

Health and Safety Executive OC 285/6

Field Operations Division

To

Factory Inspectors

FCG Specialist Inspectors (Occ Hyg)

Employment Medical Advisers

4,4'-METHYLENEDIANILINE (MDA)

This OC gives information on the current position on MDA, the application of the COSHH Regulations and introduces an Information Document (ID), which may be copied to employers and others as appropriate.

BACKGROUND

1 MDA (also known as 4,4'-diaminodiphenylmethane (DDM)) is a curing agent used in some epoxy-resins. It is currently classified as a category 3 carcinogen. Structurally, it is similar to, and often compared with MbOCA (2,2'-dichloro-4,4'-methylenedianiline). However, they are not the same and must not be treated as such.

UK USAGE

2 Over 90% of the total manufactured volume of MDA in the UK is made and used in situ at a single site, in the production of MDI for polyurethane manufacture. The remainder is used for a wide range of purposes including:

- (1) screeds and chemical-resistant coatings for flooring;
- (2) mortar and concrete repair;
- (3) high performance composites;
- (4) electrical potting and encapsulation systems;
- (5) filament-wound pipes and tubes;

(6) chemical-resistant paints and coatings; and

(7) moulding and tooling.

In addition MDA is used as one of the new materials in the manufacture of high performance polymers, eg polyester-imide wire enamel for electro-magnets in high temperature electric motors, and polybismaleimides for aerospace components.

3 MDA may be present in a number of different forms, eg:

(1) "technical" grade: prill or flake;

(2) "crude" grade: viscous brown liquid;

(3) chemical adducts in solution;

(4) putty-like material in 2-pack telecommunications jointing compounds.

4 Skin absorption provides an important route of entry into the body, possibly the major route when MDA is being used as a liquid formulation. Because of the low volatility of MDA, and its ready absorption through the skin, air monitoring may not give a true estimate of overall exposure. Despite their limitations, the results of biological monitoring may provide the most accurate indicator of the overall effectiveness of control.

5 MDA is currently listed in Table 4 of Guidance Note EH 40/92, which lists substances to be reviewed by ACTS/WATCH. The review of MDA took place in 1991 and a MEL of 0.08 mg/m³(0.01 ppm) 8-hour TWA together with a skin notation has been recommended to the HSC. If endorsed by the HSC, this will go to public consultation in the annual COSHH amendment package. If there are no significant comments, then it should come into effect on 1 January 1994. Data collection for the review included a programme of biological monitoring (by urine sampling) at a number of manufacturers' and users' premises.

6 In response to concerns expressed by the manufacturers of MDA that the review activity, together with some incautious comparisons with MbOCA, may have raised unnecessary fears about the carcinogenicity of MDA amongst employees, and have been misunderstood by employers, HSE agreed to produce interim guidance in the form of the attached ID, which:

(1) clarifies the nature and extent of the hazards to health;

(2) sets out the measures required to comply with COSHH;

(3) explains the role of biological monitoring;

(4) gives the rationale for the ACTS/WATCH review.

7 In 1991, MDA was considered by the EC Committee of Specialised Experts who agreed to classify it as a **category 2 carcinogen**. This decision will be ratified later this year, and MDA should then be included in the new Chemical Hazard Information and Packaging (CHIP) Regulations Approved Supply List at its first amendment, probably in late 1992 or early 1993. These developments have been included in the ID.

ACTION BY THE FIELD FORCE

8 Inspectors and EMAs should note the following points.

- (1) MDA is now considered to be carcinogenic to humans. However, care should be taken in making analogies to MbOCA as there are distinct differences in metabolism which may affect the degree or nature of the toxic effects.
- (2) The results of urine sampling cannot be related to health effects. In addition, for the reasons given in para 8(1) above, the biological action level (BAL) for MbOCA should not be applied to MDA .
- (3) HSE is currently developing policy on biological exposure within the COSHH framework. Although that policy development is still in progress, there may be a need to respond to industry requests for guidance on the interpretation of biological monitoring data for MDA. ACTS has agreed that HSE should promulgate, through the attached ID, a "yardstick" value of 50 nmol MDA/mmol creatinine (which is the 90th percentile of all urine samples recently analysed by HSE). This is an interim figure only, and is not intended to anticipate the outcome of the policy review on biological monitoring. Therefore, the attached ID should be copied to users in appropriate circumstances.
- (4) Where the above value is exceeded, or the biological monitoring data indicate that exposures for particular individuals or tasks are higher than for others in apparently comparable situations, employers should be advised to re-examine their COSHH assessments (reg.6) and controls (reg.7) in respect of those workers and activities.
- (5) Where biological monitoring data show the presence of MDA in urine, advice should be given on the risks arising from skin contact, as well as from airborne exposures.

Cancellation of instructions

6 FIM 1988/117 - cancel and destroy.

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ASI headings

Control of Substances Hazardous to Health Regulations 1988: methylene dianiline: toxic substances.

Health and Safety Executive Information Document

HSE 285/6

4,4'-METHYLENEDIANILINE (MDA)

4,4'-DIAMINODIPHENYLMETHANE (DDM)

INTRODUCTION

1 This document contains internal guidance which has been made available to the public. It may not be directly applicable in all cases and any queries should be directed to the appropriate enforcing authority.

2 It provides interim guidance for employers and others on the application to MDA (also known as DDM) of the Control of Substances Hazardous to Health (COSHH) Regulations 1988, and associated Approved Codes of Practice (ACoPs). It explains the role of biological monitoring and outlines work undertaken by HSE in support of a review of the control measures. Figures in square brackets relate to the references at the end of the document.

BACKGROUND

3 MDA is a substance hazardous to health as defined by the COSHH Regulations. It is currently listed in Guidance Note EH 40/92 under Table 4 "Substances to be reviewed" [1]. The review of MDA took place in 1991 and the Health and Safety Commission's (HSC) Advisory Committee on Toxic Substances (ACTS) recommended that:

- (1) a maximum exposure limit (MEL) of 0.08 mg/m³ (0.01 ppm) 8-hour TWA should be set;
- (2) a skin notation should be assigned to draw attention to the skin as a major route of uptake;
- (3) a "yardstick" value for urinary MDA of 50 nmol MDA/mmol creatinine should be cited in guidance for industry (see para 16(3)).

Subject to agreement by the HSC and Parliament, following public consultation, the MEL should co* NB: Concentrations of MDA in urine are expressed as a

proportion of the amount of a substance called creatinine. This is a natural breakdown product also present in the urine. It is produced at a fairly constant rate by the body and thus provides a reference point which is independent of urine flow.

me into effect on 1 January 1994.

4 In the meantime, exposure should be controlled in accordance with para 29 of the COSHH General ACoP [2] and the following limits should be used for guidance on the control of exposure under Regulation 7(1) of COSHH:

0.8mg/m³; 0.1 ppm: 8-hour TWA

4.0mg/m³; 0.5 ppm: 10-minute reference period.

APPLICATION OF COSHH

Regulation 6: Assessment

The hazards

5 In 1991, the European Committee of Specialised Experts considered, MDA and agreed that it should be classified as a category 2 carcinogen. This decision will be ratified later this year, and MDA should then be listed in the new Chemical Hazard Information and Packaging (CHIP) Regulations Approved Supply List at its first amendment, probably in late 1992 or early 1993. Category 2 carcinogens are defined as:

"substances which should be regarded as if they are carcinogenic to man. There is sufficient evidence to provide a strong presumption that human exposure may result in the development of cancer, generally on the basis of:

- appropriate long-term animal studies,
- other relevant information".

Classification as a category 2 carcinogen will bring MDA within the scope of the COSHH Carcinogens ACoP [2], as it will then attract the risk phrase "R 45: may cause cancer".

6 Until the changes recommended by ACTS and the EC experts come into effect, MDA should be regarded as if it were a category 2 carcinogen for the purposes of assessment. Although the COSHH Carcinogens ACoP does not at present apply to MDA, the standards outlined in that Code provide useful guidance on the measures which could be adopted to supplement those already required under the COSHH Regulations and the General ACoP.

The risks

7 The risks to health arising from each activity which may lead to exposure to MDA need to be assessed, together with the steps necessary to comply with the COSHH Regulations. In the case of MDA, particular attention should be given to controlling uptake through the skin, as there is evidence that it is rapidly absorbed following dermal contact.

Regulation 7: Prevention or control of exposure

8 Regulation 7 of COSHH requires that exposure must be prevented, or if that is not reasonably practicable, adequately controlled. Exposure to substances listed in Table 4 of Guidance Note EH40 should be controlled in accordance with para 29 of the COSHH General ACoP (see para 3).

9 Paragraph 34 of the COSHH General ACoP lists a number of measures which can be taken to prevent or control exposure. Where substitution is considered, the possibility of a carcinogenic risk arising from the use of MDA will need to be weighed against the risks associated with an alternative.

10 Particular attention should be given to the control of surface contamination and to preventing the spread of MDA to other parts of the workplace. Where personal protective equipment is a necessary part of the control measures, steps must be taken to ensure that it is suitable and sufficient for the purpose. Where there is a risk of skin contact, then gloves must be worn. They should be manufactured from materials of low permeability to MDA and should be changed regularly. The suppliers of MDA should provide information about the specification of gloves to use and the frequency of changing them. It should not be assumed that glove materials are impermeable to MDA. The provision of good hygiene and welfare facilities as outlined in paras 41-44 of the COSHH General ACoP will be necessary if uptake through the skin is to be minimised.

Regulation 8 and 9: Use and maintenance of control measures

11 Regulations 8 and 9 of the COSHH Regulations, together with paras 41-45 of the General ACoP are applicable.

Regulation 10: Monitoring

12 Monitoring for airborne MDA should be carried out where it is needed for ensuring the maintenance of adequate control of exposure. Monitoring is likely to be necessary where dusty products are used.

Regulation 11: Health surveillance

13 An employer, as part of the assessment under Regulation 6, should consider the need for health surveillance. Where exposure is likely to be significant (see para 88 of the General ACoP), then biological monitoring should form part of that surveillance (see paras 15 and 16 below). A health record must be kept irrespective of whether other health surveillance is undertaken. Details of the records required are given in the Appendix to the COSHH General ACoP.

Regulation 12: Information, instruction and training

14 The importance of information, instruction and training cannot be over-emphasised. Particular stress should be laid on the potential for exposure by skin absorption, as this aspect is often poorly understood or neglected. Employees will need to be instructed on the correct method of removing personal protective equipment (PPE) in general, and gloves in particular, to avoid skin contact with the contaminated surfaces of the PPE.

ROLE OF BIOLOGICAL MONITORING

15 The low volatility of MDA and the ease with which it is absorbed through the skin, mean that air monitoring carried out under Regulation 10 may not give an accurate estimate of overall exposure. Biological monitoring of urine for MDA and its products can often provide a more effective indicator of exposure and can thus play an important role in helping employers to assess the effectiveness of their control measures.

16 The following should be noted.

(1) Biological monitoring gives an estimate of the internal dose of MDA via all routes of exposure. However, such monitoring does not give a direct measure of external exposure. Therefore, biological monitoring cannot be used to demonstrate compliance with any occupational exposure limit.

(2) The results of biological monitoring for MDA do not give a direct measure of any risk to health. Rather, they provide a marker against which the employer can measure the effectiveness of workplace controls. No biological action level (BAL) has been established by the HSC for MDA in urine. It is inappropriate to use the BAL recommended by the HSC for those exposed to MbOCA.

(3) HSE is currently developing policy on biological exposure within the current COSHH framework. ACTS has agreed that, as an interim measure, HSE should promulgate through this Information Document, a "yardstick" value of 50 nm MDA/mmol creatinine*. This is an interim figure based on the 90th percentile of over 900 urine samples recently analysed by HSE, and is not intended to anticipate the outcome of HSE's policy review on biological monitoring. HSE understands that the Association of Plastics Manufacturers in Europe (APME) guideline value of 100µg/day approximates to the HSE "yardstick" value.

(4) Where the above value is exceeded, or the biological monitoring data indicate that exposures for particular individuals or tasks are higher than for others in apparently comparable situations, employers should re-examine their COSHH assessments (reg.6) and controls (reg.7) in respect of those workers and activities.

(5) Where biological monitoring data show the presence of MDA in urine, control measures should be focussed on preventing the possible uptake of MDA through the skin, as well as from airborne exposure.

HSE general guidance on biological monitoring for substances hazardous to health has now been published as Guidance Note EH56 [3].

ACTS/WATCH REVIEW OF CONTROL MEASURES FOR MDA

17 ACTS required the most up-to-date information possible for the review, and HSE has undertaken a survey of occupational exposures and available control

measures. One in five of the known user firms was sent a questionnaire about MDA use and HSE staff visited about one quarter of these firms. Exposure controls were examined and urine samples were taken to give an indication of the effectiveness of control. Employers and employees were informed of the results of relevant samples.

REFERENCES

1 HSE Guidance Note EH40 Occupational exposure limits (revised annually). Available from HMSO.

2 L5 (formerly COP 29) Control of Substances Hazardous to Health (General ACoP - 3rd Edition) and the Control of Carcinogenic Substances (Carcinogens ACoP - 3rd Edition). Available from HMSO - ISBN 0 11 885698 7.

3 HSE Guidance Note EH56 Biological monitoring for chemical exposures in the workplace. Available from HMSO - ISBN 0 11 885689 8.

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