1 July 2010

(Update of the version of 1 June 2009)

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

Background document for diarsenic trioxide

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 trioxide
EC Number:	215-481-4
CAS Number:	1327-53-3
IUPAC Name:	dioxodiarsoxane

2. Background information

2.1. Intrinsic properties

Diarsenic trioxide 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 1[1], 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

Diarsenic trioxide manufacturing volumes are estimated at 3000 tonnes per year (t/y). An estimated volume of 1000 t/y is produced from mining and smelting by-products, 2000 t/y is reclaimed from metal and electrical waste. Import of the substance is estimated at 1800 t/y. The volume of export is unknown. The trend of these figures is most probably stable. The total estimated use volume is around 4800 t/y.

[1] 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, there remain considerable uncertainties as to the precise quantities involved and the material flows and associated mass balances are, in some cases, rather complex. It has been not always possible to differentiate between the different arsenic sources and arsenic uses. For example, whether or not the arsenic used in particular applications was derived from diarsenic trioxide or from refined (and possibly imported) arsenic metal was not always clear. Therefore, in describing the overall mass balance, it was considered relevant to include the import of arsenic metal (750 t/y) in the overall balance.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Manufacture of diarsenic trioxide occurs in 2 sites (Belgium and Portugal) with possibly a third recycling site in Germany.

Within the EU, increasingly, the recovery of arsenic (as diarsenic trioxide) forms an integral part of metal recovery from mining waste (byproduct) streams and recyclable products. The overall manufactured volume is estimated at 3,000 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.

Table 1: Releases of arsenic and its compounds from (Possible) Manufacturing Sites (t/yr)

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	
	to Water		
Minas de Panasqueira (Portugal)	to Air	no data	
	to Water	1.08t	0.30t

Source: EPER (eper.eea.europa.eu/eper/default.asp)

2.2.2.2. Uses and releases from uses

Based on available information it is estimated that during processing for possible use in glass few, unknown locations with probably low releases to working environment and external environment are existing within the EU. Similarly, the following distribution for the EU was estimated during end use as alloy in lead-acid batteries (widespread geographical distribution), in Glass/Enamel articles (widespread geographical distribution) and as other alloys (e.g. copper) (probably widespread geographical distribution) (RPA, 2009)

Description of uses

1. Wood preservation

Diarsenic trioxide and ammoniacal copper zinc arsenate (ACZA) have been used in timber treatment but to a much lesser extent compared to wood preservative (CCA) (a preparation comprising copper (from the oxide or sulphate), chromium (from the oxide or a sodium chromate) and diarsenic pentaoxide). No quantitative data are available but it is important to stress that the use of arsenic compounds in wood protection products falls under the scope of the Biocidal directive (See section 7). Use in biocidal products within the scope of Directive 98/8/EC {Art. 56(4b)} is exempt from authorisation.

2. Paints, Varnishes etc.

Diarsenic trioxide is used in vitrifiable enamels. It can be used as an opacifier in glazes and as decolourising agent. For volumes see use in Glass and Glass Products below.

3. Pharmaceutical Preparations

The use of arsenic compounds in (Western) medicines progressively tailed off during the latter part of the 20^{th} century and had disappeared by the mid-1990s. However, the use of arsenic (as injected diarsenic trioxide) has reappeared following extensive study in China. Although (potential) medical uses are important, the associated quantities are not significant for this study. No quantitative data are available but it is important to stress that the use of arsenic compounds in medicinal products for human or veterinary use within the scope of Regulation (EC) No 726/2004, Directive 2001/82/EC and Directive 2001/83/EC {Art. 2(5a)} is exempt from authorisation.

4. Glass and Glass Products

Diarsenic trioxide is used in the manufacture of lead crystal and special glass as well as the decolourisation of glass and enamel. Furthermore, diarsenic trioxide is used as a fining agent (to remove bubbles from the glass melt) in glass production. The special glass sector produces around 6% of the glass industry output, and in terms of tonnage it is the fourth largest sector. Special glass products have a relatively high value and represent an extremely broad sector covering a wide range of products. The main products are: lighting glass (tubes and bulbs), optical glass, laboratory and technical glassware, borosilicate and ceramic glasses (cookware and high temperature domestic applications), and glass for the electronics industry (LCD panels). Until recently, the product list would have included cathode ray tube (CRT) glass for televisions and monitors. However, there has been a dramatic shift to LCD screens in recent years and CRT glass is no longer made in the EU (RPA, 2009).

Overall, the estimate for EU usage of diarsenic trioxide in glass processing has been taken as 1000 t/y, most of which is used for the production of special glass. Although no reliable data on the usage of diarsenic trioxide in vitrifiable enamels have been located, it is likely to be a much lower consumption than for glass and an estimate of 200 t/y has been assumed. The total volume of diarsenic trioxide for glass and enamel processing is estimated at **1200 t/y**.

5. Alloys

It has been assumed that the arsenic used in alloys is produced from diarsenic trioxide or is imported as arsenic metal.

5.1 Basic Iron and Steel and Ferro-Alloys

Some steels (and alloys) under particular conditions are susceptible to hydrogen embrittlement which depends on the presence of ‘dissolved’ hydrogen in the steel. The presence of arsenic promotes hydrogen diffusion into the steel (and alloys) thus enhancing the potential for hydrogen embrittlement. These factors are used in metallurgical testing (by enhancing hydrogen diffusion) to determine whether hydrogen embrittlement is likely to be significant for a particular situation.

Although no quantitative data on this use of diarsenic trioxide within the EU has been located, the quantities used will be small - as, in effect, the arsenate is being used as a test chemical in specialised laboratories. As such, no further data on usage are presented in this report (RPA, 2009).

5.2 Basic Precious and other Non-Ferrous Metals

Diarsenic trioxide may be used in the manufacture of alloys with arsenic conferring increased hardness to the other metals. Particular references can be found to lead and copper alloys.

5.2.1 Lead, Zinc and Tin

Battery grids: trace quantities (less than <0.5%) of arsenic are added to lead/antimony grid alloys used in acid batteries. A large number of ‘standard’ car batteries utilising the strengthened arsenic grids are still produced within the EU. Based on an estimated consumption of around 60 million car batteries, it is estimated that around **2250 t/y arsenic used for this purpose.** This figure has been carried forward in the analysis which follows - although it is acknowledged that this may be an overestimate.

Ammunition: the addition of arsenic (0.5–2%) improves the sphericity of lead shot. Small quantities of arsenic (<1%) may also be used to assist in the hardening of lead/antimony alloys used for casting bullets. The estimated EU consumption of lead shot was estimated to be over 30 000 tonnes in 2003 (RPA, 2009). Taking a 1% arsenic content would suggest a consumption of 300 tonnes of arsenic. With increasing (environmental) concerns over the use of lead shot, it is likely that this will have dropped as users have switched to less toxic shot.

Cable sheathing: arsenical lead is also used for cable sheathing. Lead sheathing extruded around electrical power and communication cables gives the most durable protection against moisture and corrosion damage, and provides mechanical protection of the insulation. Chemical lead, 1% antimonial lead, and arsenical lead are most commonly employed for this purpose.

5.2.2 Copper

Hardening of copper with arsenic goes back in time. At present, copper alloys such as brass (copper-zinc) containing arsenic (primarily for corrosion resistance) are used, *inter alia*, in condenser tubes, heat exchanger and distillation tubes. No further volume detail on such uses has been obtained. (RPA, 2009)

For the purposes of this analysis, it has been assumed that ‘other alloys uses’ (see table 2) could total as much as **500 t/y** (including ammunition, cable sheathing and copper alloys).

6. Electronic Components

Diarsenic trioxide is used to produce high purity arsenic which is the basis for gallium arsenide (GaAs) semiconductors. It is also suggested that the substance is used in the production of copper foil in printed circuit boards (RPA, 2009).

Although earlier studies have suggested that gallium arsenide may not be being produced within the EU, consultation for this study indicates that diarsenic trioxide is indeed being used within the EU to produce high purity arsenic metal which is either used to manufacture GaAs semiconductors or as a dopant for special semiconducting silicon qualities (RPA, 2009).

In the production of electronic components such as semi-conductors diarsenic trioxide can be considered as an intermediate. In most cases this means that the substance is transformed into another substance (e.g. gallium arsenide). Such uses are exempt from authorisation as stated in Art. 2(8b) of the REACH regulation dealing with "On-site isolated intermediates and transported isolated intermediates". More specifically, on the basis of the information presently available, we conclude that the doping process to produce special semiconducting silicon qualities can be considered as intermediate use. However, in light of future prioritisation of substances for inclusion in Annex XIV a more detailed analysis could be made of the technologies used for the doping process itself within the overall production of semi-conductors.

6.1 Gallium Arsenide Applications

Gallium arsenide (GaAs) may be used as a semiconductor substrate, as a dopant in semiconductor material, and as a substrate in LED applications (RPA, 2009).
GaAs semiconductors are used in lasers, space research and solar cells, and GaAs is an important component in light emitting diodes, which has contributed to stronger sales of GaAs. Gallium-arsenide and indium-arsenide semiconductors used in computers and electronic devices require high-purity (99.9999%) arsenic metal. GaAs wafers are used for electronics applications. A mobile phone typically contains GaAs in its microelectronic circuitry, of which the arsenic content is less than one milligram. Arsenic may be used for germanium-arsenide-selenide or GaAs specialty optical materials (USGS, 2008).

6.2 Arsenic as a Dopant

On the other hand, doping is a routine process in fabricating semiconductor devices. Arsenic is an n-type dopant (donor) in silicon (along with the other elements of Group V of the Periodic Table, notably antimony and phosphorous) N-type describes a semiconductor material that has negatively charged conductivity (a surplus of electrons).

Consultation has indicated that the use of triethyl arsenate has been developed for use in specialised doping applications (see Background report on triethyl arsenate).

6.3 Selenium Alloys

Small amounts of high-purity arsenic are used in arsenic-selenium alloys for photoconductors used in photocopiers, infrared detectors photovoltaic cells, etc. Consultation suggests that there is at least one electronics company in Western Europe using arsenic for this purpose (RPA, 2009).

Whilst the usage of arsenates in electronics is considered important, the EU consumption figures are relatively low: at **no more than 200 tonnes per annum** of high-purity arsenic (derived from diarsenic trioxide and/or arsenic metal)**.**

7. Other uses

Based on the mass flow balance of the substance (RPA, 2009) the following additional uses and volumes were identified:

- Production of diarsenic pentoxide: < 100 t/y
- Production of other arsenic compounds: 1300 t/y (uncertain estimate)

An overview of the mass balance for the wider picture of arsenic and diarsenic trioxide supply and consumption is shown in table 2. Within the timeframe for this study, it was not possible to further develop the precise material flows.

Table 2. Mass Balance for Arsenic/Diarsenic Trioxide (within EU)			
Supply		**Consumption**	
Description	**Quantity**	**Description**	**Quantity**
Arsenic metal imports to EU	750 t/yr	Arsenic in semiconductors	200 t/yr
Diarsenic trioxide imports to EU	1 800 t/yr	Arsenic in lead-acid batteries	2 250 t/yr
Diarsenic trioxide from mining/smelting by-products	1 000 t/yr	Arsenic in other alloys (ammunition, cable sheathing and copper alloys)	500 t/yr
Diarsenic trioxide recovered from metal/electrical waste	2 000 t/yr	Diarsenic trioxide in glass/ enamel processing	1 200t/yr
		Diarsenic pentaoxide	100 t/yr
		Other arsenic compounds	1 300 t/yr
Total	**5 550 t/yr**	**Total**	**5 550 t/yr**

Releases from uses

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

7.1. 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 works[2]). 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)

More generally, glass manufacture is covered by IPPC[3] resulting in a requirement to reduce emissions to the environment. This, in turn, led to the development of an *IPPC Reference Document on Best Available Techniques*[4] in 2001 which is now being updated (EC, 2008), with references to (di)arsenic trioxide.

According to information provided by the Italian Competent Authority, there seem to be problems with preventing occupational exposure in the manufacturing of hand-made decorative glass for arts and crafts. 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). Main problems are apparently the dustiness of As_2O_3, which is mixed with the other glass raw materials in form of fine powder and the high volatility of As_2O_3 at the melting temperature (at least 20% loss of the As added), which lead to inhalative exposure. About 80 manufactories with ca. 800 – 1000 workers are manufacturing As containing art glass. The annual consumption of As_2O_3 for art glass manufacture is 8.2 t in the Murano district (estimate for entire Italy 12 t/yr).

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).

7.2. Alloys (Non-Ferrous)

As for glass manufacture, the production of non-ferrous alloys is also covered by IPPC and there is an associated BREF (RPA, 2009). Although this contains many references to arsenic, these tend to be associated with the removal of arsenic impurities from other non-ferrous metals rather than with the intended addition of arsenic to alloys. As a result, many of the emissions of arsenic from metal industries (both ferrous and non-ferrous - as listed on the European Pollutant Emission Register) are associated with 'impurities' rather than with the intentional use of arsenic and its compounds.

However, the emissions of arsenic (and its compounds) associated with the production of alloys are likely to be no greater than those associated with the manufacturing sites.

7.3 Lead-acid batteries

When it comes to recycling, within the EU, the vast majority (90% or more[5]) of car batteries are collected locally, taken to centralised (regional) facilities and separated into their main constituents (acid, plastic/rubber and lead). The lead is then sent to one of the few main recovery smelters (either within the EU or overseas). On this basis, it would be expected that most of the arsenic used in lead-acid batteries would be recovered (in the large smelters) for re-use. Although not confirmed, it is

[3] Most recently codified as: Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control, OJ L24, 29.01.02008, pp 8-29.
[4] Sometimes referred to as a BREF.
[5] See, for example, information from the International Lead Association (www.ila-lead.org/)

understood that the lead used in lead-acid batteries would form a separate lead recovery stream from that used for other purposes (such as lead sheet) (RPA, 2009).

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

As already mentioned under section 2.2.2.1, manufacture of diarsenic trioxide occurs at a limited number of sites in the EU. In addition, as indicated under section 2.2.2.2, it is estimated that during processing few, unknown locations exist within the EU, whereas for known end uses probably widespread geographical distributions can be observed.

Based on the information provided by the study (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, metal and alloy industry).

Therefore it can be concluded that the supply chain for diarsenic trioxide is of rather low complexity: the substance is manufactured, imported, processed into intermediates and further used for the production of glass and alloys (see above). Based on the information presently available, the volumes of the substance applied for the production of semi-conductors can be considered as intermediate use.

2.3. Availability of information on alternatives[6]

Use in Enamels and Glass Processing

Fining Agents
Diarsenic trioxide is used as a fining agent. The industry has advised (CPIV, 2008) that arsenic acid may also be used for this purpose - albeit under different processing conditions (CPIV, 2009). Due to concerns over its use, there are various established alternative substances including:

- sodium sulphate (used in lead crystal);
- antimony trioxide (used in lead crystal);
- sodium/potassium nitrates with antimony trioxides (used in special glasses); and
- cerium oxide.

Decolourising Agents
Diarsenic trioxide is used as decolourising agents in glass and enamels[7]. The industry has advised (CPIV, 2008) that arsenic acid may also be used for this purpose - albeit

[6] Please note that this information was not used for the prioritisation.

under different processing conditions (CPIV, 2009). As with the fining agents, there are various established alternative non-arsenic substances including:

- 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).

Arsenic-Free Glass
It is of note that several major glass producers and computer companies are now promoting the use of arsenic-free glass in computer monitors.

Given the range and diversity of alternatives to the use of arsenates, it might be 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 (CPIV, 2008) has highlighted a number of applications where there are technical difficulties in replacing arsenic in special glass:

- 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/enamel 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 Regulation[8]. However, such potential effects are taken into account in developing appropriate operational practices.

Use in Alloys (Lead and Copper)

<u>Battery Grids</u>
As for ammunition (see below), various metals are added to improve the strength of the lead grids and other parameters (corrosion resistance, minimise gassing, etc.) to ensure maintenance-free service. However the main types remain those based on lead-antimony and lead-calcium alloys. Both use arsenic but the levels are much higher in lead-antimony grids (0.25%) than in those using lead-calcium alloys (<0.002%) (RPA, 2009).

[7] In enamels, diarsenic trioxide may also be used as an opacifier (i.e. to make material opaque).
[8] European Chemical Substances Information System: Diantimony Trioxide (CAS 1309-64-4).

More generally, although there has been extensive research into battery grids, use of other metals and heat treatment methods to improve the hardening of lead are still being explored (RPA, 2009).

It would be expected that the health and environmental effects of lead alloys without arsenic would be slightly less severe than those with arsenic.

Ammunition
As detailed in Kelter (undated), a wide range of bullet hardness may be obtained by varying the relative amounts of lead, antimony and tin in bullet alloys - without using arsenic. As such, arsenic is not critical for cast bullets.

In relation to lead shot, the issue is not the use of arsenic but the use of the lead itself - particularly in wetlands (see, for example, CIC, 2008). This, of course, is not a new issue and a detailed review of alternatives was commissioned in 2004 (COWI, 2004). This review concluded that there were alternative materials for shot including steel, bismuth and tungsten (and associated alloys).

Ammunition without lead and/or arsenic is likely to be less harmful to human health and the environment than lead bullets/shot containing arsenic.

Other
As for battery grids and ammunition, varying mixtures of alloys in other uses (including cable sheathing and copper alloys) have been used to produce products of a similar performance to those using arsenic.

As for the battery grids, it would be expected that the health and environmental effects of alloys without arsenic would be slightly less severe than those with arsenic.

2.4. Existing specific Community legislation relevant for possible exemption

Wood Preservative (CCA)

Especially the use of arsenic 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 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).

Pharmaceuticals

The use of arsenic compounds in medicinal products for human or veterinary use is regulated within the scope of Regulation (EC) No 726/2004, Directive 2001/82/EC and Directive 2001/83/EC {Art. 2(5a)} and is exempt from authorisation.

2.5. <u>Any other relevant information (e.g. for priority setting)</u>

No data available.

3. Conclusions and justification

3.1. <u>Prioritisation</u>

The total estimated volume used in the EU is around 3900 t/y. The volume of diarsenic trioxide used for non-intermediate uses is approximately 3000 t/y.

The main uses of diarsenic trioxide are for lead alloys (especially in lead-acid batteries) and glass production. These processes result in incorporation of the substance into matrices and/or articles. For example, during use of articles made of glass consumers will not be exposed to the arsenate trioxide as it is not present (as the original compound) in the glass. Furthermore, because the arsenic is bound into the glass matrix, the potential for migration and exposure would be expected to be insignificant. 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). For alloys, a similar assumption is made: because the arsenic is bound into an alloy, the potential for migration and exposure (to arsenic) would be expected to be very low.

As regards recycling, it is unlikely that collection and sorting of glasses leads to significant exposure to arsenic. Similarly, 90% or more of car batteries are recycled and it would be expected that most of the arsenic used in lead-acid batteries would be recovered for re-use. Although the use of arsenic containing glass and lead-acid batteries can be considered widespread, based upon available information, it is assumed that the release of arsenic compounds from those matrices/articles is most probably (very) low and hence not wide dispersive.

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). Main problems are apparently the dustiness of As_2O_3, which is mixed with the other glass raw materials in form of fine powder and the high volatility of As_2O_3 at the melting temperature (at least 20% loss of the As added), which lead to inhalative exposure. About 80 manufactories with ca. 800 – 1,000 workers are manufacturing As containing art glass. The annual consumption of As_2O_3 for art glass manufacture is 8.2 t in the Murano district (estimate for entire Italy 12 t/yr).

Verbal-argumentative approach

The volumes of diarsenic trioxide supplied to non-intermediate uses are high. Consumer exposure via articles can be considered insignificant and exposure of humans via the environment as controlled.

As regards occupational exposure there appear to exist problems with exposure control in (parts of the glass industry), in particular in manufactories for small scale manufacture of art glass. Extrapolation of the data form Italy regarding numbers of factories and workers involved would suggest that a high number of workers could be exposed and that the use of As_2O_3 for art glass manufacture should be considered as wide-dispersive.

On the basis of the prioritisation criteria, diarsenic trioxide can be considered as a candidate for prioritisation although there is some uncertainty about the extent of the problem of insufficient exposure control for workers in the glass industry.

Scoring approach

Score			Total Score
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	(= IP + V + WDU)
1 (Carcinogen, cat. 1)	7 (High volume)	Overall score: 3 * 3 = 9 Site-#: 3 (Use at a high # of sites) Release: 3 (significant exposure in (parts of) the glass industry)	17

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, diarsenic trioxide can be considered as a candidate for prioritisation.

If diarsenic trioxide is recommended for inclusion in Annex XIV it should be considered to include similar substances (e.g. As_2O_5) as well order to prevent evasion of the authorisation requirement by replacing As_2O_3 with other arsenic compounds with a similar hazard potential.

4. References

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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), available from: http://ec.europa.eu/environment/ippc/brefs/gls_d1_0208.pdf

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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.