frit consortium

CONSIDERATIONS ON THE USE OF BORATES IN THE MANUFACTURE OF FRITS AND THE AUTHORISATION PROCESS UNDER REACH

Introduction

The present document summarizes the position of the Frit Consortium regarding the possible inclusion of borates in the 6th list for authorization. The Frit Consortium considers that according to the indications of the REACH Regulation, the use of borates in the manufacture of frits should be considered as an intermediate use, and it should therefore be excluded from the authorization process. This position is in line with the indications given by ECHA [1].

Definition of frits and description of the frits sector

According to their classification as a differentiated substance under CAS No. 65997-18-4 and EINECS No. 266-047-6, Frit is a substance, produced by rapidly quenching a molten, complex mixture of inorganic raw materials, confining the atoms of those raw materials as non-migratory components of glassy solid flakes or granules that constitute the newly created substance. Frits are amorphous vitreous materials comprising mainly chemical oxides, which are the most important glass formers of technical and industrial interest in the production of glazes to be used for example in ceramic tiles.

The frits sector is concentrated mainly in Spain and in other countries like Italy, Belgium, UK, Poland and Czech Republic. The Frit Consortium was constituted on June 4th, 2009, with headquarters in Castellon, Spain, and currently groups 32 companies, all of them are aware of the need to combine progress and economic development with technological innovation, employment creation and the protection of safety and environment. The frits sector has done a considerable effort in R&D in order to achieve new products and quality improvement, with special focus on compliance with relevant environmental legislation such as the REACH Regulation, IPPC or trade emissions, among others.

The importance of the frits sector related to the uses of borates is well known, as was indicated in the Danish proposal of inclusion of disodium tetraborate anhydrous in Annex XV of REACH [2][1]. Table 4 of the mentioned document describes that glass and ceramics amount to 65% of the relative uses of borates in industry. Moreover, this document specifies that the demand for borates in the frits and ceramic sector has increased in the past years, and that the expected tendency is a 2-4% increase per year over the next five years. Besides, other reports prepared by the European Commission specifically state that “one of the largest uses of borates in Europe is in frits and glazes for ceramics [3].

1 Even though disodium tetraborate anhydrous is used in this document as the example, the rationale can be applied to all borate substances under consideration, i.e. including boric acid, diboron trioxide.

Manufacture of frits

The manufacture of frits is covered by the IPPC Directive (2008/1/EC) and is technically explained in the BREF-Document on Best Available Techniques in the Glass Manufacturing Industry [4]. Frits are manufactured using melting furnaces with a production capacity under 30 tons/day. The process is normally operated continuously (water or air cooled furnaces) but also discontinuous operation exists, i.e. in batches in rotary water cooled furnaces.

In the manufacture of frits, the starting materials are formulated and melted at 1350 to 1550 °C ensuring the vitreous matrix. As a second step the material is cooled suddenly and, thus, turned into a solid material fragmented into insoluble compounds (fritting process). Figure shows the frits production process.

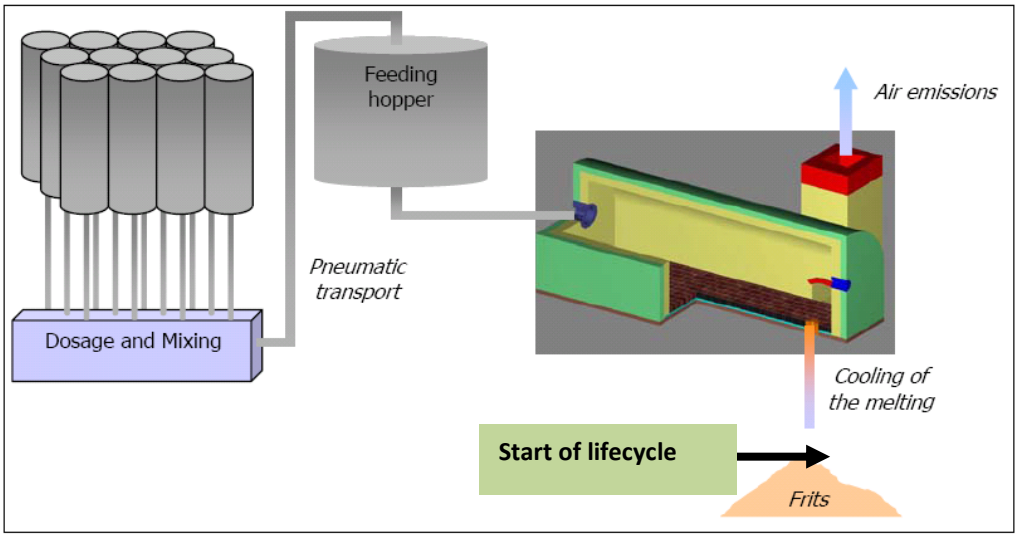

Figure 1: Manufacturing process of frits

Frits are used mainly to prepare glazes or enamels, which are then used to provide a glassy surface for protective and/or decorative purposes to a wide variety of articles. In many cases this surface is the only part of the article which is visible, and therefore it constitutes a critical part of the article. During the preparation of these articles (e.g. ceramic tiles, dinnerware, hollow glassware, automotive and architectural glass, electronic devices), different processes such as firing take place, where the glaze or enamel becomes tightly fixed to a support, with the following consequences:

- Formation of a compact, strong and resistant structure;
- Reaction and immobilization of the inorganic raw materials into complex compounds (silicates) characterized by a high chemical inertia.

Use of borates in frits

Boron is introduced in the formulation of frits by means of different raw materials that fall in the generic description of "borates" (e.g. boric acid, boric oxide, disodium tetraborate…). Borates are well-known to contribute decisively in the formation of the vitreous structure of the frit and other similar materials (e.g. glass). Together with other compounds (e.g. silica), borates are typically grouped as "network formers" due to their recognised ability to act as generators of the glassy matrix that constitute the frit. The generation of Si-O-B bonds are particularly known to take part in the generation of the vitreous matrix [5] [6].

Intermediate use of borates in the manufacture of frits

During the manufacturing process of frits, borates are chemically transformed into a complex solid solution in the form of a vitreous matrix containing boron. During the different chemical reactions that take place in the process, chemical bonds of the raw materials are broken, and atoms are rearranged within the vitreous structure of the newly formed substance, i.e. the frit. As explained above, the structural properties that borates bring to frits are extensively recognized in scientific literature. For this reason, it is considered that the use of borates in the manufacture of frits match the definition of intermediates as indicated in Article 3(15) of the REACH Regulation.

References

[1] Draft background document for Disodium tetraborate, anhydrous; Document developed in the context of ECHA's sixth Recommendation for the inclusion of substances in Annex XIV, ECHA, September 2014.

[2] Proposal for identification of a substance as a CMR Cat 1 or 2, PBT, vPvB or a substance of an equivalent level of concern; Disodium tetraborate, anhydrous, submitted by Denmark, February 2010.

[3] Assessment of the Risk to Consumers from Borates and the Impact of Potential Restrictions on their Marketing and Use, European Commission, DG Enterprise and Industry, November 2008.

[4] Best Available Techniques (BAT) Reference Document for the Manufacture of Glass, Joint Research Centre, 2013.

[5] Taylor, J. R.; Bull, A.C. Ceramics glaze technology. Oxford: Pergamon Press, 1986.

[6] Hubert, M.; Jans Faber, A. Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B (volume 55, Number 3, pp 136-158)