BROCHURE

Borates in glazes and enamels

In glazes, boric oxide reduces melting temperature and improves glaze/body. It enhances glaze appearance and can improve chemical and mechanical durability. Sodium borate is used to produce low viscosity frits for enamelling of metals, principally steel, cast iron, and aluminium.

Ceramic glazes can be divided into three categories, depending on the substrate to which they are applied:

- Tiles: Wall, floor, and sometimes clay roof tiles
- Tableware: Porcelain, china, stoneware, and earthenware
- Sanitaryware: Vitreous china and porcelain

Glazes for sanitaryware do not contain borates. Many tableware glazes do contain borates, but by far the largest consumers of boric oxide (B_2O_3) in ceramics are glazes for wall and floor tiles. Most tile glazes contain B_2O_3. The raw materials that supply this oxide are soluble in water and so cannot be used directly in glazes. They must first be rendered insoluble by incorporating them in so-called ceramic frits. This is the primary function of frits.

Frits are materials of a glassy nature, composed mainly of SiO_2, which are obtained by fusing different crystalline materials at high temperatures (around 1500ºC). The second function of ceramic frits is to “pre-melt” the ceramic glaze before the glaze ring process itself, and this helps to obtain a high glaze gloss even when using very short firing cycles.

The boric oxide content of frits depends on the type of glaze for which the frits are intended. In general:

- For glazes used in ceramic tile manufacturing process, the higher the ring temperature the lower the B_2O_3 content of the frit
- A high temperature and/or long ring cycle means a high heat work, and this reduces the amount of B_2O_3 allowable in the glaze
- With excessive B_2O_3 content, pinhole defects can result

Process	B_2O_3 content in the frits (% by weight)	Firing conditions (temperature/time)
Wall tiles: Traditional double firing	8-20	(980-1000)ºC / (360-720) min
Wall tiles: Fast double firing	4-10	(1060-1080)ºC / (30-55) min.
Wall tiles: Fast single firing	3-6	(1100-1120)ºC / (35-55) min.
Stoneware floor tiles: Fast single firing	0-3	(1140-1180)ºC / (35-55) min.

The table above lists the different tile manufacturing processes together with the B_2O_3 content of the frits used and the standard firing cycles.

Traditional double firing has virtually disappeared from all regions of the world due to higher energy and labor costs, and has been replaced by single ring. The type of frit and borate suitable for double and single ring varies, as well as the average B_2O_3 content of the frits:

- In double firing, sodium oxide (Na_2O) brings benefits and the most appropriate borate for producing these frits is a sodium borate
- In single firing (especially for wall tiles), Na_2O is often not desirable, and frits for use in this type of glaze are normally formulated with a non-sodium borate

Benefits of B_2O_3 in glazes

Boric oxide can form a glass on its own, but its dual use is as a flux and network former. The value of boron as a flux has been recognised for many years—it has become exceptional for boron not to appear in recipes for low temperature (ie, <1100ºC) glazes. Borates have an important place in glaze technology and are the second most important network-former after silicon. The benefits of boric oxide in glazes are:

A flux, that does not increase thermal expansion coefficient

This is the main reason for using B_2O_3 in tile glazes, and is true for B_2O_3 contents below 12%. It enables the production of glazes that behave appropriately at the temperatures used in current manufacturing processes, and yields lead-free ceramic tiles. There are many other fluxing oxides (eg, alkalis, alkaline earths) but all increase thermal expansion coef cient since they are network modi ers rather than formers. The one exception is lead oxide, which can be a former or modifier. However, owing to its toxic character, the use of PbO was suppressed some time ago. In ceramic tiles, the use of lead has disappeared from all frits except a few that are used for low temperature (third firing) decoration.

B_2O_3 reduces surface tension, does not crystallize from melts, and tends to hinder the crystallization process of other phases. These effects are useful in the production of glazes with high gloss, since low surface tension gives a flat glaze surface and most crystalline phases present in a glaze reduce the surface flatness and the gloss. Boric oxide increases the gloss or brilliance of a melt but does not increase the refractive index. Borates also have a strong solvent action on coloring oxides, and boron glazes are good bases for glazes colored by dissolved transition metal oxides.

Can improve chemical and mechanical durability

Correctly used, B_2O_3 can greatly improve chemical durability. In general at appropriate levels (<12% in lead-free glazes) the effect is bene cial, but at excessive levels it is negative. Mechanical strength and scratch resistance are improved after increasing the level of borates in a glaze. There are many types of glaze which would be impossible to produce without B_2O_3—for example, glazes formulated for single and double-fire wall tile manufacture. In this case, removing B_2O_3 from the frits would make it impossible to fabricate certain types of ceramic tiles, using present production cycles.

Frits for the enamelling of steel

Enamel frits are different from ceramic frits since the properties of the substrate are quite different. Ceramic bodies are typically red at temperatures above 1100°C and have a low thermal expansion coef cient. Enamelled steel on the other hand is red at around 800°C and has a thermal expansion coef cient twice that of ceramic bodies. This means that enamel frits are much softer (less viscous) than ceramic frits, and have a much higher thermal expansion. This is achieved by using more B_2O_3 and much more Na_2O in enamels than in ceramics (see table below).

Parameter	Ceramic	Enamel (steel or cast iron)
Typical B_2O_3 content	5% (SFF*)	14%
Typical Na_2O content	0.5%	14%
Preferred borate	Non-sodium	Sodium
Predominant furnace type	Continuous	Batch
Fusion temperature	1500°C	1250°C
Firing temperature	>1100°C (SFF*)	~ 800°C
Quenching method	Water	Chilled rolls

Copper and aluminum can also be enamelled using borate-based frits, but the main use of enamel frits is on steel and cast iron. *SFF = single fast

Product information

Optibor® TG boric acid is commonly used as the primary B_2O_3 source for production of frits for single-fired wall tiles, and other frits which are lead-free. It is a granular, free-flowing product with excellent bulk handling properties, and has a high and consistent level of B_2O_3.

Neobor® borax pentahydrate is the most commonly used source of B_2O_3 for frits for double firing, and some floor tile frits where sodium is a benefit. It has a high and consistent level of B_2O_3 (~49%) and very low and consistent impurity levels. It also contains 21% Na_2O which is a powerful flux in frits. *Neobor* is a free-flowing granular product; it is chemically stable and has excellent bulk handling characteristics.

Dehybor® anhydrous borax is the third option for frits. It is most attractive for enamel frits where the B_2O_3 content of the raw material batch is very high. Using *Dehybor* in place of *Neobor* significantly reduces the loss on ignition of the batch, which reduces furnace emissions and energy consumption, and increases furnace productivity. *Dehybor* is a granular, free-flowing product with excellent bulk handling properties and a very high B_2O_3 content (69%), the remainder of the composition being Na_2O.

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 650 customers with more than 1,800 delivery locations globally. We supply around 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles.

About 20 Mule Team products

U.S. Borax produces the *20 Mule Team*® borates family of products from naturally occurring minerals and have an excellent reputation for purity and safety when used as directed. Borates are key ingredients in a number of industrial applications including fiberglass, glass, ceramics, batteries and capacitors, wood preservatives, and flame retardants.

High quality, high reliability, high performance borate products. It's what we're known for.

U.S. Borax products for glazes and enamels

Borax Decahydrate

Dehybor®

Neobor®

Optibor®