Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR(1A OR 1B), PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): 2,2'-dichloro-4,4'-methylenedianiline

EC Number: 202-918-9

CAS Number: 101-14-4

Submitted by: **European Chemicals Agency at the request of the European Commission**

Version: August 2011

PUBLIC VERSION: Please note that the confidential annexes I – V referred to in the main part are not included in this version.

CONTENTS

TABLES and figures

LIST OF ABBREVIATIONS

ART	Advanced REACH Tool (for exposure modelling)
CAS	Chemical Abstracts Service
CLH	Harmonised Classification and Labelling
CSR	Chemical Safety Report
ECETOC-TRA	European Centre for Ecotoxicology and Toxicology of Chemicals – Targeted Risk Assessment tool
ECHA	European Chemicals Agency
ECPA	European Crop Protection Association
ERC	Environmental Release Category
ES	Exposure Scenario
EU	European Union
HPV	High Production Volume chemical
IOELV	EU Indicative OEL values
LEV	Local Exhaust Ventilation
MSCA	Member State Competent Authority
OECD	Organisation for Economic Co-operation and Development
OEL	Occupational Exposure Limit
PPE	Personal Protective Equipment
PU	Polyurethane
PU/AC	Polyurethane/polyacrylate
PVC	Polyvinyl chloride
REACH	Registration, Evaluation and Authorisation of Chemicals
RMM	Risk Management Measure
RPE	Respiratory Protective Equipment
SIAR	SIDS Initial Assessment Report (OECD)
SIDS	Screening Information Data Set (OECD)
SPERC	Specific Environmental Release Category
STEL	Short-Term Exposure Limit
TARC	Top-side anti-reflective coatings
TWA	Time Weighted Average
VOC	Volatile Organic Compound

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR (1A OR 1B), PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): 4,4'-methylenebis[2-chloroaniline];

2,2'-dichloro-4,4'-methylenedianiline;

MOCA

EC Number(s): 202-918-9

CAS number(s): 101-14-4

- The substance is proposed to be identified as substance meeting the criteria of Article 57 (a) of Regulation (EC) 1907/2006 (REACH) owing to its classification as carcinogen 1B[1] which corresponds to classifications as carcinogen category 2[2].

Summary of how the substance meets the criteria as category 1B carcinogen.

2,2'-dichloro-4,4'-methylenedianiline (MOCA) is covered by index number 612-078-00-9 of Regulation (EC) No 1272/2008 in Annex VI, Part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: “May cause cancer”). The corresponding classification in Annex VI, Part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen, Carc. Cat. 2, R45 (“May cause cancer”).

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogen in accordance with Article 57 (a) of REACH.

Registration dossiers submitted for the substance? Yes

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[1] Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

[2] Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I
JUSTIFICATION

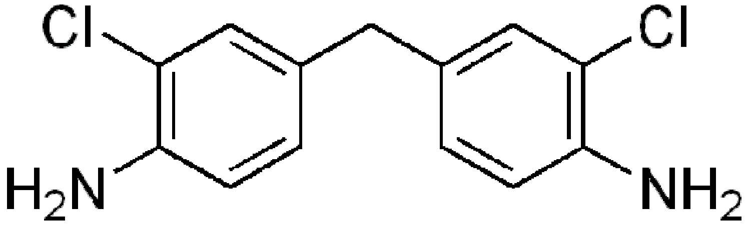
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	202-918-9
EC name:	4,4'-methylenebis[2-chloroaniline]
CAS number (in the EC inventory):	101-14-4
CAS number: **Deleted CAS numbers:**	101-14-4 29371-14-0; 51065-07-7; 78642-65-6; 126699-69-2; 142661-36-7
CAS name:	Benzenamine, 4,4'-methylenebis[2-chloro-
IUPAC name:	4,4'-Methylenebis(2-chloroaniline)
Index number in Annex VI of the CLP Regulation	612-078-00-9
Molecular formula:	$C_{13} H_{12} Cl_2 N_2$
Molecular weight range:	267.2 g/mol
Synonyms:	Bisamine A 2,2'-Dichloro-4,4'-methylenedianiline 3,3'-Dichloro-4,4'-diaminodiphenylmethane Bis(4-amino-3-chlorophenyl)methane

Structural formula:



1.2 Composition of the substance

Name: 4,4'-Methylenebis(2-chloroaniline)

Description: ---

Degree of purity: 85 - 100 %

Table 2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
4,4'-Methylenebis(2-chloroaniline)		85 - 100 %	Based on the information submitted in the registration dossiers

Table 3: Impurities

Impurities	Typical concentration	Concentration range	Remarks
See confidential Annex			Based on the information submitted in the registration dossiers

Table 4: Additives

Additives	Typical concentration	Concentration range	Remarks
None			Based on the information submitted in the registration dossiers

1.3 Physicochemical properties

Table 5: Overview of physicochemical properties

Property	Value	Reference
Physical state at 20°C and 101.3 kPa	Solid colourless crystals	Bornscheuer, U.& Roempp, 2008
Melting/freezing point	110 °C	Bornscheuer, U. & Roempp;, 2008
Boiling point	Decomposing prior boiling at 370 °C	D. S. Brassington, 2010
Vapour pressure	0.0017 hPa at 60 °C	Bornscheuer, U. & Roempp, 2008
Density	1.44 g/cm^3 at 24 °C	Bornscheuer, U. & Roempp, 2008
Water solubility	13.8 mg/l at 20 °C; pH = 7.6	Baltussen, 2010
Partition coefficient n-octanol/water (log value)	2.5 at 25 °C and pH ca. 7	Baltussen, 2010

2 HARMONISED CLASSIFICATION AND LABELLING

MOCA is covered by Index number 612-078-00-9 in Annex VI, part 3 of Regulation (EC) No 1272/2008 as follows:

Table 6: Classification according to part 3 of Annex VI, Table 3.1 ((list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	**International Chemical Identification**	**EC No**	**CAS No**	**Classification**		**Labelling**			**Spec. Conc. Limits, M-factors**	**Notes**
				Hazard Class and Category Code(s)	**Hazard statement code(s)**	**Pictogram, Signal Word Code(s**	**Hazard statement code(s)**	**Suppl. Hazard statement code(s)**		
612-078-00-9	2,2'-dichloro-4,4'-methylenedianiline; 4,4'-methylene bis(2-chloroaniline)	202-918-9	101-14-4	Carc. 1B Acute Tox. 4 * Aquatic Acute 1 Aquatic Chronic 1	H350 H302 H400 H410	GHS08 GHS07 GHS09 Dgr	H350 H302 H410			

Carc. 1B, H350	May cause cancer.
Acute Tox. 4 , H302	Harmful if swallowed.
Aquatic Acute 1 H400	Very toxic to aquatic life.
Aquatic Chronic 1 H410	Very toxic to aquatic life with long lasting effects.

Table 7: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of hazardous substances from Annex I of Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

Index No	**International Chemical Identification**	**EC No**	**CAS No**	**Classification**	**Labelling**	**Concentration Limits**	**Notes**
612-078-00-9	2,2'-dichloro-4,4'-methylenedianiline; 4,4'-methylene bis(2-chloroaniline)	202-918-9	101-14-4	Carc. Cat. 2; R45 Xn; R22 N; R50-53	T; N R: 45-22-50/53 S: 53-45-60-61		**E**

Carc. Cat. 2; R45	May cause cancer.
Xn - 22	Harmful if swallowed.
N; R50-53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

3 ENVIRONMENTAL FATE PROPERTIES

Not relevant for the identification of the substance as SVHC in accordance with Article 57a.

A QSAR model run with default values of EPISUITE 4.00 (ECHA, 2011b) shows that MOCA is mainly sorbed to soil. However, relevant amounts of MOCA are also present in the water compartment, e.g. when equal amounts are emitted to air, water and soil still about 8 % of the substance are calculated to partition to the aquatic environment.

4 HUMAN HEALTH HAZARD ASSESSMENT

See section 2 on harmonised classification and labelling of the substance.

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant for the identification of the substance as SVHC in accordance with Article 57a.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57a.

Based on information provided in the registrations (ECHA, 2011a) it is concluded that MOCA is not readily biodegradable. This was confirmed by a QSAR study with several models (ECHA, 2011b), where a calculation with CATALOGIC (using the BIOWIN module of EPISUITE v4.00 and the 28 days aerobic biodegradation model (MITI 301C) predicted a half life for primary degradation (first degradation step) of 19 months and a half life for mineralisation of more than 10 years. The Level III fugacity model from EPISUITE 4.00, based on the default values of the model, provided half lives of 60 d, 120 d and 540 d for water, soil and sediment, respectively. 3.3 h was calculated as half life in air. It appears that the substance would meet the persistent or very persistent criteria of Annex XIII REACH.

The registrant concluded from experiments and results obtained with the OECD QSAR toolbox, that the BCF values are between 173 and 398 L/kg (ECHA, 2011a). This is in accordance with the results of the QSAR study mentioned above, in which BCF values of 176 L/kg, 234 L/kg and a maximum BCF value of 396 L/kg were calculated. This shows that MOCA has a slight tendency to bioaccumulate but does not meet the numerical B criterion of Annex XIII with a threshold of 2000 L/kg for the BCF.

The T criterion of Annex XIII is in any case fulfilled due to the harmonised classification of the substance as carcinogen (see Table 6 and Table 7). However the substance is as well very toxic to aquatic organisms with a lowest NOEC for aquatic invertebrates of 9.5 µg/L (ECHA, 2011a).

Summarising, although MOCA fulfils the T criteria of Annex XIII and appears to have persistent or very persistent properties it seems not to bioaccumulate; hence it is considered to not fulfil the PBT criteria.

6.2 CMR assessment

Pursuant to Regulation (EC) No 1272/2008, MOCA is listed as entry 612-078-00-9 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 category 1B[1]. Its corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen category 2[2].

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that the substance meets the criteria for classification as carcinogen, in accordance with Article 57 (a) of REACH.

6.3 Substances of equivalent level of concern assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57a.

PART II

Part of the underlying work for development of Part II of this Annex XV report was carried out under contract ECHA/2010/175 SR27 by DHI[3].

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 MANUFACTURE, IMPORT AND EXPORT

1.1 Manufacture process and quantities

MOCA is manufactured by reaction of formaldehyde and 2-chloroaniline (IARC, 2010). No manufacturing sites have been identified within the EU. Therefore, no information on specific manufacturing conditions can be provided here.

It is reported that MOCA was produced and/or supplied in the following countries: Germany; Hong Kong Special Administrative Region; Japan; the People’s Republic of China; South Africa; Switzerland; Taiwan, China; and the USA (IARC, 2010). The production volumes of MOCA in the period from 1986 to 2002 ranged between 450 and 4500 t/y, without an observable specific trend, while for 2006 the production volume was reported to be 225-450 t (IARC, 2010).

1.2 Import, export and use quantities

According to information collected from industry, the import of MOCA into the EU was within the range of 1000 to 10000 tonnes for 2010. Information on exact annual import volumes of MOCA is considered confidential and presented in the confidential Annex.

A survey carried out by the UK Health and Safety Executive (HSE) indicated that over 200 tonnes of MOCA were imported into the UK in 2006 (HSE, 2010).

According to information provided by industry, export of MOCA from the EU was in the range 10-100 t/year in 2010 (DHI 2011).

The net volume used within the EU in 2010 was between 1000 and 10000 tonnes.

Further information on import and export is included in the confidential Annex II.

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[3] DHI, Agern Alle 5, 2970 Hørsholm, Denmark

2 USES OF THE SUBSTANCE

2.1 Overview of uses

MOCA is used primarily to procuce polyurethane articles. Polyurethanes are produced by the reaction of a liquid isocyanate with a blend of liquid polyols, catalysts and other additives. MOCA is used as an additive in the polyol blend with the purpose to give the resulting polymer specific properties. Depending on the function MOCA has within the polymer, four uses can be differentiated:

- Curing agent
- Cross-linker
- Chain extender
- Pre-polymer

The only further use registered is the use as laboratory chemical. This is in agreement with the fact that the United Kingdom Health and Safety Executive (HSE) is not aware of any industrial applications of MOCA outside the polyurethane industry in the UK (HSE, 2010).

2.2 MOCA in the polyurethane industry

In general, MOCA reacts with isocyanate to form a urea linkage. The isocyanate may be a monomer or an isocyanate-terminated pre-polymer or a polymer. Figure 1 illustrates the reaction.

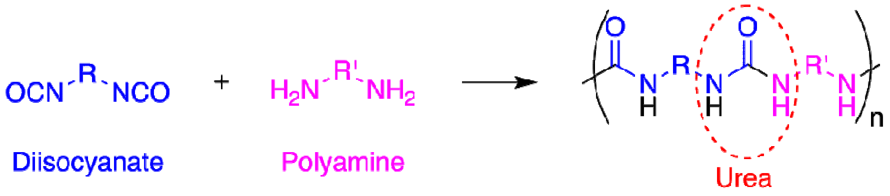

Figure 1: Reaction between diisocyanate and polyamine (e.g. MOCA) to a urea bound polymer (DHI, 2011)

This reaction is the core reaction of MOCA and basis of its function as curing agent, cross-linker and chain extender. The reaction of the amine-terminated MOCA with the polymer/pre-polymer plays an important role for the properties of the resulting polymers. Whereas the reaction of isocyanates with high molecular weight polyols results in soft segments, the reaction of low molecular weight compounds, such as MOCA, results in hard segments of the polymer.

Residual non reacted MOCA might remain in the final polymers. The amount of un-reacted MOCA is estimated to be in the range of 0 % and 4 %. This amount depends very much on the polymerisation process; in a review Araujo (2002) reported residual monomer concentrations in polymers between 100 ppm and 4 %.

2.2.1 Use as curing agent

MOCA can be used as a curing agent for polyurethane resins, polyurethane elastomers, epoxy resins and epoxy urethane resins due to MOCA's content of amine groups (IARC, 2010).

For manufacture of polyurethane plastics MOCA is mixed with di-isocyanate based pre-polymer resins, such as toluene di-isocyanate (TDI) pre-polymer, or with methylene bis-phenyl di-isocyanate (MDI) pre-polymer. MOCA is commercially available in curing products (i.e. Vibracure A 133 HS, ALCHEM MOCA) for use with TDI pre-polymers. Where MOCA is used for curing, the ratio between isocyanate and MOCA is typically 10:1 on a molar basis, although this ratio may vary depending on the polymer, it should not exceed a ratio of 1:1. A ratio of 1:1 means that all di-isocyanate is bound to MOCA, any exceeding MOCA content will remain as un-reacted substance in the polymer matrix. In the production of polyurethane products MOCA, which is a solid at room temperature, is heated to around 100°C in order to get liquid. It is then mixed with pre-heated di-isocyanate-based pre-polymer resins. The mix is then poured into preheated moulds that are placed into curing ovens (HSE, 2010). MOCA is less active than other similar substances, which slow down the reaction, giving a pot life of 0.5-1 hour, necessary for coatings (Chang et al. 1972).

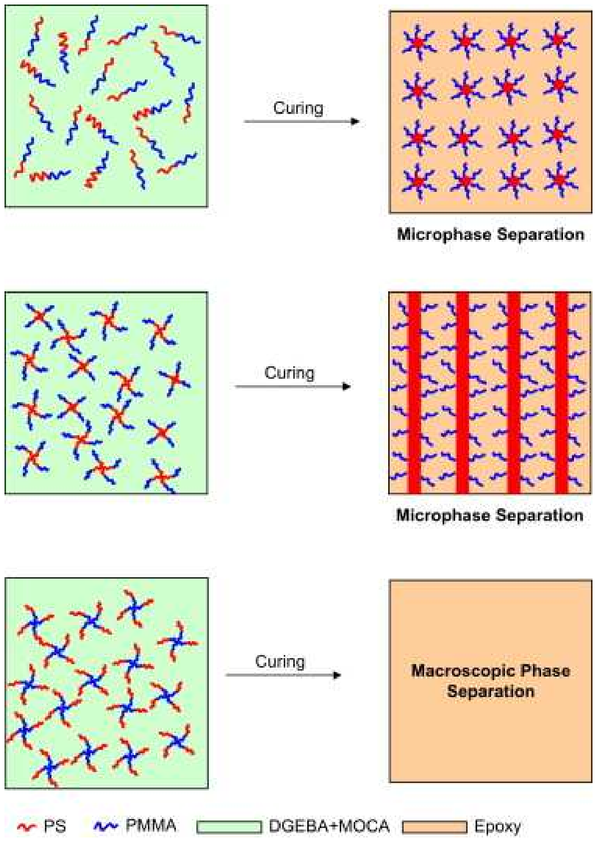

Figure 2: Curing process of polystyrene (PS) – poly(methyl methacrylate) (PMMA) copolymer with MOCA (Fan & Zheng 2008).

As shown in Figure 2, the curing process improves the structure within the polymer matrix, giving the final polymer the desired properties.

2.2.2 Use as cross-linking agent

MOCA is also used as a cross-linking agent (see Figure 3), where polymer chains are connected, creating an organised network structure. This makes the resulting polyurethanes very resistant to abrasion and adds thermal stability. These polyurethanes can be used in the production of machines, buildings, automobiles, airplanes, mining and sport equipment (Chinamoca, 2011).

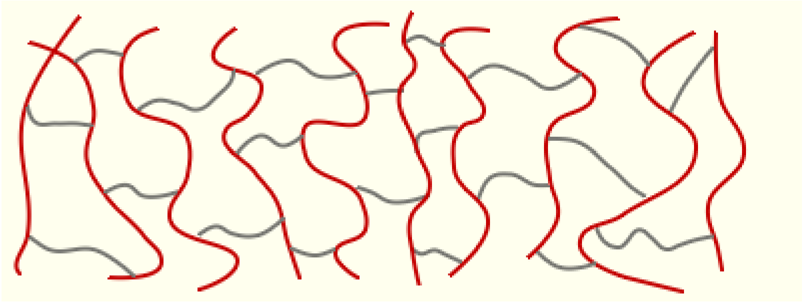

Figure 3: Structure of a cross-linked polymer where MOCA could be used to establish the cross-links between the polymer chains.

2.2.3 Use as chain extender

When the polyurethane chains need specific characteristics, the diisocyanate is first reacted with a long chain diol, obtaining a pre-polymer with soft segments. These pre-polymers are *a posteriori* reacted with a diisocyanate-MOCA mix, giving the desired amount of hard segments and resulting in thermo stable polymers (Gregori et al. 2007). Varying between soft and hard segments, like in the example in Figure 4, allows to prepare polyurethanes with very specific properties regarding hardness, thermal stability and abrasion resistance.

Figure 4: Polyurethane chain with hard segments with MOCA as short-chain diol and soft segments with long-chain diols. (Adapted from Gregori et al. 2007)

2.2.4 Use in the manufacture of pre-polymers

MOCA is used as a chain extender in the manufacture of pre-polymers. These pre-polymers are isolated and in a separate process, reacted with other monomers to yield a final polymer.

Article categories given for that use are very generic, namely rubber and plastic articles (AC 10 and AC 13, in ECHA 2011a).

2.2.5 Intermediate status of MOCA in polyurethane uses

Usually, the process steps for most uses of MOCA are as follows: The isocyanate, MOCA and the other required substances are mixed together at elevated temperatures. The liquid mixture is poured into moulds that give the desired shape. Once the polymerisation reaction has finalised, the polymer (part of an) article with the desired characteristics is obtained. Because the end result of the process is (part of) an article, this use is considered as an end use and not as a use of MOCA as an intermediate in accordance with the definition of Article 3(15) of REACH.

According to the guidance on intermediates (ECHA 2010) document a substance should not be regarded as intermediate as soon as the main aim of the chemical process is not to manufacture another substance, but rather to achieve another function, specific property, or a chemical reaction as an integrated part of producing articles (semi-finished or finished). In accordance with this statement, the end use described above and the use as curing agent described in section 2.2.1 cannot be regarded as use of MOCA as intermediate.

Similarly, it appears not possible to consider the use of MOCA as a cross-linking agent as use of the substance as intermediate.

However, its use in the manufacture of pre-polymers could possibly be covered by the intermediate definition of Article 3(15). A firm conclusion on the intermediate status of MOCA in this use requires a more detailed description of the process. In any case, according to registration information, the proportion allocated to this use seems to be lower than to the other uses. Exact quantities are however not known.

Summarising, whether a specific use of MOCA falls under the definition of use as an intermediate depends very much on the process in place and the output of this process, e.g. whether an (semi-finished or finished) article is produced or a new substance manufactured.

2.3 MOCA-containing products and articles

Polyurethanes containing MOCA have high thermal, physical and abrasion resistance and are therefore used, e.g., in construction, for wheels, cars, electric wire coating, safety belts and recently also in biomaterials such as pace makers and implants (Gregori et al. 2007). MOCA is also used in polyurethane coatings which require good flexibility or abrasion, solvent, weathering and ultraviolet light resistance (Chang et al. 1973). MOCA as curing agent in the manufacture of castable urethane rubber products, such as shock absorption pads and conveyor belting (IARC, 1993), achieves specific performance properties such as high abrasion resistance, high tensile and tear strength, heat, fuel and solvent resistance, high load-bearing and good mechanical and dynamic properties.

The Nordic SPIN database (SPIN, 2011) collects information on substances in preparations from the Product Registries of Norway, Sweden, Denmark and Finland. The database contains information on the use of MOCA from 1999 to 2009 reported for Sweden and Finland. The total amount of MOCA used is shown in Figure 5 below. A number of 4 preparations (no specification on type is provided) is reported for Sweden and Finland. The use in Sweden is indicated as industrial use for the manufacture of rubber and plastic products.

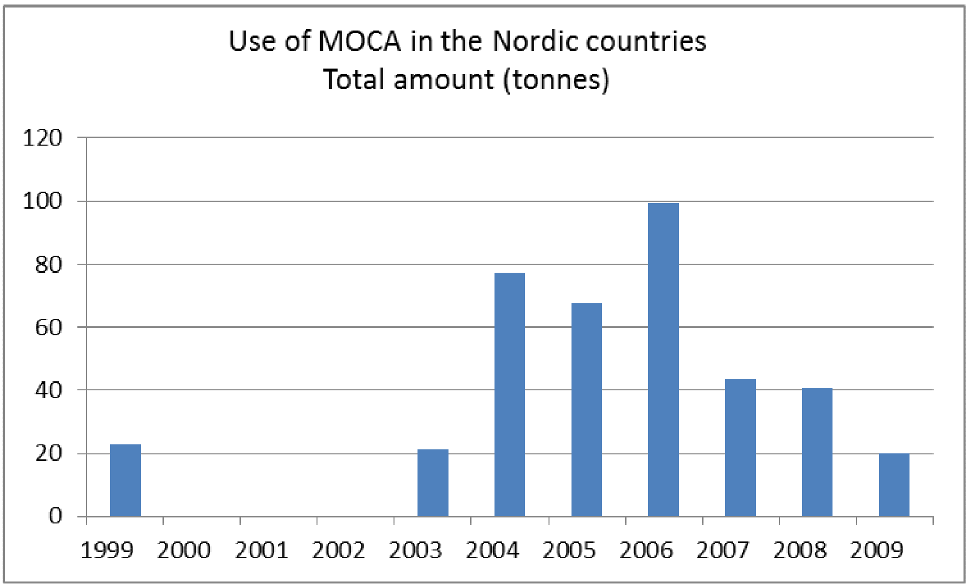

Figure 5: Use of MOCA in the Nordic countries (SPIN, 2011).

2.4 Information on the supply chain of MOCA in the polyurethane industry

HSE (2010) estimated for 2009 the presence of 30 businesses of various sizes using MOCA in Great Britain. During the study, a total of 19 sites were visited over the period April to September 2008. Seventeen of these were MOCA users manufacturing polyurethane products and two were MOCA suppliers. It can be estimated that the number of importers is relatively low, while the number of sites in Europe at which the substance is used could be several hundreds. Further details are provided in the confidential Annex.

Based on the information from the industry (DHI, 2011), the supply chain consists of importers, distributors and industrial users with a total of more than 200 use sites within the EU. MOCA is supplied as substance of its own or in mixtures containing the substance. Professional users were not identified as part of the supply chain. However, MOCA is commercially available in mixtures for the production of polyurethanes and may be used by professionals working outside industrial settings.

2.5 Use of MOCA in laboratories

In the laboratory, MOCA is used as a model compound for studying carcinogens (NTP, 2005) and is mentioned as such in many scientific articles. It can be expected that the substance is used in several hundred laboratories in the EU, but in low quantities. This use appears to be covered by the exemption of scientific research from authorisation in accordance with Article 56(3) of the REACH Regulation.

3 RELEASES FROM USES

3.1 Introduction

Figure 6 shows the life cycle of a plastic article. As MOCA is not manufactured in Europe ”raw material extraction” and “chemical production” will not be considered in this report. Releases of MOCA during the other steps of the production phase will be considered in chapter 3.2 (Releases and occupational exposure). Releases from uses of MOCA as intermediate are not considered. However, it was not always possible to decide on the basis of the process descriptions available whether the substance is used as intermediate in accordance with the definition of Article 3(15) or elsewise. Releases to professionals will be estimated in 3.3 (Workplace releases and exposure to professionals). Releases from the use phase will be estimated in chapter 3.4 (Consumer exposure) and from the end-of-life phase in chapter 3.5 (Environmental releases and exposure).

Figure 6: The life cycle of a plastic product (Lithner, 2011)

As MOCA is not present in nature, there are no natural sources for MOCA, the occurrence of MOCA in the environment is due to unintentional releases, such as spillage accidents (not covered in this report), releases from degradation of polymers or releases from polymer articles during and after the use phase. An additional known source of MOCA in the environment is the degradation of azocolourants and azodyes. However, MOCA is one of the aromatic amines listed in Appendix 8 of REACH which is referred to in entry 43 “Azocolourants and Azodyes” of Annex XVII of REACH. Annex XVII restricts the use of azodyes in articles or dyed parts thereof, (in general, articles produced from textiles and leather) which, “by reductive cleavage of one or more azo groups” would release one or more of the aromatic amines listed in Appendix 8”, in this case MOCA, in detectable concentrations, i.e. 0.003 % by weight. In cases where such azocolourants and azodyes would be used in other applications not covered by the mentioned restriction, releases to the environment could occur, however this is not covered by the present report.

3.2 Releases and occupational exposure in industrial settings

Confidential information on releases and exposure from registration dossiers and industry questionnaires is presented in the confidential Annex.

According to the IARC (2010), occupational exposure to MOCA can occur during its manufacture (i.e. MOCA-production workers) and during its use in the polyurethane industry (polyurethane production workers). Manufacture will not be considered here, as MOCA is not manufactured in the EU.

The primary route of potential human exposure to MOCA is dermal absorption after contact with contaminated surfaces while inhalation and ingestion are less pronounced (IARC, 1993).

No European-wide indicative occupational exposure limit value (IOELV) has been established; however, this matter is currently under review (DG EMPL, 2011). Occupational exposure limits (OEL) are set for long term inhalation exposure (8h) and short term inhalation exposure to MOCA in many EU Member States (see Table 8).

Table 8: Occupational exposure limits (OEL), 8 hr limit value for several EU Member States (Source: EU OSHA, 2009)

Country	**OEL in mg/m^3**
Poland	0.02
Portugal	0.01
Slovakia	0.02
Slovenia	0.02
Spain	0.01
United Kingdom	0.005
Austria	0.02
Belgium	0.11
Denmark	0.11
Netherlands	0.02
Sweden	No OEL established but use of the substance needs prior permission from the Swedish work environment authority

As the major exposure route for MOCA is the dermal route, air concentration limits might not always be the most relevant values. Instead, occupational exposure limits based on biological monitoring, such as post shift urinary concentrations of workers handling MOCA, appear to be more relevant. Such values are provided for example by the Japan Society of Occupational Health with 50 µg total MOCA per g creatinine, or by the United Kingdom Health and Safety Commission by defining a Biological Monitoring Guidance Value of 15 µmol total MOCA per mol creatinine (corresponds to 35 µg MOCA / g creatinine).

3.2.1 Handling of MOCA as raw material

According to industry MOCA is available in the form of powders, as flakes and as granules. Granules may either be provided as small granules (size of < 1 mm) or as big granules (size of 3 mm). The small granules are less likely to form dust than the bigger granules. Also powders and flakes can form dust during handling.

In many cases MOCA is being handled in glove boxes, from which it is passed on by means of suction to hermetically closed smelters. From the smelters, MOCA is being pumped (also in hermetically closed circuits) to a mixing head where it is mixed with polyurethane pre-polymers. Thus contact with MOCA and exposure to MOCA in solid or liquid form is reduced to an absolute minimum.

3.2.2 Use of MOCA in the polyurethane industry

MOCA-containing mixtures are used in combination with di-isocyanates for manufacture of rotational and hot cast elastomers. According to industry, MOCA reacts with NCO-containing substances to form polyurea and thus is transformed to a solid, non-thermoplastic polymer during use. MOCA is covalently bound in the polymer.

Methods exist to reduce the amount of free MOCA in the polymer (Araujo et al., 2002), and, according to industry information, this is achieved in most of the industrial settings. Concentration of MOCA in the final product is reported by industry as 0%. This estimate is based on stoichiometric considerations and not verified by chemical analysis (DHI, 2011). In such applications the concentration of free MOCA might be below 100 ppm as reported by Araujo et al. (2002).

It is summarized in the RoC (2009) that persons with the greatest possible risk of exposure to MOCA are those involved in the manufacture of polyurethane and plastic products during the curing process. When used as a curing agent, MOCA is melted before mixing into elastomer formulations and it may volatilize and be released with the waste gas and waste water from the facilities in which it is used.

The HSE estimates that in the years 2005 / 2006 300 workers in the UK were directly exposed to MOCA during polyurethane-elastomer production, and more than 1,000 workers, such as office staff, were indirectly exposed (HSE, 2007). The HSE study (2010) reported that MOCA and isocyanate handling systems vary at the different user sites. Enclosed weighing, melting and mixing systems exist at some sites. At other sites open processes with significant manual operation steps take place. Most often LEV is applied at sites where weighing, melting and mixing is carried out whereas casting may be performed with or without use of LEV. The dermal exposure route is reported as the most significant for MOCA and exposure can be highly dependent on individual working practices and relatively subtle differences in the way that protective equipment, especially gloves, are used. The HSE report suggests that reducing the MOCA exposure of these individuals could be achieved by improved training and supervision rather than by implementation of additional technical measures (HSE, 2010).

During the last decades, post shift urine samples of workers in the polyurethane industry have been monitored in several studies (IARC, 2010). The measured values are in some cases above the limit concentrations imposed by Japan and the UK (50 and 35 µg total MOCA per g creatinine respectively, see 3.2 and Table 9). As the dermal exposure route is the most relevant, MOCA concentrations on workplace surfaces give indication of the potential exposure. The most recent study with such data is from HSE (2007) and shows quite high concentrations of MOCA on different surfaces at industrial sites (Table 10).

Table 9: Urinary levels of MOCA in workers in the polyurethane industry (Extracted from IARC, 2010.

Country	Year	Task	Number of samples	Concentration of MOCA (µg/g creatinine)
Australia	1998	Polyurethane manufacture workers	12	0.9-115
France	1999	Mixer (n=6)	17	0.5-149
		Moulder (n=10)	26	0.5-22
		Maintenance (n=6)	17	0.5-456
		Others (n=13)	38	0.5-28
United Kingdom	2005/ 2006	Casting	3	7.8-40
		Moulding	12	5.2-59
		All exposed	40	3.1-59

Table 10: MOCA levels in workplace surface wipe samples from the United Kingdom (HSE, 2007)

Task	Number of samples	MOCA concentration (geometric mean, µg/100 cm^2)
Fume cupboard	27	3800
Storage	34	2700
Weighing/pouring	21	2660
Mixing	9	1910
Oven	21	1910
Hopper	4	96000
Casting	6	790
Other	34	2340

Information on exposure to MOCA has recently been included in the SPIN database. The exposure information provided indicates that MOCA is only used in some few applications in Denmark and Sweden in 2009. No direct exposure of MOCA to surface water, air, soil and consumers seems to result from these applications. However, potential exposure to waste water may occur from several uses in Sweden. No information related to worker exposure was provided for 2009.

3.3 Workplace releases and exposure to professionals

No information on exposure to professionals was received during consultation of industry (DHI, 2011), and in the registration dossiers use by professionals has not been taken into account. However, professionals may use MOCA-containing mixtures for the production of polyurethane articles outside industrial settings without consideration of the necessary operational conditions and risk reduction measures (DHI, 2011). MOCA seems to be available to professionals as part of bi component resins, in particular for application in construction work and arts (e.g. opera and theatre). No further information on exposure of professionals to MOCA is currently available.

3.4 Consumer exposure

Regarding the general population, IARC (2010) reports that the public can be exposed to MOCA in areas contaminated with MOCA or upon consumption of root crops grown in MOCA-contaminated soil. Also, family members of exposed workers have been reported to be exposed indirectly (IARC, 2010).

According to DHI (2011), information on the content of MOCA in finished articles, either as bound or as free MOCA, is missing and therefore measured data on releases or migration of MOCA from articles cannot be provided here. Furthermore, no relevant information on exposure of the general population was obtained in the context of consultation of industry and authorities (DHI 2011). An additional request to provide respective information was sent to selected stakeholders, but did not yield responses.

As MOCA increases abrasion, temperature and solvent resistance of articles, releases of MOCA from the polymer matrix of articles during their use phase are expected to be very low and to not result in adverse effects.

3.5 Environmental releases and exposure

No specific information other than on accidental releases is currently available for MOCA itself. Exposure to the environment could potentially occur from industrial processes in which the substance is used or from use by professionals. These exposure routes have not been covered in the registration dossiers. The substance may potentially be released into the environment with waste gas and waste water emissions from installations that produce polymers/elastomers and/or articles containing these polymers.

It is also possible that MOCA is released into the environment during and after use of articles containing the substance. Possible release routes are abrasion, particularly from wheels, but also machinery and other articles used under adverse physical conditions. In addition, the free un-reacted MOCA from the polymer/elastomer material might be released to the environment from articles. Release of MOCA during the waste stage of articles can also not be excluded.

According to Dow Corning (1997), degradation of polymers follows a sequence in which the polymer is first converted to its monomers after which the monomers are mineralized. This is confirmed by Gajewski (1990) stating that the ester and urea bounds (the case of MOCA), followed by the urethane bounding, are the most susceptible to hydrolytic degradation. Hydrolysis and biodegradation are the predominant processes of polyurethane degradation (Gregori et al. 2007).

Rutkowska et al. (2002) have shown that polyurethanes cross linked with MOCA were more resistant to degradation in sea water than non cross linked polyurethanes, nearly not being degraded during the two years of their experiments. However, in other environments degradation might proceed much faster. Gajewski (1990) showed that polyester TDI-MOCA systems hydrolyse quite rapidly, two or four times faster than polyether-TDI MOCA systems; however he also stated that degradation depends on the environmental conditions.

MOCA may be released from plastic waste under environmental conditions, mainly due to physical deterioration, hydrolysis and biodegradation. Evidence of MOCA releases from landfills is reported by White & Claxton (2004).

Taking into account that MOCA appears to be persistent and very toxic to aquatic organisms (NOEC for aquatic invertebrates is 9.5 μg/L, ECHA, 2011a), adverse effects to the environment cannot be excluded.

Data available (ECHA, 2011a) show that the substance has a vapour pressure of < 0.0147 Pa, a log K_{OC} of 3.56, and a water solubility of 13.8 mg/L. Therefore, the substance can be expected to strongly adsorb to soil and sediment but also to be present in water in concentrations above the NOEC. EPI Suite modeling indicates that about 8 % of the substance can be expected in the aquatic environment if it is released to air, soil and water in equal proportions (see ECHA, 2011b).

4 CURRENT KNOWLEDGE ON ALTERNATIVES

4.1 Introduction

The term “alternatives” refers to either the use of an alternative substance, an alternative technique or technology or a combination of these, including changes that make the process step involving the use of the substance redundant. Further confidential information on alternatives can be found in the confidential Annex.

4.2 Alternatives to MOCA

According to an internet search (using the google search engine; DHI 2011), different aqueous urethane dispersion systems consisting of pre-polymers and aromatic amines for curing purposes are available on the market for use in the production of polyurethane products and cast elastomers. Products from industry (i.e. Chemtura) include five different systems without MOCA. Other companies (i.e. Lyondellbasell) are offering butanediol (BDO) based systems as alternative to the MOCA systems. However, the quality of the final products made with these MOCA-free curing agents, i.e. strength, abrasion resistance, temperature resistance etc. has not been evaluated and compared to the MOCA based systems.

Generally, the requirements the final elastomer has to meet are very demanding with respect to its mechanical properties such as abrasion, tear, tensile and elongation strength, compression set and resilience but also in terms of its resistance to physico-chemical attacks such as by sunlight, acids, grease, oil etc.

Industry acknowledges the availability of alternative curing products but also claims that the final products produced with the alternatives will not have as good properties as the MOCA based ones. This lack of performance is considered the main limiting factor for using the alternative curing products but also the price is important as the alternative materials are more expensive than MOCA.

One company stated that many R&D activities around the world have been conducted for decades to find suitable MOCA alternatives, with very limited success. From the chemical point of view there are no viable alternatives. The R&D work today focuses on safe processing equipment for handling MOCA and MOCA-containing products. MOCA has the perfect structure and leads to elastomers with unique physical and chemicals properties, e.g. longevity and resistance. Any variations will drop properties, reduce the pot life and increase the price considerably. Furthermore, the replacement products have not been extensively studied for their toxicological properties, their toxicity is only partly known. According to the company, MOCA cannot be replaced in the hot cast process, which is the far most relevant manufacturing process whereas MOCA might be replaceable in the rotational cast process. (DHI 2011)

Another company stated that it takes years to introduce a new curing product and to obtain the same technical performance as with MOCA. In addition, the final product has to be tested during many years, which is hampered by difficulties in obtaining the needed data from the supplier of the alternative.

Several consultees from industry indicated that the downstream users are aware of the possible alternatives already available today but may leave the EU if MOCA is banned. If industry could not realise the required properties with alternative curing products, they may decide to produce or buy the final product produced with MOCA outside the EU in order to be able to compete on the global market. As there has been tremendous R&D work done in the past, no one would today look for new alternatives. Many alternatives have been developed by Bayer, Albemarle, Polacure, Lonza, etc.

The following substances are potential alternatives to MOCA (DHI, 2011):

- **3,5-diamino-4-chlorobenzoacid isobutylester** (EC No 251-311-5; CAS No 32961-44-7)
  Advisory classification (Danish EPA,2010): R43 N; R51/53
  Advisory CLP classification (Danish EPA,2010):Skin Sens1 Aquatic Chron2

  - Has been used for 30-40 years to replace MOCA.
  - However, some mechanical properties of articles produced with this replacement product are not as good as those produced with MOCA.
  - Reactivity comparable to MOCA.
  - Estimated market share is 1% of the world-wide market (MOCA = 100%).
  - The price compared to MOCA is much too high (factor 4).

- **Dimethylthiotoluenediamine** (DMTDA) (isomers) (EC No 403-240-8; CAS No 106264-79-3)
  Classification according to Regulation (EC) No 1272/2008 of the European Parliament and of the council of 16 December 2008: Acute Tox4 Skin Sens1 Aquatic Acute1 Aquatic Chronic1; H302 H317 H400 H410.

  - Commercial name Ethacure 300
  - Has been used for decades to replace MOCA
  - Most of the mechanical properties of the products produced with DMTDA are not as good as MOCA-based products; also the aging properties (e.g. hydrolysis) are inferior.
  - Reactivity in most applications is to short compared to MOCA. It exhibits a slightly higher level of reactivity than MOCA and the end processor must consider this aspect.
  - Estimated market share is 5% of the world-wide market (MOCA = 100%).
  - The molecule has an unpleasant smell.
  - An advantage is that the product is liquid at ambient temperatures. However, in most applications the properties of the produced products are not sufficient to replace MOCA.
  - The price compared to MOCA is much too high (factor 2-3).

- **DETDA-80** (isomers) (EC No 270-877-4; CAS No 68479-98-1)
  Classification according to Regulation (EC) No 1272/2008 of the European Parliament and of the council of 16 December 2008: Acute Tox4 STOT Re2 Eye Irrit2 Aquatic Acute1 Aquatic Chronic1; H312 H302 H373 H319 H400 H410

  - A theoretical alternative, as the reaction time is much too low for cast elastomer applications.
  - It can be used in some reactive applications (rotational cast elastomers) <<< 1%.

- **MCDEA** (EC No 402-130-7; CAS No 106246-33-7)
  Self-classification from registration dossier (ECHA, 2011a): Aquatic Chron4; H413

- Has been used for years and provides products with better mechanical properties than MOCA.
- The reaction time is much too fast to process this amine in most applications.
- About 6 times more expensive than MOCA.
- Today, it is used in niche applications where high dynamic is needed, a high price can be paid and a short reaction time can be accepted.

➢ **MDA** (CAS No 101-77-9)

Classification according to Regulation (EC) No 1272/2008 of the European Parliament and of the council of 16 December 2008: Carc1B Muta2 STOT Se1 STOT Re2 Skin Sens1 Aquatic Chronic2; H350 H341 H370 H373 H317 H411

- MDA is named as a potential alternative to MOCA due to its chemical structure being similar to that of MOCA. However, MDA is not suitable to replace MOCA due to higher toxicity and faster reactivity in the application than MOCA.

Further information regarding the presented alternatives is given in Table 11.

Table 11: Hazard and other relevant information for substances presented as potential alternatives to MOCA

Substance name	**EC number**	**CAS number**	**Harmonised classification***	**SVHC properties**	**Registrations (by July 2011)**
3,5-diamino-4-chlorobenzoacid isobutylester	*251-311-5*	*32961-44-7*	None	Not available	None
Dimethylthiotoluene-diamine	*403-240-8*	*106264-79-3*	Acute Tox. 4 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	Not available	None
Diethylmethylbenzene-diamine	*270-877-4*	*68479-98-1*	Acute Tox. 4 Acute Tox. 4 STOT RE 2 Eye Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1	Persistent, but not bioaccumulative (ECHA, 2011a)	Yes
4,4'-Methylene-bis-(3-chloro-2,6-diethylaniline)	*402-130-7*	*106246-33-7*	None Self classification (ECHA, 2011a): Aquatic Chronic 4	Persistent (no further information in ECHA, 2011a)	Yes

*Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances

4.3 Conclusions

According to the industry, there are alternatives to MOCA available but these are not fully compatible to MOCA either from the chemistry (limited performance compared to MOCA) or financial point of view (often too expensive).

There has been ongoing for decades (and still is) a continuing research and development effort by industry to develop viable alternatives to MOCA. However it takes years to introduce a new curing agent as testing of its technical properties and of the final product is very time consuming. Given the efforts required to develop the currently available alternatives it is doubted by industry that more efforts and resources will be dedicated to the development of new alternatives. Instead, industry will focus on safe use of MOCA containing products or produce / buy the MOCA containing final products outside the EU.

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