ANNEX XV REPORT

AN ASSESSMENT OF WHETHER THE USE OF MDA IN ARTICLES SHOULD BE RESTRICTED IN ACCORDANCE WITH ARTICLE 69(2) OF REACH

SUBSTANCE NAME(S): 4,4'-Diaminodiphenylmethane (MDA)

IUPAC Name(s): 5-tert-butyl-2,4,6-trinitro-m-xylene

EC NUMBER(S): 202-974-4

CAS NUMBER(S): 101-77-9

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A. Conclusions

A.1 Conclusions based on the assessment

4,4'-Diaminodiphenylmethane (MDA) is classified in Regulation 1272/2008 (CLP) as a carcinogen (category 1B), it has been included on the candidate list (2008/10/28; ED/67/2008) and included in Annex XIV of REACH (Commission Regulation (EU) No 143/2011) with a sunset date of 21 August 2014.

ECHA has gathered information on the uses of MDA in articles from various sources. According to the records MDA has been registered in the tonnage band 10,000 - 100,000 tonnes per annum but there are no identified uses in articles, there are no SiA notifications made under Article 7(2) and there have been no applications for authorisation (AfAs) made for the substance.

Following an assessment of the available evidence, ECHA considers that there is no use of the substance itself in articles. The main use of MDA is in the production of MDI, which is further processed to polyurethanes; there is no evidence from the relevant CSRs from registrants that any residual MDA remains in the MDI produced. In any case, as MDI will be further processed to polyurethanes before being used in articles, any potential impurity would be negligible.

Therefore, under Article 69(2), ECHA's view is that the requirements to develop and submit an Annex XV dossier for restriction are not met. This conclusion will be tested in a call for evidence to last from 13 May 2015 to 15 July 2015 [8 weeks].

A.2 Targeting

The report is targeted on the potential use of MDA in articles and whether or not such use should be restricted.

This targeting is based on the requirement of Article 69(2) that requires ECHA to consider if the use of the substance in articles is adequately controlled and prepare an Annex XV dossier for an appropriate restriction if this is not the case.

A.3 Summary of the justification

A.3.1 Identified hazard and risk

Information on uses

Production of MDA was reported as approximately 1,400,000 tonnes per annum at the time of candidate listing (ENTEC 2008). The main use of MDA is as an intermediate in the synthesis of MDI; this represents more than 98% of the total EU production volume (EC, 2001). Non-MDI uses such as an intermediate in the manufacture of high performance polymers and for processing to 4-4' methylenebis(cyclohexaneamine) are estimated at more than 4000 t/y (ENTEC, 2008). In addition, it has also been used as hardener in epoxy resins and adhesives (ENTEC, 2008).

According to current information there are no registrations for MDA indicating there are uses as in an article[1], there are no SiA notifications made under Article 7(2) and there have been no applications for authorisation (afa) of the substance. The uses as an intermediate are not subject to authorisation and in addition wouldn't be subject to restriction (Article 68(1) 2nd sub paragraph). As there were no afa for the use in epoxy resins and adhesives it is concluded this is a historical use.

Information on hazards

MDA is classified in Annex VI of CLP as: Carc. 1B H350; Muta. 2 H341; STOT SE 1 H370; STOT RE 2 H373; Skin Sens. 1 H317; Aquatic Chronic 2 H411. MDA is candidate listed and included on Annex XIV for its carcinogenic properties.

Information on emissions/release

There is no information available on emission/release of MDA from articles.

Characterisation of risk

No risk has been identified for the use of MDA in articles.

A.3.2 Justification that action is required on a Union-wide basis

No restriction is proposed.

A.2.3 Justification that the proposed restriction is the most appropriate Union-wide measure

No restriction is proposed.

B. Information on hazard and risk

B.1 Identity of the substance(s) and physical and chemical properties

B.1.1 Name and other identifiers of the substance(s)

Chemical name: 4,4'-Diaminodiphenylmethane

EC Number: 202-974-4

CAS Number: 101-77-9

IUPAC Name: Bis (4-aminophenyl)methane

B.1.2 Composition of the substance(s)

Chemical name: Bis (4-aminophenyl)methane

EC Number: 201-329-4 202-974-4

[1] MDA has been registered in the tonnage band 10,000 - 100,000 tonnes per annum by 10 registrants (with 2 further inactive registrants): http://apps.echa.europa.eu/registered/data/dossiers/DISS-9c7b34e3-c5c4-7414-e044-00144f67d249/DISS-9c7b34e3-c5c4-7414-e044-00144f67d249_DISS-9c7b34e3-c5c4-7414-e044-00144f67d249.html.

CAS Number: 81-15-2 101-77-9

IUPAC Name: 1-tert-butyl-3,5-dimethyl-2,4,6-trinitrobenzene Bis (4-aminophenyl)methane

Molecular Formula: C12H15N3O6 C13H14N2

Structural Formula: -

Molecular Weight: 297.3 198.3 g/mol

Synonyms: 4,4'-Methylenedianiline, 4,4'-Diaminodiphenylmethane, 4,4'-Diphenylmethane diamine, 4,4'-Methylendibenzolamine, 4,4'-Methylenebisbenzeneamine, 4-(4-Aminobenzyl)aniline, MDA

Technical-grade MDA is used as an intermediate in the form of an isomer mixture with a varying content of tri- and polynuclear amines (so-called „polymers“). A typical standard product with a purity between 59 and 61 %(w/w) is liquid at room temperature and comprises the following:

Impurity Content	***CAS no.***	***EC no.***	***Molecular formula***
MDA polymers ca. 36 % w/w			
2,4'-MDA ca. 3.5 % w/w	1208-52-2	214-900-8	C13H14N2
2,2'-MDA < 0.1 % w/w	6582-52-1	229-512-4	C13H14N2
water < 300 ppm	7732-18-5	231-791-2	H2O
aniline < 100 ppm	62-53-3	200-539-3	C6H7N

Pure 4,4'-MDA (purity ³ 98 % w/w) is also used as an intermediate and has the following composition:

Impurity Content	***CAS no.***	***EC no.***	***Molecular formula***
2,4'-MDA (2.2- + 2.4) MDA max. 2 % w/w	1208-52-2	214-900-8	C13H14N2
2,2'-MDA (2.2- + 2.4) MDA max. 2 % w/w	6582-52-1	229-512-4	C13H14N2
4-amino-4'-methylaminodiphenylmethane traces aniline traces	62-53-3	200-539-3	C6H7N

B.1.3 Physicochemical properties

REACH ref Annex	*Property*	*Value*	*Reference*
VII, 7.1	Physical state at 20º C and 101.3 kPa	Powder	
VII, 7.2	Melting / freezing point	89 °C	
VII, 7.3	Boiling point	398-399 °C at 1013 hPa	
VII, 7.5	Vapour pressure	2.87 * 10-8 hPa at 20 °C	
VII, 7.7	Water solubility	1.25 g/l at 20 °C	
VII, 7.8	Partition coefficient noctanol/water (log value)	1.59	

B.1.4 Justification for grouping

Not relevant

B.2 Manufacture and uses

B.2.1 Manufacture, import and export of a substance

It is reported in the EU Risk Assessment Report (RAR; EC, 2001) that 10 manufacturing sites in several Member States that existed in 1989 and at the time of candidate listing there were 5 or 6 companies producing MDA and MDI (ENTEC, 2008). According to information from industry the production of MDA at the time of candidate listing could amount to 1,400,000 tonnes per annum (ENTEC, 2008). MDA has been registered in the tonnage band 10,000 - 100,000 tonnes per annum by 10 registrants (with 2 further inactive registrants)[2].

B.2.2 Uses

The main use of MDA is as an intermediate in the synthesis of MDI (EC, 2001). Other uses, such as an intermediate in the manufacture of high performance polymers, for

[2] As reported on ECHA's website on 22/4/2015.

processing to 4-4' methylenebis(cyclohexaneamine) and as hardener in epoxy resins and adhesives, have also been identified (ENTEC, 2008).

The use of MDA as intermediate in the synthesis of MDI represents more than 98% of the total production volume. MDI is mainly used in the production of rigid polyurethane foams (EC, 2005). It is assumed the overall European consumption of MDA in non-MDI uses remained fairly constant at the figure of 4000 tonnes per annum used in the EU RAR (EC, 2001; ENTEC, 2008).

The information available on the use of MDA as hardener in adhesives indicates that it is not likely to be used in adhesives or is being phased out from that use (ENTEC, 2008). No applications for authorisations were received for this use, so that will support the conclusion that it is a historical use.

B.2.3 Uses advised against by the registrants

Uses by workers and consumers.

B.2.4 Description of targeting

Targeting is based on the hazard for which the substance was included on Annex XIV.

B.3 Classification and labelling

Classification according to CLP

4,4'-Diaminodiphenylmethane (MDA) was inserted in Annex I to Directive 67/54/EEC with the 19th ATP and revised by the 29th ATP. It is classified as: Carc. 1B H350; Muta. 2 H341; STOT SE 1 H370; STOT RE 2 H373; Skin Sens. 1 H317; Aquatic Chronic 2 H411.

Classification according to the Classification and Labelling Inventory

There have been 942 notifications to the C&L inventory all reproducing the harmonised classification with no additional endpoints covered.

B.4 Environmental fate properties

Not relevant

B.5 Human health hazard assessment

A comprehensive risk and hazard analysis has been carried out in the EU RAR (EC, 2001).

B.6 Human health hazard assessment of physicochemical properties

Not relevant

B.7 Environmental hazard assessment

A comprehensive risk and hazard analysis has been carried out in the EU RAR (EC, 2001).

B.8 PBT and vPvB assessment

B 8.1 Assessment of PBT/vPvB Properties – Comparison with the Criteria of Annex XIII

Not relevant

B 8.2 Emission Characterisation

Not relevant

B.9 Exposure assessment

B.9.1 General discussion on releases and exposure

The main use of MDA is in the production of MDI, which is further processed to polyurethanes. There is no evidence from the relevant CSRs of MDA registrants that any residual MDA remains in the MDI produced. In addition, any MDA residue is not indicated in either the RAR for MDA or the RAR for MDI (EC, 2001; EC, 2005). In any case, MDI is further processed to polyurethanes before being used in articles, so any potential impurity would be negligible. It is possible that MDA is imported or exported in articles containing/made of epoxy resins or adhesives but no information to confirm this exists.

B.9.1.1 Summary of the existing legal requirements

MDA is restricted in accordance with entry 29 of Annex I to Directive 76/769/EEC and entry 28 of Annex XVII of REACH Regulation; it shall not be placed on the market for supply to the general public as a substance on its own or in mixtures.

B.10 Risk characterisation

Not relevant for this dossier as no use in articles has been identified.

B.11 Summary on hazard and risk

The main use of MDA is as an intermediate in the synthesis of MDI; this represents more than 98% of the total EU production volume (EC, 2001). According to the records there are no registrations for MDA indicating there are uses as an article, there are no SiA notifications made under Article 7(2) and there have been no applications for authorisation of the substance.

Information on hazards

MDA is a carcinogen (category 1B) according to Article 59, it has been included on the candidate list and into Annex XIV of REACH.

Information on emissions

There is no information available on emission of MDA from articles.

Characterisation of risk

No risk has been identified for the use of MDA in articles.

C. Available information on alternatives

Not relevant

D. Justification for action on a Community-wide basis

No restriction is proposed as no uses of MDA in articles have been identified. ECHA concludes that it is not in a position to prepare a restriction dossier that would conform to the requirements of Annex XV of the REACH Regulation.

E. Justification why the proposed restriction is the most appropriate Community-wide measure

Not applicable for the report.

F. Socio-economic Assessment of Proposed Restriction

Not applicable for the report.

G. Stakeholder consultation

The Annex XV report was subject to a Call for evidence from 13 May 2015 to 15 July 2015 (8 weeks).

[To be updated following CfE.]

H. Other information

Not relevant.

References

EC (2001): Risk-Assessment Report Vol.09, November 2000 on 4,4'-methylenedianiline, CAS#: 101-77-9, EINECS#: 231-634-8. Publication: EUR 19727 EN

EC (2005): Risk-Assessment Report Vol.59, November 2005 on methylenediphenyl diisocyanate (MDI), CAS#: 26447-40-5, EINECS#: 247-714-0. Publication: EUR 22104 EN

ENTEC (2008): Data on manufacture, import, export, uses and releases of 4,4'diaminodiphenylmethane as well as information on potential alternatives to its use. Report prepared for ECHA

RCOM (2009): "Responses to comments" document. Document compiled from the commenting period 14.01-14.04.2009.