Kirk-Othmer Encyclopedia of Chemical Technology.
Copyright © John Wiley & Sons, Inc. All rights reserved.

AMINES, AROMATIC, METHYLENEDIANILINE

Commercial production of 4,4′-methylenedianiline [101-77-9] (4,4′-MDA) is carried out by the acid catalyzed reaction of formaldehyde with aniline. All processes produce polymeric MDA (PMDA), which consists of mixtures of isomers and oligomers of MDA. The amounts of MDA and oligomers are varied to produce products that have different applications. The isomeric distribution and the amount of MDA in the PMDA can be varied within wide ranges, depending on the needs of the consumer. More than 99% of the manufactured PMDA products are used in reactions with phosgene to produce the corresponding isocyanates for use in polyurethanes. The resultant polymeric isocyanates (PMDI) are either sold commercially or are purified to isolate 4,4′-methylenediphenyldiisocyanate (MDI) [101-68-8]. Only 15–20% of the total PMDI manufactured in the United States is consumed in the monomeric form. MDI is an important intermediate in the manufacture of spandex fibers, thermoplastic resins, and coatings, and it is used in reaction injection molding (RIM) for automotive applications. The primary use of PMDI products is in rigid foam insulation, but they are also used in semiflexible foams, foundry core binders, and particle board manufacture. Nonisocyanate uses for MDA or PMDA include epoxy curing agents, filament wound pipe, wire coatings, and military applications.

It is very difficult to treat MDA as a single entity because the manufacturing processes of PMDA and MDA are essentially identical, with the exception of a separation step. This article focuses on the technology of 4,4′-MDA, and it also includes properties of isomers and oligomeric mixtures when they are of commercial importance. The 4,4′-MDA is a suspected human carcinogen, and therefore special handling of this material is required. All of the MDA and PMDA produced is consumed in industries that are “destructive” of MDA’s chemical identity. Thus MDA loses its unique chemical identity and is not encountered by household consumers.

The terminology commonly used to describe MDA and PMDA material is confusing to those new to the field. The term MDA is sometimes used for pure 4,4′-MDA as well as the oligomeric mixture PMDA. Similar inconsistencies are encountered for the isocyanate derivatives (MDI and PMDI). Synonyms for 4,4′-methylenedianiline include MDA, 4,4′-MDA, methylenedianiline, 4,4′-methylenebisaniline, dianilinomethane, 4-(4′-aminobenzyl)aniline, 4,4′-diaminodiphenyl-methane, 4,4′-methylene-bis(benzenamine), bis(*p*-aminophenyl)methane, DADPM, DAPM, and DDM. The *p,p*′- and 4,4′-designations are used interchangeably. Synonyms for the oligomeric MDA mixtures include polyaminopolyphenylamine, polymethylenepolyphenylamine, and PMDA. In this article MDA will stand for 4,4′-MDA and/or its isomers, and PMDA is a mixture of MDA and MDA oligomers.

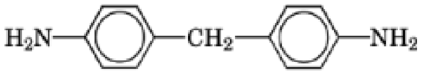
1. Physical Properties

The physical and chemical properties of 4,4′-MDA and a typical PMDA are listed in Table 1.**12**

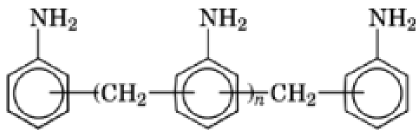
Table 1. Physical and Chemical Properties of MDA and PMDA

Property	4,4′-MDA	PMDA[a]
CAS Registry Number	[101-77-9]	[25214-70-4]
molecular formula	$C_{15}H_{14}N_2$	
RTECS accession number[b]	BY5425000	
molecular weight	198.3	
active hydrogen equivalent weight	49.6	51
melting point, °C	93	60–80
heat of vaporization, kJ/mol[c]	95.4	
specific heat, J/(g·°C)	2.1	2.1
heat of fusion, kJ/mol[c]	19.6	~19.6
flash point, °C	227	238
boiling point, °C	238 at 1.33 kPa[d]	398 at 101.3 kPa[d]
vapor pressure, Pa[d]	2.7×10^{-5} at 25°C	1.3 at 100°C
density, g/mL	1.070 at 103°C	1.07 at 70°C
viscosity, mPa·s(= cP)	8.3 at 100°C	80 at 70°C
approximate solubility, g/100 mL solvent at 25°C		
acetone	273.0	
benzene	9.0	
carbon tetrachloride	0.7	
ethyl ether	9.5	
methanol	143.0	
water	0.1	

[a] For PMDA containing approximately 70% MDA.
[b] Registry of Toxic Effects of Chemical Substances.
[c] To convert kJ to kcal, divide by 4.184.
[d] To convert kPa to mm Hg, multiply by 7.5.



4,4′-methylenedianiline (MDA)



polymeric MDA (PMDA)

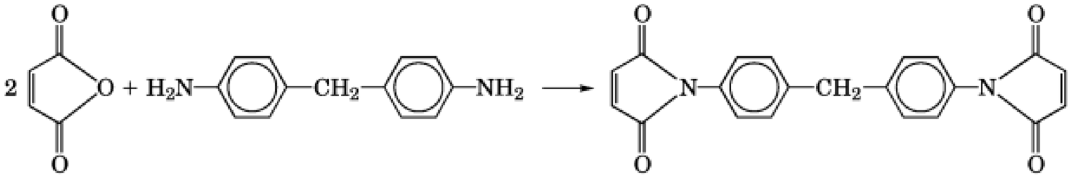
Purified 4,4′-MDA is a light tan to white crystalline solid with a faint aminelike odor. It slowly oxidizes in air with a darkening in color. PMDA mixtures are yellow to brown supercooled liquids or waxy solids.

2. Chemical Properties

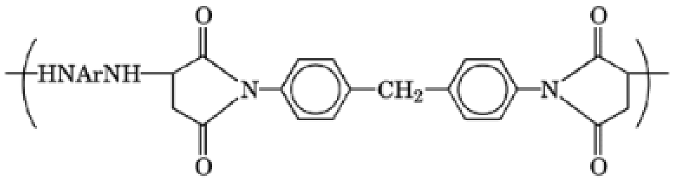
MDA reacts similarly to other aromatic amines under the proper conditions. For example, nitration, bromination, acetylation, and diazotization (1–3) all give the expected products. Much of the chemistry carried out on MDA takes advantage of the difunctionality of the molecule in reacting with multifunctional substrates to produce low and high molecular weight polymers.

The most important commercial process is the reaction of MDA with an excess of phosgene to form the corresponding isocyanate, 4,4′-methylene-diphenyldiisocyanate, MDI, $C_{15}H_{10}N_2O_2$. The reaction proceeds through the formation of a primary carbamyl chloride that is decomposed with heating and the removal of HCl.**3**

MDA reacts with acid anhydrides to form amides. In the reaction with maleic anhydride both of the amino hydrogens are replaced to form the imide, *N,N*′-(methylenedi-*p*-phenylene) dimaleimide [1367-54-5] $C_{21}H_{14}N_2O_4$.**4**



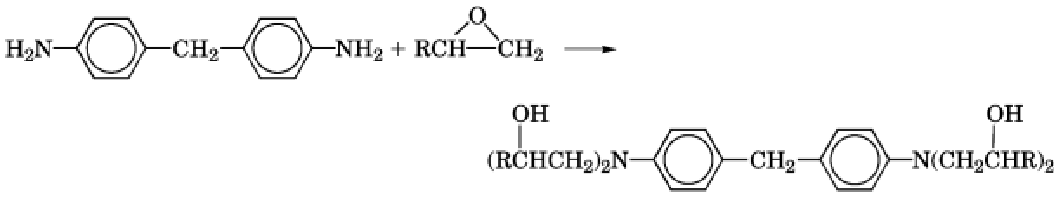
The bismaleimide can then be polymerized by reaction with additional amine to form polyaminobismaleimide or by radiation-induced homopolymerization to form polybismaleimide (4).**5**



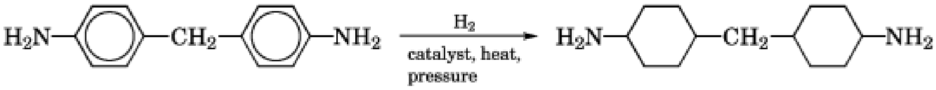
polyaminobismaleimide

The reaction of diphenic anhydride with excess MDA proceeds through an imide ring opening to produce a linear polymer, or it can react with PMDA to form a cross-linked polymer (5).

All of the amine hydrogens are replaced when MDA or PMDA reacts with epoxides to form amine based polyols. These polyols can be used in reactions with isocyanates to form urethanes or with additional epoxide to form cross-linked thermoset resins.**6**



High temperature and high pressure reactions of MDA with hydrogen in the presence of noble metal catalysts convert 4,4′-MDA into bis(4-aminocyclohexyl)methane (H_{12}MDA) [1761-71-3] ($C_{13}H_{26}N_2$). The products are a mixture of cis and trans isomers that can be controlled to some extent by the proper choice of catalyst and reaction conditions (6–12).**7**



3. Manufacture and Processing

MDA and oligomers (PMDA) are produced by the acid catalyzed condensation of aniline [62-53-3] (C_6H_7N) with formaldehyde [50-00-0] (CH_2O). The reaction does not lead to a single product, but to a mixture of 4,4′-, 2,4′-, and 2,2′-isomers and oligomeric MDAs. The amounts of MDA isomers and oligomers formed depend on the ratios of aniline, formaldehyde, and acid used, as well as the reaction temperature and time. Figure 1 shows a simplified pathway to the formation of 4,4′-MDA. Similar routes can be drawn for the formation of 2,4′-MDA, 2,2′-MDA, and higher oligomers. The initial reaction of aniline with formaldehyde produces *N*-methylolaniline [61224-32-6] (C_7H_9NO). This product loses water rapidly to form the Schiff base (intermediate A) (12, 13). The Schiff base reacts with aniline to form two types of aminals, linear (LA) and cyclic (HHT). The relative amounts of the aminals formed depend on the ratio of aniline to formaldehyde. For example, when aniline: formaldehyde molar ratios of $>2:1$ are employed, the predominant product is the linear aminal with $n = 1$. If the reaction is carried out in base or in neutral solution, the reactions stop at this stage.

MDA does not form in the absence of acid. The aminals and the *N*-methylolaniline decompose rapidly in acid solution to form an anilinium ion (intermediate B). This reactive intermediate combines with aniline to form *N*-(*p*-aminobenzyl)aniline [17272-83-2] ($C_{13}H_{14}N_2$) which reacts with intermediate B in the presence of acid to form oligomeric benzylamines (PBA) that exist in equilibrium with the monomer. The formation of this equilibrium mixture completes the condensation phase of the synthesis. Almost all of the side reactions take place during the condensation phase of the reaction. The typical side products formed are the N-methyl and quinazoline derivatives of aniline and MDA (12, 14). Commercial processes have been successful in minimizing these side reactions.

The final step (rearrangement stage of the reaction) is decomposition to form the *p*-aminobenzyl carbonium ion (intermediate C) and alkylation of aniline to form 4,4′-MDA. In this step all of the secondary amine intermediates are converted to primary amine final products. Direct alkylation of PBA with aniline has also been hypothesized to form MDA without the formation of intermediate C (16). The formation of MDA is not reversible under normal reaction conditions. Almost all of the other reactions depicted are reversible to some extent. From a commercial standpoint the most important reactions taking place are the formation of oligomers, ie, the reaction of MDA with intermediate C or PBA. It is these reactions, which cannot be suppressed, that are responsible for the current development of MDA technology. MDA is formed slowly during the reaction and therefore is susceptible to further alkylation to form 2,4-bis(*p*-aminobenzyl)aniline [25834-80-4] ($C_{20}H_{21}N_3$). Further alkylations produce an oligomeric mixture.

The reaction of aniline with formaldehyde can be carried out in a single reactor (Fig. 2). However, most commercial processes probably use multiple reactors, which provide greater control of the MDA isomer distribution and oligomeric content of the final product (16–19). Use of hydrochloric acid and high reaction temperatures necessitates the use of corrosion resistant metallurgy. Normally the acid is first mixed with excess aniline, which causes an exotherm. Formaldehyde is then added, with efficient agitation and at low temperatures ($<50^\circ C$), to the aniline–aniline hydrochloride solution. The reaction is usually staged to control the condensation and rearrangement steps. The final reaction temperatures are normally 80–120°C. After completion of reaction, the acidic PMDA is treated with aqueous sodium hydroxide to neutralize the excess acid. A large amount of salt is formed during this step; thus the plants must be located near an outlet capable of handling the generated salt water (normally a seacoast). Processes that recycle the acid and eliminate the salt disposal problem have been patented (20, 21). The organic layer is then washed with water and stripped to remove unreacted aniline and water. The unreacted aniline is recycled back to the beginning of the reaction.

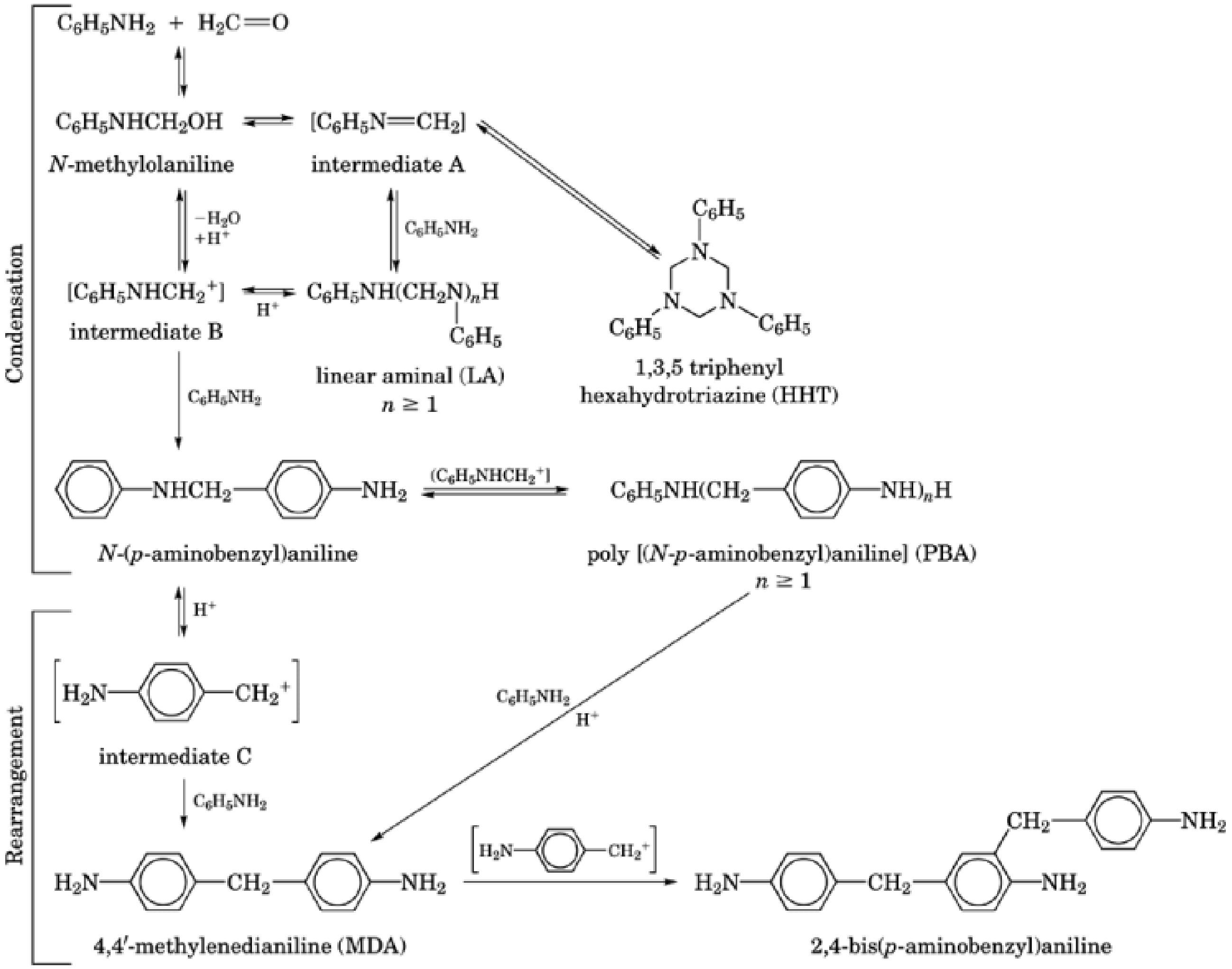


Fig. 1. Reaction of aniline with formaldehyde.

The product may be purified to isolate pure 4,4′-MDA, packaged for shipment, or treated with phosgene to produce the corresponding isocyanate. The 4,4′-MDA is normally sold in flaked or granular form in lined steel drums. Depending on the MDA content, PMDA is sold as a waxy solid or a yellow to brown viscous supercooled liquid in steel drums.

Process parameters can be varied to change the MDA isomer distribution and oligomeric content of PMDA products. Generally, aniline to formaldehyde molar ratios of 2 to 5 are used. To increase the MDA content, higher ratios of aniline to formaldehyde are employed. Increasing the acid to aniline ratio also increases the 4,4′-MDA content of the diamine fraction. Historically, the polyurethane industry consumes as much of the 4,4′-MDI isomer as possible. Recently, however, there has been an increasing demand for higher 2,4′-MDI and 2,4′-PMDI products to be used as replacements for toluenediisocyanate (TDI). Low acid and high aniline to formaldehyde ratios increase the 2,4′-MDA content of the diamine fraction. At the lower aniline to formaldehyde ratios the tendency is to form higher oligomers. The 2,4′-MDA is more reactive toward alkylation than the 4,4′-MDA

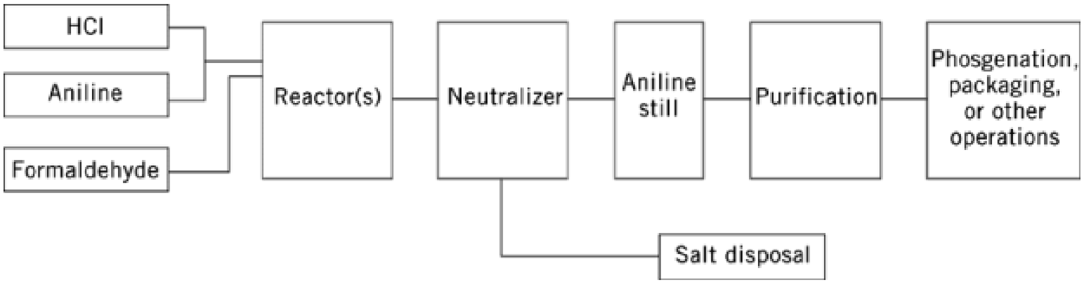


Fig. 2. Methylenedianiline process.

isomer. Commercial processes do not employ molar excesses of acid to aniline. Acid catalysis is necessary to form MDA, and HCl is the acid of choice. Silica (23), clay (23–25), ethanesulfonic acid (27), and tungsten (27, 28) are among the catalysts that have been patented. All of these processes possess some commercial drawbacks, eg, high expense, severe reaction conditions, and/or poor yields of 4,4′-MDA. High reaction temperatures result in a decrease in the MDA content of the product. Reaction time and water content also affect the oligomeric distribution of the product; both should be minimized for maximum MDA formation (30). Water is introduced into the reaction from the hydrochloric acid used to make the aniline hydrochloride solution, from the formaldehyde, which is normally sold in water solution (formalin), and as a reaction product in the condensation phase of the reaction.

Commercially, the PMDA mixtures are normally treated with phosgene to produce the corresponding isocyanates. These isocyanate mixtures, commonly called polymeric MDI (PMDI), are sold directly and have varied chemical compositions. The 4,4′-MDI can be separated from the PMDI products by distillation or crystallization (30, 31). The amount of 4,4′-MDI that is removed depends on marketing conditions. The residues are also viable commercial products.

Commercially, a small amount of the 4,4′-MDA is isolated by distillation from PMDA. Depending on the process employed, the removal of MDA can be partial (as is done with the isocyanates) or total. Partial removal of MDA gives some processing latitude but yields of 4,4′-MDA are reduced. Distillation residues from PMDA manufacture that contain less than 1% MDA pose a disposal problem. Processes for the regeneration of MDA by heating these residues in the presence of aniline and an acid catalyst have been patented (32–34). Waste disposal of PMDA is expensive and reclamation processes could become commercially viable. The versatility of the isocyanate process, however, can be used to avoid the formation of low MDA content distillation residues.

4. Economic Aspects

The data in Table 2 represent the total MDI (MDI and PMDI) that is produced on a global basis.

The estimated growth rate to the year 2000 for total MDI is 4–5% in the United States and 6% globally. In 1987 and 1988 U.S. plants were estimated to be 96 and 97% utilized (39). Additional capacities of over 400,000 t by the end of 1993 have already been announced (39–43). Approximately 20% of the total MDI manufactured in the United States is exported (37, 38, 44). Of the 500,000 t of PMDI mixtures manufactured annually in the United States it is estimated that only 75,000–100,000 t are sold as 4,4′-MDI. The current bulk selling price for 4,4′-MDI is $2.75/kg and for PMDI $2.20. The 4,4′-MDA sells for $5.00–6.50/kg and crude PMDA is $2.90–3.25/kg. Approximately 450–900 t of pure 4,4′-MDA are imported (45, 46), MDA and PMDA products are sold commercially under the names of MDA (BASF), Araldite Hardener (CIBA-GEIGY), Curithane (Dow), Ancamine (Pacific Anchor), and TONOX (Uniroyal).

Table 2. 1989 Global Production Capacity for MDI and Polymeric MDI

Manufacturer	Location	Capacity[a], 10^3 t
United States[b]		
BASF	Geismar, La.	68
Dow	La Porte, Tex.	150
Mobay	Baytown, Tex.	100
	New Martinsville, W. Va.	50
Rubicon	Geismar, La.	141
Total United States		*509*
Western Europe[c]		
BASF	Antwerp, Belgium	60
Bayer	Krefeld, FRG	126
Bayer	Leverkusen, FRG	20
Bayer	Tarragona, Spain	6
Bayer-Shell	Antwerp, Belgium	26
ICI	Fleetwood, UK	45
ICI	Rosenberg, Holland	40
Montedison	Brindisi, Italy	70
Dow	Isopor, Portugal	50
Dow	Delfzijl, Holland	70
Total Western Europe		*513*
Asia[d]		
Dow-MDK	Yokkaichi, Japan	36
Mitsui Toatsu	Omuta, Japan	35
Nippon Polyurethane	Nanyo, Japan	50
Sumitomo Bayer	Niihama, Japan	36
Total Asia		*157*
other (Eastern Europe and South America)		ca 61
Global total		*1,240*

[a] The conversion factor for PMDA to PMDI is 1.25–1.35; eg, 80 kg of MDA produces 100 kg of MDI.
[b] Ref. 36.
[c] Ref. 37.
[d] Ref. 38.

5. Specifications and Standards

The 4,4′-MDA is sold commercially with a diamine assay of 98–99%. The major impurity is the 2,4′-MDA isomer, which can be present in amounts up to 3%. PMDA products are normally defined by hydrogen equivalent weight and viscosity. Typical products exhibit a 50 hydrogen equivalent weight and a viscosity of $80 - 140\mathrm{mPa{\cdot}s}(= \mathrm{cP})$ at 70°C. PMDA products normally contain, in addition to the isomers and oligomers of MDA, small amounts of aniline, water, chlorides, and various alkylated amines. All MDA products should be stored in sealed containers in a cool dry area.

6. Analytical and Test Methods

The characterizations of MDA and PMDA are similar to those normally used for aromatic amines. In the manufacture of PMDA, the MDA isomer distribution and the formation of side products is determined primarily by gas chromatography (47, 48). The amine content is determined by acid titration or diazotization. PMDA oligomeric distributions are determined by hplc or gpc techniques (49) and are estimated by viscosity measurements. Liquid chromatographic and spectrophotometric monitoring methods have been developed to determine ppm to low ppb quantities in workplace environments (49, 50), urine (52), reacted polyurethanes (53), and epoxy systems (54). All of the environmental methods of analysis employ a collection technique that is sensitive to the presence of aerosols and are capable of quantitating MDA down to 10 ppb (v/v). OSHA recommends using Method #57 for monitoring purposes (55).

7. Health and Safety Factors (Toxicology)

All of the toxicity data on MDA have been collected using either 4,4′-MDA or the corresponding hydrochloride salt. The information discussed in this section can also be used for commercial products containing MDA or PMDA. Because MDA is a potentially hazardous chemical, worker exposure should be kept to a minimum. For complete health and safety information on MDA consult references 46 and (55–58).

The recommended threshold limit value (TLV) of MDA is 100 ppb for an 8-h time-weighted average (TWA) skin. MDA is a suspected human carcinogen (55, 57, 58). The oral LD_{50} = 830 mg/kg. In May of 1989 OSHA proposed a new standard for regulating MDA. The proposal cites a permissible exposure limit (PEL) for occupational exposure of MDA to an 8-h TWA of 10 ppb and a STEL (short-term exposure limit) of 100 ppb for a 15-min TWA (50). The standard does not apply if initial monitoring shows less than the action level of 5 ppb for an 8-h TWA (airborne) and if no dermal exposure is likely. The employer is required to implement engineering and work practices (eg, respirators) to maintain employee exposure levels at less than or equal to the permissible exposure limit. The proposal also includes having a changing room and showers for changing all contaminated clothing after a work shift; employer laundering of clothing; removal of clothing prior to eating, drinking, smoking, etc; and washing hands and face prior to eating. If food and beverages are consumed in the work area, the employer is expected to provide a positive pressure eating area. All surfaces must be maintained as free as possible from visible accumulations of MDA. The employer is responsible for conducting medical surveillance and record keeping, as well as for conducting periodic monitoring of the area according to existing exposure level guidelines.

The major exposure route in workers who experience MDA poisoning is by skin contact. If there is a likelihood of skin or eye contact, proper protective clothing (including gloves, head coverings, impervious shoes, aprons, coveralls, or other full body clothing) must be worn. Skin absorption is increased if the MDA is dissolved in an organic solvent. Face shields and/or goggles should be worn where appropriate. Care must be taken to minimize contamination of individuals and their personal environment from exposure to MDA. The low vapor pressure of MDA poses a minimum risk of MDA inhalation. However, grinding and drumming of MDA produces dust and vapors, which can cause inhalation problems. In addition, many operations require heating MDA to keep the material molten. It is therefore recommended that respirators be worn while handling MDA to keep exposures to a minimum.

There are no reports of cancer in humans as a result of MDA exposure. Acute exposures of MDA have caused epigastric pain, fever, jaundice, and other symptoms consistent with hepatitis. These effects, however, appear to be reversible. No liver damage has yet been observed from chronic exposure to MDA. Skin sensitivity and staining occurs in some individuals. In animals, chronic administration of MDA produces hepatic cirrhosis, liver lesions, and enlargement of the spleen, liver, and kidneys. MDA has also proved to be carcinogenic in rats and mice, causing liver and thyroid tumors. No cancers have been formed in dogs. Structurally similar compounds have been shown to cause cancer in laboratory animals (58). If appreciable amounts of MDA are swallowed, vomiting should be induced. If eye exposure does occur, the eyes should be flushed with water for 30 min. Skin exposures should be washed with soap and water. Medical attention should be obtained promptly whenever an exposure occurs. There are always dangers involved with the misuse of any chemical. However, with attention to proper work practices and policies, this valuable intermediate can be utilized safely.

8. Uses

More than 99% of all the PMDA produced is used directly in the manufacture of the corresponding isocyanates (MDI and PMDI). Two types of isocyanates are sold, monomeric (MDI) and polymeric (PMDI). The PMDI products are available commercially in varying viscosities from 50 to $2000\text{mPa}\cdot\text{s}(= \text{cP})$, containing from 25 to 60% monomeric MDI. The major use for PMDI products (65–75%) is in the manufacture of rigid foam, which is primarily used in housing and refrigeration insulation applications. Other uses for PMDI products include semiflexible foam, elastomers, foundry core binders, and particle board adhesives. MDI contains approximately 98% of the 4,4′-isomer and is used to manufacture thermoplastic resins (eg, films, gaskets, tubing), spandex fibers, and coatings. Because MDI is a solid at room temperature, a significant portion of the commercially produced pure MDI is converted to liquid products by either modifying the MDI with carbodiimide linkages or reaction with polyols to produce isocyanate terminated prepolymers. These products are used in automotive reaction injection molding (RIM), coatings, and recreation and military applications. MDI and PMDI products containing more than 10% of the 2,4′-MDI isomer are becoming available for use in nonrigid foam applications. These products are able to compete with toluenediisocyanate (TDI) in physical properties of the final products without the severe handling limitations normally needed for TDI. Nonisocyanate uses for MDA or PMDA include epoxy resin curing agents, wire coating applications, plastic fibers, polyurethane coreactants, an intermediate for pigments and dyes, intermediates for the preparation of polyamide–imide resins, reinforced composite materials, and military applications. Perhydrogenated 4,4′-MDA (H_{12}MDA or PACM) is used in light-stable elastomers and coatings. The H_{12}MDA is converted to the corresponding isocyanate, bis(4-isocyanatocyclohexyl)methane [5124-30-1] ($C_{15}H_{22}N_2O_2$) or H_{12}MDI, and is used in automotive safety glass and biomedical applications.

BIBLIOGRAPHY

"Amines, Aromatic (Methylenedianiline)" in *ECT* 3rd ed., Vol. 2, pp. 338–348, by William M. Moore, Dow Chemical U.S.A.

Cited Publications

1. H. King, *J. Chem. Soc.* **117**, 988 (1920).
2. G. D. Parkes and R. H. H. Morley, *J. Chem. Soc.* **139**, 315 (1936).
3. C. L. Butler, Jr. and R. Adams, *J. Am. Chem. Soc.* **47**, 2610 (1925).
4. M. A. J. Mallet, *Mod. Plast.* **50**, 78 (1973).
5. M. E. B. Jones and M. S. Chisholm, *Polymer* **29**, 1699 (1988).
6. U.S. Pat. 2,606,927 (Aug. 12, 1952), A. E. Barkdoll and G. M. Whitman (to E. I. du Pont de Nemours & Co., Inc.).
7. U.S. Pat. 2,606,928 (Aug. 12, 1952), A. E. Barkdoll, C. D. Bell, and E. R. Graef (to E. I. du Pont de Nemours & Co., Inc.).
8. U.S. Pat. 2,606,924 (Aug. 12, 1952), G. M. Whitman (to E. I. du Pont de Nemours & Co., Inc.).
9. U.S. Pat. 2,494,563 (Jan. 17, 1950). W. Kirk, Jr., C. Hundred, R. S. Schreiber, and G. M. Whitman (to E. I. du Pont de Nemours & Co., Inc.).
10. A. E. Barkdoll, H. W. Gray, and W. Kirk, Jr., *J. Am. Chem. Soc.* **73**, 741 (1951).
11. Brit. Pat. 619,706 (Mar. 14, 1949), W. Kirk, Jr., R. S. Schreiber, and G. M. Whitman (to E. I. du Pont de Nemours & Co., Inc.).
12. Ger. Pat. 842,200 (June 23, 1952), O. Stichnoth and L. Wolf (to BASF).
13. E. C. Wagner, *J. Org. Chem.* **19**, 1862 (1954).
14. M. M. Sprung, *Chem. Rev.* **26**, 297 (1940).
15. C. Ringel, H. Böhm, H. Kroschwitz, and D. Scheller, *SYSpur Reporter 1981*, **19**, 143 (1981).
16. H. J. Twitchett, *Chem. Soc. Rev.* **3**, 209 (1974).
17. U.S. Pat. 3,954,867 (May 4, 1976), B. D. Funk, Jr., J. Mongiello, and W. J. Rabourn (to the Upjohn Co.).

18. U.S. Pat. 3,931,320 (Jan. 6, 1976), W. Eifler, R. Raue, E. H. Rohe, and J. Finkel (to Bayer AG).
19. Brit. Pat. 1,378,423 (Dec. 27, 1974), R. S. Mason, P. D. Rough, and H. W. Twitchett (to Imperial Chemical Industries, Ltd.).
20. U.S. Pat. 3,476,806 (Nov. 4, 1969), H. O. Wolf (to E. I. du Pont de Nemours and Co., Inc.).
21. U.S. Pat. 4,061,678 (Dec. 6, 1977), H. Knöfel and G. Ellendt (to Bayer AG).
22. Ger. Pat. 2,238,920 (Mar. 7, 1974), H. Knöfel (to Bayer AG).
23. Belg. Pat. 677,830 (Dec. 1, 1965), R. B. Lund and J. Vitrone (to Allied Chemical).
24. U.S. Pat. 4,071,558 (Jan. 31, 1978), F. E. Bentley (to Texaco Development Corp.).
25. U.S. Pat. 4,039,580 (Aug. 2, 1977), F. F. Frulla, A. A. R. Sayigh, H. Ulrich, and P. J. Whitman (to the Upjohn Co.).
26. U.S. Pat. 4,039,581 (Aug. 2, 1977), F. F. Frulla, A. A. R. Sayigh, H. Ulrich, and P. J. Whitman (to the Upjohn Co.).
27. U.S. Patent 4,212,821 (July 15, 1980), (to Texaco Development Corp.).
28. U.S. Pat. 4,286,107 (Aug. 25, 1981), (to Texaco Inc.).
29. U.S. Pat. 4,284,816 (Aug. 18, 1981), (to Texaco Inc.).
30. U.S. Pat. 3,277,173 (Oct. 4, 1966), E. L. Powers and I. B. Van Horn (to Mobay Chemical Company).
31. U.S. Pat. 3,892,634 (July 1, 1975), J. D. Hajek and H. R. Steele (to the Upjohn Co.).
32. Brit. Pat. 1,423,993 (Feb. 4, 1976), D. Adsley and R. C. Smith (to Imperial Chemical Industries, Ltd.).
33. Brit. Pat. 1,127,347 (Sept. 18, 1968), J. A. Hall and B. L. Yates (to Imperial Chemical Industries Ltd.).
34. U.S. Pat. 4,089,901 (May 16, 1978), P. Ziemek, R. Raue, and H. J. Buysch (to Bayer AG).
35. U.S. Pat. 4,083,870 (Apr. 11, 1978), H. J. Buysch, P. Ziemek, and R. Raue (to Bayer AG).
36. *1989 Directory of Chemical Producers*, SRI International, Menlo Park, Calif., 1989, p. 712.
37. Ref. 36, p. 1365.
38. *Urethane Industry Digest, Part B Marketing Guide*, C. J. Swanson, Publisher, Holiday, Fla., June 1988.
39. *The North American Markets for Polyurethane Products 1988/1989—Chem Systems Final Report*, Polyurethane Division of the Society of the Plastics Industry, Tarrytown, N.Y., July 1989.
40. *Chem. Mark. Rep.*, 12 (July 3, 1989).
41. *Urethanes Technology*, 6 (Apr./May 1989).
42. *Eur. Chem.*, 28 (Mar. 1989).
43. *Chem. Week.* 64 (June 28, 1989).
44. *Mod. Plast.* 140 (Nov. 1989).
45. Ernst and Whinney, *Isocyanates Reports, SPI Committee on Resin Statistics*, Washington, D.C., 1989.
46. *NIOSH Current Intelligence Bulletin—4,4′-Methylenedianiline (MDA)*, 47 (July 25, 1986).
47. *An Estimate of Industry Regulatory Compliance Costs and Economic Impact for Meeting an OSHA Workplace Exposure Standard for 4,4′-Methylenedianiline (MDA)*, Heiden Associates, Inc., Washington, D.C., Dec. 12, 1986.
48. I. P. Krasnova, E. N. Boitsov, Y. N. Golovistikov, and B. M. Tsigin, *Zsvod. Lab.* **43**, 1324 (1977).
49. P. Falke, R. Tenner, and H. Knopp, *J. Prakt. Chem.* **328**, 142 (1986).
50. C. C. Anderson and E. C. Gunderson, *Methods Validation Study of High Performance Liquid Chromatographic Technique for Determining the MPDA and MDA Content of Air Samples*, SRI International, Menlo Park, Calif., 1986.
51. D. W. Meddle and A. F. Smith, *Analyst (London)* **106**, 1082 (1981).
52. J. Cocker, L. C. Brown, H. K. Wilson, and K. Rollins, *J. Anal. Toxicol.* **12**(1), 9 (1988).
53. D. A. Ernes and D. T. Hanshumaker, *Anal. Chem.* **55**, 408 (1983).
54. R. E. Smith and W. R. Davis, *Anal. Chem.* **56**, 2345 (1984).
55. C. J. Elskamp, *OSHA Analytical Method #57—4,4′-Methylenedianiline (MDA)*, OSHA Analytical Laboratory, Salt Lake City, Utah, Jan. 1986.
56. *Federal Register* **54**, 20672–20744 (May 12, 1989).
57. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 5th ed., American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1989.

58. N. M. Bernholc, S. C. Morris, III, and J. E. Brower, *Biological Effects Summary Report 4,4′-Methylenedianiline* (BNL-51903), Brookhaven National Laboratory, Upton, N.Y., 1985.
59. *Threshold Limit Values and Biological Exposure Indices for 1989–1990*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1989.

STEVEN LOWENKRON
The Dow Chemical Company

Related Articles

Isocyanates, organic; Foamed plastics; Urethane polymers