 1.0 weight %.

6. The glass composition of claim 1, comprising greater than 5 weight % of the recycled glass cullet.

7. The glass composition of claim 6, comprising up to 55 weight % of the recycled glass cullet.

8. The glass composition of claim 1, comprising up to 55 weight % of the recycled glass cullet.

9. The glass composition of claim 1, wherein the alkali metal oxide comprises Na_2O and one or more alkali metal oxides selected from the group consisting of K_2O and Li_2O.

10. The glass composition of claim 1, comprising Li_2O in an amount up to 5 weight %.

11. The glass composition of claim 1, comprising 3.5 to 5.5 weight % B_2O_3.

12. The glass composition of claim 1, wherein the glass composition has a T_{log3} temperature of less than 2300°F.

13. The glass composition of claim 1, wherein the glass composition has a T_{log3} temperature of less than 2220°F.

14. The glass composition of claim 1, wherein the glass composition has a T_{log3} temperature of less than 2160°F.

15. The glass composition of claim 1, wherein the glass composition has a liquidus temperature at least 100°F less than the T_{log3} temperature of the glass composition.

16. The glass composition of claim 1, wherein the glass composition has a liquidus temperature at least 140°F less than the T_{log3} temperature of the glass composition.

17. The glass composition of claim 1, wherein the glass composition has a liquidus temperature at least 160°F less than the T_{log3} temperature of the glass composition.

18. A method of making fiberglass, the method comprising:

i) providing a combination of recycled glass cullet and minerals, wherein the minerals include borax;

ii) heating the combination to a melting temperature for the recycled glass cullet and minerals to form a molten material; and

iii) forming the molten material into fiberglass;

wherein the fiberglass comprises:

a) 12 to 25 weight % CaO;

b) 12 to 16 weight % Al_2O_3 ;

c) 52 to 62 weight % SiO_2;

d) 0.05 to 0.8 weight% Fe_2O_3;

e) 3 to 8 weight % alkali metal oxide wherein the alkali metal oxide comprises at least 3 weight percent sodium oxide; and

f) up to 10 weight% B_2O_3, wherein the B_2O_3 is provided by the borax.

19. The method of claim 18, wherein the fiberglass is formed using a non-PURh bushing.

20. Use of the glass composition of any one of claims 1-17 to make fiberglass.