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GDCh-Advisory Committee
on Existing Chemicals of
Environmental Relevance (BUA)

4,4‘-Diamino-3,3‘-Dimethyldicyclohexylmethane (Dimethyldicyclohexylmethane)

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on Existing Chemicals of Environmental Relevance (BUA)

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Foreword

The German Chemicals Act (Chemikaliengesetz - ChemG) of 1980 stipulates that certain existing chemicals must be reported to the competent authority, if they exhibit properties which indicate that they may be hazardous, either alone or in combination with other substances.
In the summer of 1982, an Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) was set up by the German Chemical Society (Gesellschaft Deutscher Chemiker - GDCh). It brings together representatives from the scientific community, the chemical industry and the governmental authorities. This Advisory Committee is responsible for elaborating appropriate solutions for substances of relevance for health and the environment on the basis of voluntary measures. It selects and examines existing chemicals from the aforementioned angles. The testing and evaluation are based on scientific criteria alone.
It was, therefore, necessary to develop priority setting procedures. In a first phase reports were only prepared for priority chemicals. Within the framework of a first priority setting procedure, chemicals were compiled from several priority lists and 135 chemicals were selected for detailed substance reports.
In a second priority setting procedure the survey of the German Chemical Industry Association (VCI) on all substances with a production volume of more than 10 tons per year was used as a starting list. Since this survey covered 4,600 chemicals, BUA decided to process the corresponding list in several stages. The first stage included approx. 1,050 substances with a production volume of more than 1,000 tons per year.
Detailed reports are drawn up on chemicals suspected of having a hazard potential and abridged reports on those presenting only a minor hazard potential, according to the current state of knowledge.
The detailed BUA reports take in both the published literature and data from industry. If data for the evaluation of the chemicals are not available, additional studies are recommended and the results are published as updates to the reports. The reports serve as a basis for the instigation of administrative measures, when there are indications of risks to health or the environment.

Tübingen, May 1993

Ernst Bayer
Chairman of the Advisory Committee
on Existing Chemicals
of Environmental Relevance

Contents

Summary and Conclusions ..... **XI**

Recommendations ..... **XVI**

4,4'-DIAMINO-3,3'-DIMETHYLDICYCLOHEXYLMETHANE (DMD)

1. Chemistry of 4,4'-Diamino-3, 3'-Dimethyldicyclo-hexylmethane **1**
1.1 Chemical Identity 1
1.2 Composition of the Technical Product 2
1.3 Chemical Properties 2

2. Physical Properties **6**

3. Analysis **8**
3.1 Determination in Air 9
3.2 Determination in Water 10
3.3 Determination in Soil, Sediment, and Biological Material 10
3.4 Determination in Plastics 12

4. Introduction into the Environment through Production, Processing, Application, and Waste Disposal **13**
4.]. Production Method 13
4.2 Manufacturer and Processors, Production Quantities, Export, Import, Total Consumption 13
4.3 Processing, Application, Consumption Quantities 14
4.3.1 Processing 14
4.3.2 Application 16
4.4 Introduction into the Atmosphere 16
4.4.1 Introduction through Production and Processing 16
4.4.2 Introduction through Application of DMD-Cured Epoxy Resins 17

4.5 Introduction into the Hydrosphere 18
4.5.1 Introduction through Production and Processing 18
4.5.1.1 Introduction through Production 18
4.5.1.2 Introduction through Processing 18
4.5.2 Introduction through Application of DMD-Cured Epoxy Resins 18
4.6 Introduction into the Geo- and Biosphere 19
4.7 Introduction through Wastes and Their Treatment 19
4.8 Balance of Environmental Introduction 20

5. Environmental Occurrence 21
5.1 Atmosphere 21
5.2 Hydrosphere 21
5.3 Geosphere 21
5.4 Biosphere 21
5.5 Natural Sources 21
5.6 Plastics 21

6. Environmental Behavior 22
6.1 Transformation, Degradation, and Degradation Products 22
6.1.1 Biodegradation 22
6.1.1.1 Aerobic Degradation 22
6.1.1.2 Anaerobic Degradation 22
6.1.2 Hydrolysis 22
6.1.3 Photolysis 22
6.2 Accumulation 23
6.2.1 Bioaccumulation 23
6.2.2 Geoaccumulation 23
6.3 Distributional Behavior and Transport Processes within and between Environmental Compartments 24
6.3.1 Henry‘s Law Constant 24
6.3.2 n-Octanol/Water Partition Coefficient 24
6.3.3 Soil Sorption Coefficients 24
6.4 Environmental Fate 25

7. Ecotoxicity 27
7.1 Effects on Aquatic Organisms 27
7.1.1 Microorganisms 27
7.1.2 Plants 27
7.1.3 Invertebrates 27
7.1.4 Vertebrates 28
7.2 Effects on Terrestrial Organisms 28
7.3 Effects on Ecosystems 28

8. Toxicity to Warm-Blooded Animals 29
8.1 General Effects 29
8.2 Mode of Action 29
8.3 Metabolism, Toxicokinetics 29
8.4 Acute Toxicity 29
8.5 Skin and Mucous Membrane Tolerance 30
8.6 Sensitization 32
8.7 Subacute, Subchronic, and Chronic Toxicity 32
8.8 Genotoxicity 36
8.9 Carcinogenicity 36
8.10 Reproduction Toxicity 36
8.11 Other Effects 37
8.12 Human Cases 37
8.12.1 Acute Poisoning 37
8.12.2 Epidemiological Data 37

9. Substance-Specific Legal Regulations 39

10. References 42

BUA Report on 4,4‘-Diamino-3,3‘-Dimethyl dicyclohexylmethane (DMD)

Summary and conclusions

Ecological aspects

Introduction through Production and Application

In 1991 DMD was produced by one manufacturer in the Federal Republic of Germany, at an amount of between 1 000 and 3 000 tonnes. The capacity is less than 5 000 t/a. The substance is not further processed by the manufacturer.
DMD is not known to be manufactured or processed in the former GDR.
Considerably more than half of the production was exported; imports are not known. Several hundred tonnes are sold annually in the Federal Republic of Germany.

The only known application in the Federal Republic of Germany is in epoxy resins. DMD is added to low-molecular epoxides as a hardener. The reactivity of the four H atoms of the amino groups with the epoxide groups permits a multiple cross-linkage of DMD during hardening, and thus chemical binding in the cross-linked resins. The presence of traces of free DMD in the hardened material cannot be excluded, however. An introduction into the environment is rather unlikely, due to the difficult diffusion in the cross-!inked system. Analytical results on DMD are not available, however.

Epoxy resins cross-linked with DMD are used mainly for coating concrete and other building materials, as raw material for the varnishes, and in anti-corrosive paints. These resins can also be employed in shipbuilding and for coating pipelines.

According to one processor DMD is also used as a hardener in the wet laminating of heavy-duty fiber composite materials. As diamine, DMD can be condensed into poly-amides. No manufacturer of such products is known in the Federal Republic of Germany.

There is no known application without chemical conversion in the Federal Republic of Germany.

As the German manufacturer incinerates exhaust forming during the synthesis, continuous distillation and storage in tanks, atmospheric emissions are not expected.

No waste water forms through the actual synthesis of DMD. Via the waste water formed in generating a vacuum for the distillation apparatus, which requires treatment and is passed to the biological sew plant, < 42 kg DMD/a is introduced into the hydrosphere.

Distillation residues accumulating through production are disposed of in a residue incineration plant.

Quantitative data on the environmental introduction of DMD through processing are not available. However, no atmospheric introduction is expected through epoxy resin hardening at room temperature or higher temperatures, due to the reactivity of the substance with the epoxide groups and the low vapor pressure. As plants using higher hardening temperatures are connected to incinerators, no substantial introduction is anticipated here. Inadequate exhaust suction or extensive processing under unfavorable conditions can cause contamination of breathable air. DMD is not expected to enter the environment by splitting again into fragments of the initial epoxy resins and whole DMD molecules.

No water forms during the cross-linking of epoxy resins with DMD, thus ruling out an introduction min the hydrosphere through processing. An introduction during handling and transport is possible but not quantifiable.

Epoxy resins hardened with DMD show no decomposition through swelling and hydrolysis; even under extreme conditions, such as use in shipbuilding, decomposition or appreciable leaching are not observed. Material testing has shown that resins hardened with DMD are susceptible to hydrolysis under extreme, non-environmentally relevant conditions.

Considering the areas of use and the almost complete conversion expected during processing, no appreciable introduction into the geo- or biosphere is anticipated.

Environmental Occurrence

Data are not available on the occurrence of DMD in the atmosphere, hydrosphere, geosphere or biosphere. There are indications of its presence at the workplace.

Degradation

Under the laboratory conditions cited, no biodegradation of DMD takes place aerobically. Data are not available on its biodegradation under anaerobic conditions or in soil. On the basis of data at hand, DMD should be characterized as sparingly volatile in water; volatilization into the atmosphere is thus not expected. Due to the substance‘s chemical structure, no hydrolysis is anticipated.

DMD can be degraded photochemically in the atmosphere. The half-lives for the reaction of DMD with OH radicals in the gas phase are about 2.8 and 3.1 hours (values calculated empirically).

Accumulation

The log P_{OW} of 2.51 for DMD (although inaccurate, due to its Lewis base character) indicates a low bioaccumulation potential. Experimental investigations on the bioaccumulation and geoaccumulation are not available. Since binding is thought to occur through Ion exchange, mobility in soil is not suspected.

Ecotoxic Effects

In the short-term respiratory test according to ISO/DIS 8192 (Part B) an EC_{20} (30 minutes) of 160 mg/l was determined.

In the cell growth inhibition test with *Pseudomonas putida* (experiment carried out according to a draft for DIN 38412, Part 8), an EC_{50} of 96 mg/l was determined for an exposure period of 17 hours.

A cell growth inhibition test with green algae (*Scenedesmus subspicatus*; performed according to DIN 38412, Part 9) determined an EC_{50} (72 h) of 2.1 mg/l, an EC_{10} (96 h) of 0.41 mg/l and an EC_{50} (96 h) of 1.55 mg/l.

An acute toxicity test for daphniae (performed according to procedure C2 of Appendix V for Guideline 79/831/EEC) gave the following values: EC_{50} (24 h) 25.19 mg/l, EC_0 (48 h) 6.25 mg/l and EC_{50} (48 h) 15.16 mg/l.

In an investigation performed in accordance with DIN 38412 (Part 11) with the golden orfe (*Leuciscus idus*) the LC_{50} (96 h) was found to be between 22 and 46 mg/l ($NOEC_{acute}$: 21.5 mg/l).

Data on the effects on terrestrial organisms are not available.

Toxicological Aspect

The oral LD_{50} for the rat is > 320 mg/kg bw. The dermal LD_{50} is > 200 mg/kg bw in the rabbit. The inhalative LC_{50} after aerosol exposure of rats is 0.42 mg/l/4h. Earlier studies on the acute toxicity describe impairment of heart function, mucous membrane corrosion, and changes in the kidney and urinary tract.

DMD has a highly irritating to corrosive effect on the skin and eye. The available studies gave no indication of a sensitizing effect.

After repeated administration, in addition to damage to the liver, kidney and nasal mucosal epithelium, changes in skeletal and cardiac muscles were described. The no effect dose or concentration in the rat was 2.5 mg/kg bw (NOEL) in a 90-day exploratory study and 2 µg/l (NOEC) in a 90-day inhalation study.

In exposed persons sclerotic skin changes have been described and indications of liver damage were found; the skin changes were also seen in animal experiments after high intraperitoneal doses.

Several in vitro studies with the pure substance gave no indication of a genotoxic effect.

Studies on the carcinogenic effect and reproductive toxicity are not available.

Recommendations

Ecological Aspects

Environmental introductions through DMD production are very low. In DMD processing, the presence of appreciable amounts of DMD in the finished, hardened epoxy resin is probably slight. No analytical investigations are available, however.

The following tests are thus recommended to dose this gap:

- Determination of the free DMD impurity in a DMD - epoxy resin combination tested in practice,

- Determination of the environmental introduction which may thus result through migration and leaching.

Toxicological Aspects

Studies on the carcinogenic effect and reproductive toxicity are not available. Considering the structure, the exposure situation, and the lack of a genotoxic potential, a clarification of the end point carcinogenicity is not of high priority. Since no appreciable exposure is anticipated, studies on the reproductive toxicity are not of urgent demand.