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(Update of the version of 1 June 2009)

This document has been updated because new information on the uses of diarsenic pentaoxide in the manufacture of decorative glass for arts and crafts became available, in particular on potential worker exposure to the substance during manufacturing of the glass.

Background document for diarsenic pentaoxide

Document developed in the context of ECHA's second Recommendation for the inclusion of substances in Annex XIV

1. Identity of the substance

Chemical name: diarsenic pentaoxide

EC Number: 215-116-9 CAS Number: 1303-28-2

IUPAC Name: 1,3-dioxodiarsoxane 1,3-dioxide

2. Background information

2.1. Intrinsic properties

Diarsenic pentaoxide was identified as a Substance of Very High Concern (SVHC) according to Article 57(a) as it is classified according to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008 as a carcinogen, category 1¹, R45 (may cause cancer) and was therefore included in the candidate list for authorisation on 28 October 2008, following ECHA's decision ED/67/2008.

2.2. Imports, exports, manufacture and uses

2.2.1. *Volume(s), imports/exports*

The overall manufacturing quantities within the EU for this substance are estimated at less than 100 tonne per year (t/y) (RPA 2009). Import volumes have been estimated based on international trade data, however, it remains difficult to produce reliable trade figures for the different arsenic species. For diarsenic pentaoxide it is estimated that less than 200 t/y is imported within the EU. Exports are unlikely to be significant.

This corresponds to a classification as carcinogen 1A, H350 (may cause cancer) in Annex VI, part 3, Table 3.1 of Regulation (EC) No 1272/2008 (List of harmonised classification and labelling of hazardous substances)

However, in relation to preparations, one potential export has been identified from the consultation: that of a wood preservative (CCA) containing diarsenic pentaoxide at less than 100 t/y. All the volumes reported most likely show a downward trend (RPA 2009). The total estimated use volume is less than 210 t/y.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Manufacture of diarsenic pentaoxide occurs at two sites (Belgium and Portugal) with possibly a third recycling site in Germany. At present, it has been assumed that the associated manufacturing quantities are less than 100 t/y.

Indicative information on releases of arsenic and its compounds can be derived from the European Pollutant Emission Register (EPER). The results for the possible manufacturing sites are shown in Table 1.

2.2.2.2. Uses and releases from uses

Possible use in glass is suggested to be relevant for few, unknown locations, with probably low releases to working environment and external environment. The consumer use of special glass is probably widespread, but it is important to state that consumer articles as such do not contain the diarsenic pentaoxide but arsenic.

| Table 1: Releases of arsenic and its compounds from (Possible) Manufacturing Sites (t/y) | | | | | |
|--|-------------|------------|-------|--|--|
| Location | Compartment | 2001 | 2004 | | |
| Umicore (Hoboken and Olen facilities, Belgium) | to Air | 0.74t | 0.57t | | |
| | to Water | 0.28t | 0.22t | | |
| PPM Metals (Germany) | to Air | not listed | | | |
| PPM Metals (Germany) | to Water | | | | |
| Mines de Denes que ins (Bentucal) | to Air | no data | | | |
| Minas de Panasqueira (Portugal) | to Water | 1.08t | 0.30t | | |
| Source: EPER (eper.eea.europa.eu/eper/default.asp) | | | | | |

Quantitative figures have been generated for the following uses (RPA, 2009):

1. Wood preservation

CCA (a preparation comprising copper (from the oxide or sulphate), chromium (from the oxide or a sodium chromate) and diarsenic pentaoxide) is applied to the wood under pressure and, hence, is often referred to as pressure-treated wood (RPA, 2009). Increasing concerns over its use, however, led to a series of regulatory actions (see below, section 7). Although wood newly treated with CCA may not be imported or placed on the market, one company (in a Nordic country) has been identified which formulates CCA for export. The estimated volume for this use is **less than 100 t/y** (RPA, 2009).

However, certain types of old CCA treated wood are still permitted to be reused (and imported) under the details of Directive 2006/139/EC (RPA, 2009). The extent to which this reuse is practised is not known.

2. Glass and Glass Products

Diarsenic pentaoxide is reportedly used in the manufacture of special glass. In response to consultation for this study, the European glass industry trade association has suggested that diarsenic pentaoxide is not used within Europe (CPIV, 2008a). However, according to information provided by the Italian Competent Authority, diarsenic pentaoxide is used in the small scale manufacture of decorative glass for arts and crafts in manufactories. As a conservative estimate, it was assumed that any usage within the EU is likely to be small (<10 t/y) (RPA, 2009).

3. Intermediate for other arsenic compounds

During the study it was reported that one site in Western Europe uses diarsenic pentaoxide as an intermediate for other arsenic compounds at less than 100 t/y (RPA, 2009).

An overview of the uses and corresponding volumes can be found in table 2.

Table 2. Use processes and corresponding volumes of diarsenic pentaoxide.

| Use Process | Amount used | Number of sites of use within EU |
|--|-------------|----------------------------------|
| Formulation of CCA (wood preservative) | <100 t/y | 1 |
| Intermediate for other arsenic compounds | <100 t/y | 1 |
| Possible use in glass and/or glazes | <10 t/y | probably few |
| Total | <210 t/y | Probably few |

Conclusion

Based on this table, it is clear that the volume which is relevant for the Authorisation procedure under the REACH regulation can be considered as low (< 10 t/y).

Releases during the uses described above will tend to be associated with processing. As such, releases will rather occur under controlled working conditions. Further details on the use in glass processing are presented below. Data on release from uses which are not relevant for the Authorisation procedure can be found in RPA (2009).

Glass Processing

The use of arsenic in the glass industry has long been recognised as requiring care for both the health of the workers and the surrounding environment. Although major glass production facilities within the EU do use significant quantities of arsenic, their emissions to the environment are less than for many other facilities (such as power stations and major steel works²). Nevertheless, there are several glass manufacturing facilities (across the EU) each with arsenic emissions in the range 0.1 to 0.7 t/y.

² By inspection of the European Pollutant Emission Register (eper.eea.europa.eu/eper/default.asp).

As regards occupational exposure, there seem to be problems with preventing such exposure in the manufacturing of hand-made decorative glass for arts and crafts, as can be inferred from information provided by the Italian CA.. Biological monitoring of workers in glass manufactories in the Murano district, carried out through urinary arsenic measurement, revealed that workers employed in the mixture preparation and in the furnace work are still significantly exposed to arsenic despite the technical preventive measures adopted (mean concentrations of different As species in urine samples of workers are 2-3 times higher than the upper limit of reference for the non exposed population (Montagnani et al., 2006). The investigations of Montagnani et al. are based on the use of As2O3, however, similar worker exposure could reasonably be expected if As_2O_5 was used.

Many items of special glass may be collected and, possibly, recycled. However, it is of note that the collection and physical sorting of different glasses is unlikely to lead to significant exposures to arsenic (at least within the EU) (RPA, 2009).

2.2.2.3. Geographical distribution and conclusions in terms of (organisation and communication in) supply chain

As already mentioned under section 2.2.2.1, manufacture of diarsenic pentaoxide occurs at two sites (Belgium and Portugal) with possibly a third recycling site in Germany. In addition, as already mentioned under section 2.2.2.2, possible use in glass is suggested to be relevant for few, unknown locations, with probably low releases to working environment and external environment. The consumer use of special glass is probably widespread.

According to the available information (RPA, 2009) it can be concluded that:

- 1) the supply chain of this substance contains only few levels (from the manufacturer/importer to the last actor affected by a possible authorisation decision).
- 2) the supply chain contains limited types of industry branches. In addition, these industry branches are well organised in effective industry associations (glass industry and possibly metal and alloy industry).

Therefore it can be concluded that the supply chain for diarsenic pentaoxide is of rather low complexity: the substance is manufactured, imported, processed into intermediates and further used for the production of glass (see above) (RPA, 2009).

2.3. Availability of information on alternatives³

Use in Glass Processing

Diarsenic pentaoxide as decolourising agent in glass has various established alternative non-arsenic substances including:

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³ Please note that this information was not used for the prioritisation.

- antimony trioxide (decolourising agent for glass and an opacifier in ceramics and enamels);
- selenium (particularly in lead crystal); and
- cerium oxide (in special glass and as an opacifier in enamels/ceramics).

The industry has advised that arsenic acid may also be used for this purpose - albeit under different processing conditions (CPIV 2008; CPIV, 2009).

Given the range and diversity of alternatives to the use of arsenates, it is expected that alternatives would be available with suitable technical and economic characteristics for most applications. Although it is accepted that there are alternatives for most domestic (lead crystal) applications, the glass industry has highlighted a number of applications where there are technical difficulties in replacing arsenic in special glass (CPIV, 2008):

- pharmaceutical packaging glass which would require further investigation into the suitability of any alternative materials;
- although some glass-ceramic hobs (cooker tops) are now arsenic-free, producing clear glass hobs remains a difficult challenge;
- some optical filter glass relies on the intrinsic properties (i.e. optical wavelengths) of arsenic for which there are no alternatives; and
- use of alkali-free glass in opto-electronic applications.

Many of the alternatives to the use of arsenic in glass processing may be considered potentially harmful to human health and the environment. By way of example, antimony trioxide is the subject of an (as yet unpublished) EU Risk Assessment Report under the Existing Substances Regulation⁴.

2.4. Existing specific Community legislation relevant for possible exemption

Wood Preservative (CCA)

Especially the use of CCA treated wood has been extensively covered by other regulations. Although initially it was considered suitable for general indoor and outdoor use, increasing concerns over its use led to a series of regulatory actions including:

Directive 89/677/EEC (amending for the eighth time Directive 76/769/EEC on Marketing and Use restrictions) stipulated that arsenic compounds may not be used as substances and constituents of preparations intended for use in the preservation of wood unless solutions of inorganic salts of the CCA type were used in industrial installations using vacuum or pressure to impregnate wood.

Several years later, **Directive 2003/2/EC** (adapting Directive 76/769/EEC to technical progress for the tenth time) restricted the use of CCA-treated timber to a limited number of end uses where structural integrity is required for human or livestock safety

⁴ European Chemical Substances Information System: Diantimony Trioxide (CAS 1309-64-4).

and skin contact by the general public is unlikely. This had to be implemented by 30th June 2004. These limited end uses account for a small proportion of the requirement for treated timber.

Another issue of importance to the evolution of the EU markets for wood treatment formulations is the **Biocidal Products Directive** (98/8/EC). Arsenic pentaoxide was notified by industry as an active substance following the provisions of the Directive; however, a dossier was not eventually submitted. This effectively prevents the use of arsenic in wood preservatives in the EU (but see points on imports below).

Directive 2006/139/EC (adapting Directive 76/769/EEC to technical progress), prescribes that arsenic shall not be used in the preservation of wood. Under Point 20 of Annex 1 to Directive 76/769/EEC as amended by Directive 2006/139/EC, CCA type C cannot be used to treat wood in the EU due to the fact that it has not been authorised under Directive 98/8/EC. A request for authorisation could, however, be made in the future in line with the requirements of Directive 98/8/EC (EC, 2008).

2.5. Any other relevant information (e.g. for priority setting)

No data available.

3. Conclusions and justification

3.1. Prioritisation

The volume supplied to non-intermediate uses is <110 t/y. However, the main part is used for biocidal products (wood protection), for which authorisation does not apply. A volume of <10 t/y is probably supplied to uses in the scope of authorisation.

The main use of diarsenic pentaoxide, which is relevant for the authorisation procedure under the REACH regulation, is for special glass production (<10~t/y). This conservative estimate is uncertain as the European glass industry trade association has suggested that the substance is not used within Europe for this purpose. However, according to information provided by the Italian Competent Authority As_2O_5 may be used in the small scale manufacture of decorative glass for arts and crafts.

Nonetheless, consumers will not be exposed to the arsenate trioxide as it is not present (as the original compound) in the glass (arsenic instead). Furthermore, because the arsenic is bound into the glass matrix, the potential for migration and exposure would be expected to be very low. A study into elemental migration from glass in contact with food found that, in general, accelerated migration testing did not result in detectable levels of various elements (including arsenic). Although the use of special glass articles can be considered widespread, based upon available information, it is assumed that the release of arsenic compounds from the glass matrix is most probably very low and hence not wide dispersive.

However, as the substance may be used for similar technical purposes as diarsenic trioxide in the small scale manufacture of art glass, the same problems with the control of occupational exposure may occur.

Verbal-argumentative approach

On the basis of the prioritisation criteria, diarsenic pentaoxide may be considered as a borderline candidate for prioritisation because of the low volume used, the low release potential from articles produced but the potentially significant exposure of workers during manufacture of As containing glass.

Scoring approach

| Score | | | Total Score |
|---------------------------|-------------------|--|------------------|
| Inherent properties (IP) | Volume (V) | Uses - wide dispersiveness (WDU) | (= IP + V + WDU) |
| 1 (Carcinogen, cat. 1) | 1 (Low volume) | Overall score: 2 * 3 = 6 Site-#: 2 (Use at a medium # of sites) Release: 3 (potentially significant exposure in (parts of) the glass industry) | 8 |

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, diarsenic pentaoxide can be considered as a borderline candidate for prioritisation. If however similar arsenic compounds (e.g. diarsenic trioxide) are considered to be prioritised, it should be considered to prioritise diarsenic pentaoxide as well because otherwise it may in certain cases be possible to bypass the authorisation requirement by substitution.



4. References

- CPIV (2008): CPIV Answer to the Questionnaire of Arsenic Uses in the Glass Industry, detailed response to RPA consultation, dated October 2008.
- CPIV (2008a): CPIV Answer to the Questionnaire of Arsenic Uses in the Glass Industry, detailed response to RPA consultation, dated October 2008.
- CPIV (2009): Responses to additional RPA questions, dated January 2009.
- EC (2008): Draft Reference Document on Best Available Techniques in the Glass Manufacturing Industry, Draft of February 2008 (updating the previous BREF dated December 2001), European Commission, available from: http://ec.europa.eu/environment/ippc/brefs/gls_d1_0208.pdf
- Montagnani, R, M Campagna, S Gasparello, A Hreiglich, P Apostoli (2006): L'esposizione ad arsenico nella produzione artigianale della bacchetta di vetro. Risultati del monitoraggio biologico e indicazioni preventive. G Ital Med Lav Erg 2006; 28:2, 158-162.
- RPA (2009): Data on manufacture, import, export, uses and releases of: diarsenic trioxide (CAS no: 1327-53-5); diarsenic pentaoxide (CAS no: 1303-28-2); lead hydrogen arsenate (CAS no: 7784-40-9); and triethyl arsenate (CAS no: 15606-95-8), as well as information on potential alternatives to their use. Report prepared for ECHA.