Abteilung Umweltschutzpolitik

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STN

ZVEI Answers to

1st Stakeholder Consultation – Questionnaire for diantimony trioxide (CAS 1309-64-4; EC 215-175-0)

Abbreviations

EEE	Electrical and Electronic Equipment

Background

The Oeko-Institut and Fraunhofer IZM have been appointed by the European Commission, within a framework contract[1], among others to support the review of the list of restricted substances and to assess seven substances with a view to their possible future restriction under Directive 2011/65/EU (RoHS 2).

Diantimony trioxide was specified in the project terms of reference for a detailed assessment. Initial substance information for diantimony trioxide are compiled and available on the substance specific webpage of the stakeholder consultation (http://rohs.exemptions.oeko.info/index.php?id=290).

The questions below outline the need for information.

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Questions

1. Applications in which diantimony trioxide is in use

a. Please provide information concerning products and applications in which the substance is in use.

i. In your answer please specify if the applications specified are relevant to EEE products and applications or not.

The applications are relevant to EEE products. Antimony trioxide is used in components that will be incorporated in EEE. Examples are:

- Insulation bodies
- Hoods for electrics, electronics and connectors
- Reactive component in plastics for laser printing (durability and legibility of laser printings are product safety relevant – e.g. Low Voltage Directive, Machinery Directive, Ecodesign, blue guide)
- Resistors in semiconductors

Antimony trioxide is mostly used in ABS and PBT plastics. Regarding further uses and use amounts please refer to the answer of i2a to this question 1.a.i.

ii. Please elaborate if substitution of the substance is already underway in some of these applications, for example in relation to the properties for which diantimony trioxide is used (for example synergist for halogenated flame-retardants) and/or in relation to specific applications in which it is used (for example in specific plastic materials, etc.) and where relevant elaborate which chemical or technological alternatives may be relevant for this purpose.

The most common use of antimony trioxide is as synergist to brominated flame retardants. While there might be also alternative synergists for brominated flame retardants no use of such synergists is known to us. Therefore possible alternatives to the system brominated flame retardant/antimony trioxide are usually halogen-free flame retardant systems based on phosphorus or nitrogen.
The substitution of halogenated by halogen-free materials is a very big challenge due to several technical requirements especially for existing parts. In consequence to no case of a successful substitution in existing parts is known.
For further details, please refer to part 4. Substitution.

b. Please specify if you are aware, if aside from actual use of the substance, it may be re-introduced in to the material cycle through the use of secondary materials.

i. Please detail in this case what secondary materials may contain diantimony tri-oxide impurities and at what concentrations as well as in the production of what components/products such materials are used.

ii. If possible please provide detail as to the changing trends of diantimony trioxide concentrations in such secondary materials as well as the changing trend of use of the respective secondary material in EEE manufacture.

Plastics that contain brominated flame retardants, and thus also antimony trioxide, have to be removed from WEEE according to 2012/19/EU Annex VII.
At the moment no process for material recovery of plastics from WEEE containing brominated flame is applied. In Germany such materials originating from EEE are therefore completely used for thermal recovery. Thus, no contamination of secondary materials with antimony trioxide originating from WEEE exists.

Production residues containing antimony trioxide may be used in other products that are usually not EEE, like floor covering. For these products a re-introduction of antimony trioxide cannot be excluded.

c. Please specify in which applications diantimony trioxide is used as a material constituent, as an additive or as an intermediate and what concentration of diantimony trioxide remains in the final product in each of these cases (on the homogenous material level).

If diantimony trioxide is used as a synergist flame retardant, please specify the brominated flame retardant with which it is used and at what concentrations they are applied.

In EEE and components for EEE antimony trioxide is usually used as synergist to brominated flame retardants. It is an additive and not covalently bound to a polymer.

For EEE and components thereof several fire protection requirements exist. Examples for such requirements are standards for railway and households. Due to the high complexity of the supply chains, it is usually for the component manufacturer and its direct customer not possible to decide in which equipment a component will be incorporated for its final use. Therefore fire safety became a general market requirement that is usually applied in the whole electric and electronic industry.
Antimony trioxide is usually used as synergist in PBT, ABS and other plastics.

2. Quantities and ranges in which diantimony trioxide is in use

a. Please detail in what applications your company/sector applies diantimony trioxide and give detail as to the annual amounts of use. If an exact volume cannot be specified, please provide a range of use (for example – 50-100 tonnes per annum).

b. Please provide information as to the ranges of quantities in which you estimate that the substance is applied in general and in the EEE sector.

c. 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.

According to one plastics manufacturer based on an own market analysis the global use of antimony trioxide in PBT and Polyamides can be estimated as ca. 14000 tons per year.

The International Antimony Association i2a gives in its answer to this questionnaire an overview over the uses of antimony trioxide.

PINFA estimates the use of antimony trioxide as ca. 209000 tons in 2013 and 228000 tons in 2016. The consumption as a flame retardant in Europe is estimated as ca. 20000 tons in 2015.[1]

3. Potential emissions in the waste stream

a. Please provide information on how EEE applications containing diantimony trioxide are managed in the waste phase (with which waste is such EEE collected and what treatment routes are applied)?

According to information we got from associations of WEEE treatment entities in Germany we want to state the following:

Antimony trioxide is usually used as synergist to brominated flame retardants. It is therefore contained only in plastics containing brominated flame retardants. These

[1] Flame Retardants in Electric and Electronic Applications, pinfa, 2017.

fractions are removed from WEEE according to 2012/19/EU. Different plastic fractions in the waste stream can be separated by density. Fractions with high content of antimony trioxide are due to the high density of antimony trioxide (ρ = 5,7 g/cm^3) even more easy to separate. Such plastic fractions will be mixed with other (halogen-free) fractions and used for thermal recovery. Printed circuit boards that contain brominated flame retardants and antimony trioxide usually are treated by copper smelters to recover the copper. The plastic material is also in this case used for thermal recovery.

PVC cables that might also contain antimony trioxide are usually first separated from WEEE and then recycled separately.

b. How are waste wire and cables containing diantimony trioxide managed in the waste phase and how is copper extracted from such waste to enable recycling?

Usually external cables are separated from WEEE. The cable will then be dismantled to recover the copper. Plastic isolation material that contains brominated flame retardants and antimony trioxide will be used for thermal recovery.

c. How are waste glass and ceramics containing diantimony trioxide dealt with in the waste phase?

Glass and ceramics do not contain antimony trioxide. While it is common to name the constituents of glass and ceramics as the oxides of the contained metals or semimetals this does not mean that these oxides are contained in pure form. In glass and ceramics the antimony ion will be embedded in the glass or ceramics matrix with ionic bonds/semi-covalent bonds to other atoms like oxygen, silicon etc. Therefore, glass and ceramics will contain some kind of oligomeric or polymeric mixed antimony and silicon oxides but this is not antimony trioxide.

d. Please detail potentials for emissions in the relevant treatment processes.

We do not expect specific emissions of antimony trioxide. It may be contained in dust as constituent of plastic particles. A potential biologic effect would in this case be an unspecific effect caused by plastic dust and not a substance specific effect of antimony trioxide.

4. Substitution

a. For which applications is substitution underway?

i. For which applications is substitution scientifically or technically not practicable or reliable and why?

ii. Please specify in this respect which alternatives are available on the substance level (substitution) and which are available on the technological level (elimination). For example, which alternatives can be applied instead of diantimony trioxide used in PVC cables or in plastic components and which alternative isolating materials can be applied instead of PVC in order to eliminate the need for diantimony trioxide in such applications?

iii. What constraints exist to the implementation of the named substitutes in a specific application area (provide details on costs, reliability, availability, roadmap for substitution, etc.). For example for what range of the diantimony trioxide applications can specific substitutes be used for?

i)

As shown in 1. c. for many electrical and electronic components high requirements on fire safety exist. Thus the substitution of a flame retardant plastic by a plastic without flame resistance is usually no option. To obtain the required flame resistance in general two ways are possible. Either plastics with inherent flame resistance can be used or a flame retardant can be added to a plastic.

As plastics with inherent flame resistance mainly liquid crystal polymers (LCP) are used in the E&E industry. In general these polymers have several very good properties but they also show specific drawbacks that make them no suitable substitute for halogenated PBT or ABS materials.

The Comparative Tracking Index (CTI) shows the electrical breakdown properties of an insulating material. The CTI of LCPs is often too low for specific applications, e.g. electrical and electronic connectors. This can be explained by application of EN 60664-1 - Insulation coordination for equipment within low-voltage systems - Part 1: Principles, requirements and tests. This standard is also harmonized to the Low Voltage Directive 2014/35/EU. The standard specifies the requirements for clearances, creepage distances and solid insulation for equipment based upon their performance criteria. Creepage distance is defined according to EN 60664-1 as follows:

“shortest distance along the surface of a solid insulating material between two conductive parts”

It is very important that electrical or electronic connectors and other installations comply with the requirements on creepage distances because otherwise a high danger of fire exists.

The required creepage distance is derived from the applied voltage, the distance of the pins to each other and the CTI value of the insulating material. The applied voltage is usually defined by the application and cannot be changed. The same is the case for the distance of the pins that is usually defined by the mating face. The general trend of minimizing requires a small distance between conductive parts for a high variety of components. Thus the minimum requirement for the CTI value cannot be changed.

The CTI value can be derived by application of IEC 60112 and is grouped by EN 60664-1. Typical CTI values of liquid crystal polymers are 125 to 200V[2]. This is much lower than typical CTI values of PBT or ABS which are usually > 580V[3]. Thus for applications where a high CTI value is required a substitution of PBT or ABS by LCP is not possible. This is for example the case for small electronic connectors with many pins in small distance.

The findings regarding the low CTI value are valid for all plastic materials with inherent flame resistance as all these materials have a benzoidal structure in common.

For plastics materials without inherent flame resistance a flame retardant has to be added. Many such plastic materials are available with halogenated and halogen-free flame retardant. While of course others are in use we want to focus in our answer on Polybutylene terephthalate (PBT).

Usually the choice of a specific material with specific flame retardant system is based on macroscopic properties of the material.

The most important antimony trioxide containing PBT materials for the E&E industry can be sorted in three groups:

- Halogenated, not reinforced
- Halogenated, not reinforced, elastomer modified

[2] https://plastics.ulprospector.com/generics/17/c/t/liquid-crystal-polymer-lcp-properties-processing/sp/3

[3] https://plastics.ulprospector.com/de/generics/1/c/t/acrylnitril-butadien-styrol-abs-properties-processing
https://plastics.ulprospector.com/de/generics/37/c/t/polyester-polyester-properties-processing

- Halogenated, glass fiber reinforced, hydrolysis stabilized

Halogen- and antimony trioxide free materials show a much lower elongation at break than materials with halogenated flame retardants. Thus, the material is less elastic and breaks more easily. Especially for parts with a mechanical connecting function this is very problematic as connecting elements will break during installation.

Antimony trioxide is a very fine powder and the used halogenated flame retardants can be melted. This makes the system antimony trioxide / halogenated flame retardant very well dispersible in the plastic material which is usually not the case for halogen-free systems. The consequence of this are inhomogeneities in case of the halogen-free material that cause the lower elongation at break.

Elastomer modifiers can usually be burned very easily. As they show negative side effects with halogen-free flame retardants at the moment no equivalent alternatives to halogenated and elastomer modified PBTs are commercially available.

Materials that are halogen-free flame protected and also hydrolysis stabilized are neither reinforced nor not reinforced available. According to the material manufacturers such materials are not achievable.

So far no halogen-free PBT exists that fulfills the UL requirements of self-extinguishing in combination with inflammability (V2 plus HWI or HAI).

Halogen-free PBTs often show an unfavorable behavior during processing in comparison to halogenated PBTs. The main reason for this is the lowered temperature resistance of the melt of halogen-free PBTs compared to the melt of halogenated PBTs. So, the melt of halogen-free PBTs may not be heated as high as the one of halogenated PBTs.

For injection molding the melt of the PBT is pressed in a tool. During this process friction occurs which causes an additional heating of the melt. Especially for thin parts the additional heating due to friction can have a significant share in the total temperature of the melt. As the melt of halogen-free PBTs is less temperature stable overheating can occur. The consequence is material degradation and thus the formation of parts that cannot be used. The additional heat due to friction is not even distributed through the melt of the material and it is hard to control. Due to these findings the processing of halogen-free PBTs is often less stable than in case of halogenated PBTs and the percentage of scrap parts produced is much higher.

As substitutes of halogenated flame retardants often aluminum, phosphorus or nitrogen compounds are used.

Especially for phosphorus compounds it is not completely sure that this is in no case a regrettable substitution. Sweden introduced in 2017 a tax on chemicals in certain electronics.[4] This tax can be reduced by 90% for certain electronic products that do not any phosphorus compound added as an additive in circuit cards or plastic parts weighing more than 25 grams. In the Notification Detail to this Draft Act[5] Sweden stated:

"The aim of the legislation is to reduce the introduction of hazardous substances into people's homes and thereby protect the health and life of humans and animals."

[4] https://www.skatteverket.se/servicelankar/otherlanguages/inenglish/businessesandemployers/payingtaxesbusinesses/taxonchemicalsincertainelectronics.4.5c281c7015abecc2e2019351.html

[5] http://ec.europa.eu/growth/tools-databases/tris/en/search/?trisaction=search.detail&year=2016&num=582

Therefore before substituting a halogenated flame retardant with a phosphorus based flame retardant a manufacturer has to make sure that the phosphorus based flame retardant will not have hazardous properties. In addition the manufacturer has to keep in mind that the 90% tax reduction in Sweden will then not possible for the parts in scope. Both hinders the possibility of substituting halogenated flame retardants with phosphorus based flame retardants.

Due to the findings above we agree with the statement of PINFA[2]:

"There is not a universal flame retardant (as there is not a universal plastic, or a universal metal usable everywhere for every application). Each material has its own properties and compatibilities. This applies to flame retardants too."

Plastics that contain no antimony trioxide exist and show many convincing properties. But several applications of antimony trioxide exist for which a substitution with an antimony free flame retardant systems is not possible. Specific examples with this situation are:

- Electrical and electronic parts with thin walls, e.g. electrical and electronic connectors
- Electrical and electronic parts with short distance between conductors, e.g. electrical or electronic connector with high density of pins
- Parts with mechanical connecting function due to the lower elongation at break, e.g. parts for installation in profile rail.

ii)

Substitution: There is no alternative synergist in PVC.

Elimination: For specific applications instead of PVC other materials like elastomers and thermoplastic polymers can be used. For them if no halogen-free flame retardant system is used usually also the system brominated flame retardant/antimony trioxide is applied. A system without synergist antimony trioxide would lead to higher contents of halogenated flame-retardants. This would have severe negative impact on the macroscopic material characteristics (e.g. higher hardness, less flexibility). Therefore, a cable that complies with the flame resistance requirements of the E&E industry that contains a halogenated flame-retardant only but no antimony trioxide does not exist.