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SCIENTIFIC COMMITTEE ON TOXICITY, ECOTOXICITY AND THE ENVIRONMENT (CSTEE)

Opinion on the results of the Risk Assessment of:

METHYLENEDIPEHNYL DIISOCYANATE (MDI)

Environmental part

CAS N°: 26447-40-5

EINECS N°: 247-714-0

Carried out in the framework of Council Regulation (EEC) 793/93 on the evaluation and control of the risks of existing substances[1]

Adopted by the CSTEE during the 43rd plenary meeting of 28 May 2004

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[1] Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of those substances if they are produced or imported into the Community in volumes above 10 tonnes per year. The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC)1488/94, which is supported by a technical guidance document.

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Terms of Reference

In the context of Regulation 793/93 (Existing Substances Regulation), and on the basis of the examination of the Risk Assessment Report the CSTEE is invited to examine the following issues:

1. Does the CSTEE agree with the conclusions of the Risk Assessment Report

2. If the CSTEE disagrees with such conclusions, the CSTEE is invited to elaborate on the reasons for this divergence of opinion.

According to the Technical Guidance Document on Risk Assessment – European Communities 2003:

- conclusion i): There is a need for further information and/or testing;

- conclusion ii): There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already;

- conclusion iii): There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Introduction

Within the EU, a total MDI of 790 ktonnes is produced at 11 sites. Of this, 105 ktonnes is exported. The term 'MDI' refers to a number of isometric forms of $C_{15}H_{10}N_2O_2$. The substance is used in the industrial production of rigid polyurethane foams (56%), flexible polyurethane foams (13%), C.A.S.E. products (26%; i.e. coatings adhesives, sealants and elastomers), thermoplastic polyurethanes (4%) and fibres (1%).

General comments

The CSTEE finds that, in general, the RAR is written in a manner consistent with the Regulation and covers most aspects of the environmental risk assessment of MDI . However, the CSTEE would like to raise a number of fundamental concerns on the risk evaluation of sparsely soluble substances in general, and the way the RA was performed for MDI, in particular. The concerns, data gaps and some minor specific comments are given hereunder.

The CSTEE notes that although the environmental exposure and effects assessments and the risk characterization are conducted using procedures recommended by the TGD

(1996), assessments for certain environmental compartments were not included in the RAR.

The CSTEE notes the following:

1. The lack of transparency in the PEC calculations and the complete absence of any measured environmental MDI concentrations;

2. The CSTEE cannot agree with the proposed PNECs due to the methodological uncertainties explained above;

3. The absence of certain section(s) in the RAR;

4. The uncertainties associated with, and absence of data on, the environmental concentrations and toxicity of the reaction products of MDI.

Based on these conclusions, the CSTEE is of the opinion that the conclusion (ii) proposed in the RAR is not supported by the scientific evidence presented in this Report. The CSTEE suggests that the concerns expressed in this opinion are addressed in a revised version of the RAR.

In general, the environmental exposure and effects assessments and the risk characterisation are conducted using procedures recommended by the TGD (1996). Where appropriate, realistic worst-case scenarios were used. The CSTEE would like to point out that for both the exposure and effects assessment, the available data seems to be limited.

Specific comments

Physico-chemical properties

The RAR states that the determination of solubility of MDI is difficult due to the reactivity of it's NCO with OH groups. Consequently it was not possible to measure the solubility of MDI in water using standard EC methods.

The solubility was thus calculated using a regression method, developed with MDI by Yakabe, linking log Pow and log water solubility. As the report of this study was not available to the CSTEE, we were unable to evaluate this approach and the proposed calculated solubility of 0.02mg/l. Still based on the report by Yakabe, the RAR concludes that 0.02 mg/l solubility limit is the maximum achievable concentration in water. Although it is stated in the RAR that this value was taken as a worst case for the subsequent risk assessment, the CSTEE notes that in the several sections (e.g. bioconcentration assessment, effects assessment, PNEC derivation) of the RAR, nominal MDI – i.e. added concentrations – and not the 0.02 mg/l value was used in the assessments. Considering the importance of solubility, the CSTEE suggest that these sections are appropriately revised.

Exposure assessment

The RA reports states that releases to water, sediment and soil during production is expected to be non-existent or negligible since production takes place in a closed system. Releases of the MDI to the environment to the atmosphere might occur during the production but are expected to be low as exhaust gases are incinerated or scrubbed. The

RAR states that waste water from cleaning and decontamination procedures are not expected to contain any MDI but rather polyurethanes and polyureas which are insoluble and inert.

Emissions of MDI to soil, waste water and sediment during processing are expected to be negligible and polyurethanes products neither contain generic isocyanates nor biologically available isocyanate groups.

The CSTEE notes that most of these statements are not supported by data or literature references

In contact with water, MDI forms a solid crust encasing partially unreacted or unreacted material. Degradation through hydrolysis was experimentally established (simulated realistic environmental conditions) and a half-life of 143 hours was derived. Several experimental studies also demonstrated that MDI additions to water yield no aqueous MDI concentrations and very low MDA concentrations (0,13 to 2 %). The RAR also mentions the degradation (and solubility) of MDI in an experimental field study. Heimbach (1993) detected no MDI (detection limit 0.006 mg/l) in a 112 day artificial pond study in which polymeric MDI had been added up to a concentration of 10 g/l .

Two independent studies demonstrate that MDI and its reaction products with water are not biodegradable. No data are available for MDI degradation in soil. The rate constant calculated by EUSES was used in the RAR. A sediment half-life of 80 days was derived from the above-mentioned experimental pond study. The calculated tropospheric half-life of 4,4 MDI is 1.3 days.

Two studies reporting on the accumulation of MDI in aquatic environment are discussed in the RAR. In the artificial outdoor pond study, MDI was added at a concentration of 10 g/l and it's concentration was monitored in water, fish (rainbow trout) and sediments for 112 days. MDI and MDA was not detected in the water (detection limit 0,01 mg/l) or in fish (detection limit for MDI 0.5 mg/l). In the second study, carp were exposed to 0.1 mg/l in a river model exposure system for 8 weeks. No MDI was detected in the fish (detection limit: 0.1 mg/kg). From this, the RAR concludes that bioacummulation is unlikely to occur.

The CSTEE agrees with the evaluation of the available data, the selected rate-constants used in the RAR and the conclusions proposed in this section of RAR.

The section on the predicted environmental concentrations (3.1.5) is not transparent and thus does not allow verification of the validity of the PECs. The CSTEE suggests that this section is revised.

PEC calculations were provided for five life stages. Additionally, release information - provided by producers and users were also presented. Local and regional PECs were calculated using EUSES 1.00 ad the default emission scenarios (A and B-tables). However, for the local PECs the release estimation output from EUSES was overridden by release estimations calculated and provided by Industry. It is unclear to the CSTEE how these estimates were obtained. The PEC calculations could not be verified as the results of the EUSES calculations were not available to the CSTEE (Annex 3). The combination of: (1) limited information provided on the standard EUSES calculations, (2) the fact that some were and some were not adjusted with Industry data and (3) the very concise reporting style, results in a non-transparent section.

The RAR states that depending on the life stage, local PECs varied from $1.5x10^{-5}$ to $8.1x10^{-7}$ mg/m^3 for air, $1.4x10^{-4}$ to $5.4x10^{-5}$ mg/kg for agricultural soil, from $1.9x10^{-4}$ to $6x10^{-7}$ mg/kg for grassland and $1.4x10^{-6}$ mg/l and $1.7x10^{-4}$ mg/kg for water and sediment, respectively. PEC regional was $1.4x10^{-6}$ mg/l, $2.1x10^{-7}$ mg/m^3, $4.2x10^{-5}$ mg/kg, $4.2x10^{-5}$ mg/kg and $6.9x10^{-5}$ mg/kg for water, air, agricultural soil, natural soil and sediment, respectively.

No measured values of MDI concentrations in surface waters or any other environmental compartment are reported in the RAR.

Effects assessment

A discussion on the difficulties (due to it's low solubility) of testing MDI is given. The RAR also considers that MDA and other breakdown products may be (in part) responsible for the observed toxicity. The quality and relevance of the ecotoxicity data was evaluated although no real selection (based on the reliability index) of the reported data was performed. The criteria for assigning the tests to a certain category are not reported in the RAR.

Acute toxicity tests are available for 2 fish species exposed to nominal concentrations, i.e. added to the test medium, of 500 to 3000 mg/l of MDI. The actual MDI concentration present in the test medium was not measured. The MDA concentration in the tests with one species was measured and was 3.5 -4 mg/l. Results of long-term studies with 2 fish species are summarized in the RAR. In one study, rainbow trout were exposed in outdoor ponds for 112 days. A mixture of 4,4 MDI and polymeric MDI was added at concentration of 1000 and 10000 mg/l. No MDA was detected in the water. From the RAR it is unclear if the MDI concentration in the water was measured. At 10000 mg/l (nominal) a weight reduction of the fish was noted due a decrease of the cladoceran abundance in the pond. In the second study, carp were exposed of in a river model ecosystem to an added polymeric MDI concentration of 0.1 mg/l. Actual MDI and MDA concentrations in the water were not measured. No mortality was noted.

Acute toxicity test results are available or two invertebrate species (daphnid and a snail). Added concentrations in these tests were from 0.5 to 1000 mg/l MDI. In one of the daphnid tests, in which the MDI was dispersed through high speed shearing, a 24h EC50 of 130 mg/l was obtained. In all other tests the EC0 was higher than the highest test concentration. Actual MDI and MDA concentrations in the water were not measured. The results of one standard chronic toxicity test with *Daphnia magna* are reported in the RAR. The added polymeric MDI concentrations were 1 to 10 mg/l. No effects on reproduction were noted. Actual MDI and MDA concentrations in the water were not measured. The effects of MDI (1000 and 10000 mg/l of added MDI) on the copepod and cladoceran populations present in the long-term pond study were also summarized in the RAR. However, the information provided is too limited to draw conclusions on the toxicity of MDI.

Two studies on the effects of MDI on aquatic plants are summarized in the RAR. A standard algal growth test exposed to (up to) 1640 mg/l of added MDI was performed. No effects were observed. Actual MDI and MDA concentrations in the test medium were not measured. The second study concerns observations on the phytoplankton and macrophyte biomass in the pond studies performed by Heimbach (1996). Although the RAR states that no effects (at added concentrations of 1000 and 10000 mg/l) were observed in the latter study, the information provided on this study is too limited to allow

evaluation by he CSTEE. The RAR does mention a 72h EC for *Scenedesmus* of 21 mg/l (added?) and attributes this to the toxicity of MDA.

In summary, the RAR reports acute (L(E)C0s of >1000, > 1000 and > 1640 mg/l for fish, daphnids and algae. In the chronic daphnid test no effects were observed at the highest added concentration tested (10 mg/l).

From these data, using an assessment factor of 1000 and based on the acute toxicity data, the RAR derives a $PNECw_{ater}$ of >1 mg/l The RAR suggests that this approach is *'probably more suitable given the reactivity of the substance'*. To the CSTEE it is unclear what is meant with this statement. Furthermore, the CSTEE is not convinced of this argument as the residence time of the substance in the chronic test is the same (48h) as in most acute tests.

More fundamentally, the CSTEE is concerned that no toxicity data are available for which measured (in the test vessel) MDI data are reported. As shown by the study of Heimbach (1993) MDI detection limits are sufficiently low to measure this compound in laboratory toxicity tests.

Given the low reliability of the toxicity test results and other concerns expressed above, the CSTEE cannot support the proposed PNECaquatic of > 1 mg/l. The PNEC should be set at the solubility limit of MDI, i.e. 0.02 mg/l.

The RAR does not contain a section of the effects of MDI on benthic organisms, Hence, no PNEC for sediment compartment was calculated. The CSTEE suggests this section is included in the RAR and that the EQP method (using the aquatic toxicity data), in the absence of toxicity data on benthic organisms, could be used to derive this value.

Data of three terrestrial toxicity tests (invertebrate and 2 plants) are presented. The RAR states that no effects were noted at nominal MDI concentrations ranging from 10 to 1000 mg/kg. However, 14d EC50s of 444, 353 and 128 mg/kg dw soil for *Eisenia, Avena* and *Lactuva* are mentioned in the report, but it is concluded that this is due to MDA formation. The CSTEE does not understand how this can be stated if neither MDI no MDA concentrations are measured in the tests. Based on these concerns the proposed PNEC of > 1000 mg/kg / 1000 = > 1 mg/kg cannot be supported by the CSTEE.

Two studies on the toxicity of MDI to micro-organisms are summarized in the RAR. Added test concentrations ranged from 1 to 100 mg/l. Actual MDI and MDA concentrations in the water were not measured. No PNEC is proposed in the RAR.

For the atmospheric compartment the effects of MDI - assessed through inhalation tests with rats - is also described in the RAR. The CSTEE welcomes the integration of this type of rodent data in the environmental risk assessment. .

Risk characterisation

The risk characterisation in the Report is performed according to the procedure recommended by the TGD (1996). The RAR states that the calculated PEC/PNEC ratio's for all environmental compartments are 4 to 7 orders of magnitude < 1. The CSTEE does not support the risk characterisation presented in the RAR.

Due to the lack of information, a quantitative risk assessment for the atmospheric compartment could not be performed.

Based on the cited bioaccumulation, the RAR concludes that secondary poisoning is unlikely to occur. The CSTEE agrees with this conclusion.

The RAR finally very briefly assesses the possible risk due to MDA formed when MDI enters the water. PECs of MDA were calculated (using worst cause assumptions) and compared to $PNEC_{water}$ of MDA (3 µg/l). From this it is concluded that MDA resulting from MDI hydrolysis will not pose a risk to the aquatic environment. The CSTEE finds this evaluation to brief and unclear and can thus not support the conclusion on MDA.

Given the following concerns/observations:

1) The lack of transparency in the PEC calculations and the complete absence of any measured environmental MDI concentrations;

2) The CSTEE cannot agree with the proposed PNECs due to the methodological uncertainties explained above;

3) The absence of certain section(s) in the RAR;

4) The uncertainties associated with, and absence of data on, the environmental concentrations and toxicity of the reaction products of MDI;

The CSTEE is of the opinion that the conclusion (ii) proposed in the RAR is not supported by the scientific evidence presented in the Report. The CSTEE suggests that the concerns expressed in this opinion are addressed in a revised version of the RAR.

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