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| (54) Title: ARSENIC-FREE GLASSES | | | |
| (57) Abstract | | | |
| <p>This invention is related to glasses for use as substrates in flat panel display devices, more specifically to a family of aluminosilicate glasses in which less than .2 mole percent and preferably no As_2O_3 is used as a fining agent and the β-OH of the glass is maintained below about .5.</p> | | | |
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ARSENIC-FREE GLASSES

Related Applications

This application claims the benefit of U.S. Provisional Application No. 5 60/022,193, filed July 19, 1996.

Field of the Invention

This invention is directed to arsenic-free glass compositions and methods of making such glasses which are suitable for use as substrates in flat panel display devices without having to use arsenic containing materials.

Background of the Invention

Liquid crystal displays (LCDs) are passive flat panel displays which depend upon external sources of light for illumination. They are manufactured as segmented displays or in one of two basic configurations. The substrate needs (other than being transparent and capable of withstanding the chemical conditions to which it is exposed during display processing) of the two matrix types vary. The first type is intrinsic matrix addressed, relying upon the threshold properties of the liquid crystal material. The second is extrinsic matrix or active matrix (AM) addressed, in which an array of diodes, metal-insulator-metal (MIM) devices, or thin film transistors (TFTs) supplies an electronic switch to each pixel. In both cases, two sheets of glass form the structure of the display. The separation between the two sheets is the critical gap dimension, of the order of 5-10 μm .

25 Intrinsically addressed LCDs are fabricated using metal deposition

techniques, typically at temperatures $\leq 350^{\circ}\text{C}$, followed by standard metal etching procedures. As a result, the substrate requirements therefor are often the same as those for segmented displays. Soda-lime-silica glass with a barrier layer has proven to be adequate for most needs. A high performance version of intrinsically addressed LCDs, the super twisted nematic (STN) type, has an added requirement of extremely precise flatness for the purpose of holding the gap dimensions uniform. Because of that requirement, soda-lime-silica glass made using the float glass manufacturing process must be polished. Such polishing processes are expensive and time consuming, and generate a large amount of glass particles which have the potential to negatively impact further processing of the glass sheets. Alternatively, glass can be formed using a process which does not require polishing, e.g. fusion downdraw.

Extrinsically addressed LCD's can be further subdivided depending upon the nature of the electrical switch located at each optical element (subpixel). Two of most popular types of extrinsically (or active matrix, AMLCD) addressed LCD's are those based on either amorphous (a-Si) or polycrystalline (poly-Si) silicon thin film transistors (TFT's).

U.S. Pat. No. 4,824,808 (Dumbaugh, Jr.) lists four desirable properties for a glass to exhibit in order to fully satisfy the needs of a substrate for extrinsically addressed LCD's:

First, the glass must be essentially free of intentionally added alkali metal oxide to avoid the possibility of alkali metal contamination of the TFT;

Second, the glass substrate must be sufficiently chemically durable to withstand the reagents used during the manufacture of the TFT;

Third, the expansion mismatch between the glass and the silicon present in the TFT array must be maintained at a relatively low level even as processing temperatures for the substrates increase; and

Fourth, the glass must be capable of being produced in high quality thin sheet form at low cost; that is, it must not require extensive grinding and polishing to secure the necessary surface finish.

That last requirement is most difficult to achieve inasmuch as it demands a sheet glass production process capable of producing essentially finished glass sheet. A process capable of meeting this requirement is a particular downdraw process known as the overflow downdraw, or fusion, sheet manufacturing process. The overflow downdraw process is described, for example, in U.S. Pat. No. 3,338,696 (Dockerty) and U.S. Pat. No. 3,682,609 (Dockerty). Fusion formed glass sheets, unlike float glass sheets, are sufficiently flat that they do not need to be polished after forming. Two glasses which meet the above requirements, Corning Incorporated Codes 10 7059 and 1737 sheet glass, are currently employed as substrates for extrinsically addressed LCD's. These glasses are made using the overflow downdraw process, and hence do not require polishing after forming.

Recent improvements in the resolution of extrinsically addressed LCD's have led to the development of a fifth glass requirement, that is, a high glass 15 strain point. This property is used as an indication of the thermal shrinkage of the glass. As can be appreciated, the lower the strain point, the greater is this thermal shrinkage. Low thermal shrinkage is desirable for precise alignment during successive photolithographic and other patterning steps during the TFT processing. Consequently, glasses having higher strain points are generally 20 preferred for extrinsically addressed LCD's, particularly those which employ poly-Si TFT technology. Thus, there has been considerable research to develop glasses demonstrating high strain points so that thermal shrinkage is minimized during device processing. Corning Code 1737 glass, which has the highest strain point (666° C) in the AMLCD substrate industry, is rapidly 25 becoming an industry standard. Concurrent with their high strain points, these glasses often have high melting temperatures, e.g. on the order of 1550-1650° C.

Another technology termed "chip-on-glass" (COG) has further 30 emphasized the need for the substrate glass to closely match silicon in thermal expansion. Thus, the initial LCD devices did not have their driver chips mounted on the substrate glass. Instead, the silicon chips were mounted

remotely and were connected to the LCD substrate circuitry with compliant or flexible wiring. As LCD device technology improved and as the devices became larger and required finer resolutions, these flexible mountings became unacceptable, both because of cost and of uncertain reliability. This situation led to Tape Automatic Bonding (TAB) of the silicon chips. In that process the silicon chips and electrical connections to the chips were mounted on a carrier tape, that subassembly was mounted directly on the LCD substrate, and thereafter the connection to the LCD circuitry was completed. TAB decreased cost while improving reliability and increasing the permitted density of the conductors to a pitch of approximately 200 μm -- all significant factors. COG, however, provides further improvement over TAB with respect to those three factors. Hence, as the size and quality requirements of LCD devices increase, COG is demanded for those devices dependent upon the use of integrated circuit silicon chips. For that reason, the substrate glass preferably demonstrate a linear coefficient of thermal expansion closely matching that of silicon; i.e., a linear coefficient of thermal expansion (0° : 0.0° C) between about 32-46 $\times 10^{-7}/\text{°C}$, most preferably 32-40 $\times 10^{-7}/\text{°C}$.

Many of the glasses manufactured for flat panel display applications, particularly those which are formed by downdraw processes (e.g., the fusion or slot draw processes), are melted or formed using manufacturing equipment comprised of refractory metals, e.g. platinum or platinum alloys, particularly in the fining and conditioning sections of the process, where refractory metals are employed in order to minimize the creation of compositional inhomogeneities and gaseous inclusions caused by contact of the glass with oxide refractory materials. In addition, many of these manufacturing processes employ arsenic as a fining agent. This is because arsenic is among the highest temperature fining agents known, meaning that, when added to the molten glass bath, it allows for O₂ release from the glass melt even at high melting temperatures (e.g. above 1450° C). This high temperature O₂ release, (which aids in the removal of gases during the melting and fining stages of glass production), coupled with a strong tendency for O₂ absorption at lower conditioning

temperatures, (which aids in the collapse of any residual gaseous inclusions in the glass), results in a glass product essentially free of gaseous inclusions. In addition, the oxidizing nature of the arsenic fining package allows for protection of the platinum based metal systems by preventing contamination as a result of tramp metals reduction. Other fining agents typically melt and release their oxygen far too early when added as fining agents to high melting temperature glasses and reabsorb O₂ too late during the conditioning process, thereby disabling their fining abilities. From an environmental point of view, it would be desirable to find alternative methods of making such high melting point and strain point glasses without having to employ arsenic as a fining agent. It would be particularly desirable to find methods for making such glasses via downdraw (especially fusion-like) processes. Unfortunately, previous efforts at doing so have been hindered by the production of unacceptable amounts of bubbles in the glass. This has been a particular problem with glasses which employ refractory metals such as platinum or platinum containing alloys in their molten glass delivery systems. This is because platinum can cause an electrochemical reaction to occur with the glass which results in bubble formation on or near the platinum (commonly referred to as blistering) contacting region of the glass.

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Summary of the Invention

We have found that by maintaining a low amount of water in the glass during the glass forming process, other fining constituents which are normally less efficient at high melting temperatures (melting temperature is defined herein as the temperature at which the glass exhibits a viscosity of 200 poise), e.g. Sb₂O₃, CeO₂, SnO₂, Fe₂O₃, and mixtures thereof, can be employed if needed in place of As₂O₃ to facilitate successful fining of the glass. Maintaining a low amount of water in the glass thus enables the formation of high melting point glasses (i.e., glasses wherein the temperature at which the viscosity corresponds to 200 poise is greater than about 1500°C) which are essentially or substantially arsenic-free. By substantially arsenic-free it is

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meant that such glasses have less than 0.02 mole percent As_2O_3 (such amounts are normally present as a result of raw material impurity). The invention also enables the formation of such high melting point glasses using manufacturing systems which employ platinum or platinum containing alloys which contact the glass during the melting or forming steps of the manufacturing process. These methods are particularly suited for forming glasses which are formed using a downdraw process, such as, for example, Corning Code 1737.

One manner of measuring the water content in the glass is by measuring beta-OH ($\beta\text{-OH}$). $\beta\text{-OH}$, as used herein, is a measure of the hydroxyl content in the glass as measured by IR spectroscopy, and is determined using the fundamental hydroxyl absorption, which for this material occurs at about 2809 nm. The $\beta\text{-OH}$ is the linear absorption coefficient (absorbance/mm thickness) of the material at 2809 nm. The equation below shows how $\beta\text{-OH}$ is calculated from the sample's IR transmittance spectrum.

$$\beta\text{-OH} = (1/X) \text{LOG}_{10}(T_1/T_2)$$

where X is the sample thickness in millimeters, T_1 is the sample transmittance at the reference wavelength (2600 nm) and T_2 is the minimum sample transmittance of the hydroxyl absorption wavelength (2809 nm). The reference wavelength compensates for signal loss due to surface reflections, scatter, and refraction in the sample, and is chosen from a region of low absorption and as close as possible to the absorption wavelength of interest.

In a preferred embodiment of the present invention for forming low arsenic containing glasses via a downdraw sheet forming process, the batch constituents are selected so that the resultant glass has a water content therein, as indicated by $\beta\text{-OH}$ level, which is less than .5, preferably less than .45, more preferably less than .4, and most preferably less than .35.

Preferably, the glasses formed in accordance with the invention are formed using less than 0.1 mole percent As_2O_3 , and most preferably are

essentially free of As_2O_3 in the resultant glass. We have found that silicate glasses (especially aluminosilicate and borosilicate glasses) formulated to result in such β -OH values in the resultant formed glass can be fired using less than 0.02 mole percent As_2O_3 , expressed as the amount of As_2O_3 present in the resultant glass. Even when formed using a downdraw process employing a platinum based metal delivery system, such glasses can be formed without any significant amounts of electrochemical blistering occurring. In the most preferred embodiment, in order to facilitate firing of these glasses, Sb_2O_3 , CeO_2 , SnO_2 , Fe_2O_3 , and mixtures thereof are added to such glasses, alone or in combination, in an amount between about .02-2 mole percent. In a preferred embodiment, Sb_2O_3 is added in an amount between about 0.2-0.5 mole percent.

The water content or β -OH value of the glass can be reduced in a variety of ways. For example, simply by appropriate selection of batch materials, the water level in the glass can be adjusted to some extent. Further water reduction can be achieved by adding drying agents, such as halide materials. For example, halide containing materials may be added in an amount which results in the final glass having a composition between about 0.1 to 4 mole percent halide, more preferably 0.1 to 2 mole percent halide, and most preferably about 0.1 percent halide. In a preferred embodiment for forming the glass composition disclosed in the example, .4 mole percent chlorine is batched, e.g. as $CaCl_2$, resulting in about .15 to .19 mole percent Cl in the resultant glass.

Additionally, it is desirable to keep the sum of the partial pressures of all dissolved volatile gases below 1 atmosphere. One method of facilitating this result is by limiting the amount of sulfur in the resultant glass by appropriate selection of batch materials. Preferably, selection of batch materials should be made so that the sulfur, expressed as SO_3 , in the resultant formed glass is as low as possible, preferably less than 100 ppm, more preferably less than 50, and most preferably less than 25 ppm.

The methods in accordance with the present invention are useful for

forming silicates containing large amounts of Al_2O_3 and B_2O_3 , e.g., glasses having 60-77 mole percent SiO_2 , 8-14 mole percent Al_2O_3 , and 5-17 mole percent B_2O_3 .

The methods in accordance with the present invention are particularly advantageous in forming high strain point aluminoborosilicate glasses such as, for example, those having a composition, expressed in terms of mole percent on the oxide basis, of

| | | | |
|-------------------------|-------|--------------|------|
| SiO_2 | 60-73 | MgO | 0-5 |
| Al_2O_3 | 8-14 | CaO | 1-13 |
| B_2O_3 | 5-17 | SrO | 0-8 |
| TiO_2 | 0-5 | BaO | 0-14 |
| Ta_2O_5 | 0-5 | | |

More preferably, the base glass has a composition, expressed in terms of mole percent on the oxide basis, of

| | | | |
|-------------------------|--------|---|-------|
| SiO_2 | 64-70 | MgO | 0-5 |
| Al_2O_3 | 9.5-14 | CaO | 3-13 |
| B_2O_3 | 5-12 | SrO | 0-5.5 |
| TiO_2 | 0-5 | BaO | 2-8 |
| Ta_2O_5 | 0-5 | $\text{MgO}+\text{CaO}+\text{SrO}+\text{BaO}$ | 10-20 |

With the exception of the low water content, glasses within this preferred composition range are disclosed, for example, in U.S. Patent No. 5,374,595, the specification of which is hereby incorporated by reference.

Preferred glasses formed in accordance with the present invention exhibit linear coefficients of thermal expansion over the temperature range of 0° - 300°C between 32 - $46 \times 10^{-7}/^\circ\text{C}$, more preferably between 32 - $40 \times 10^{-7}/^\circ\text{C}$, strain points higher than 630°C , more preferably higher than 640°C , and most preferably greater than 650°C liquidus temperatures less than 1125°C , liquidus viscosities which are sufficient to enable formation by a downdraw manufacturing process, preferably greater than 400,000, and more preferably

greater than 600,000 poises (60,000 Pa·s), a weight loss of less than 2 mg/cm² after immersion for 24 hours in an aqueous 5% by weight HCl solution at 95°C, long term stability against devitrification at melting and forming temperatures, and melting viscosities of about 200 poises (20 Pa·s) at less than 1675°C.

5 The methods of the present invention may be employed in glasses having compositions within the boundaries set forth above, such as, for example, glasses listed as examples in U.S. Pat. No. 5,374,595, thereby enabling such glasses to be fined and formed without having to use arsenic.

10 In the most preferred glasses, in addition to the low water level, the level of Al₂O₃ will exceed that of B₂O₃ and in the most preferred glasses the composition will consist essentially, expressed in terms of mole percent, of about

| | | | | |
|----|--------------------------------|-------|-----------------|-------|
| | SiO ₂ | 65-69 | MgO | 1-5 |
| | Al ₂ O ₃ | 10-12 | CaO | 3-9 |
| 15 | B ₂ O ₃ | 7-10 | SrO | 1-3 |
| | TiO ₂ | 0-3 | BaO | 2-5 |
| | Ta ₂ O ₅ | 0-3 | MgO+CaO+SrO+BaO | 11-16 |

Preferably, the ratio Al₂O₃: B₂O₃ in such glasses is greater than 1.

20 The invention thus enables the formation of silicate sheet glasses having high melting points (greater than 1500°C.), as well as the formation of silicate sheet glasses using manufacturing processes which employ refractory metals such as molybdenum and platinum in their forming regions. Forming region, as used herein, refers to the portion of the manufacturing process prior to which the final form of the glass is imparted to the glass, and includes the melting, conditioning, and fining portions of the manufacturing process.

BRIEF DESCRIPTION OF THE DRAWINGS

30 Figure 1 illustrates a humidity controlled enclosure for use in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to silicate glass compositions and methods of making such silicate glass compositions while employing little or no arsenic. The preferred glasses are aluminosilicate or borosilicate glasses. The preferred manufacturing processes for such glasses is via a downdraw sheet manufacturing process. As used herein, downdraw sheet manufacturing process refers to any form of glass sheet manufacturing process in which glass sheets are formed while traveling in a downward direction. In the fusion or overflow downdraw forming process, molten glass flows into a trough, then overflows and runs down both sides of a pipe, fusing together at what is known as the root (where the pipe ends and the two overflow portions of glass rejoin), and is drawn downward until cool. The overflow downdraw sheet manufacturing process is described, for example, in U.S. Patent No. 3,338,696 (Dockerty) and U.S. Patent No. 3,682,609 (Dockerty). One advantage to the fusion forming process is that the glass sheet can be formed without the glass surface contacting any refractory forming surfaces. This provides for a smooth, contaminant-free surface. In addition, this technique is capable of forming very flat and thin sheets to very high tolerances. Consequently, fusion formed glass sheets, unlike float glass sheets, do not require costly polishing steps for TFT and STN LCD applications.

Other forms of downdraw sheet forming techniques include the slot draw and redraw forming techniques. In the slot draw technique, molten glass flows into a trough having a machined slot in the bottom. The sheets of glass are pulled down through the slot. The quality of the glass is obviously dependent on the accuracy of the machined slot. Redraw processes generally involve preforming a glass composition into a block of some shape, then reheating and drawing the glass downwardly into a thinner sheet product.

The glasses of the present invention preferably have less than .2 mole percent As_2O_3 , more preferably less than .1 mole percent As_2O_3 , and most

preferably less than .02 mole percent As_2O_3 (an amount which is normally present as a result of raw material impurity).

It is believed that the method described herein are applicable to a wide variety of glasses, particularly those formed via downdraw manufacturing processes which employ platinum in their forming regions. Application of the invention to Corning Code 1737 glass, for example, is demonstrated as follows, with reference to Table I below. These glasses were prepared in a laboratory-scaled continuous melting unit similar to the overflow downdraw melting units typically used for commercial production of this type of product. This experimental melting unit employs a platinum/rhodium alloy refractory metal delivery system, wherein the molten glass contacts the platinum alloy metal. Example 4 of Table I corresponds closely to commercially available Corning Code 1737 glass, and was fined accordingly using an amount of arsenic which resulted in about 0.4 mole percent being present in the resultant glass. Examples 1, 2, and 3 illustrate the effect that decreasing amounts of water has on these compositions. As the β -OH values of the glass decrease, so do the gaseous inclusions (Inc./lb.) in glass. In these examples, gaseous inclusions are primarily a result of electrochemical blistering caused by the platinum alloy pipes which deliver the molten glass, and consequently accurately mimic the manufacturing processes employing metals such as platinum. Gaseous inclusions were measured on a per pound basis over a period of two to three days. As illustrated by the examples, the inclusions per pound dropped significantly with each decrease of β -OH value. The fact that this was done without having to use As_2O_3 as a fining agent makes this accomplishment significant.

Table I records similar glass compositions of varying β -OH levels, expressed in terms of parts by weight on the oxide basis, illustrating the invention. Inasmuch as the sum of the individual constituents totals or very closely approximates 100, for all practical purposes the reported values may be deemed to represent weight percent. Table IA records the same glass compositions expressed in terms of mole percent on the oxide basis. The

actual batch ingredients may comprise any materials, either oxides or other compounds, which, when melted together with the other batch components, will be converted into the desired oxide in the proper proportions. For example, SrCO_3 and CaCO_3 can provide the source of SrO and CaO , respectively. In Example 3, Cl was added as CaCl_2 at a level of 0.2 weight percent in excess of the batch, resulting in about .087 weight percent Cl retained in the resultant glass. About 2.7 weight percent water in excess of the batch was added to Examples 1 and 4.

Table I also lists measurements of several chemical and physical properties determined on the glasses in accordance with techniques conventional in the glass art. Thus, the linear coefficient of thermal expansion (CTE) over the temperature range 0°-300°C. expressed in terms of $\times 10^{-7}/^\circ\text{C.}$, and the softening point (S.P.), annealing point (A.P.), and strain point (St.P.) expressed in terms of °C., were determined by fiber elongation. The durability (HCl Dur.) in HCl was determined by measuring the weight loss (mg/cm^2) after immersion in a bath of aqueous 5% by weight HCl at 95°C. for 24 hours.

The liquidus temperatures (Liq.Temp.) of the glasses were measured using the standard liquidus method, which involves placing crushed glass particles in a platinum boat, placing the boat in a furnace having a region of gradient temperatures, heating the boat in an appropriate temperature region for 24 hours, and determining by means of microscopic examination the highest temperature at which crystals appear in the interior of the glass. The melting temperature (M.P., in °C) (defined as the temperature at which the glass melt demonstrates a viscosity of 200 poises [20 Pa.s]) was calculated employing the Fulcher equation as fit to the high temperature viscosity data. The liquidus viscosity (Liq. Vis.) was also calculated using the Fulcher equation coefficients, and is expressed in terms of $\times 1,000,000$ poises (100,000 Pa.s). SnO_2 was added to examples 1-3 in an amount suitable to replicate melting conditions in production, wherein the tin electrodes employed in melting the glass result in residual tin oxide in the resultant glass.

TABLE I

| | | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> |
|----|--------------------------------|----------|----------|----------|----------|
| | SiO ₂ | 59.49 | 58.82 | 58.91 | 57.07 |
| 5 | Al ₂ O ₃ | 16.4 | 16.7 | 16.58 | 16.46 |
| | B ₂ O ₃ | 8.29 | 8.3 | 8.21 | 8.35 |
| | MgO | 0.737 | 0.739 | 0.765 | 0.77 |
| | CaO | 4.109 | 4.111 | 4.116 | 4.21 |
| | SrO | 1.889 | 1.883 | 1.887 | 1.88 |
| 10 | BaO | 8.6 | 8.59 | 8.61 | 9.49 |
| | SnO ₂ | 0.062 | 0.09 | 0.092 | |
| | Sb ₂ O ₃ | 1.857 | 1.852 | 1.856 | 0 |
| | As ₂ O ₃ | 0 | 0 | 0 | 1.11 |
| | % Added H ₂ O | 2.70 | 0 | 0 | 2.7 |
| 15 | Cl | 0 | 0 | 0.087 | 0 |
| | β-OH | 0.481 | 0.41 | 0.358 | 0.440 |
| | Inc./lb. | 15.2 | 2.06 | 0.26 | .21 |
| | S.P. | 973 | 976 | 977 | 968 |
| | M.P. | 1641 | 1638 | 1644 | 1625 |
| 20 | St.Pt. | 660 | 665 | 664 | 658 |
| | A.P. | 717 | 719 | 720 | 714 |
| | Liq.Temp. | 1080 | 1080 | 1090 | 1050 |
| | Liq.Vis. | 1.37 | 1.4 | 1.06 | 2.51 |
| | HCl Dur. | 0.46 | 0.44 | 0.45 | 0.61 |
| 25 | CTE | 36.3 | 36.6 | 36.6 | 37.6 |

TABLE IA

| | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> | |
|----|--------------------------------|----------|----------|----------|------|
| 5 | SiO ₂ | 68.6 | 68.2 | 68.3 | 67.3 |
| | Al ₂ O ₃ | 11.1 | 11.4 | 11.3 | 11.4 |
| | B ₂ O ₃ | 8.25 | 8.31 | 8.22 | 8.5 |
| | MgO | 1.27 | 1.28 | 1.32 | 1.35 |
| | CaO | 5.08 | 5.11 | 5.11 | 5.32 |
| 10 | SrO | 1.26 | 1.27 | 1.27 | 1.28 |
| | BaO | 3.89 | 3.9 | 3.91 | 4.39 |
| | SnO ₂ | 0.03 | 0.04 | 0.04 | -- |
| | Sb ₂ O ₃ | 0.44 | 0.44 | 0.44 | -- |
| | As ₂ O ₃ | | | 0.4 | |

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These examples, which are meant to be illustrative and not limiting, demonstrate that aluminoborosilicate glasses such as those falling within the compositional ranges described above can be made using downdraw manufacturing processes.

In a preferred embodiment of the invention, the glass is formed in a manufacturing system which employs platinum, molybdenum, palladium, rhodium or an alloy thereof in contacting relationship with the glass, and the partial vapor pressure of hydrogen outside this portion of the manufacturing system relative to the partial vapor pressure of hydrogen in the glass or inside that manufacturing vessel. The partial pressure of hydrogen outside the vessel can be controlled, for example, by enclosing part of the vessel in an enclosure, and varying the partial pressure of hydrogen, or the dew point, inside the enclosure as desired. By so controlling the relative partial pressures of hydrogen inside versus outside the platinum or molybdenum containing portion of the glass manufacturing system, we can control, and if desired, reduce the amount of surface blisters which were heretofore problematic in

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such glass manufacturing systems which employed platinum or molybdenum. The partial vapor pressure of hydrogen inside and outside the system can be controlled, for example, by controlling the partial vapor pressure of water inside and outside the system. The desired relative partial pressures inside versus outside the forming vessels depends upon whether the forming vessel contains platinum or molybdenum (or palladium or rhodium) as a glass contacting material.

For example, platinum is desirable for use in glass forming vessels primarily because of its inert properties. However, platinum enables hydrogen migration to occur from the glass melt through the platinum, thereby creating an oxygen rich layer at the glass/platinum interface which results in surface blisters. Consequently, for the platinum glass manufacturing vessels, it is most desirable to maintain the relative inside and outside partial pressures of hydrogen to be substantially equal, so that no migration of hydrogen, either in or out of the glass manufacturing vessel, occurs. However, if any migration is to occur, it is more desirable that it occur from the outside in, and thus in another embodiment the partial pressure of hydrogen outside the platinum or molybdenum manufacturing vessel is maintained at a higher level than is present inside the vessel.

On the other hand, molybdenum acts as a reducing material toward oxide melts. Therefore it is desirable to maintain a partial pressure of hydrogen outside the molybdenum containing forming vessel which is lower than that inside the forming vessel, to reduce the amount of blisters formed as a result of reduction of the glass constituents (e.g. formation of SO_2 bubbles as a result of reduction of dissolved SO_3).

In another preferred embodiment, a measurement device is used to measure the relative partial pressures of hydrogen inside versus outside the manufacturing vessel, and the humidity or dew point outside the vessel is then controlled accordingly. A preferred such measurement apparatus is shown in Figure 1. Platinum vessel 10 includes platinum walls 12 through which molten glass 13 is flowing. The platinum walls 12 of vessel 10 can have any shape

(e.g. round or rectangular in cross-section), and the direction of flow of the molten glass through vessel 10 is not important. A platinum flag electrode 14 is immersed into the molten glass. By platinum flag, it is meant a flat sheet of platinum, so that the both sides of the platinum contact the molten glass, and therefore the flag does not experience hydrogen permeation. Also immersed into the molten glass 13 is a platinum tube 20, the interior of which is in contact with the atmosphere outside platinum vessel 10. Both flag electrode 14 and the platinum tube 20 are isolated from the platinum manufacturing vessel 10 via an insulating material 24. The flag electrode 14 and platinum tube 20 are then connected as illustrated in Fig. 1. Controller 15 is used to adjust the voltage from variable d.c. power source 16 necessary to maintain the target potential between electrodes 14 and 20. The current necessary to sustain this voltage is then read from ammeter 17 as an indicator of the flow of hydrogen through the platinum wall 20, and thus platinum wall 12 as well. For example, an increase in current indicates a net decrease in the rate of hydrogen migration out of the glass and into the atmosphere outside the Pt system. Conversely, a decrease in current would indicate a net increase in the rate of hydrogen migration out of the glass and into the atmosphere.

The apparatus illustrated in Fig. 1 is enclosed by enclosure 30 (shown schematically), which enables the control of the partial pressure of hydrogen surrounding the platinum vessel 10. Thus, if the measurement system described above indicates a change from the target potential, the humidity inside enclosure 30 can be adjusted to correct for this change. Other variations within the scope of the claimed invention will be apparent to those skilled in the art. For example, the potential between flag 14 and platinum tube 20 could be monitored simply by a voltage regulator, and a signal produced relative to the voltage measured, the signal then being sent to a control device capable of increasing or decreasing the humidity or dew point in the enclosure in response to the signal. In addition, while in Fig. 1, only a portion of the vessel 10 is enclosed, in a preferred embodiment the entire portion of the manufacturing process employing platinum vessels is enclosed. Clearly, a

similar control system can be devised if the partial pressure of hydrogen is varied directly.

Such control of the relative partial pressures of hydrogen, as well as the measuring device described above, are explained in more detail in U.S. Patent 5 Application No. 08,736,848, the specification of which is hereby incorporated by reference.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose and variations can be made therein by those skilled in the art without departing 10 from the spirit and scope of the invention which is defined by the following claims.

WHAT IS CLAIMED IS:

1. A method of making a silicate glass comprising:

5 melting and forming a silicate sheet glass using a downdraw glass manufacturing process and selecting batch constituents so that the resultant glass contains less than .2 mole percent arsenic expressed as As_2O_3 , and the β -OH of said glass is below about .5.

10 2. The method of claim 1, wherein said downdraw glass manufacturing process is a sheet forming downdraw process.

15 3. The method of claim 2, wherein the batch constituents and process control variables in said melting step are adjusted so that the β -OH is below .4.18 4. The method of claim 2, wherein the batch constituents and process control variables in said melting step are adjusted so that the β -OH is below .35.

20 5. The method of claim 2, wherein said melting step comprises forming said sheet using a downdraw process wherein glass is contacted with platinum during the melting or forming process.

25 6. The method of claim 5, wherein said downdraw process in said melting step is a fusion process.

7. The method of claim 2, wherein said melting step further comprises employing a fining agent selected from the group consisting of Sb_2O_3 , CeO_2 , SnO_2 , Fe_2O_3 , halide containing compounds, and mixtures thereof.30 8. The method of claim 3, wherein the batch constituents and process control variables are adjusted so that said glass comprises less than 0.1 mole percent As_2O_3 .

9. The method of claim 5, wherein the batch constituents and process control variables are adjusted so that said glass in said melting step is essentially free of arsenic.

5 10. The method of claim 2, wherein said melting step comprises employing antimony containing material in an amount which results in the resultant glass having between .02 to 1 mole percent Sb_2O_3 .

10 11. The method of claim 7, wherein said melting step comprises employing a halide containing compound in an amount sufficient to result in about .1 to 2 mole percent halide in the resultant glass.

12. The method of claim 11, wherein the halide in said melting step is chlorine.

15 13. The method of claim 2, wherein the resultant glass comprises an aluminoborosilicate glass, expressed in terms of mole percent on the oxide basis, having:

| | | | | |
|----|--------------------------------|-------|-----|------|
| | SiO ₂ | 60-73 | MgO | 0-5 |
| 20 | Al ₂ O ₃ | 8-14 | CaO | 1-13 |
| | B ₂ O ₃ | 5-17 | SrO | 0-8 |
| | TiO ₂ | 0-5 | BaO | 0-14 |
| | Ta ₂ O ₅ | 0-5 | | |

25 14. The method of claim 13, wherein the resultant glass is essentially free of alkali metal oxides and exhibits a strain point higher than 630°C., and a linear coefficient of thermal expansion over the temperature range 0°-300°C. between 32-46X10⁻⁷/°C.

30 15. A silicate glass sheet formed using the method of claim 1.

16. A silicate glass sheet formed using the method of claim 13.

17. The glass sheet of claim 16, wherein the β -OH is below .4.

5 18. The glass sheet of claim 16, wherein the β -OH is below .35.

19. The glass sheet of claim 16, wherein said glass comprises less than 0.1 mole percent As_2O_3 .

20. The glass sheet of claim 16, wherein said glass is essentially free of As_2O_3 .

21. A flat sheet glass substrate for use in flat panel displays in accordance with claim 19.

15 22. The glass sheet of claim 16, wherein said glass is essentially free of alkali metal oxides and exhibits a strain point higher than 630°C., and a linear coefficient of thermal expansion over the temperature range 0°-300°C between $32-46 \times 10^{-7}/^\circ\text{C}$.

20 23. The glass sheet of claim 16, wherein said glass comprises a strain point greater than about 650°C.

24. A flat, transparent glass sheet substrate made using a downdraw process and having less than .3 mole percent As_2O_3 , and a β -OH below about .5.

25 25. The substrate of claim 24, further comprising a strain point higher than 630°C., a linear coefficient of thermal expansion over the temperature range of 0°-300°C. between $32-46 \times 10^{-7}/^\circ\text{C}$., said glass being essentially free from alkali metal oxides and consisting essentially, expressed in terms of mole percent on the oxide basis, of:

| | | | |
|----------------|-------|--------------|-----|
| SiO_2 | 64-73 | MgO | 0-5 |
|----------------|-------|--------------|-----|

| | | | |
|--------------------------------|--------|-----|------|
| Al ₂ O ₃ | 9.5-14 | CaO | 1-13 |
| B ₂ O ₃ | 5-17 | SrO | 0-8 |
| TiO ₂ | 0-5 | BaO | 0-14 |
| Ta ₂ O ₅ | 0-5, | | |

5 and a fining agent selected from the group consisting of Sb₂O₃, CeO₂, SnO₂, Fe₂O₃, and mixtures thereof.

26. The substrate of claim 25, further comprising a strain point above about 640°C.

10

27. The substrate of claim 26, wherein the β-OH is below .4.

28. The substrate of claim 26, wherein the β-OH is below .35.

15

29. The substrate of claim 26, wherein said glass comprises less than 0.1 mole percent As₂O₃.

30. The substrate of claim 26, wherein said glass is essentially free of As₂O₃.

20

31. The substrate of claim 29, wherein said glass has properties suitable for formation via a downdraw process.

25

32. The substrate of claim 27, wherein said glass is made by a downdraw process employing a platinum component which contacts the glass during melting or forming.

33. A method of making a silicate glass sheet comprising:

melting, in the presence of platinum, a silicate glass mixture having a melting point greater than 1500°C, selecting batch constituents in said melting step so that the resultant glass contains less than .2 mole percent arsenic expressed as As₂O₃, and the β-OH of said glass is below about .5, and

30

forming a glass sheet from said mixture.

34. The method of claim 33, wherein the batch constituents and process control variables are adjusted so that the β -OH is below .4.

5

35. The method of claim 33, wherein the batch constituents and process control variables are adjusted so that the β -OH is below .35.

10 36. The method of claim 33, wherein said melting step comprises forming said sheet using a process which does not employ floating of the glass sheet on a molten tin bath.

15 37. The method of claim 34, wherein said melting step comprises forming said sheet using a downdraw process wherein glass is contacted with platinum during the melting or forming process.

38. The method of claim 37, wherein said downdraw process is a fusion sheet forming process.

20 39. The method of claim 36, wherein the batch constituents and process control variables are adjusted so that said glass comprises less than 0.1 mole percent As_2O_3 .

25 40. The method of claim 37, wherein the batch constituents and process control variables are adjusted so that said glass in said melting step is essentially free of arsenic.

30 41. The method of claim 36, wherein said glass in said melting step comprises an aluminoborosilicate glass, expressed in terms of mole percent on the oxide basis, having:

| | | | |
|----------------|-------|--------------|-----|
| SiO_2 | 60-73 | MgO | 0-5 |
|----------------|-------|--------------|-----|

23

| | | | |
|--------------------------------|------|-----|------|
| Al ₂ O ₃ | 8-14 | CaO | 1-13 |
| B ₂ O ₃ | 5-17 | SrO | 0-8 |
| TiO ₂ | 0-5 | BaO | 0-14 |
| Ta ₂ O ₅ | 0-5. | | |

5

42. The method of claim 41, wherein said glass in said melting step is essentially free of alkali metal oxides and exhibits a strain point higher than 630°C., and a linear coefficient of thermal expansion over the temperature range 0°-300°C. between 32-46X10⁻⁷/°C.

10

43. A silicate sheet glass having a melting point greater than about 1500°C. and comprising at least one fining agent selected from the group consisting of Sb₂O₃, CeO₂, SnO₂, Fe₂O₃, halide containing compounds, and mixtures thereof, having less than .3 mole percent As₂O₃, and a β-OH below about .5 and consisting essentially, expressed in terms of mole percent on the oxide basis, of:

| | | | |
|--------------------------------|-------|-----|------|
| SiO ₂ | 60-73 | MgO | 0-5 |
| Al ₂ O ₃ | 8-14 | CaO | 1-13 |
| B ₂ O ₃ | 5-17 | SrO | 0-8 |
| TiO ₂ | 0-5 | BaO | 0-14 |
| Ta ₂ O ₅ | 0-5. | | |

44. The glass of claim 43, wherein the β-OH is below .4.

25

45. The glass of claim 43, wherein the β-OH is below .35.

46. The glass of claim 43, wherein said glass comprises less than 0.1 mole percent As₂O₃.

30

47. The glass of claim 43, wherein said glass is essentially free of As₂O₃.

48. The glass of claim 43, wherein said glass has properties suitable for formation via a downdraw process.

5 49. The glass of claim 43, wherein the liquidus viscosity of said glass is greater than about 600,000 poises.

50. The glass of claim 43, wherein said glass is essentially free of alkali metal oxides and exhibits a strain point higher than 630°C., a linear coefficient of thermal expansion over the temperature range 0°-300°C.

10 between 32-46X10⁻⁷/°C., and a weight loss of less than 2 mg/cm² after immersion for 24 hours in an aqueous 5% by weight HC₁ solution.

51. The glass of claim 50, further comprising a strain point above about 640°C.

15 52. A silicate sheet glass formed in the presence of platinum or molybdenum during a melting, conditioning, fining, or forming portion of a manufacturing system, said glass comprising at least one fining agent selected from the group consisting of Sb₂O₃, CeO₂, SnO₂, Fe₂O₃, halide containing compounds, and mixtures thereof, having less than .3 mole percent As₂O₃, and a β-OH below about .5.

20 53. The method of claim 1, wherein the batch constituents and process control variables in said melting step are adjusted so that the β-OH is below about .45.

25 54. The substrate of claim 25, wherein the β-OH is below about .45.

55. The method of claim 1, wherein said melting and forming step comprises employing a fining agent therein.

30 56. The method of claim 1, wherein the resultant glass comprises a silicate

glass, expressed in terms of mole percent on the oxide basis, having: 60-77 SiO₂, 8-14 Al₂O₃, and 5-17 B₂O₃.

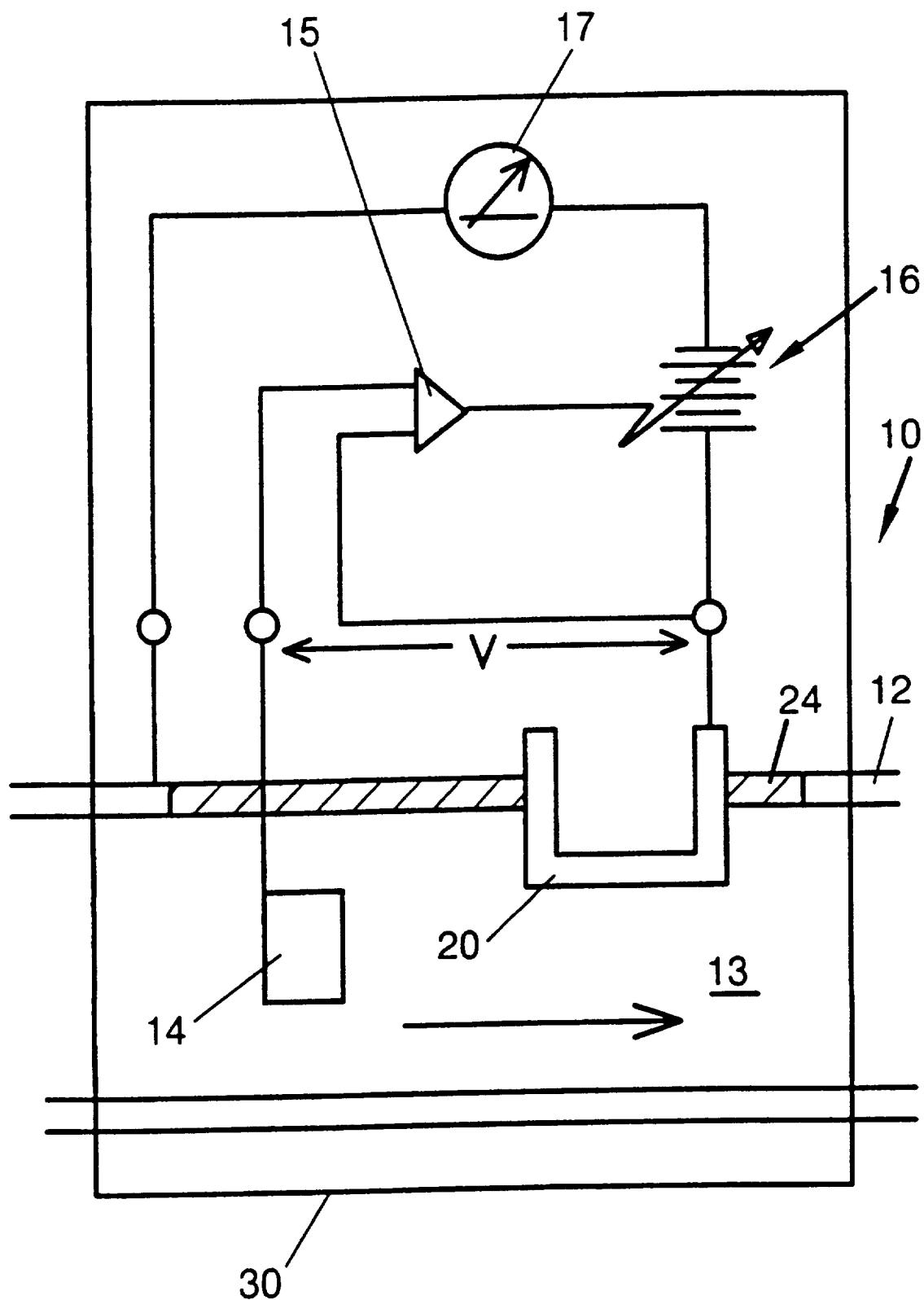


Fig. 1

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/US 97/12140

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C03C1/00 C03B17/00 C03B17/06 C03B5/08 C03B5/167
 C03B5/225

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)

IPC 6 C03C C03B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 97/12140

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INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 97/12140

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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Information on patent family members

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