Position Paper of the European Glass Industries on the Proposed Inclusion of Arsenic Acid on Annex XIV

Brussels, 18 September 2012

Glass manufacturers support the REACH Regulation and believe that a reduction of the risk associated with worker exposure and the environmental impact of dangerous substances is welcome in the EU Market. Glass Alliance Europe welcomes the opportunity to provide its contribution to the public consultation on the insertion of arsenic acid in ECHA's 4th recommendation for the authorisation list.

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FUNCTION OF ARSENIC ACID IN THE PRODUCTION OF GLASS

The Draft background document for Arsenic acid (Document developed in the context of ECHA's fourth Recommendation for the inclusion of substances in Annex XIV) dated from 20 June 2012 as published on ECHA's webpage, refers to Arsenic acid being *"used as fining agent in the manufacture of speciality glass"* (see page 2, point 2.2.2.2 of the above mentioned document). Furthermore the document states as follows: *"Although in the registrations considered as use of the substance as an intermediate, this use of arsenic acid rather appears to be as a "processing agent", similar to the use of diarsenic trioxide (As_2O_3) in glass making (Annex XV, 2011; ECHA, 2010). In glass production arsenic acid has the same function as diarsenic trioxide (As_2O_3), i.e. fining agent. Both substances can and appear to be used interchangeably in the glass sector. For As_2O_3 it was concluded that there seem to be problems regarding* ***occupational exposure control*** *in (parts of) the glass industry although there is uncertainty about the extent (ECHA, 2010)."* (see pages 2 and 3 of the above mentioned document). The document also refers to Arsenic acid and Diarsenic trioxide being used as fining agents to remove bubbles from the glass melt (see page 3, point 2.2.2.3 of the document).

As will be shown in the following paragraphs, these statements do not display the role of Arsenic acid in the "synthesis" of speciality glass. Arsenic acid as well as Diarsenic trioxide (As_2O_3) and Diarsenic pentaoxide (As_2O_5) are used in the glass production as intermediates under the REACH Regulation.

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The nature of glass

Glass is a substance of variable composition, which for simplicity is expressed by convention in terms of oxide of the constituent elements (the oxides: SiO_2, Na_2O, CaO, B_2O_3, etc). Although conventionally glass compositions are expressed as oxides of the different elements, **glass is a non-crystalline or vitreous inorganic macromolecular structure**, which does not show behaviour of the individual different raw materials or oxides. The individual raw materials undergo chemical reaction and are transformed into a silicate glass.

The raw materials used to manufacture glass react to create a new chemical substance, totally different from the starting materials. Glass is not a mixture of compounds such as metals or oxides. The physico-chemical, toxicological and eco-toxicological properties of the substance glass are totally different from those of the individual raw materials or oxides.

Under REACH, glass is classified as a UVCB substance (substance of unknown or variable composition, complex reaction products or biological materials – Annex V (11) REACH). It is exempted from the REACH registration requirement under certain conditions laid down in Annex V (11) REACH.

The flow chart of the production can be described as follows:

Arsenic acid, as all the other raw materials used in the production (synthesis) of glass, reacts with other raw materials (substances) at high temperature to produce the new substance glass. During this process, the oxides from the raw materials form a new random network, where different elements are linked together by oxygen bridges. Arsenic acid is completely consumed during this chemical reaction and no longer contained as such in the final substance glass.

Raw materials
Glass substance
Glass article

The general chemical reaction to form silicate-glasses can be illustrated by the following simplified equation:
a SiO_2 [sand] + b Na_2CO_3 [soda] + c $CaCO_3$ [lime] + d $CaMg(CO_3)_2$ [dolomite] + e Na_2SO_4 [sodium sulphate] + f Arsenic Acid….. → x $Si_mNa_nCa_oMg_pAs_f……O_s$) [glass] + y CO_2 ↑+ z SO_2 ↑ + O_2 ↑…..

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Please note that the composition of glass is expressed by convention as oxides of the elements constituting the network. This does not mean that glass is a mixture of non-bonded different oxides.

The physico-chemical properties of the new substance glass (chemical resistance, mechanical resistance, transmittance, colour, inertness etc.) are a function of the composition and the network formed. A different composition leads to a different glass (chemical / molecular) structure and consequently different physico-chemical properties of the final product.

The function of arsenic acid in the production of glass

Several chemical substances, so-called "glass formers" are able to form the network structure and thereby the glass. These are mainly inorganic chemical oxygen bounded substances such as silica, boron, germanium, phosphor and arsenic. Thus, arsenic compounds are considered as "glass formers".

Arsenic acid is a raw material used to produce different kinds of glass, mainly domestic glass and special glass (e.g. pharmaceutical glasses, optical glasses, display glass, glass-ceramics,…). It participates in the chemical reactions to create the glass network and is completely consumed in the new substance glass (N.B.: the arsenic does not evaporate, and stays in the substance glass) and therefore contributes to the functional structure of the new substance. During the chemical reaction it contributes to the generation the oxygen bonds between the elements. In addition, by a redox reaction, it thereby also releases gaseous oxygen that helps to remove bubbles in the glass.

Arsenic acid acts clearly as a precursor to make glass and it cannot be regarded just as an "auxiliary agent" (catalyst, processing agent, solvent). On a molecular scale arsenic acid enters the glass network as a tightly bonded constituent and therefore becomes an integral part of the glass structure. The presence of arsenic ions in the network structure confers unique properties to the glass such as a specific redox state, clarity, colour, transmittance, absence of bubbles, lack of inclusion, etc…, which are critical to the function of glass.

Intermediate status of arsenic acid

Raw materials that are used in the manufacture of glass meet the definition of transported isolated intermediates as they are produced elsewhere and transformed into a new substance (glass) at the glass manufacturers' site.

In the case of Arsenic acid this can be further explained as follows: Arsenic acid (A) acts as raw material for glass (B) manufacturing. The structure of this (crystalline) substance (A) - crystallographically a well-defined cubic structure - is changed during the glass manufacturing

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process, where by means of a mineralogical transformation a stable non-crystalline, vitreous substance (B) is generated. The reason for the arsenic acid to be considered as an intermediate is that during the transformation another substance (glass) is synthesized. The glass network structure shows properties which differ totally from the sum of the properties of the individual raw materials. Arsenic acid acts as network former i.e. new chemical bonds are formed (with tetrahedral and/or trigonal chemical bonding could you refer to literature that indicates these types of bonding?) in the non-crystalline glass configuration and thus, arsenic acid is together with silica, boron oxide and for instance alumina a prime candidate for the glass synthesis. Therefore, it displays the features of an intermediate.

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AVAILABILITY OF ALTERNATIVES

The background document refers to an input made by CPIV (now Glass Alliance Europe), saying that there are a number of applications in speciality glass that show technical difficulties in replacing arsenic (see background document p. 4, point 2.3). The document also refers to sodium/potassium nitrates with antimony trioxides as alternatives for arsenic in speciality glasses.

Those substances can't be used for special applications where a very high glass quality is required. In the opinion of the European glass industries, it is also not advisable to replace a substance that possesses all required properties for a certain product, by another substance that is potentially harmful but degrading the glass quality level. The background document recognises this dilemma by saying: *"Many of the alternatives to the use of arsenic in glass/enamel processing, e.g. antimony trioxide, may be considered potentially harmful to human health and the environment"* (see p. 4 of the background document, point 2.3). A prioritisation of replacing or banning arsenic acid for the use in the (speciality) glass production is not rational, as it would result in the use of other potentially harmful substances in combination with products of inferior quality.

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OCCUPATIONAL EXPOSURE AT THE WORKPLACE

The background document also refers to occupational exposure saying: *"Consumer exposure via articles resulting from the uses is considered to be insignificant but there might be potentially significant occupational exposure."* (see page 5, point 3.1 of the background document).Occupational health is regulated in Member States by separate legislations, which provide sufficient safety standards to workers. Occupational exposure should therefore be regulated through such legislation as it is not a main task of the REACH Regulation. As the

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background document states correctly, consumer exposure via glass articles resulting from using the uses is insignificant. This is due to the scientifically proven and generally recognised inertness of the substance silicate glass. Accordingly, a prioritisation of arsenic acid resulting in an insertion in Annex XIV of the REACH Regulation is not justified.

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About Glass Alliance Europe

Glass Alliance Europe (former CPIV) is the European Alliance of Glass Industries. It is composed of 19 national glass associations and of the main sectors of the glass industries: container glass, flat glass, special glass, domestic glass and continuous filament glass fibres.

Over Europe the glass industry represents ca. 1.200 companies and about 150.000 workers. The size of the glass companies range from small furnaces (SME) to big multinationals present in several countries.

The European glass industry is very diverse and covers a variety of very different types of products and technologies, investing in research and developing glass products fit for a sustainable, resource-efficient and low-carbon society such as fully recyclable bottles & jars, energy efficient windows, weight-lightening continuous filament glass fibres (CFGF), flaconnage, tableware, optical fibres and special glass (Photovoltaic glass modules, glass for TVs and monitors, lighting glass, optical glass, laboratory and technical glassware, borosilicate and glass ceramic (cookware), X-Ray shielding and nuclear windows protection, etc).

In 2010, total EU-27 glass production reached a volume of more than 34 million tonnes, making the EU-27 the largest glass producer in the world. The production value amounted to ca. € 36 billion.

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