Partnership for Sustainable Textiles

Antimony

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Content

1. Identification and classification

Antimony (Sb) is a semi-metal with 51 as atomic number. The CAS-no is 7440-36-0. As it naturally also appears in elemental form, antimony is classified as a mineral.

In 2015, about 184,000 t of antimony have been globally processed (USGS 2016). China is the largest producer. Antimony has various applications such as in alloys, in the electric industry, as catalyst for the production of polyester fibres (especially for polyethylene terephthalateT), in the optical and ceramic industry or in the manufacture of glass (Ullmann's, 1985; Winnacker/Küchler Metalle, 2006).

2. Existing regulations

Under REACh, due to its potential carcinogenic effect and its potential risk for workers in the polyester fibre manufacturing as well as in the polyester fibres processing industry, antimony is evaluated within a Community Rolling Action Plan (CoRAP).

The German Ordinance on Hazardous Substances (GefStoffV 2010) does not exist and occupational exposure limit (OEL) for antimony yet. Antimony and its compounds belong to those compounds the subcommittee III of the Committee for Hazardous Compounds is currently working on with the aim to propose an OEL for the Technical Rule for Hazardous Substances (TRGS 900) or to derive exposure-risk-relation according to TRGS 900.

The German Federal Soil Protection and Contaminated Sites Ordinance (BodSchV 1999) contains a trigger value for antimony of 0.01 mg/l to assess the pathway soil-groundwater.

The Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy does not classify antimony as priority substance. The limit for antimony for drinking water is 0.005 mg/l (Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption).

WHO has issued a limit for drinking water of 0.02 mg antimony/l (WHO 2011).

3. Use in wet textile production processes

In the textile sector, antimony is used as a flame retardant (only in combination with other flame retardants) and as a catalyst for the production of polyester fibres. The latter application dominates by far.

For producing polyester fibres, catalysts on the basis if antimony(III) oxide or antimony acetate are used for the polymerization reaction of polyethylene terephthalate (Schönberger/Schäfer, 2003; Winnacker/Küchler PES, 2005). The antimony content of PES fibres is up to 300 ppm. During aqueous textile pretreatment steps including alkaline treatment processes but mainly during high temperature polyester dyeing processes, a substantial percentage of antimony is released. Measurements show that about one third of the antimony content is released during polyester high temperature dyeing (the content in the polyester decreased from 255 to 174 mg/kg) (Thier-Grebe, 2000).

In addition, in the textile sector, antimony is sometimes used as flame retardant but only in combination with halogenated compounds such as chlorinated paraffins or brominated compounds (Ullmann’s, 1985, Sato et al., 1998).

The exposure of the final consumer primarily occurs through skin contact when wearing polyester textiles. An additional exposure is possible by oral ingestion or inhalation of particles from polyester abrasion (Laursen et al. 2003).

The investigation of 433 samples of different garments sourced from the German market with different polyester contents revealed total antimony contents between 87 and 147 mg per kg textile (one maximum value, not considered in the given range was 270 mg antimony/kg textile) (BfR, 2012). Form these samples, 0.33-4.57 mg antimony/kg polyester fibres were released during sweat testing (BfR, 2012).

4. Hazard potential

Acute and chronic human toxicity

In general, antimony exhibits similar toxic effects as the closely related arsenic. Trivalent antimony is usually more toxic than pentavalent antimony (Filella et al., 2007); Inorganic antimony has more toxic effects than organic antimony (Merian et al 1984, Rish 2004).

Acute oral uptake of antimony leads to gastrointestinal symptoms such as vomiting or diarrhea. Thereby, the minimum lethal dose is between 300 mg for children and 1.200 mg for adults. Therefore, antimony is classified as "harmful, toxic or life-threatening fatal if swallowed" (H300, H301 and H302). Metallic antimony is preferably taken up by inhalation (GESTIS). It can be "harmful by inhalation" and "can irritate respiratory tract"

(H332 and H335). In occupational exposure, the dermal uptake of antimony does not play any role, even if resorption of small quantities is possible with permanent contact (GESTIS).

Antimony (III) oxide is classified as "probably can cause cancer (H351)" (GESTIS), this effect refers to a repeated inhalation exposure. The International Agency for Cancer Research (IARC) classifies antimony (III) oxide as a possible carcinogen for humans (Group 2B) due to an inhalation study with rats (group 2B); in this study, the carcinogenicity of antimony sulfide was not classified (Group 3). The exact cellular mechanisms leading to genotoxicity and carcinogenicity of trivalent antimony are not known (De Boeck et al., 2003), however, antimony could interfere with proteins involved in nucleotide excision repair (Grosskopf, Schwerdtle, Mullenders & Hartwig, 2010)) .Guo et al. (2016) do correlate antimony exposure with heart diseases. According to that, antimony exposure positively correlates with increased mortality due to cardiopathy and an increased prevalence of specific heart diseases such as congestive heart failure and myocardial infarction (Guo et al., 2016). Choe et al. (2003) demonstrated an estrogenic activity and hence hormone-like efficacy of antimony.

Ecotoxicity

With respect to its toxicity, antimony shows differences for some species: it is very toxic to amphibians while being only moderately toxic or toxic to fish and zooplankton. Generally, soil organisms show higher effect concentration than aquatic organisms. Antimony was classified in the range ‘harmful’ (dangerous) up to toxic by different registrants (H411, H412, H413) (Merian 1984; Rish 2004).

5. Environmental behaviour

Antimony is mainly released to the environment via anthropogenic sources (WHO 2003). Its environmental behavior is similar to those of arsenic: the water-soluble forms are mobile in the water phase while insoluble forms bind to soil particles (WHO, 2003). No bioaccumulation has been observed. The concentration of antimony in sea water and in non-polluted rivers is below 0.5 ppb (Merian, 1984; Reimann/de Caritat, 1998).

6. Possible substitutes

PES fibres can also be produced with catalysts based on titanium/silicium mixed oxides or titanium acid esters which are stable to hydrolysis (Thier-Grebe, 2000). However, this option has not found its way into industrial practice yet. The mechanical properties of PES fibres produced by means of titanium-containing catalysts are the same as for antimony-containing catalysts but the ageing resistance has still to be checked (Thier-Grebe, 2000). The production costs of PES fibres produced with titanium-containing catalysts are higher but need their dyeing requires less energy and a lower dyestuff consumption compared with PES fibres produced with antimony-containing catalysts (Thier-Grebe, 2000).

7. Summary

The most important relevance of antimony in the textile industry is its use as a catalyst for polyester production. During textile finishing, it is released from various processes, mainly from high temperature processes and related washing operations. From the toxicological point of view, the remaining content of antimony in the textile product has not been substantially questioned so far with respect to human toxicology.

The hazard potential of antimony is given due to its toxic impact when swallowed and by inhalation as well as because of its assumed carcinogenic effect in case of repeated respiration. The toxic effects on water organisms is of minor relevance.

Antimony oxide is still the most important catalyst for the production of polyester fibres. It has been suggested to substitute it by titanium/silicon mixed oxides but for that, additional research and development is required to improve the fibre quality of polyester produced with this catalyst.

8. References

BBodSchV (1999): Bundes-Bodenschutz- und Altlastenverordnung vom 12. Juli 1999 (BGBl. I S. 1554), die zuletzt durch Artikel 102 der Verordnung vom 31. August 2015 (BGBl. I S. 1474) geändert worden ist.

Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (2016): Bearbeitungsliste des AGS – UA III zur TRGS 900 und TRGS 910. http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/pdf/Bearbeitungsliste-TRGS-900.pdf?__blob=publicationFile (01.12.2016)

Bundesinstitut für Risikobewertung (BfR) (2012), Einführung in die Problematik der Bekleidungstextilien, Aktualisierte Stellungnahme Nr. 041/2012 des BfR vom 6. Juli 2012,

http://www.bfr.bund.de/cm/343/einfuehrung-in-die-problematik-der-bekleidungstextilien.pdf

GefStoffV (2010): Gefahrstoffverordnung vom 26. November 2010 (BGBl. I S. 1643, 1644), die zuletzt durch Artikel 2 der Verordnung vom 3. Februar 2015 (BGBl. I S. 49) geändert worden ist.

GESTIS Stoffdatenbank Mobil (2016): Antimon http://gestismobil-de.itrust.de/#dasStoffDiv (31.10.2016)

Herbst, K.A.; Rose, G.; Hanusch, K.; Schumann, H.; Wolf, H.U. (1985), Antimony and Antimony Compounds, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A3, VCH Verlagsgesellschaft, Weinheim, 55-76

IARC (1989): Monographs on the evaluation of carcinogenic risks to humans. Some organic solvents, resin monomers and related compounds, pigments and occupational exposures in paint manufacture and painting. Vol. 47. IARC, Lyon: 1989. 291-305.

International Programme on Chemical Safety IPCS (2001): Environmental Health criteria: Arsenic and Arsenic Compounds, Geneva.

Laursen, S.E.; Hansen, O.C.; Hansen, J.; Pommer, K.; Pedersen, E.; Drøjdahl, A.; Bernth, N. (2003), Survey of chemical compounds in textile fabrics. 23, -115. Danish Environmental Protection Agency - Danish Ministry of Environment and Energy.

http://www.mst.dk/NR/rdonlyres/B9CDE217-9E41-4F27-A8A3-921D5B50A737/0/23.pdf

Merian, E.; Stemmer, K.L. (1984), Antimon, in: Merian, E. (Hrsg), Metalle in der Umwelt, Verlag Chemi, Weinheim, 309-317

Reimann, C.; de Caritat, P. (1998), Chemicals Elements in the Environment – Factsheets for the Geochemist and Environmental Scientist – Antimony, Springer-Verlag, Berlin, 298-301

Richtlinie 98/83/EG des Rates über die Qualität von Wasser für den menschlichen Gebrauch, Anhang I, Teil B. http://eur-lex.europa.eu/legal-content/DE/TXT/HTML/?uri=CELEX:01998L0083-20151027&from=EN (30.11.2016)

Richtlinie 2008/105/EG des europäischen Parlaments und des Rates über Umweltqualitätsnormen im Bereich der Wasserpolitik und zur Änderung und anschließenden Aufhebung der Richtlinien des Rates 82/176/EWG, 83/513/EWG, 84/156/EWG, 84/491/EWG und 86/280/EWG sowie zur Änderung der Richtlinie 2000/60/EG, Anhang II. http://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:32008L0105&from=EN , (30.11.2016)

Rish, M.A. (2004), Antimony, in Merian, E. et al. (Hrsg), Elements and Their Compounds in the Environment, Wiley-VCH Verlag, Weinheim, 659-670

Sato, H.; Kondo, K., Tsuge, S.; Ohtani, H.; Sato, N. (1998); Mechanisms of thermal degradation of a polyester flame-retarded with antimony oxide/brominated polycarbonate studied by temperature-programmed analytical pyrolysis, Polymer Degradation and Stability 62, 41-48

Schönberger, H., T. Schäfer (2003): Beste verfügbare Techniken in Anlagen der Textilindustrie. Im Auftrag des Umweltbundesamts. Berichtsnr.: UBA-FB 000 325.

Thier-Grebe, R; Rabe, M. (2000): Polyester mit neuem Titandioxid-Katalysator Melliand 81: 977-980.

Verordnung (EG) Nr. 1272/2008 des europäischen Parlaments und des Rates über die Einstufung, Kennzeichnung und Verpackung von Stoffen und Gemischen, zur Änderung und Aufhebung der Richtlinien 67/548/EWG und 1999/45/EG und zur Änderung der Verordnung (EG) Nr. 1907/2006. Tabelle 3.1. http://www.reach-clp-biozid-helpdesk.de/de/Downloads/CLP-VO/CLP_GHS_VO.pdf?__blob=publicationFile&v=2 (30.11.2016)

Winnacker/Küchler (2005), Chemische Technik, Band 5 – Organische Zwischenverbindungen, Polymere - Polyester, 5. Auflage, Wiley-VCH Verlag, Weinheim, 1016

Winnacker/Küchler (2006), Chemische Technik, Band 6b – Metalle - Antimon, 5. Auflage, Wiley-VCH Verlag, 1016

World Health Organization WHO (2003): Antimony in Drinking-water. WHO/SDE/WSH/03.04/74

World Health Organization WHO (2011): Guidelines for Drinking-water Quality. 4th edition. 314. http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf (30.11.2016)