1st Stakeholder Consultation – Questionnaire for diantimony trioxide

Part of the Study to support the review of
the list of restricted substances and
to assess a new exemption request
under RoHS 2 (Pack 15)

Contribution of the

German Hightech Industry Association SPECTARIS e. V.

14.06.2018

Confidential

Wenko Süptitz, Ph.D.
Head of Photonics Division
SPECTARIS e. V.
Werderscher Markt 15
10117 Berlin
Germany
Phone: +49 30 41 40 21-25
suepititz@spectaris.de

Ms. Yifaat Baron
Oeko-Institut e.V.
P.O. Box 1771
79017 Freiburg
Germany
rohs.exemptions@oeko.de

13 June 2018

Dear Ms. Baron,

the EU has recognized photonics as a key enabling technology that supports the general objectives of the EU set out in the Horizon 2020 and glass is often a key component in electrical and electronic equipment. In parallel, in the current stakeholder consultation of the RoHS-Regulation referenced in [1],[2] the substance *diantimony trioxide* has been named and technically specified as *flame retardant* as 1 of 7 substances for assessment, resp. for review and possible amendment of the list of restricted substances specified in RoHS Annex II. Diantimony trioxide is used as an intermediate in the glass manufacturing processes [3a, 4] and as such essential for the glass characteristics. Although the technical specification of diantimony trioxide as flame retardant is not applicable on optical glasses, the availability of Sb_2O_3 is essential for todays and future applications of optical glass, being a key material in components in electrical and electronic equipment.

Please find below the SPECTARIS statement on diantimony trioxide for further consideration within the pack 15 procedure. The structure of the statement follows the provided questionnaire referenced in the Guidance Document [1].

Please do not hesitate to contact us, in case of any questions.

Best regards,

Wenko Süptitz, Ph.D.
Head of Photonics Division
SPECTARIS

Confidential

Statement concerning the 1st consultation on the planned restriction of diantimony trioxide

1. **Applications in which Sb_2O_3 is in use**

   a **Products and applications relevant to electric and electronic equipment? Is substitution under way? What are possible technological alternatives?**

i. Glass is being used as an optical material applied in a broad range of components. No matter what glass type or geometry of the components, optical materials provide the key functions of optical systems such as refraction, reflection, selective transmission and other special physical characteristics like electrical insulation, enabling optical systems and special functions in electrical and electronic equipment.
Optical systems provide key functions for research (measurement equipment, light guiding components and else), diagnosis, surveillance and quality assurance in medicine, scientific research, general industry, safety installations, environment monitoring, automotive and aviation. Special filter glasses, lenses, displays, insulation interlayers, optical glass in fluorescent light tubes (Sb-cations allow visible light), glass solders, glass wafers for optical augmented reality applications, sensors, cameras, photocopiers, binoculars and a vast amount of other applications are the end applications, please refer to [6],[7],[8].

ii. A substitution of glasses within optical systems by other materials like plastics, coatings or by digital solutions is not feasible due to limited optical performance of those substitutions. A substitution of diantimony trioxide has to take the substitution efforts within the 1990s into consideration, when the substance Sb_2O_3 had been itself already a substitute for diarsenic trioxide (As_2O_3). Both are used as an intermediate in the synthesis of optical glasses to provide specific characteristics, mainly on improving the transmission. The effect on enhanced transparency by improving photon transmission is based on physical interactions within the glass melting process and within the complete transformation into the glass network. The adding of Sb_2O_3 in the glass ingredients results in indispensable effects on the optical glasses for optical transmission, turbidity due to transformations of the polyvalent Sb-cations with other glass network building ingrediences into the glass network. Specifically, the redox reaction with Fe+2, as an impurity (iron oxide) of few other glass raw materials, has to be named: By oxidizing the Fe ions and thus preventing the color of Fe+2 ions and reducing the amount of Fe+2 it increases the solar and light transmission, improving photon transmission. The complex redox reactions within the glass melting process and the glass network building within are explained in [9];[10];[11]. The adding of Sb_2O_3 in the glass ingredients brings indispensable effects on the molten glasses for optical transmission, turbidity and bubbles removal. It is also used to produce special glass inhibiting the reduction of solarisation effects, also but not exclusively for example for fiber optics, which would be malfunction, if due to solarisation the transmission decreases. The requirements from the end applications on the optical performance lead to a loss of competitiveness in Europe, if the state-of-the-art transmission is no longer available within optical systems in EEE.

   b. Recycling of glass components with Sb_2O_3 as an intermediate raw material

Confidential

i. Recycling of optical and colored glass is not possible. The precisely specified properties [15] require raw material being very pure and homogeneous. Waste glass in no longer used systems is characterized by small amounts widely distributed. Only in certain business-to-business relations special glass is recycled. If recycled in the b-t-b cases, the cullets are used only glass type-specific in re-melting processes and thus the typical properties of glass as a substance remain.
Under REACh-Regulation the use of Sb_2O_3 within the glass melting process is classified as intermediate [4],[5]. The diantimony trioxide is a glass network builder and as such no longer available in the glass like the substance identification described in the compilation of initial substance information [1]. It is completely transformed in the melting process into the network of the glass. Due to this Sb_2O_3 will be not recycled from glass – the energy efficiency is to low and therefor not in the right balance to the ecological benefit.

ii. (non applicable; please refer to i.)

c. In which applications is Sb_2O_3 used as constituent / additive / intermediate and what is the content of Sb_2O_3 in the final product ?

In glass, Sb_2O_3 is used as an intermediate and is a glass network builder, constituting the glass network in a 3-dimensional glass structure. Due to the essential optical properties of the glasses based on the antimony cations in the network, the typical percentage of diantimony trioxide in the raw material mixtures is below 1.0 w/w-%. Again referring to the percentage within the raw material, more than 70% of the glass types have more than 0.1 w/w-%. For the molted glass, no such percentages can be provided due to the network of the glass (please refer to chapter b. i.). Scientific research based on Raman-Spectroscopy for structural analysis of glass networks showed, that the substance as such cannot be identified due to being an integrated part of the network [13];[14].
Sb_2O_3 is not used in any glass type at any time as a flame retardant.

2. **Quantities and range in which Sb_2O_3 is in use**

a. In the glass melting process diantimony trioxide is used as an intermediate. Within the glass melting process, it is an ingredient of the mixed raw material. In [1] the annual consumption of Sb_2O_3 is stated as 250t.
Within special optical glass producing companies, the typical quantity used as raw material is about 3.0 t p.a. in a range of 1t – 4t p.a. depending on the customer requested glass types within a year. Only for the use within special glass inhibiting the reduction of solarisation effects about another range of 1t – 3t p.a. are used. For the application please refer to chapter 5.

b. An exact ratio of the quantities in general- and in EEE-related applications cannot be provided; it is estimated as being the absolute majority, since optical glasses are key components for EEE.

c. Since the substitution is feasible only based on special polyvalent cations, their physical effect within the glass matrix and the optical properties like transmission, the substitution is limited to As_2O_3 and Sb_2O_3 vice versa. The substitution had been analyzed in the 1990s with extensive research efforts to look for other technical options, to stay on the level of high transmission and also low bubble level in the molted glass, taking typical technics used in the glass melting process into consideration (using TiO_2, Sn, Zn, Cr and other substances, see for example

[9];[10];[11];[12]). The result is, that especially the transmission can be only reliable on a competitive level, if Sb_2O_3 is used, thus no technical and reliable substitution is available.

3. Potential emissions in the waste stream

a. For applications containing Sb_2O_3, detail how it is managed in the waste phase

The environmental relevance of Sb_2O_3 in optical glass is negligible. Glass as a substance is not hazardous. The antimony cations are a constituent of the glass matrix. In contrast to the application of Sb_2O_3 as a flame retardant within plastics, Sb_2O_3 is not present in the final product (glass). Optical glass is also a very rare part of general waste and even of electrical equipment waste. With final disposal on waste dumps glass will remain unchanged for very long times without a relevant leaching if exposed to water in form of rain on a waste dump. The total amount of optical glass produced worldwide is comparatively small (approximately 20,000 tons per year, based on data of [7]).

b. *(non applicable for optical glass)*

c. How are waste glass containing Sb_2O_3 dealt with in the waste phase?

Please refer to 3.a. Recycling of optical and colored glass is not possible. On the one hand due to the precisely specified properties [15] requesting raw material being very pure and homogeneous. On the other hand glass components being no longer used in electrical and electronic equipment is characterized by small volumes and wide geographical spread as well as unknown by its glass type (which usually is not noted on the product or in its documentation). The effort to identify the glass type after long times of operation and collecting the different glass types from many different places for reuse in melting processes would outweigh any benefit from both criteria economics and ecology.

d. Potential emissions during waste treatment processes?

If no longer used the EEE will be either dismantled and the glass alone will be finally disposed on waste dumps or the entire EEE will be disposed. In both scenarios the glass will remain unchanged for very long times without a relevant leaching if exposed to water in form of rain on a waste dump, so that there is no Sb_2O_3 emissions to be expected.

4. Substitution

a. i. Is substitution scientifically or technically not practicable or reliable and why?

Substitution is not reliable and thus not feasible because considered alternative substances (Tin oxide, Titanium oxide, Chromium oxide, Zinc oxide, also Vanadium oxide or even Cl as a different substance) result in severe alterations of the final product properties, mainly limiting the optical performance as the key characteristics of optical glass (strong color tint, lower light transmission etc.) [9];[10];[11];[12]. Technically the light guiding requirements do not allow a reduced transmission even by few percentages, when glass for example is used in medical applications such as glass fibers used in endoscopes or fiberscopes for IT-infrastructure to name only two examples. While technically the physical equilibrium in the melting process between Sb(III) and Sb(V) is similar to the polyvalent cation As and explains, why this vice versa substitution exists, the temperature range of this equilibrium within the melting process, the impact on glass viscosity, interaction to Fe-cations and also the refining effect without risks of metal inclusions and critical reactions within the glass melting process is indispensable compared to using the named substance above.

ii. Alternatives on substance level and /or on technological level?

Sb_2O_3 is already an alternative to As_2O_3. There exists no other alternative as explained in chapter 4.a.i. On technological level an alternative is also not feasible, because of the physical effects of the polyvalent antimony cations being within the glass network.

iii. Constraints to substitution (costs, reliability, feasibility?)

No reliable alternatives are available (please refer to chapter 4.a.i.)

5. Socio-economic impact of a possible restriction

See also picture 1 in the confidential appendix.

Given that there is no feasible and reliable substitution neither on substance level (except with As_2O_3) nor on technological level the obligation to request an exemption every five years, would be both, not effective and not efficient within the purpose of the RoHS-Regulation. It would rather generate business uncertainty and would have negative impacts on reaching the objectives of the EU set out in the Horizon 2020 program.

The loss of the availability of Sb_2O_3 as an intermediate within the glass production would result in a loss of the majority of optical glass types, not losing only competitiveness but also long-term experiences in designing of optical systems within EEE as well as producing and processing of optical components. This would affect many different important applications:

- Endoscopes for minimally-invasive surgery or technical inspections (transmission over long glass paths limited, color trueness with reduced reliability of those applications)
- Surgical microscopes (transmission and color trueness)
- Ophthalmic instruments (transmission and color trueness over long glass paths)
- Near UV-region fluorescence microscopy (excitation of fluorescence with UV-light needs high throughput of UV-radiation; Antimony within the glass networks shifts the UV transmission spectrum)
- Safety eye protection (incl. sun glasses, steep slope filter characteristics, high blocking efficiency needed for safety)
- Optical glass for industrial metrology (filter characteristics for distinct separation of transmitted and blocked wavelengths in combination with high transmission; full range of optical glass types for designing high resolution objectives and optical systems)
- High end photography (transmission and color trueness over long glass paths)
- Cinematographic camera lenses (transmission and color trueness over long glass paths)
- Movie projection lenses (transmission and color trueness over long glass paths, energy saving by reducing heat losses)
- Aviation safety (transmission and color trueness of airport traffic control lighting)

Facility safety (Invisible infrared illumination through deep red long pass filters)
Many more secondary impacts due to the affected applications can be named, however, the Abbe-Diagram shows already the severeness of the consequences in the confidential appendix.

6. Further information

There is no point in glass being in the scope of the RoHS with regard to Sb_2O_3, since this substance is used as an intermediate in all cases, and is not present in the final glass product as such. The special glass industry therefore suggests that glass is specifically be excluded from the scope of the RoHS with regard to Diantimony trioxide and/or be granted a permanent exemption since the physical laws of optics will not change.

References

1	**RoHS Evaluations, substance information on diantimony trioxide** [08th of June, 2018] A http://rohs.exemptions.oeko.info/index.php?id=290 B http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/Diantimony-trioxide_Substance_info_1st_cons_Pack-15.pdf C Stakeholder consultation: Guidance Document, 20.04.2018 of Öko-Institute e.V. and Fraunhofer IZM
2	**1st Stakeholder Consultation – Questionnaire for diantimony trioxide** [08th of June, 2018] http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/Questionnaire/Diantimony_trioxide_Questionnaire_RoHS_Pack15_1st_Cons.pdf
3	**I2a International Antimony Association** A http://www.antimony.com/en/detail_exposure-scenarios_30.aspx B http://www.antimony.com/files/cms1/exposure%20scenario/overview-uses-of-8--sb-compounds-for-es-may2013-web.pdf
4	**Diantimony trioxide ECHA Information on Chemicals, registered substances (in full; intermediate)** [08th of June, 2018] https://echa.europa.eu/information-on-chemicals/registered-substances/-/disreg/substance/100.013.796
5	**Arsenic trioxide in the glass synthesis - an “intermediate” under REACh**, PROF. DR. HELMUT A. SCHAEFFER , 2011
6	P. Hartmann: **Optical glass: past and future of a key enabling material**, Adv. Opt. Techn., Vol. 1 (2012), pp. 5–10
7	P. Hartmann, U. Hamm: **Optical glass and the EU directive RoHS**, Proc. SPIE 8065, p.806511, (2011)
8	P. Hartmann: **EU regulations threaten availability of raw materials for optics**, SPIE Professional (2014)
9	E. Meechoowas, M. Müller, C. Rüssel: **Redox relaxation in a sodium borosilicate glass doped with copper and arsenic, antimony or tin**, Journal of Non-Crystalline Sollids 356 (2010) 2528-2533
10	C. Stalhandske: **The impact of refining agents on glass colour**, Glasteknisk Tidskrift, nr. 3, Vol 55, 2000
11	C. Rüssel, E. Freude: **Voltammteric Studies of the redox bahaiviour of various multivalent ions in soda-lime-silica glass melts**, Physics and Chemistry of Glasses, Vol 30, No 2, April 1989
12	GT20 Progress Report: **Fining and Glass Quality of Ultra Clear Soda Lime Silica Glass for Solar Applications**, Summary, Sep13 (presentation on CelSian)
13	S. A. Brawer & W. B. White: **Raman spectroscopic investigation of the structure of silicate glasses. I. The binary alkali silicates**. J. Chem. Phys. 63, 2421-2432 (1975).
14	T. Furukawa, K. E. Fox & W. B. White: **Raman spectroscopic investigation of the structure of silicate glasses. III. Raman intensities and structural units in sodium silicate glasses.** J. Chem. Phys. 75, 3226-3237 (1981).
15	ISO 12123:2010(E) **Optics and photonics — Specification of raw optical glass** International standard (2010).
	Company internal experiences & research knowledge on using diantimony trioxide as an intermediate in glass melting.

Confidential