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Background document for formaldehyde, oligomeric reaction products with aniline (technical MDA)

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

Information comprising confidential comments submitted during public consultation, or relating to content of Registration dossiers which is of such nature that it may potentially harm the commercial interest of companies if it was disclosed, is provided in a confidential annex to this document.

1. Identity of the substance

Chemical name:	Formaldehyde, oligomeric reaction products with aniline
EC Number:	500-036-1
CAS Number:	25214-70-4
IUPAC Name:	Formaldehyde, oligomeric reaction products with aniline

2. Background information

2.1. Intrinsic properties

Formaldehyde, oligomeric reaction products with aniline (technical MDA) was identified as a Substance of Very High Concern (SVHC) according to Article 57 (a) as it is classified in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008 as carcinogen 1B[1] (H350: "May cause cancer"), and was therefore included in the Candidate List for authorisation on 19 December 2011, following ECHA's decision ED/77/2011.

[1] This corresponds to a classification as carcinogen cat. 2 (R45: "May cause cancer") in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) N° 1272/2008

2.2. Imports, exports, manufacture and uses

2.2.1. Volume(s), imports/exports

According to information provided in the registrations, most of the volume (> 500,000 t/y) of technical MDA is registered as intermediate, mainly for the manufacture of methylene diphenyl diisocyanate (MDI).

Still, a relatively high amount (100 – 1000 t/y) is registered as being imported for uses within the scope of authorisation (Germany, 2011; registration information). No information on exports is available.

In addition to the use in the manufacture of MDI, the Annex XV report (Germany, 2011) indicates the following uses for technical MDA:

- as hardener for epoxy resins in
    - adhesives
    - the production of rolls with composite cover
    - the production of chemically resistant pipes
    - the production of moulds
- in the production of high performance polymers
- as a starting point for the synthesis of 4,4'-methylenebis (cyclohexane-amine)

However, only the uses in the production of rolls, pipes and moulds have been included in the full registration dossiers (ECHA, 2012a). The other registrations only refer to uses of the substance as intermediate (ECHA, 2012b).

The uses as hardener / curing agent are sometimes interpreted as intermediate uses (see Annex XV report on 2,2'-dichloro-4,4'-methylenedianiline (MOCA); ECHA, 2011); however, according to ECHA's guidance on intermediates, they are not. Even though a chemical reaction is taking place, the purpose is not the synthesis of a new substance but to add desired properties and functions to the polymers[2] or adhesives (ECHA, 2010). Given this frequent misinterpretation, it might be possible that some registrants erroneously deem their use of the substance as a curing agent or hardener to be covered by their registration of technical MDA as intermediate. Therefore, a (likely small) part of the overall tonnage registered as intermediate might in fact be allocated to uses in the scope of authorisation.

Therefore, similar to the approach taken for MDA (ECHA, 2009), the volume of 100 – 1000 t/y in the scope of authorisation should be regarded as the minimum, but a higher volume cannot be excluded.

[2] Nevertheless, when a cross-linker is used in the manufacturing of a cross-linked polymer substance as such (e.g. a polymer substance isolated as powder or pellets), the use of such cross-linker can be regarded as an intermediate use. Still uses during which the cross-linking reaction takes place at the "in mould" phase where (a part of) an article is produced would rather be uses in the scope of authorisation.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Technical MDA is synthesised by reaction of formaldehyde and aniline in the presence of hydrochloric acid (Germany, 2011). The main constituent of technical MDA is MDA itself (about 60 %). In fact, MDA is manufactured by distillation from technical MDA (EU RAR, 2001).

The manufacture of technical MDA takes place in closed systems and it is transferred at dedicated facilities (ECHA, 2012b). According to the EU RAR (2001), exposure might take place during less controlled activities such as maintenance, cleaning or sampling. However, a high level of implementation of Risk Management Measures can be expected at the manufacturing sites.

2.2.2.2. Uses and releases from uses

Both MDA and technical MDA have the same functions as curing agent for polymers and hardener in epoxy resins and adhesives, as described above. The full registration dossiers submitted for technical MDA (similar to the registrations of MDA) advise against the use of the substance by professionals or consumers.

Further specific applications were reported when the substance was up for public consultation in the context of the process that led to its identification as a SVHC (RCOM, 2011): e.g. use in ion exchange resins in nuclear power plants (a matrix used to contain radioactive waste). This use also falls within the scope of authorisation. Nevertheless, industry informed (RCOM, 2011) that due to the nature of the application (nuclear power plant), the use is highly automated and contained. Also, the further life cycle of the substance is expected to be highly controlled, with low releases of technical MDA.

The registered uses described on ECHA's dissemination website (ECHA, 2012a), include processes like dipping and pouring, transfer at non-dedicated facilities and others that seem to have high potential for exposure of workers.

Some workplace measurements in the MDA sector were provided in the EU RAR (2001), with values of the 95 percentile above or around the DMEL derived for MDA (ECHA, 2012c) in different activities, such as using flake MDA, processing of resins, sack emptying flake MDA (EU RAR, 2001). More recent data, provided in the Annex XV report (2011) indicate that worker exposure takes place to a lesser extent in the plastic and foam industry, but to a significant extent in steel foundries (measured data above derived DMEL), where (technical) MDA is used for the preparation of moulds when steel is casted (EPA, 1990). The fact that significant levels of MDA are also measured during the casting process might indicate that the curing agent MDA is released from the finalised moulds. Thus, this life cycle stage should be taken into account in the further risk assessment in case the substance would be subject to the authorisation requirement.

In conclusion it is assumed that the uses of technical MDA in the scope of authorisation bear a high potential for significant exposure to workers.

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

No conclusive information is available regarding the supply chain structure of the uses of technical MDA in the scope of authorisation.

However, the Annex XV report (Germany, 2011) assumes for technical MDA a similar supply chain as for MDA. The use of MDA as hardener in epoxy resins and adhesives is expected to take place in the entire EU and to result in exposure of workers, in particular in smaller companies.

Regarding the use as curing agent, the EU RAR (2001) on MDA (sometimes referring also to technical MDA), describes tens of different formulations containing MDA in one-component and two-component applications, in liquid, paste, granular or powder form and containing MDA in concentrations between 0.1 and 60 %. Formulations containing MDA/technical MDA seem to be prepared in industrial settings and then further distributed to downstream users (RAR, 2001; Entec, 2008). This suggests a similar structure of the supply chain as for MOCA (for similar uses and applications), where information is available indicating the existence of tens of formulator sites and hundreds of use sites in the EU (ECHA, 2011).

Therefore it appears reasonable to assume that technical MDA is also used at a high number of sites.

2.3. Availability of information on alternatives[3]

The Annex XV report (Germany, 2011) suggests that other aromatic amines or aliphatic amines can be used as alternative curing agents in some circumstances, although information on alternatives for specific applications has not been found.

Also for the use of (technical) MDA as a hardener in epoxy resins some promising alternatives have been identified (as evidenced by a number of patents, ECHA, 2011). According to information provided during public consultation on the draft recommendation for the Authorisation List (RCOM, 2012), it seems that for the use of technical MDA in ion exchange resins in nuclear power plants a suitable alternative does exist and might be in place by end 2015, ahead of the proposed sunset date.

Two potential "alternative" substances, namely MDA (4,4'-Diaminodiphenylmethane, EC 202-974-4, CAS 101-77-9) and MOCA (2,2'-dichloro-4,4'-methylenedianiline, EC 202-918-9, CAS 101-14-4) are already included in Annex XIV (MDA) or the Candidate List (MOCA). It could be expected that technical MDA could replace MDA (main constituent of technical MDA) in many of its applications and could replace MOCA as a curing agent in some applications. However, these substances are not considered to be alternatives and such substitution would not be appropriate, as the overall risk would not be reduced because all three substances (MOCA, MDA and technical MDA) are carcinogens.

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

2.4. Existing specific Community legislation relevant for possible exemption

There seems to be no specific Community legislation in force that would allow consideration of exemption(s) of (categories of) uses from the authorisation requirement on the basis of Article 58(2) of the REACH Regulation.

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

Not available.

3. Conclusions and justification

3.1. Prioritisation

The substance is used in "relatively high" to "high" volumes in the scope of authorisation. The substance is expected to be used at a high number of sites, with significant potential for worker exposure.

Verbal-argumentative approach

On the basis of the prioritisation criteria, formaldehyde, oligomeric reaction products with aniline (technical MDA) gets high priority for inclusion in Annex XIV.

Scoring approach

Score			Total Score
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	(= IP + V + WDU)
1 Art. 57 (a); Carc 1B	5-7 (Relatively high to high volume used in the scope of authorisation)	Overall score: 3 * 3 = 9 Site-#: 3 (Substance is used at a high number of sites) Release: 3 (Significant potential for worker exposure from uses within the scope of authorisation)	15-17

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, formaldehyde, oligomeric reaction products with aniline (technical MDA) gets high priority for inclusion in Annex XIV.

Furthermore, a very similar substance with similar uses, namely MDA (main constituent of technical MDA), is already included in Annex XIV. Considering regulatory effectiveness (i.e. that technical MDA could at least in some uses replace MDA) further supports the prioritisation of this substance.

Additionally, technical MDA should be seen as a potential alternative to MOCA (on the Candidate List), even though it might not be suitable to replace this substance in all its applications.

Therefore, it is proposed to prioritise formaldehyde, oligomeric reaction products with aniline (technical MDA) for inclusion in Annex XIV.

4. References

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