1 June 2009

Background document for 4,4'-Diaminodiphenylmethane (MDA)

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

1. Identity of the substance

Chemical name:	4,4'-Diaminodiphenylmethane (MDA)
EC Number:	202-974-4
CAS Number:	101-77-9
IUPAC Name:	Bis (4-aminophenyl)methane

2. Background information

2.1. Intrinsic properties

MDA was identified as a Substance of Very High Concern (SVHC) pursuant to Article 57(a) as it is classified as Carcinogenic, Category 2[1] and it was therefore included in the candidate list for authorisation following ECHA's decision ED/67/2008 on 28 October 2008.

2.2. Imports, exports, manufacture and uses

2.2.1. Volume(s), imports/exports

According to the EU Risk Assessment Report (EC, 2001), in 1993, the production capacity of 4,4'-methylene diphenyl diisocyanate (MDI), the subsequent product of MDA was estimated to be 540,000t in Western Europe. For this, about 432,000 t of MDA were needed. Since then, there has been a significant increase in volumes of MDI (and hence MDA) manufactured in the EU. Anecdotal information from industry suggests that the current production of MDA is around 3-4 times higher than in 1993 (corresponding to an approximately 8% annual compound growth) and is therefore estimated to amount to 1,400,000 t/y (ENTEC, 2008).

The use of MDA as intermediate in the synthesis of MDI represents more than 98% of the total production volume. Apart from this use, non-MDI uses are also identified (EC, 2001), for which the annual tonnage is estimated to be more than 4000 t/y (ENTEC, 2008). This tonnage includes other intermediate uses than the synthesis of

[1] This document refers (here and in its other parts) to classification in accordance with Directive 67/548/EEC to keep the references in line with the entry in the published Candidate list. ECHA will update the Candidate list to follow the CLP Regulation ((EC) No 1272/2008) in future.

MDI, such as intermediate in the manufacture of high performance polymers and processing to 4-4' methylenebis(cyclohexaneamine).

Regarding the non intermediate uses no information on the quantities of MDA used as hardener in adhesives is available. It is estimated by one company that the overall EU consumption of MDA as hardener in epoxy resins is around 200 t/y, however this figure should be regarded as a minimum. Furthermore, at least 150t/y of MDA is used exclusively for another application of hardener in epoxy resins (ENTEC, 2008).

In conclusion, the manufacture of MDA for non intermediate uses is estimated to be around 350 t/y but this volume should be regarded as a minimum as it does not include the amount of MDA used as hardener in adhesives and the figure for the use of MDA as hardener in epoxy resins might be underestimated.

No precise information is available on EU import and export volumes of MDA. MDA is imported by some manufacturers as finished curing systems containing MDA. In addition, it seems that at least one company acts as a distributor and imports and exports MDA from/to the EU (ENTEC, 2008).

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

ISOPA (the European trade association for producers of diisocyanates and polyols) has indicated that there are currently 5 or 6 companies producing MDA and MDI in the EU but the number and location of the sites is not known (ENTEC, 2008). In the EU RAR (EC, 2001) 10 producing sites were reported for 1989. It is expected that there are manufacturing facilities in several Member States.

2.2.2.2. Uses and releases from uses

As stated above more than 98% of the total production of MDA was used on-site as an intermediate for the production of 4,4´-methylene diphenyl diisocyanate (MDI) (EC, 2001). MDI is further used for polyurethane production. Given the significant increase in MDA/MDI production, it is considered likely that the percentage used in MDI production is at least 98% and may well be greater (ENTEC, 2008).

Apart from its use in the synthesis of MDI, the following uses for MDA were identified (EC, 2001):

- Intermediate in the manufacture of high performance polymers
- Intermediate in processing to 4-4'methylenebis(cyclohexaneamine)
- Hardener in epoxy resins
- Hardener in adhesives

Based on the information from the Nordic product registers it is assumed that for the period between 2000 and 2006 the overall European consumption of MDA in non-MDI uses remained fairly constant (at least within an order of magnitude). Therefore it is assumed that the figure of 4000 t/y used in the EU RAR (EC, 2001) is still valid or is at least within an order of magnitude.

The first two uses (intermediate in the manufacture of high performance polymers and processing to 4-4'methylenebis(cyclohexaneamine), which is used as a hardener in epoxy resins are intermediate uses.

Regarding the use of MDA as hardener in epoxy resins, the available information indicates that MDA is used as a hardener in epoxy resins curing agents for coatings as well as a hardener for the manufacture of pipes using filament winding process. The tonnage values available indicate that at least 200 t/y of MDA are used as a hardener in epoxy resins curing agent and at least 150t/y of MDA is used exclusively in the filament wound pipe application (ENTEC, 2008).

The information available on the use of MDA as hardener in adhesives indicates that MDA is not likely to be used in adhesives or is being phased out from that use. MDA-containing hardener is still used in the automotive industry in binders for 'sand forms' to cast engine parts. No information on the quantities of MDA used as hardener in adhesives is available (ENTEC, 2008).

The use of MDA as hardener in epoxy resins and adhesives is not considered as a use of an intermediate in a manufacturing process of another substance but as an end use of the substance since it does not result in another substance which is manufactured/imported or placed on the market as such or in a preparation (RCOM, 2009).

Releases of MDA into the environment from non-intermediate uses (hardener in epoxy resins and adhesives) are considered not to be significant (EC, 2001).
However releases are expected from these uses resulting in exposure of the workers in the skilled trade area (small and medium-sized companies) (ENTEC, 2008). It seems that some companies do not sell epoxy resins curing agents containing MDA to the skilled trade area and that these products are intended to be applied in an industrial environment. However it is unclear if this is the case for all the companies dealing with curing agents containing MDA (ENTEC, 2008).

As a consequence it can not be excluded that there might be exposure of workers in the skilled trade area due to the use of hardener in epoxy resins and adhesives containing MDA.

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

As already indicated in a section above, according to the available information, MDA is currently manufactured by 5 or 6 companies in the EU, but the number and location of the sites is not known (ENTEC, 2008).

According to the available information, the non-intermediate uses of MDA may then involve rather short supply-chains.
Furthermore, although a high number of professional and industrial actors throughout EU may potentially be involved, this would apply to a limited number of relatively similar industrial sectors and professional user groups.

2.3. Availability of information on alternatives[2]

There appears to be information available on alternatives to MDA for its non-intermediate uses. Furthermore the available information indicates substitution of MDA is already ongoing for these non-intermediate uses, and in particular for its use as hardener in adhesives (ENTEC, 2008). There appears also to be information on the limitation of the applicability of the alternatives for certain uses as hardener in epoxy resins (ENTEC, 2008). Therefore, the available information on potential alternatives facilitates preparing an analysis of alternatives for uses for which actors wish to apply for.

Consequently, the available information suggests that potential applicants would be well prepared to develop an application, in particular the analysis of alternatives.
Hence, the available information justifies an early application date.

2.4. Existing specific Community legislation relevant for possible exemption

It is noted that MDA is restricted in accordance with entry 29 of Annex I to Directive 76/769/EEC and entry 28 of Annex XVII[3] of REACH Regulation.

Pursuant to entry 29 of Directive 76/769/EEC (and 28 of Annex I of Annex XVII of REACH Regulation) substances (e.g., MDA) which appear in Annex I to Directive 67/548/EEC classified as carcinogenic category 1 or 2, shall not be placed on the market for supply to the general public as a substance on its own or in preparations when equal to or greater than either the relevant concentration specified in Annex I to Directive 67/548/EEC, or the relevant concentration specified in Directive 1999/45/EC (i.e., is equal to or greater than 0.1%). Thus, placing on the market for supply to the general public of MDA in concentrations lower than 0.1% is permitted.

Article 56(6)(b) of REACH provides that the authorisation requirement does not apply to the use of substances in preparations below the lowest of the concentration limits specified in Directive 1999/45/EC or in Annex I to Directive 67/548/EEC. Accordingly, the concentration limits specified for MDA in Directive 76/769/EEC (and in Annex XVII of REACH) are in fact the same as the concentration limits referred to in Article 56(6)(b). Therefore, the use of MDA below the concentration limits set out in Directive 76/769/EEC (and Annex XVII of REACH) does not need to be subject to an exemption from authorisation.

Furthermore, pursuant to entry 29 of Directive 76/769/EEC (and 28 of Annex XVII of REACH) the concentration limits described above do not apply to medicinal or veterinary products, cosmetic products, motor fuels, mineral oil products intended for use as fuel, fuels sold in closed systems, and artists' paints.

Pursuant to Articles 2(5)(a), 56(4) (c) and (d) and 56(5)(a) the provisions on authorisation under REACH do not in any event apply to medicinal or veterinary

[2] Please note that this information was not used for prioritisation.
[3] Annex XVII shall apply from 1 June 2009, until that Directive 76/769/EEC applies.

products, cosmetic products[4], motor fuels, mineral oil products intended for use as fuel and fuels sold in closed systems. Use of MDA in these products therefore does not need to be exempted from authorisation under Article 58(2) of the REACH Regulation.

However, the use of MDA in artists' paints covered by Directive 1999/45/EC is not automatically exempted from authorisation under the REACH Regulation. In light of the fact that such use was already permitted under Annex XVII of REACH Regulation which is legislation imposing minimum requirements relating to the protection of human health, an exemption from the authorisation pursuant to Article 58(2) of the REACH Regulation for the use of artists' paints could be considered.

It should be noted that it is not possible to grant an authorisation that would constitute a relaxation of a restriction set out in Annex XVII (Art 60(6) of REACH). Therefore, it is not possible to authorise, and by that not meaningful to apply for an authorisation for the placing on the market of MDA as such or in preparations for the supply for generic public.

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

No data available.

[4] In the case of substances that are subject to authorisation only because they meet the criteria in Article 57(a), (b) or (c) or because they are identified in accordance with Article 57(f) only because of hazards to human health.

3. Conclusions and justification

3.1. Prioritisation

According to information from industry the current production of MDA could amount to1,400,000 t/y. The volume of MDA used for non-intermediate uses is estimated to be at least 350 t/y. In addition, there may be uses of MDA as hardener in adhesives. It is however not clear whether these are still actual uses and what amounts are supplied to these uses.

The uses as hardener in epoxy resins and in adhesives are expected to potentially occur across the entire EU and are therefore considered to be widespread. Furthermore releases to the working environment and as a consequence exposure of workers in the skilled trade area cannot be excluded. The uses of MDA as hardener in epoxy resins and adhesives in the skilled trade area are therefore considered to be wide dispersive.

Given the relatively high volume of MDA supplied to uses and applications that must be considered as wide dispersive, ECHA recommends to include 4,4'-Diamino diphenyl methane in Annex XIV.

3.2. Recommendation for Annex XIV entry

3.2.1. Transitional arrangements

Based on the available information, it is anticipated that the preparation of applications for authorisation would be facilitated by rather short supply-chains, which consist of actors from a limited number of relatively similar industrial sectors and professional user groups.

Furthermore, the available information indicates an already ongoing substitution of MDA with alternative substances. There appears also to be information on the limitation of the currently available alternatives for certain uses. Therefore, the available information on potential alternatives facilitates preparing an analysis of alternatives for uses for which actors wish to apply for. Consequently, the available information suggests that potential applicants would be well prepared to develop an application, in particular with respect to the analysis of alternatives.

Hence, in light of the available information, ECHA recommends the following early transitional arrangements:

- *Latest application date*:
  24 months after the entry into force of the Decision to include the substance in Annex XIV

- *Sunset date*:
  42 months after the entry into force of the Decision to include the substance in Annex XIV

3.2.2. Review periods for certain uses

Neither the available information for MDA nor the comments following the public consultation of 14 January 2009 provide information that would support defining review periods for any uses in accordance with article 58(1)(d).

ECHA therefore recommends not to include any review periods for uses of MDA.

3.2.3. Exempted (categories of) uses

Recommendation:

ECHA recommends not to include any exemptions for uses of MDA.

Justification:

Exemption for use in artists' paints:
Directive 76/769/EEC sets out the restrictions on the uses of substances as well as specific exemptions to these restrictions. These restrictions (and their exemptions) are incorporated in Annex XVII of the REACH Regulation which will replace the entries in Directive 76/769/EEC from 1 June 2009. The recitals of Directive 76/769/EEC and the directives amending it provide that these restrictions have an objective to protect human health and/or the environment. Directive 76/769/EEC could therefore constitute specific Community legislation imposing minimum requirements relating to the protection of human health and the environment for the use of a substance within the meaning of Article 58(2) of the REACH Regulation.

On this basis, ECHA considers that where an entry in Annex XVII exempts a specific use of a substance from the restrictions, Article 58(2) could be used to exempt that specific use from authorisation in the two following situations:

i) Annex XVII includes a restriction on a specified use of a substance and this restriction specifies condition(s) under which the restriction does not apply

ii) Annex XVII includes a generic ban on a substance and a specified use is exempted from this generic ban. Such an exemption can be subject to further conditions.

Entries 28 to 30 of Annex XVII provide that all substances classified as CMR (Category 1 and 2) may not be used in substances and mixtures placed on the market for sale to the general public. However, these entries exempt from restriction the use of such substances in artists' paints.

In the draft recommendation published by ECHA on 14 January 2009 ECHA considered that as MDA is one of the CMR substances concerned by entries 28 to 30 of Annex XVII and that recital (80) of the REACH Regulation requires that a proper interaction should be ensured between the provisions of authorisation and restriction, an exemption from the authorisation requirement should be granted pursuant to

Article 58(2) of the REACH Regulation for the use of MDA in artists' paints on the basis that this use has been specifically exempted in Annex XVII.

In its opinion of 20 May 2009 ECHA's Member State Committee (the MSC) considered that no exemption should be granted from the authorisation requirement for the use of MDA in artists' paints. This opinion was based on the following considerations.

First, some members of the MSC expressed doubts as to whether the exemption from restrictions of the use in artists paints could be regarded as meeting the criteria for exemption from authorisation set out in Article 58(2) as the exemption to the restriction was based on socio-economic grounds rather than on health and risk considerations.

On this point ECHA considers that in determining whether an exemption to a restriction should benefit from an exemption from the authorisation requirement it is not possible to simply dissociate the exemption from the restriction. The restriction and its related exemptions must be examined as a whole in order to determine whether an exemption under Article 58(2) of the REACH Regulation should be granted.

Second, all members of the MSC considered that an exemption should not be granted for the use of artists' paints on the basis that the exemption from the restriction requirement of that use in entries 28 to 30 of Annex XVII covers a category of substances (i.e., all CMRs) rather than a specific substance (i.e., only MDA or group of specified substances). In the MSC's view an exemption to a restriction covering a wide range of substances may not necessarily meet the requirements from exemption from authorisation under Article 58(2) of the REACH Regulation.

On this latter point ECHA shares the MSC's concern. On the basis of the information available ECHA cannot determine whether such an exemption can be justified under Article 58(2) of the REACH Regulation. ECHA therefore decided on the basis of the MSC's opinion and the deliberations leading to that opinion to amend its recommendation and not propose an exemption from the authorisation requirement for the use of MDA in artists' paints.

ECHA however urges the European Commission to examine on the basis of the information at its disposal whether such exemption should be introduced after all, and to further clarify under what conditions specific exemptions to restrictions set out in Annex XVII should be taken into account when determining exemptions from the authorisation requirement under Article 58(2) of the REACH Regulation.

<u>Exemptions requested by third parties</u>:
During the public consultation on the draft recommendation, ECHA received a number of requests for use-specific exemptions of MDA.

ECHA did not see grounds for recommending general exemptions for MDA for the reasons set out in the "*Responses to comments*" document.

3.2.4. Application of authorisation to product and process oriented research and development (PPORD)

Neither the available information for MDA nor the comments following the public consultation of 14 January 2009 provide information that would support introducing exemptions from the authorisation requirement for product and process oriented research and development (PPORD) on the basis of Article 56(3) of the REACH Regulation.

Therefore ECHA does not recommend to exempt the use of MDA in PPORD from authorisation.

3.3 Possible route for authorisation

The substance meets the criteria in Article 57(a) and according to available information it is not possible to determine a toxicological threshold in accordance with section 6.4 of Annex I. Therefore, pursuant to article 60(3) of the REACH Regulation it would appear that an authorisation can only be granted in accordance with Article 60(4) ('socio-economic route').

4. 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

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.