European Flame Retardants Association

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Subject: Feedback to the Öko-Institute "Questionnaire for Substance Prioritisation" under RoHS

EFRA appreciates the opportunity to comment and to participate in this survey. Our comments relate only to TBBPA and Antimony Trioxide[1]. We already provided a detailed feedback to the first version of the HBCD assessment dossier by Austrian UBA last autumn. We do not have any information about 2,3-dibromo-1-propanol since none of the EFRA member companies manufacture this substance. We thus also believe that its use in E&E should be negligible, if it takes place at all. ICL-IP, one of the EFRA member companies, will provide information on the substance Dibromo-neopentyl-glycol individually.

Question 4: Application in which substance is in use

a) Please provide information concerning products and applications in which the substance indicated in Question 3 is in use.

TBBPA is used as reactive flame retardant (FR) in printed circuit boards for EEE products and as additive FR in housings (mainly ABS) of EEE products.

ATO is mainly used in EEE as flame retardant synergist for halogenated flame retardants (HFR); with a typical ATO-HFR ratio of 1:3), or in polymers containing halogens such as PVC. The addition of ATO in combination with HFRs allows that about 2-3 times less HFRs have to be added to meet the same flame retardancy performance. HFRs in combination with ATO are typically used for E&E housings (e.g. computers, TVs etc.) and cabling. ATO is also used as catalyst in PET production.

b) In your answer please specify if application is relevant to EEE products and applications or not.

The applications are relevant for EEE

c) Please elaborate if substitution of the substance indicated in Question 3 is already underway in some of these applications, and where relevant elaborate which chemical or technological alternatives may be relevant for this purpose.

TBBPA: FR4 Epoxies are the current industry standard and thus the most common type of printed circuit boards today. Typically, they have to meet the flammability requirement UL 94 V-1 or V-0. Around 80-90% of these printed circuit boards are based on brominated epoxy resins, i.e. on TBBPA, because brominated epoxy-based FR-4 boards provide the best combination of mechanical properties, thermal

[1] Information on Antimony Trioxide was received through the International Antimony Association, i2a: www.antimony.com

stability[2], moisture uptake[3], electrical performance[4] and cost-effectiveness. Brominated epoxies also have low levels of failure during drilling and assembly operations, especially for multi-layer laminates. TBBPA is chemically reacted to form a TBBPA-epoxy resin. This resin is then used to make a pre-impregnated composite, which is then fully cured to make a laminate. The laminates are then used to make circuit boards. The reaction is close to 100% which means that TBBPA as such is not identifiable any more in the final printed circuit boards.

Besides brominated epoxies, epoxy resins can also incorporate a phosphorus-based flame retardant. The most successful solution to date is DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). Due to the monofunctional nature of its structure, DOPO has to be reacted into specific multifunctional epoxies. However, only about 6-7% of the FR-4 printed wiring boards currently on the market are partly based on this technology by our understanding, as brominated epoxy resins provide the best combination of all requirements.

To meet fire safety requirements, phosphorous resins are used in combination with metal oxides such as Aluminium Tri-hydroxide (ATH) or Aluminium Oxide-hydroxide (AOH) – around 20-30% by weight loading – and sometimes with other additive flame retardants. These formulations have good thermal stability, but tend to face technical challenges, such as higher water uptake, increased brittleness[5], higher Dk, and higher failure rate at assembly stage, making them unsuitable for high-reliability battery-powered consumer electronics.

Metal phosphinates such as aluminium or zinc salts of diethylphosphinic acid (AlPi, ZnPi) have recently been tested in wiring boards. They are typically used as additives in combination with synergists, such as melamine polyphosphate.

With printed wiring boards, the interaction of metal hydroxides with fire (dilution of combustible gases via water release under thermal stress) can lead to the presence of water in the laminate during soldering operations, potentially increasing the assembly failure rate and affecting electrical properties. In practice, ATH is essentially used in intrinsically less-flammable flexible wiring boards for smaller devices like mobile phones or cameras.[6]

TBBPA in ABS can in theory be replaced by other brominated flame retardants in combination with antimony trioxide, or by phosphorus flame retardants. However, in this case also the polymer has to change, and one needs to use alloys such as PC/ABS since phosphorus-based flame retardants cannot be used in virgin ABS alone. A change in the polymer might lead to other disadvantages for certain plastic manufacturers and/or OEMs such as a necessary equipment change, potentially higher cost and limited material choice.

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[2] The ban in 2006 on the use of lead in all electronic and electrical appliances as required by the first EU RoHS Directive brought a considerable challenge for the production of PWBs. Instead of lead-containing solder, new alloys are now used to connect the chips and sockets to the conductive layers. These new alloys have a higher melting point (on average 40°C to 50°C higher), which means that the polymer substrates used in PWBs need to retain all their properties at higher soldering temperatures (typically 250°C to 360°C).

[3] Apart from its potential impact on electrical properties, moisture plays a key role in determining whether a material can withstand lead-free soldering conditions. At high temperatures, the vapour pressure of trapped moisture absorbed in the plastic laminate can lead to rapid deterioration (delamination), resulting in the printed wiring board and the attached electronic components being discarded even before useful service life begins. The less moisture present in the material, and the lower moisture uptake potential, the better. Thus, moisture uptake and retention of the flame retardant is a major factor in its selection.

[4] Such as dielectric permittivity (Dk) for example. Electrical properties are directly linked with the chemical composition of the polymers used in the wiring boards. The availability of best solutions for printed wiring boards is therefore a prerequisite for continued progress in electronics. For example, electronic components are usually designed to perform best at a certain dielectric permittivity (3.6 < Dk < 3.9 are common values for the industry-standard brominated epoxies). The higher average dielectric permittivity of alternative formulations currently available (~4.0 < Dk < 5.2) can affect the functioning of highly sensitive electronic components such as microprocessors, with higher risk of failure for the end product.

[5] Brittleness can cause issues with pad detachment, poor drilling capability and more rapid wear on drill bits.

[6] For all information given under Question 4c): http://www.cefic-efra.com/images/stories/IMG-BROCHURE-2.4/EFRA_E&E_brochure_oct2011_v04.pdf

ATO: The use of Brominated Flame Retardants (BFRs) together with ATO as synergist is for certain applications indispensable. Some examples:

- ABS and HIPS are today one of the preferred (technically and economically) polymers for E&E enclosures. The BFR-ATO combination is still one the most cost-effective FR system. Alternatives often do not fulfil the same combination of functionalities as the BFR-ATO system. Replacement by polymer alloys is possible, but this might lead to higher costs and still requires up to 0,5% halogen addition (PTFE).
- The BFR-ATO system is also often the material of choice for thermoplastic elastomers used in cabling for E&E.

Question 5: Quantities ranges in which the substance is in use

a) Please provide information as to the ranges of quantities in which the substance indicated in Question 3 is applied in general and in the EEE sector.

TBBPA: In 2011, EFRA member companies sold TBBPA in a range of 1000-2500 tonnes in Europe according to the 2012 VECAP report[7]. Exact figures cannot be provided due to antitrust rules. Around 90% of this volume was used in printed circuit boards.

ATO: in 2005, 24.500 tonnes were used in the EU-15, of which 38% was used for flame retardancy purposes in non-PVC plastics and 36 % in PVC, and 4% in PET production (EU-RAR, 2008). The use as flame retardant synergist in rubber/textile is **NOT** relevant for EEE. According to Roskill, the EU tonnage (incl. Russia and Ukraine) was 19500 t ATO in 2011. ATO concentration range in products: 1-10% in non-PVC polymer depending on type of polymer and/or choice of HFR (typical concentration: 3-5%), and 3.5-20% in PVC depending on the use of other FRs.

b) If substitution has begun or is expected to begin shortly, please estimate how the trend of use is expected to change over the coming years.

TBBPA: We see no major trend in replacing TBBPA in printed circuit boards. It is the flame retardant of choice for this application, as it provides the best combination of technical properties and requirements and economic considerations.

ATO: We see no major trend in replacing BFR-ATO. However, the choice of the flame retardant system in E&E enclosures depends mainly on the choice of the polymer (i.e. virgin polymers or alloys).

Question 6: Further information and comments

a) The substance profiles made available on the consultation page have been prepared as a summary of the publicly available information reviewed so far. If relevant, please provide further information in this regard.

TBBPA is a well-known substance that has been risk assessed by the EU (human health part[8] published in 2006 and environmental part finalized in February 2008[9]) and by the WHO[10] with the result that TBBPA

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[7] http://vecap.info/flipbook/annual2012/index.html

[8] TBBPA EU Risk Assessment report (2006) for human health can be found at: http://echa.europa.eu/documents/10162/32b000fe-b4fe-4828-b3d3-93c24c1cdd51

[9] Experts found no risk to the environment when TBBPA is used as a reactive component in printed circuit boards, and a low risk on the environment (water and sediment) when TBBPA is used as an additive to plastics. Potential risk was identified when sludge containing TBBPA is applied to agricultural soil. A Risk Reduction Strategy (RRS) was drafted to address the local risk identified and recommended to reduce emissions only at one ABS compounding site in Europe through the IPPC (Integrated Pollution Prevention and Control) Directive. *The final version of the environmental part of the risk assessment was not published on the internet, however, respective EU authorities should have access to it.*

does not pose a risk to human health. TBBPA was REACH-registered in 2010[11]. TBBPA was classified as H410 (R50/53) “very toxic to aquatic life with long lasting effects”. However, there will be negligible risk to the environment once TBBPA is encapsulated in an E&E casing or reacted within a printed circuit board, as there will be no contact with water during the use phase and end of life, if treated according to standards. The above-mentioned EU risk assessment states that for workers, consumers, humans exposed via the environment, combined exposure and human health (risk from physic-chemical properties), conclusion (ii) was reached: “There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.” (p. VI-VII)

ATO has been risk assessed by the EU (‘EU-RAR’); finalised in May 2008, and the data of EU RAR are approved by the OECD members under the SIAP program (14 October 2008). ATO has been REACH registered in November 2010 (>1000 t/y; http://echa.europa.eu/information-on-chemicals/registered-substances).

Risk assessments by the Canadian government (2010), the Dutch government (2011) and the U.S. EPA (2013 – draft version) are available as well. ATO is classified in the EU as Carcinogen cat 2- H351 ‘Suspected of causing cancer via inhalation’ (CLP Annex VI). It was agreed by expert toxicologists of TC NEC (Technical Committee for New and Existing Substances) that these effects are most likely caused by particle overload and impaired lung clearance ultimately leading to the formation of tumours (particle effect, no substance specific effect). ATO is considered a threshold carcinogen with an OEL of 0.5 mg/m³ (with the critical concentration expected to be 10 times higher). The inhalation hazard does neither apply via dermal or oral exposure (cfr. EU-RAR (2008), OECD-SIAP (2008) and ‘SCHER opinion on the risks of antimony trioxide in toys’ (November 2011)), nor does it apply when ATO is added to a polymer as flame retardant synergist (ATO gets mixed homogeneously into the polymer matrix during the extrusion process, ATO is not present in a respirable form anymore and the inhalation exposure potential to workers and consumers is negligible (cfr. EU-RAR)). The EU-RAR and EU-REACH dossiers confirm that ATO can be safely used throughout its entire lifecycle (production -> disposal).

b) Please provide further information and documents that you believe to have additional relevance for this review, as well as references where relevant to support your statements.

Technical requirements for printed circuit boards and EEE casings, as well as further information about the use of flame retardants in EEE is provided in the EFRA E&E brochure, which can be found here: http://www.cefic-efra.com/images/stories/IMG-BROCHURE-2.4/EFRA_E&E_brochure_oct2011_v04.pdf

TBBPA is also subject to the VECAP programme, which is run by the EFRA member companies together with customers and downstream users to decrease and, where possible, eliminate potential emissions for flame retardants during manufacturing and processing. The latest VECAP report shows the results over the past years as well as the tonnage band of the sold volume: “The coverage of the programme increased to 95% while potential emissions remained steady at the lowest rate. Total potential emissions at participating sites were reported to be below 0.003 metric tonnes per year.” (p. 10) www.vecap.info

Market and scientific information on ATO is summarized here: http://www.antimony.com/en/antimony-compounds.aspx. Publications that might be of interest (factsheets, statements etc.) are available at http://www.antimony.com/en/publications.aspx

Risk Assessment information ATO:

EU-RAR available at http://esis.jrc.ec.europa.eu/doc/risk_assessment/REPORT/datreport415.pdf

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[10] World Health Organisation International Programme on Chemical Safety (IPCS): Environmental Health Criteria 172 : Tetrabromobisphenol A and Derivatives, 1995. The report can be found here: http://www.inchem.org/documents/ehc/ehc/ehc172.htm

[11] http://apps.echa.europa.eu/registered/data/dossiers/DISS-9d928727-4180-409d-e044-00144f67d249/DISS-9d928727-4180-409d-e044-00144f67d249_DISS-9d928727-4180-409d-e044-00144f67d249.html

OECD-SIAP (2008) – available at http://webnet.oecd.org/hpv/ui/handler.axd?id=13e93c97-6605-4eac-961f-8af23cc6ad32)

RA Canada (2010 – available at http://www.ec.gc.ca/ese-ees/9889ABB5-3396-435B-8428-F270074EA2A7/batch9_1309-64-4_en.pdf)

Assessment Dutch government (2011 – available at http://www.gezondheidsraad.nl/sites/default/files/201133%20Antimony%20and%20compounds.pdf)

Risk Assessment US EPA (2013 – draft available at http://www.epa.gov/oppt/existingchemicals/pubs/TSCA_Workplan_Chemical_Risk_Assessment_of_ATO.pdf

About EFRA

EFRA (the European Flame Retardants Association) brings together the major companies which manufacture substances used as flame retardants in Europe. EFRA covers all types of substances used as flame retardants: chemicals based on bromine, chlorine, phosphorus, nitrogen and inorganic compounds. EFRA is a Sector Group of Cefic, the European Chemical Industry Council.

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