Technical Bulletin

Borates in glasses

1. Introduction

Boric oxide (B_2O_3), added as borates, is important in glass technology because it brings combinations of properties that would be either technically impossible or prohibitively expensive to achieve in other ways. It is used as a flux to reduce processing temperatures in situations where the addition of alkalis needs to be limited; for example, where there is a need for low thermal expansion to achieve thermal shock resistance, or a need for high chemical durability or low electrical conductivity.

Glass accounts for three major borate applications (insulation fiberglass, textile fiberglass and technical borosilicate glass) in addition to a multitude of minor vitreous end uses.

Insulation fiberglass, or glass wool, is one of the principal insulating material used in the construction industry. Composed of very thin fibers spun from molten glass, its purpose is to trap and hold air. Borates are incorporated into the formulation to aid melting, inhibit devitrification and improve the aqueous durability of the finished product. Borates also ensure that the insulation fiberglass has adequate recovery after prolonged compression in order to save transportation.

Another major glass application is the production of textile fiberglass also referred to as continuous strand fiberglass. Originally these glasses were used for electrical purposes, and low sodium levels were important. Nowadays their major applications are reinforcements for plastics, but the low sodium tolerance still applies.

Borosilicate glass is a general classification referring to glasses having the common characteristics of containing a relatively high level of B_2O_3. Borates impart many distinct properties to borosilicate glass: thermal shock resistance, chemical resistance, aqueous durability and physical strength. Uses include oven-to-table cookware, laboratory ware, pharmaceutical containers, lighting lenses and tubing. Nuclear waste encapsulation relies on the high chemical durability of borosilicate glass.

Small quantities of borates are used in other vitreous products including container glasses and art glasses. Optical glasses, microspheres, glass-ceramics, "Vycor" glass, sealing frits and high-tech glass for space exploration applications all rely on boron to assist in melting or to fine-tune the final product properties.

2. Insulation fiberglass

Insulation fiberglass (IFG) consisting of intermingled straight and curled glass fibers, is one of the principal insulation material used in the construction industry. Smaller quantities are used for industrial applications in and for specialty insulation (automobiles and appliances). IFG is composed of 5 micron diameter fibers which are spun from a molten glass normally produced in all electric or oxy-gas furnaces. The purpose of the fibers is to entrap air and to reduce the transmission of infrared radiation, thereby inhibiting the transfer of heat and sound. The effectiveness for both functions of IFG depends on diameter of fibers, bulk density as well as thickness of material. Acoustical properties of IFG can be improved through greater density, increased thickness, and decreased fiber diameter of the insulation material.

The level of borate in glass wool is typically 4 to 7% B_2O_3. It is added to the batch raw materials as borax pentahydrate (e.g. *Neobor®*), although mineral borates such as ulexite may also be used.

Glass wool is formulated to satisfy the property requirements of both the production process and the finished product. Cr/Ni super-alloy spinners produce high quality discontinuous fibres, around 5 microns in diameter that are required for producing effective thermal and acoustic insulating materials. The upper temperature limit of the spinner is typically 1050°C.

The glass is formulated to give a fiberising viscosity ($T_{vis=log3}$) of say 1050°C and a liquidus temperature 100°C lower. This prevents crystallisation of the melt in the spinner holes, important for maintaining productivity. The aqueous durability of the fibers has to be controlled, because the fibers are susceptible to attack from atmospheric moisture. Products such as attic insulation are compressed for packaging and need to recover to a designed thickness during installation. Moisture attack can cause fiber breakage and failure of the fiber-resin bond, leading to poor recovery. The use of B_2O_3 in the glass is essential to protect from these modes of product failure. In addition, borate improves the thermal properties of the insulation by increasing the IR absorption of the glass. This allows the density of the product to be reduced while maintaining thermal performance, effectively increasing productivity by reducing the glass to product ratio. The B_2O_3 content of the glass is variable and is optimised for cost/ productivity. B_2O_3 also helps to improve the solubility of fibers in lung fluids, providing an extra margin of safety in the incidence of inhalation.

3. Textile fiberglass

Continuous fibers are used in the manufacture of composites (fiberglass reinforced plastics) and woven fabrics for electrical and fire resistant applications. The most common form is E-glass, which is a calcium aluminoborosilicate. Fiber diameter is typically in the range 7 to 25microns. This is essentially a low or alkali free glass that combines good tensile strength and durability. B_2O_3 is used as a flux to reduce the melting and fiberising temperature through control of viscosity and liquidus temperature. Alkali increases electrical conductivity and reduces chemical resistance; its use is therefore limited to typically, 1.0 to 1.5% maximum. Improvements in melting and fiberising technology have allowed the level of B_2O_3 to be reduced (and eliminated) although fiberising becomes increasingly difficult. It is essential to keep the fiber breakage to a minimum to maintain productivity and control costs.

Major applications are automotive composites (underhood components, body panels, mechanical parts, and interparts for cars or trucks), consumer durables (appliances, business machines, power tools, housewares, sporting goods), construction products (shower stalls, bathtubs, windows, doors, flooring, spas), industrial equipment (glass-reinforced thermoset pipe, containers, tanks, pumps, meters, valves), electrical/electronics (circuit boards, connectors, switches, relays), marine (boat hulls and components), and aerospace applications. Roofing products are primarily asphalt shingles for new and re-roofed residential properties and built-up asphalt roofing for commercial applications. Flooring includes reinforced PVC tiles. Fiberglass can also be found in reinforced gypsum wallboard, industrial filters (air conditioning systems and clean rooms), and concrete reinforcement.

Borates are added as colemanite or boric acid (*Optibor TG®*), some sodium borate such as borax pentahydrate is also added up the maximum permitted alkali content. This aids melting and reduces raw material costs.

4. Borosilicate glass

Borosilicate glass is a general term referring to a host of technical glasses, all having the common characteristic of containing relatively high levels of B_2O_3 (5-20%). Common examples are:

- "Pyrex type" glass, which is used for cookware, microwave dishes, laboratory ware, tableware and lighting/tubing. Its main characteristics are very good thermal shock resistance, good chemical resistance and physical strength.
- "Neutral" or "pharmaceutical" glass, which is used for medical applications. Its main characteristics are high chemical durability and pH neutrality.
- "LCD-TFT" glass for display panels; used in computer screens, TVs and projection equipment.

Borates in glasses

The B_2O_3 content of "Pyrex type" glass and "neutral" glasses are 12.5% and 10.0%, respectively.

Borates are particularly valuable in the production of technical glasses, where there is a requirement to lower or control thermal expansion or achieve chemical durability and neutrality. These glasses are made with to fulfill very specific properties for a wide range of applications, including: cooking and tableware, laboratory and process plant, lighting, sealing, pharmaceutical, optical and fire resistant glazing. They show very low thermal expansion, because using B_2O_3 as a flux allows the alkali level to be reduced. Alkalis increase thermal expansion because, as network modifiers, they break up the silicate structure. During the cooling of a borosilicate glass, the $[BO_3]$ converts into a $[BO_4]$ coordination; the structure become more rigid and shows lower thermal expansion.

Neutral glasses have a very high chemical durability; they can be sterilised at >120°C and give minimal release of alkali allowing use for medical and pharmaceutical applications. These glasses are often based on the Na_2O-SiO_2-B_2O_3 system, and stabilised with alumina to prevent phase separation. The compositions are optimised for the desired property requirements and it does not follow that increasing B_2O_3 will always improve properties. In addition to B_2O_3 and Na_2O, technical glasses may also contain Al_2O_3, BaO and smaller amounts of CaO and K_2O. The alumina improves chemical durability whilst also suppressing the tendency for crystallisation. To achieve the highest possible chemical durability it is necessary to ensure that the glass contains as few non-bridging oxygen atoms as possible. Each mole of Al_2O_3binds one mole of Na_2O. Additional Na_2O should only be sufficient to form $[BO_4]$; the optimum ratio is Na_2O: B_2O_3 = 1:3.

The thermal expansion is dictated by the sodium to boron ratio in the glass. Pyrex has the lowest thermal expansion coefficient of the borosilicate glasses, 33 x10-7/ °C. This contains about 4.5% Na_2O and 12.4% B_2O_3 and is achieved by using a mixture of boric acid and borax pentahydrate in the batch. A higher expansion glass of ~40 x10-7/ °C can be formulated using borax pentahydrate only. Anhydrous borax (*Dehybor*®) is used where enhanced melting is needed to achieve e.g. high furnace pull rate.

The following are examples of borosilicate glasses:

4.1 Heat resistant glasses (cookware and laboratory ware)

Such glasses comprise domestic ovenware/microwave dishes and laboratory ware which must possess a high degree of thermal shock resistance. The thermal expansion coefficients for these glasses are low compared to soda-lime glass, ranging from 33 to 45 x10-7/ °C. Borosilicate flat glass (Borofloat) is produced for fire resistant architectural glazing using float technology.

4.2 Lighting glass

Many of the components used to manufacture lighting products are made of hard borosilicate glass where temperature and thermal shock resistance, or corrosion resistance are important. Borate glass is also used in the frits that seal glass to metal (see 4.4 below). The glass used in the sealed-beam headlights is made of borosilicate glass containing up to 8%B_2O_3. This glass possesses the properties not only of high electrical resistance but of considerably greater strength, chemical durability and thermal shock resistance. The high pressure mercury vapor lamps are employed almost exclusively for street lighting and involve the use of a hard glass to seal to the molybdenum surface. In this application, boric oxide is employed to maintain the necessary thermal expansion required for the molybdenum seal. In the outer soda glass bulb, boric oxide may be introduced for the benefit it incurs on melting rate, strength, chemical durability and flame working properties of the glass. Sodium vapor lamps also use a combination of glasses, some requiring boric oxide for their basic properties and others with a potential use for boric oxide in manufacturing processes. In addition, a sheathing glass of small diameter tubing is required to sheath the copper-clad leads from direct contact with sodium resistant glass layer in order to provide adequate electrical insulation. The sodium resistant glasses contain probably the highest proportion of B_2O_3 (up to 48%) employed in technical glass for large-scale commercial production. The fluorescent lamp is an example of low pressure mercury vapor lamps used for domestic, factory and office and street lighting.

4.3 Thin film transistor liquid crystal display (TFT -LCD)

TFT-LCD is a variant of LCD and has virtually replaced the CRT for television and computer displays. The manufacturing technology has advanced rapidly to allow the production of large TV screens now in common use. The liquid crystal is sandwiched between two thin (0.7mm) glass sheets. The glass is an alkali-earth aluminoborosilicate; ~10% B_2O_3 is added as a flux to control viscosity and liquidus temperature. It is an alkali free formulation and the borate is added as boric acid (H_3BO_3) or boric oxide (B_2O_3). The sheets are formed using two possible methods; the Corning Fusion process, and the float process that uses a molten tin bath on which the glass melt is formed into a flat sheet.

4.4 Sealing glasses

Sealing glasses are used for creating glass to glass and glass to metal seals. This is analogous to soldering where relatively low temperatures can be used to join different materials. These sealing glasses are formulated to have specific properties e.g. glass transition temperature, viscosity and thermal expansion. They will be used commonly in lighting for joining different types of glass and for sealing in metal components e.g. filaments.

Tungsten and molybdenum glass-metal seals are probably the most widely used combinations of glass and metal and encompass the manufacturing of lamps, transmitting valves and other electronic equipment. The choice of glass composition depends on requirements other than thermal expansion - e.g. chemical durability, electrical resistivity and working range, etc. A hard borosilicate glass is required if strain-free seals are to be made to tungsten or molybdenum. Typical sealing glasses are in the family of borosilicate glass compositions that includes Pyrex.

Solder glass is a form of a glass powder suspended in volatile liquids and is applied to the surfaces to be joined. This type of glass has comparatively low softening temperatures, and may contain lead oxide.

4.5 Neutral glasses (ampoules, vials, cosmetic containers, and vacuum flasks)

The ability of boric oxide to give increased resistance to chemical attach either by water, alkali or acid solutions, is most ably demonstrated in the manufacture of neutral glass. This is usually produced in the form of machine-drawn tubing and may be clear, white or amber glass. From these types of tubing are ampoules and vials used in medical profession. These glasses contain boric oxide at an intermediate level around 8% to 10%. Neutral glass also includes cosmetic containers. Chemical and aqueous durability is essential to these products.

5. Miscellaneous glasses

Examples of other borate-based glasses are summarized as follows:

5.1 Optical glasses (prisms and lenses)

In the production of optical glass, the use of boric oxide enables the manufacture of glasses with specific optical properties with respect to refractive index and light dispersion. Some optical glasses are produced in continuous tank furnaces completely lined with platinum to prevent contamination of any kind. The glass melt is sent to automatic press equipment for the production of lens blanks. The boric oxide content normally found in optical glasses can range from nil to about 40% in the more recently introduced rare earth borate glasses.

5.2 Glass microspheres

There are two different kinds of glass microspheres: solid (glass beads) and hollow. Glass beads can be made from soda lime glass or boron-containing glass. Glass beads with a refractive index of 1.5 (low index) are generally manufactured from soda lime glass. They are mainly used for reflectors in road delineation systems. Beads with a refractive index of 1.9 - 2.5 (high index) are made from the B_2O_3/TiO_2/BaO glass compositions (3-5% B_2O_3). The high index glass beads are widely used for drop-on reflectors of runways, taxiways, threshold markings, and holding areas at military and civilian airports.

Glass beads have also been used as a reinforcement-extender in plastics. The microspheres used are usually made of soda lime glass. However, some glass beads for plastics fillers contain borate (3-8% B_2O_3).

Hollow glass microspheres are one of the promising new materials which may be widely used in various fields of engineering. The low density, high compressive resistance, good heat and sound insulation properties make hollow glass microspheres light-weight fillers for composite polymeric materials.

5.3 Glass ceramics

Glass ceramics have a variety of established uses dependent on their uniform reproducible fine-grain microstructures, absence of porosity and wide-ranging properties which can be tailored by changes in composition and heat treatment. Because the glass ceramic process begins with a glass, all the well established glass-forming techniques including blowing, casting, pressing, and rolling can be employed to manufacture components with a variety of complex shapes. Subsequently the glass component is readily converted into a fine-grained polycrystalline ceramic by a controlled nucleation and crystal growth heat treatment. The established compositions and uses of glass ceramics are extensive, including cookware, cooker range tops, heat-resistant windows and telescope mirror blanks. A good example of a borate glass/ceramic is Macor (Corning), containing 8.5% B_2O_3, which is machinable and has applications as precision electrical insulators, windows for microwave tubes and gamma ray telescope frames.

In recent years, new compositions, processing methods and applications have begun to emerge. Among the recent developments considered are new phosphate-based compositions, the use of sol-gel processing, glass ceramic matrix composites, glass ceramics in microelectronics packaging, glass ceramics bonded to metals and joining media, high-strength and high-toughness materials and machinable compositions in the calcium-phosphate-based glass ceramic system.

New optical glass ceramics have recently been developed. These include integrated lens arrays, luminescent materials, and zero-expansion passive optical materials, the latter recently used in the ring-laser gyroscope. An interesting new range of glass ceramics with very low thermal expansion has been recently reported in the calcium, strontium and barium aluminoborate systems. These glass ceramics were produced from powdered glass compacts, sintered and crystallized below 1000°C. They have high strength, high fracture toughness and excellent electrical properties. Potential applications in substrates for microelectronics packaging, sealing frits for low-expansion materials, coatings for metals and thermal shock resistant ceramics.

5.4 Art glass

Boric oxide is often used the manufacture of high quality hand-made decorative ware. The glass is a modified soda-lime-silica formulation; the borate improves the workability of the glass.

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5.5 Soda-Lime-Silica glass

Soda-lime-silica is the most commonly produced glass in the world, representing >80 of total production. Applications include both containers and flat glass, together with decorative ware. In the 1950's, many glassmakers included a small amount of B_2O_3 (0.3-1.5%) additions to their glass formulations. However, borate is rarely used in the modern soda-lime glass formulations.

In certain applications the addition of small level of borate gives benefits in terms of improved resistance to moisture corrosion, increased furnace pull, lower melting temperature and increased machine speed. It tends to be used in the manufacture of high quality containers e.g. for cosmetic applications.

Boric acid is used as an interleavant for flat glass to prevent atmospheric moisture corrosion during storage.

5.6 Vycor glass

Low expansion ware such as Vycor contains more than 90% silica. This glass is produced by etching and heating of a borosilicate glass. The first step in their manufacture is to produce a glass which may contain up to 30% B_2O_3. This glass is subjected to a special chemical treatment which dissolves nearly all constituents except silica. A skeleton of silica containing practically nothing but a little residual boric oxide is left. Heat treatment consolidates this skeleton to a clear glass, the physical and chemical properties of which approach those of pure silica, i.e. with a very low thermal expansion coefficient (0.8 x 10-6/°C), excellent thermal shock resistance and high chemical durability. Vycor is used to join quartz with Pyrex glass and also used to produce material of controlled porosity for bio-technical applications. Vycor was originally used for chemical ware and lamp envelopes. It was also used as re-entry protection tiles for the early space shuttles. It is still also used in military and aerospace applications.

5.7 Space protection glass

A cesium borosilicate glass has been used to protect solar cells on satellites from the harmful radiation encountered in outer space.

5.8 New specialty glasses

Specialty glasses clearly include optical glasses in bulk or fibrous form as well as glasses used for pharmaceutical or electronic packaging. Use in optical applications dominates, e.g. television, optic and ophthalmic, optical communications and IC photomasks. It is directly linked with the huge optoelectronic/electronic industries which can afford the immense resources for research and development. Other new specialty glasses including photochromic glass, photosensitive glass, laser glass, conductive film substrate, dielectric glass, and graded index glass are under development. In addition to an expansion of the range of application fields, research and development continues for in established applications.

For example, in automotive glazings the trend to increase the size of the car windows has expanded the market and use level for specialty glasses for heat protection, security and fogging problems. Certain residential building standards requiring low emissive coatings or triple glazing as well as new European standards for lowering energy consumption and CO_2 output will favor the extensive use of coated architectural glasses.

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About U.S. Borax

U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 500 customers with more than 1,700 delivery locations globally. We supply 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles east of Los Angeles. We pioneer the elements of modern living, including:

- Minerals that make a difference: Consistent product quality secured by ISO 9000:2001 registration of its integrated quality management systems
- People who make a difference: Experts in borate chemistry, technical support, and customer service
- Solutions that make a difference: Strategic inventory placement and long-term contracts with shippers to ensure supply reliability

About *20 Mule Team*® products

20 Mule Team® borates are produced from naturally occurring minerals and have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.