A Borate Supplier's View of the Glass Industry

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Abstract. Borates find a wide variety of industrial uses ranging from fertilizers to fire retardants. The manufacture of vitreous products, including various types of glass and ceramic glazes, represents the single largest application area, accounting for more than half of the roughly 1.7 million B_2O_3 equivalent tons consumed globally by industry. Significant among these consumers are fiberglass used for insulation and composites, borosilicate glasses used for solar water heaters, lighting, and laboratory and kitchen wares, flat-panel glass used in liquid crystal displays, and other specialized glasses. The production of borates and their history in glass making will be discussed, as well as potential future uses such as high-dielectric glass layers for supercapacitors.

Introduction

Borates find a tremendous range of industrial applications in products as diverse as fertilizers, industrial fluids, construction products, and fire retardants.(1) However, the manufacture of various types of glass represents the largest end use sector for industrial borate products. Boric oxide, supplied in the form of metal and non-metal borate products, is important to the glass industry because it provides combinations of desirable properties that are either technically impossible or uneconomical to achieve using other additives.

Many academic glass scientists around the world are engaged in important studies of glass formation, structure, and properties. These studies often involve glass compositions that are primarily of scientific interest or glasses that are produced commercially in relatively small volumes. The borate industry, on the other hand, is mainly concerned with borate glasses produced on large industrial scale, typically requiring thousands of tons per year of borate products. Thus, the perspectives from these two vantage points can be very different. The objective of this paper is to provide a brief overview of the glass industry from a borate supplier's perspective.

The manufacture of borosilicate glasses, including heat resistant, optical, sealing, lighting, and chemically inert types, as well as different kinds of fiberglass, are all well established markets for borate products.(2) In recent years, the manufacture of glass used for electronic displays, including flat screen televisions, computers, mobile devices, appliances, advertising displays, and devices incorporated into modern architectural designs, has become a major use of borates. Borosilicate glass is also increasingly used in solar energy applications. In addition, borates are extensively used the production of ceramic glazes and porcelain enamels having increasing importance as a result of global urbanization trends.

Borate Sources and Products

More than 200 boron-containing minerals are known, but relatively few of these have commercial importance.[3-6] Only four minerals provide the source of more than 90% of the world's industrial borate products. These are the sodium borate minerals borax and kernite, the sodium–calcium borate ulexite, and the calcium borate mineral colemanite. Various magnesium borate minerals and the calcium borosilicate mineral datolite provide the remaining industrial borate production. These minerals are extracted largely in California and Turkey, and to a lesser extent in China, Russia, and South America. Compositions and principal geographic origins of the commercially important borate minerals are listed in Table 1. These primary borate minerals are used to produce refined borate products. The refined borate products most commonly used in large scale commercial glass manufacture are listed in Table 2. [7,8] It can be noted that traditional borax, found as the mineral tincal, is the decahydrate (sodium tetraborate decahydrate). While this is a commercial product that is sometimes used in glassmaking, borax pentahydrate (sodium tetraborate pentahydrate), which occurs in nature as the mineral tincalconite, is much more widely used in large-scale glass manufacture. This lower hydrate, which is produced from sodium borate minerals, is generally more economical, easier to handle, and more efficient to melt than the higher hydrate. The mineral tincal actually converts into the more stable lower hydrate tincalconite upon expose to dry air.

Table 1. Commercially important borate minerals

Mineral	Chemical Formula	Oxide Formula	Wt% B_2O_3	Geographic Origin
Borax (tincal)	$Na_2B_4O_7 \cdot 10H_2O$	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	36.5	USA, Turkey, Argentina
Kernite	$Na_2B_4O_7 \cdot 4H_2O$	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$	51.0	USA, Turkey
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$	43.0	Turkey, S. America
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	50.8	Turkey
Hydroboracite	$CaMgB_6O_{11} \cdot 6H_2O$	$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$	50.5	Argentina
Datolite	$Ca_2B_2Si_2O_9 \cdot H_2O$	$2CaO \cdot B_2O_3 \cdot 2SiO_2 \cdot H_2O$	21.8	Russia

Table 2. Borate products used in large scale commercial glassmaking

Product	Chemical Formula	Oxide Formula
Borax Pentahydrate (sodium tetraborate pentahydrate)	$Na_2B_4O_7 \cdot 5H_2O$	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$
Boric Acid	$B(OH)_3$	$B_2O_3 \cdot 3H_2O$
Anhydrous Borax (anhydrous sodium tetraborate)	$Na_2B_4O_7$	$Na_2O \cdot 2B_2O_3$
Boric Oxide	B_2O_3	B_2O_3

Brief history of borates in glass

Smith reviewed the history of borate use in glassmaking.[9] There is some controversy regarding the earliest use of borates in this application. Use by ancient artisans would have required ease of attainment, either through proximity to borate mineral deposits or to major trade routes. Borates were transported along ancient trade routes between the Far Eastern and Islamic worlds, where borates were used in metallurgy by Arab goldsmiths. The likely source of this borate was Tibet, which contains borate deposits accessible on the surface. There is some evidence of early borate use in the Middle East prior to 800 AD, suggesting that the technology may have spread initially from that region.[10] One of the earliest documents on borates in glassmaking is a Chinese document from 1225 that refers to Arab glassmakers using borax to make glass that resists thermal extremes without cracking, suggesting that this advantages of borates has been known for a long time.[10] Possibly the earliest uses of borates in vitreous applications was in ceramic glazes. Pot shards from the Liao dynasty (916-1125 AD) have been found decorated with a borate glaze.[11] Previous to this period, boron-free lead oxide glazes were common.

As the melting point of pure silica is about 1720 ºC and the resulting melt has high viscosity, manufacture of articles made from pure silica glass was prohibitive. Therefore, glass makers continued to seek glass batch additives allowing lower melt temperatures as well as higher quality glass with lower dwell times, resulting in the early development of soda lime type glasses. By the 17th century borates were being used in Germany as flux in glass melting for the fabrication of artificial gems. However, borates were little used in glassmaking as they remained a scarce and expensive commodity.

The discovery of borates in North and South America in the mid-19th century resulted in greatly improved availability and lower prices. This prompted further study investigations, ultimately leading to greater understanding of the advantages of borates in glassmaking. The first modern borosilicate glass was developed by Otto Schott in late 19th century and marketed as a commercial product under the name Duran® (a trademark of the Schott AG). Wider recognition of the particular advantages of borosilicate glass with respect to its fluxing properties and the ability to improve the thermal characteristics and durability of glass led to increased use in early 20th centuries with brands such as Pyrex® (a trademark of the Corning Inc.). This was followed by further increases in the 1930's resulting from the growth of fiberglass industry and wider household use of borosilicate glass. Borate was used 1937 as a component of the process for making Vycor® (a trademark of the Corning Inc.), which made use of the limited immiscibility of boric oxide in silica in form phase separated glass compositions.[12] Borates have since been used in an ever increasing number of applications as the glass industry has found new ways to take advantage of the special benefits imparted to glass by borate, which both improvements in glass processing as well as finished product quality.

Generic borosilicate glass, such as those known as Pyrex® and comparable types, typically contain 8-15% B_2O_3. This B_2O_3 can be supplied to the glass batch as either boric acid or commercial technical grade amorphous boric oxide. Other borosilicate glass varieties that can tolerate higher alkali levels can utilize borax pentahydrate as the borate source.

Modern borate glasses

Millions of tons of borate products, with a B_2O_3 equivalent content of more than 1.7 million tons, are used annually by modern industries around the world. More than half of this borate volume is used in the manufacture of various types of glass. The manufacture of fiberglass products, including both insulation and textiles varieties, still represents a large sector of this market; but many new high tech applications for glass that are essential to modern living have increasing importance. Borosilicate glass is increasingly used manufacture of flat panel displays used in large screen televisions, mobile devices, and other advanced technologies. In addition, borosilicate glasses are used in thermal solar devices for heating water and generating electricity and also find a range of industrial and household uses. Some of these uses include the following:

- advanced lighting devices
- heat resistant kitchenware and cooking panels
- laboratory glassware and equipment
- neutral glass pharmaceutical vials and tubing
- precision optics for instruments and medical devices
- porcelain enamel products
- ceramic frits and glazes

Typical composition ranges in common commercial glasses are given in Table 3.

Table 3. Typical Borate Content of Commercial Glasses

Glass Type	wt % B_2O_3
Fiberglass	
Textile (E-glass)	0-10
Insulation	4-8
TFT (flat panel display) glass	8-10
Optical glass (crown glass)	~10
Sealing glass	8-30
Heat resistant (e.g., Pyrex®)[a]	8-15
Vycor® [a]	20[b]
Porcelain enamel (frit)	10-20
Ceramic frit	0-15

[a] Pyrex and Vycor are registered trademarks of Corning Inc.
[b] Percent B_2O_3 in the phase separated glass before leaching to form Vycor.

Insulation fiberglass. Insulation fiberglass (IFG) or glass wool is a major insulating material used in residential and commercial construction and plays a major role in energy conservation. Fiberglass is also widely used in sound insulation for buildings, automobiles, machinery and appliances. Composed of thin intermingled fibers spun from molten glass, IFG traps and holds air to form an effective thermal barrier. IFG is also widely used for acoustical insulation, finding extensive use in automobiles and consumer appliances.

IFG is a soda lime borosilicate glass, formulated to satisfy the performance requirements of the finished product as well as improving manufacturing requirements.(13) The presence of borate in the glass composition lowers the liquidus temperature and viscosity of the glass melt and reduces surface tension, assisting in fiber formation and reducing fiber breakage. Reduced liquidus temperatures can be achieved by addition of alkali metal, e.g., Na_2O, but reliance of this component alone results in poor corrosion resistance of the final product. Corrosion resistance can be improved by Al_2O_3, but this result in increased liquidus temperatures. Thus, borate is added to the IFG formulation to balance these effects and achieve maximum benefits in terms of practical fiberizing conditions and final product durability. Borate in the composition is believed to reduce the mobility of alkali from the bulk glass to the surface, reducing fiber degradation under humid conditions. Borates also give resiliency to fiberglass, allowing it to recovery after the prolonged compression required during transport. In addition, the borate component in IFG improves the R-value or thermal insulating performance of the fiberglass.

Fiberglass contributes significantly to the energy efficiency and sustainability of residential and commercial buildings. According to the North American Insulation

Manufacturers Associate, NAIMA, fiberglass installed in buildings saves up to 12 times as much energy per unit weight in the first year of use as required to manufacture it.[14] Buildings are major contributors to greenhouse gas emissions due to energy consumption for heating and cooling. Since fiberglass can greatly reduce the energy requirements of buildings, demand for this product is likely to increase. As this occurs, reformulation to higher B_2O_3 compositions can help alleviate possible capacity constraints of fiberglass manufacturers.

The borate content of insulation fiberglass is typically 4-8% B_2O_3. It is typically added to the glass batch raw materials as borax pentahydrate, ($Na_2B_4O_7 \cdot 5H_2O$ = $Na_2O \cdot 2B_2O_3 \cdot 5H_2O$), although beneficiated mineral borates, such as ulexite, are also used.

Textile fiberglass. Another type of glass that often contains borate is textile fiberglass (TFG), also called E-glass.[15,16] This is a continuous strand lime aluminosilicate glass having little or no alkali metal content. This type of glass combines good tensile strength with high durability for use in many commercial applications. The low sodium content of TFG limits its electrical conductivity, allowing for use as a reinforcement material in electronic circuit boards. It is also extensively used as reinforcement in automotive, marine, household, and construction products, including auto bodies, boat hulls, appliances, housewares, power tools, sporting goods, tank and pipe wrapping, roofing shingles, and flooring tiles. Textile fiberglass is also used in reinforced gypsum wallboard and heating/air conditioning filters.

Borate is used in TFG compositions as a flux to reduce melting and fiberizing temperatures through control of viscosity and liquidus temperature. Since the presence of alkali metals in glass increases its electrical conductivity and reduces its chemical resistance, they are usually limited to 1.0-1.5%. Although TFG is now widely used as reinforcement for polymer composites used in construction products, the low sodium requirement needed for electronic applications still applies in most cases.

The primary borate products used in the manufacture of textile fiberglass are either colemanite ($Ca_2B_6O_{11} \cdot 5H_2O = 2CaO \cdot 3B_2O_3 \cdot 5H_2O$) or boric acid [$B(OH)_3 = B_2O_3 \cdot 3H_2O$]. A limited amount of sodium-containing borate, such as ulexite and borax pentahydrate, may also be added up to a maximum permitted alkali content to aid in melting and reduce raw material costs.

Specialized borosilicate glasses. Borosilicate glass is a general classification for glasses having the common characteristics of containing relatively high levels of B_2O_3. Borates impart many unique properties to glass, such as thermal shock resistance, chemical inertness, and durability. Few other glass additives provide the same combination of attributes. Physical treatments, such as coatings and tempering, can be applied to glass to duplicate some of these properties, but are often problematic and costly. Thus borosilicate glasses find many uses including kitchenware, such as coffee pots and oven-to-table cookware, lighting products, metal-to-glass seals, laboratory ware, optical lenses, glass tubing, pharmaceutical vials, and many other applications requiring durable, inert, and thermal change resistant glass. Borosilicate glass is also used in solar-thermal electrical generating and water heating systems.

Most borosilicates glasses require the use of refined borate products and cannot tolerate the impurity levels found in mineral products. The primary borate products used in the manufacture of borosilicate glasses are boric acid, boric oxide, borax pentahydrate, and anhydrous borax.

Borosilicate glass is used for optical elements in a wide range of instruments and devices. This application requires glass having low refractive index and optical dispersion that can be fabricated with precise curvatures that are minimally affected by temperature changes. Precision instruments, from telescopes to medical devices, rely on borosilicate glass to meet these requirements.(17)

Ceramics

Closely related to glass, ceramics represents another significant market for borates. Increased use of ceramic tile surfaces and porcelain enamel household products relates to global urbanization trends and the desire for higher quality, durable, functional, and esthetically pleasing architectures and conveniences.

The ceramics industry generally uses borates in the form of frit, which is a powdered glass employed in the formulation of ceramic glazes and porcelain enamel compositions. Borates are also applied to the surface of ceramic roofing tiles before firing to improve appearance and performance, including freeze-thaw resistance. In cases where borosilicate frits are employed, as in the manufacture of many types of colored floor and wall tiles and high performance enamels, the ceramic industry generally uses boric acid, borax pentahydrate, or colemanite as raw materials.

Notable developments in the glass industry

Electronic panel displays. The emergence of modern display technologies has resulted in considerable growth in demand for optically clear, thin, and nearly flawless glass having appropriated physical properties for component use. Large flat panel televisions, computer monitors, mobile phone, and appliance displays all require high-quality, thin glass, and the technology for manufacturing large continuous sheets with minimal defects. Modern display technologies make use of flat-panel glass in LCD and OLED devices, including touch screen technologies. Not only does borosilicate glass meet the technical requirement for internal device components, but it also provides the strength and durability needed for protective surfaces.

Thin Film Transistor-Liquid Crystal Display (TFT-LCD) glass is used in modern displays that have largely replaced cathode ray tubes (CRTs) for televisions, computer displays. The ability to fabricate these devices in very thin profiles has lead to their increasing use in advertising signs, automotive displays, and appliances. Increasing demand for ever larger television and advertising displays has resulted in rapid advancements in technology for this type of glass.

LCD displays are constructed of multiple layers that may employ different types of glass. The TFT glass, which may be less than 0.7mm in thickness, is surface deposited with a TFT-LCD array. This glass must be free of defects and nearly free of alkali metals. The requirement for low alkali is to avoid adverse performance effects that can result from diffusion of alkali ions to the glass surface where they can contaminate silicon of the TFT.(17) Borate is added to this alkaline earth aluminoborosilicate glass, which contains 8-10% B_2O_3, either as boric acid or boric oxide. OLED devices utilize organic light emitting diode arrays instead of light crystals arrays deposited on panel glass.

Specialized borosilicate sealing glasses are also used to seal together the component layers at the edges of display panels. OLED materials, in particular, are easily oxidized when exposed to air and moisture. To prevent such oxidization, the OLED must be well encapsulated in glass.

In addition, there is increasing use of borosilicate compositions for display cover glasses. These glasses are chemically toughened using surface ion exchange technologies to impart excellent scratch resistant properties to display devices.

Solar thermal glass. Solar thermal is among the most efficient solar energy capture methods. This rapidly growing technology employs solar energy collectors designed to capture heat from sunlight for specific applications. Roof-top mounted solar thermal devices are widely used to heat water or air for residential use and large-scale concentrated solar power (CSP) installations are used for electric power generation. Thermal solar devices currently produce hot water for millions of households and CSP is a rapidly growing technology that already adds hundreds of megawatts of power to electric grids.

Many solar thermal devices employ borosilicate glass collector tubes surrounding metal tubes through which a heat transfer fluid, which may reach temperatures of several hundred degrees Celsius, circulates. The tubes are arranged in a concentric configuration with the space between the tubes evacuated. These tubes may run along the axis of parabolic reflector troughs in large-scale installations or have metal reflector plates positioned inside the glass tube in smaller-scale devices. Attributes of borosilicate glass that make it particularly suitable for this application include:

1) Low emissivity, preventing absorbed heat from being re-irradiated away,
2) High thermal stability, preventing thermal shock due to high extremes.
3) Low linear expansion coefficient
4) High durability and weatherability for long outdoor life.

There is also interest in using borosilicate as cover glass for photovoltaic devices. This interest stems from the ability of borosilicate glasses to form extreme tough, scratch resistant sheets, as used for display devices, with good optical transmission properties.

Other applications of dielectric glass. Aside from their existing use in electronic displays, borosilicate glasses shows promise as a dielectric materials for new generations of high energy capacitors known as double-layer capacitors, supercapacitors, and ultracapacitors. These devices may play important roles in novel power storage applications including for electric vehicles and renewable energy systems. A new generation of these devices utilizes high dielectric constant borosilicate glass as dielectric layers. For example, a Pennsylvania State University research group achieved a capacitor having a breakdown strengths of 12 MV/cm and energy density over 35 J/cm^3 using a barium boroaluminosilicate glass.(19)

Conclusions

Borates have long history of use in glassmaking. The incorporation of boric oxide into glass formulations allows combinations of properties that are technically impossible or prohibitively expensive to achieve with other additives. Because of the unique effects of boric oxide, including improved batch melting and enhanced physical qualities and durability, borosilicate glasses are valuable for use in many technology driven products and devices, including advanced displays and solar thermal energy applications.

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