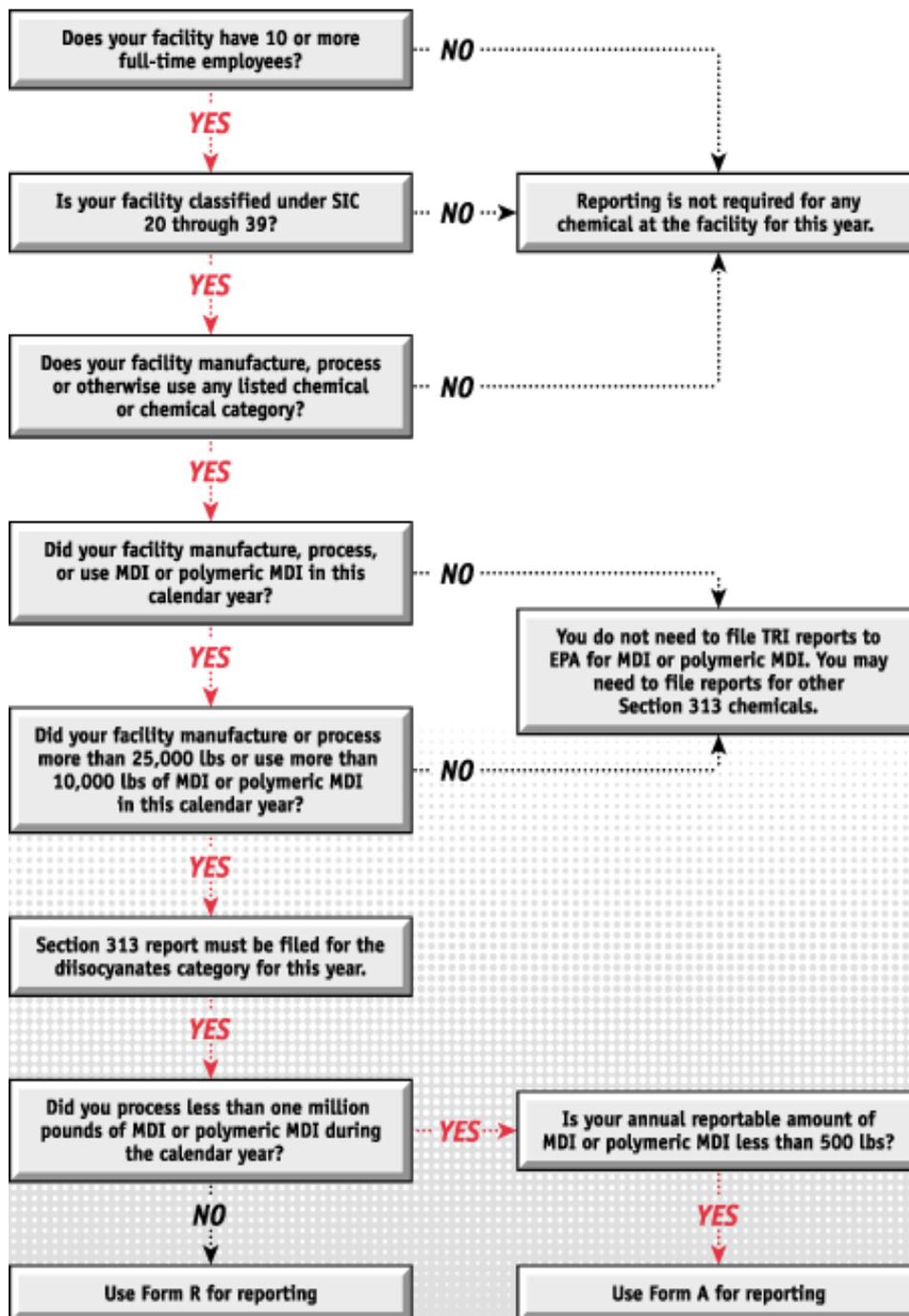


MDI/Polymeric MDI Emissions Reporting Guidelines For the Polyurethane Industry



For Section 313 of EPCRA and State Reporting

Note to Readers:

This document reviews the requirements and offers guidance for reporting releases of certain listed chemicals of interest to members of the polyurethane industry under the provisions of Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA). Its principal purposes are to:

- Assist companies in the polyurethane industry in completing the Environmental Protection Agency's (EPA) Form A or Form R,
- Outline suggested techniques for estimating emissions for certain chemicals in the "diisocyanates" category listing under EPCRA, specifically 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI), and
- Provide examples of calculating MDI/polymeric MDI emissions associated with storage tank losses, fugitive releases, and stack emissions based on applied applications.

The methodologies used to estimate releases of 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI) have been developed using standard techniques, but may not be suitable for estimating releases of other chemicals. The information provided in this document is offered in good faith and believed to be reliable, but is made **WITHOUT WARRANTY, EXPRESS OR IMPLIED, AS TO MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ANY OTHER MATTER**. This document is not intended to provide emissions data for any particular product or process. Scenarios that have been selected are believed to be representative of situations where releases may occur. Other scenarios not reflected in this document may involve releases as well. It is the responsibility of all manufacturers, processors or users of any listed chemical to know and understand the reporting obligations, and to provide accurate information, in accordance with the provisions of the law. Consult your own legal and technical advisors for specific advice applicable to your own facility.

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Alliance For the Polyurethanes Industry
A Business Unit of the American Plastics Council

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Introduction and Background

The purpose of this document is to provide manufacturers, processors and other users of certain chemicals in the polyurethane industry with guidance on fulfilling their obligation to report releases of listed chemicals in accordance with the provisions of Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA). In particular, this document outlines approaches for estimating emissions from the processing and use of 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI) in the absence of specific data on emissions. MDI and PMDI are EPCRA-listed chemicals in the "diisocyanates" category listing for which reports must be filed.

Section 313 requires affected facilities to provide information on (1) routine and accidental releases of specific listed chemicals and mixtures of chemicals into the environment, (2) transfers to off-site facilities, and (3) waste treatment methods, and the efficiency of those methods. It also requires reporting on the name, location and type of business; the identity of the listed chemical(s) or chemical mixture(s) involved, and whether the chemical is manufactured, processed or otherwise used at the facility; and an estimate of the maximum amount of the chemical present at the facility at any time during the year. EPCRA-required information must be reported on the Annual Section 313 Toxic Chemical Release Form R. In certain circumstances, however, facilities may be able to report using the 313 Toxic Chemical Release Form A, which requires significantly less information.

Facilities are also required to comply with the provisions of the Pollution Prevention Act of 1990 (PPA). The PPA requires that source reduction and detailed information about on-site waste treatment and recycling be reported. Definitions of "source reduction," "treatment," "recycling" and the like should be reviewed and your activities reported accordingly.

Reported information is placed in the Environmental Protection Agency's (EPA) Toxic Release Inventory (TRI) database, where it is made publicly available via the Internet and through the annual publication of the Toxic Release Inventory.

Use of TRI Database

The TRI database is widely used by the public and private sectors alike. EPA and state regulators review information contained in the database to evaluate the possible need for special reductions in use and/or emissions of a particular listed chemical, and the need for implementation of special controls to reduce releases. Environmental groups, news reporters and others also closely scrutinize these data. It is not uncommon for EPA, its counterpart state agencies, environmental groups and local newspapers to publish reports summarizing TRI data reported by local facilities. Typically, "top polluters" are prominently highlighted in these reports. Citizens action groups and others may use TRI data to oppose projected plant expansion plans or to insist on special controls for companies that manufacture, process or use particular listed chemicals. EPA analyzes TRI data to establish priorities for reducing use of certain chemicals as part of its risk management process. For example, TRI data were used in developing the list of 189 "hazardous air pollutants" included in Title III of the Clean Air Act Amendments of 1990. MDI is on that Title III list, and has been on the EPCRA list since its inception.

Therefore, it is important that reports be as accurate as possible. Overestimating emissions can lead regulators and others to seek imposition of controls that are not scientifically justified, while underestimating emissions risks enforcement action by the Agency.

Historical Perspective on TRI Reporting for Diisocyanate Users

MDI was part of the original list of toxic chemicals subject to EPCRA §13. In 1994, however, EPA created a “diisocyanates” category, containing 18 specific isocyanates. Beginning in Reporting Year 1995, a covered facility that exceeded a threshold for the diisocyanate category had to file a TRI report.

Specifically, instead of submitting separate reports for MDI, PMDI and other isocyanates, reports must be aggregated for all isocyanates used and released by a facility. For example, if a facility processes 10,000 pounds of MDI and 15,000 pounds of polymeric MDI, it now meets the 25,000-pound threshold for reporting, and the release of both chemicals must be reported as a cumulative number. The requirement to aggregate exists for all isocyanates in the category. Formerly, only MDI releases were reported, and processing the above amounts would not meet the threshold for reporting.

Almost all facilities in the polyurethane industry process or use PMDI rather than pure MDI. PMDI is typically used as a mixture of MDI, a solid at ambient temperatures, dissolved in polymeric MDI, which is a liquid. Polymeric MDI has a lower vapor pressure than pure MDI. Consequently, MDI/PMDI mixtures have lower vapor pressures than pure MDI, and release estimates that were based in the past on the vapor pressure of pure MDI often significantly overstated emissions - particularly air release estimates. In response to the addition of the diisocyanates category to the EPCRA reporting requirement, these guidelines provide a means of adjusting emission estimates to reflect more accurately the possible releases from facilities that use MDI/PMDI mixtures. This workbook, however, does not provide guidance on estimating emissions of other isocyanates included in the diisocyanate category. Check with your supplier and your own technical or legal advisors for assistance.

EPCRA Overview

To put the Section 313 requirements in perspective, this chapter very briefly reviews the provisions of the Emergency Planning and Community Right-to-Know Act (EPCRA), and the Pollution Prevention Act (PPA). Additional materials addressing EPCRA requirements are available from the Alliance for the Polyurethanes Industry (API).

EPCRA, also known as Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA), was enacted on October 17, 1986. EPCRA has four major sections: emergency planning (Section 301-303), emergency release notification (Section 304) hazardous chemical inventory reporting requirements (Section 311-312), and toxic chemical release reporting/emissions inventory (Section 313). A summary of these sections follows.

Section 301-303: Emergency Planning

The emergency planning provisions of EPCRA are specifically designed to allow for emergency response and preparedness through coordination and planning at the state and local level. The concept involves a multi-tiered system capable of coordinating emergency activities. The governors of each state must designate a state emergency response commission (SERC), which, in turn, must designate local emergency planning districts (LEPD), and appoint local emergency planning committees (LEPC). SERCs are responsible for supervising and coordinating the activities of the LEPCS, for establishing procedures for receiving and processing public requests for information, and for reviewing local emergency plans. These commissions and committees are required to have broad representation from the public and the private sector, including community groups, representatives of the media, and representatives of facilities subject to emergency planning requirements. The LEPCs must develop emergency response plans that meet minimum criteria.

Section 304: Emergency Release Notification

Any time there is a release of a listed CERCLA hazardous substance (*see* 40 CFR Section 302.4) or an EPCRA extremely hazardous substance (*see* 40 CFR Part 355) that exceeds the reportable quantity (R.Q.) for that substance, the facility must immediately (within 15 minutes) notify the LEPC, SERC and National Response Commission (NRC). In addition to following the notification requirements, the facility must submit a follow-up written emergency notice that sets forth the actions taken to respond to the release and any risks posed by the incident.

Section 311-312: Hazardous Chemical Inventory Reporting

The chemical inventory reporting requirements under EPCRA Sections 311 and 312 apply to manufacturers, importers, processors, and users of substances for which material safety data sheets (MSDS) must be maintained under the Occupational Safety and Health (OSH) Act. Under EPCRA Section 311, such facilities must prepare or have available MSDS's and submit either copies of the MSDS's or a list of the hazardous chemicals to the LEPC, SERC, and local fire department if more than a threshold level is stored onsite at any one time.

The threshold level varies depending on how the chemical is classified. For hazardous chemicals that are not extremely hazardous substances (EHS), the threshold is 10,000 pounds. On the other hand, if the hazard chemical is also an EHS (listed in 40 CFR Part 355, Appendices A and B), the reporting threshold is 500 pounds or that chemical's threshold planning quantity

(TPQ), whichever is lower.

Section 312 requires an annual submission of an emergency and hazardous chemical inventory form, known as the Tier One or Tier Two Report, to the LEPC, SERC and local fire department.

Section 313: Toxic Chemical Release Reporting/ Emissions Inventory

As noted above, EPCRA Section 313 requires affected facilities to provide information on routine and accidental releases of specific chemicals, among other things. A “release” includes vaporization or discharge of the chemical into the air, discharge of the chemical into a sewage system, and disposal of the chemical in landfills, either directly or via a waste management contractor.

<p>10 full-time employees = 20,000 hours of work in a year. Add the hours worked by all employees during the calendar year, including the hours worked by contract employees, part-time employees, and sales and support staff. Divide by 2,000, if the resulting number is greater than 10, the criterion has been met.</p>
--

Section 313 of EPCRA requires that a report be filed by an owner and/or operator of a facility that meets all of the following criteria:

- ! The facility has 10 or more full-time employees; and
- ! The facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20-39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under the RCRA Subtitle C, 42 U.S.C. section 6921 *et seq.*), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and
- ! The facility manufactures (defined to include importing), processes, or otherwise uses any EPCRA Section 313 chemical in quantities greater than the established threshold in the course of a calendar year.

Form A Certification Statement Introduced

In 1994, EPA established the Form A Certification Statement—known as Form A- to simplify and reduce the compliance burden associated with EPCRA Section 313. Like the Form R, the Form A must be submitted annually, but instead of a five-page report, the Form A consists of only two pages. Part I requires facility identification information, and Part II requires information on the toxic chemical's identity.

A facility may submit a Form A rather than a Form R if --

- (1) The total annual reportable amount for the toxic chemical does not exceed 500 pounds; and
- (2) The facility does not manufacture, process or otherwise use greater than 1 million pounds of the toxic chemical.

The Form A, however, should not be used for the reporting of any PBT chemical, as identified under 40 CFR Section 372.28.

The “total annual reportable amount” is equal to the combined total quantities of the toxic chemical released at the facility, disposed within the facility, treated at the facility, (as represented by amounts destroyed or converted by treatment process), recovered at the facility as a result of recycle operations, combusted for the purpose of energy recovery at the facility, and amounts transferred from the facility to off-site locations for the purpose of recycle, energy recovery, treatment, and/or disposal. These volumes correspond to the sum of amounts reported on the Form R, section 8, data elements 8.1 through 8.7.

Since 1998, Form A may be used to report up to four chemicals that meet the criteria listed above. If more than four chemicals meet the criteria, they may be listed on additional copies of Part II: Chemical Identification (page 2). A complete report for Form A consists of at least two pages for each submission.

Pollution Prevention Act of 1990

The Pollution Prevention Act of 1990 (PPA) requires facilities subject to the reporting requirements of EPCRA Section 313 to provide information concerning pollutant source reduction and recycling activities. Pollution prevention information must be included with the annual section 313 Toxic Chemical Release “Form R.”

On May 27, 1992, EPA published revisions to the Form R, incorporating required pollution prevention information. Mandatory source reduction and recycling activity information and detailed information regarding on-site waste treatment and recycling must be reported.

The PPA requires reporting of the following information:¹

1. The quantity of each reportable chemical entering any waste stream prior to recycling, treatment, or disposal;
2. The amount of each chemical from the facility which is recycled, including the percentage change from the previous year and the process of recycling used;
3. Source reduction practices used with respect to each chemical for each of the following categories:
 - a. Equipment, technology, process, or procedure modifications;
 - b. Reformulation or redesign of products;
 - c. Substitution of raw materials;
 - d. Improvements in management and operations;
4. The projected quantity of each chemical recycled for two calendar years immediately following the reporting year;
5. A ratio of production (or other activity) in the reporting year to production (or other activity) in the previous year that adequately characterizes the primary influence on the quantity of a toxic chemical entering wastes;
6. Techniques that were used to identify source reduction opportunities;
7. The amount of any toxic chemical released into the environment which results from a catastrophic event; and
8. The amount of any reportable chemical that is subject to treatment (other than in-process source reduction or recycling) during any calendar year and the percentage change from the previous year.

A challenging element for companies reporting pollution prevention information is developing production ratio/activity indices for operations. The production ratio is intended to reflect the extent to which year-to-year changes in release estimates are due to source reduction activities versus changes in business activity. Companies are currently free to identify the most appropriate methods or activities on which to base production ratios for each chemical. This may be a difficult task for facilities that may use section 313 chemicals in many different operations.

¹ The PPA should be consulted for the exact language of the reporting requirements.

Are You Subject to EPCRA Reporting Obligations?

A general decision tree for determining if you must report releases under section 313 of EPCRA is provided on the front cover of this document. This section of the booklet expands upon the questions in the decision tree by summarizing the general steps that must be taken to determine if you must report releases of MDI, MDI and polymeric MDI mixtures and other section 313 listed chemicals that you manufacture, process, or use.

Is Your Facility Subject to Section 313 Reporting?

Section 313 reporting requirements apply to facilities in Standard Industrial Classification (SIC) Codes 20-39, among others. SIC Codes 20-39 include chemical manufacturers, plastic resin, foam, and other plastic product manufacturers, foundries, boat builders, and automotive and recreational vehicle manufacturers. *Foam contractors who install foam insulation in houses or businesses or by spraying polyurethane on-site are **NOT** subject to reporting at this time.* Be aware, however, that this could change in the future, so these requirements need to be monitored.

Do You Manufacture, Process or Otherwise Use MDI, PMDI or Other Substances That Are On the Section 313 List?

Both 4,4'-methylene diphenyl diisocyanate (4,4'-MDI or MDI) and polymeric MDI (PMDI) are included in the diisocyanate category. 4,4'-MDI is identified by Chemical Abstract Services (CAS) Registry Number (RN) 101-68-8 and should be aggregately reported with other isocyanates in Category N120. Synonyms for MDI are provided in Table 1.

Table 1
Synonyms for MDI

1,1'-methylenebis [4-isocyanato benzene]	methylenebis (4-phenylene isocyanate)
bis(4-isocyanatophenyl) methane	methylenedi-p-phenylene isocyanate
diphenylmethane 4,4'-diisocyanate	4,4'-diisocyanatodiphenylmethane
methylenebis (4-isocyanatobenzene)	methylenebis(p-phenylene isocyanate)
MBI	methylenebis (p-phenyl isocyanate)
4,4'-MBI	bis (1,4-isocyanatophenyl) methane
isocyanic acid, methylenedi-p-phenylene ester	methylenebis -p-phenylene diisocyanate
bis(p-isocyanatophenyl) methane	4,4'-methylenediphenylene isocyanate
p,p'-methylenebis (phenyl isocyanate)	4,4'-diphenylmethane diisocyanate
4,4'-methylenebis (phenyl cyanate)	p,p'-diphenylmethane diisocyanate
methylenebis (4-phenyl isocyanate)	4,4'-methylenedi-p-phenylene diisocyanate
methylenedi-p-phenylene diisocyanate	diphenylmethane diisocyanate
	di(4-isocyanatophenyl) methane
	diphenylmethylene diisocyanate
	4,4'-methylenebis(isocyanatobenzene)
	methylenebisphenylene diisocyanate
	isocyanic acid, diphenylmethylene ester

The most widely used MDI/PMDI mixture consists of approximately 50% monomeric 4,4'-methylene diphenyl diisocyanate (MDI, CASRN 101-68-8) which was on the Section 313 list even before EPA promulgated the November 1994 rule - and 50% higher molecular weight oligomers (PMDI, CASRN 9016-87-9) of variable composition.² This MDI/PMDI mixture generally exists as an amber, viscous liquid at ambient temperatures. As described in the discussion above, MDI and PMDI are aggregated with other isocyanates for TRI reporting. Only a single cumulative quantity is reported using the diisocyanates Category Code N120. *Please note that individual CAS Registry Numbers should NOT be used when reporting under Category Code N120.*

Users and processors must report releases of all chemicals in any listed category listing as a single number. *Different estimation techniques will likely be needed for the various members of the diisocyanates category. This book provides guidance on MDI and PMDI only.* Table 2 lists all the isocyanates in the category. **Please note** that TDI is not a member of the diisocyanates category, and that release estimates for TDI should be reported separately.

²

59 Fed. Reg. 61,432 (November 30, 1994).

Table 2
Isocyanates in the Section 313
Diisocyanates Reporting Category

Chemical Name	CASRN
Methylenebis (phenyl isocyanate) (MDI)	101-68-8
1,3-Bis(methylisocyanate)-cyclohexane	38661-72-2
1,4-bis(Methylisocyanate)cyclohexane	10347-54-3
1,4-Cyclohexane diisocyanate	2556-36-7
Diethyldiisocyanatobenzene	134190-37-7
4,4'-Diisocyanatodiphenyl ether	4128-73-8
2,4'-Diisocyanatodiphenyl sulfide	75790-87-3
3,3'-Dimethoxybenzidine-4,4'-diisocyanate	91-93-0
3,3'-Dimethyl-4,4'-diphenylene diisocyanate	91-97-4
3,3'-Dimethyl diphenylmethane-4,4'-diisocyanate	139-25-3
Hexamethylene-1,6-diisocyanate	822-06-0
Isophorone diisocyanate	4098-71-9
4-Methyldiphenylmethane-3,4-diisocyanate	75790-84-0
1,1-Methylenebis(4-isocyanatocyclohexane)	5124-30-1
1,5-Naphtalene diisocyanate	3173-72-6
1,3-Phenylene diisocyanate	123-61-5
1,4-Phenylene diisocyanate	104-49-4
Polymeric diphenylmethane diisocyanate (PMDI)	9016-87-9
2,2,4-Trimethylhexamethylene diisocyanate	16938-22-0
2,4,4-Trimethylhexamethylene diisocyanate	15646-96-5

There are other section 313 chemicals that may also be used in your process as blowing agents, catalysts, polyols and additives. A list of other section 313 listed substances that are commonly used with MDI is provided in Table 3. **This is not an exhaustive list.** Please consult the most recent year's TRI reporting list, which is updated yearly and printed in the "TRI Reporting Form R and Instruction" book, for a complete list of substances for which Section 313 reporting may be required. The list of TRI reportable chemicals is also in the Code of Federal Regulations at 40 C.F.R. § 372.65.

Table 3
Other Section 313 Chemicals Used by the Polyurethane Industry

Additive Type/Chemical Name	CASRN
Diisocyanates	
Toluene-2,4-diisocyanate	584-84-9
Toluene-2,6-diisocyanate	91-08-7
Toluene diisocyanate (mixed isomers)	26471-62-5
Curing Agents	
Ethylene glycol	107-21-1
Certain glycol ethers	category
Diethanolamine	111-42-2
Catalysts	
Lead compounds	category
Mercury compounds	category
Fillers	
Barium compounds (except barium sulfate)	category
Colorants	
Cadmium compounds	category
Cobalt compounds	category
Copper compounds (excluding certain phthalocyanine-based pigments)	category
Solvents	
Toluene	108-88-3

Do You Manufacture, Process or Otherwise Use Greater Than a Threshold Amount of Any Section 313 Chemical?

Application of the TRI reporting requirements is based on whether a facility manufactures, processes or otherwise uses greater than a threshold amount of a toxic chemical. Historically, if you met the requirements above, and either (1) manufactured or processed more than 25,000 pounds of a listed chemical or chemical category, or (2) used more than 10,000 pounds of a listed chemical or chemical category, you had to comply with the EPCRA reporting requirements.³

“Manufacture:” to produce, prepare, compound or import a listed toxic chemical, including the coincidental production of a toxic chemical (*e.g.*, as a by product or impurity).

“Process:” preparation of a listed toxic chemical, after its manufacture, for distribution in commerce (*e.g.*, the intentional incorporation of the chemical into a product).

“Otherwise use:” any activity involving a listed toxic chemical that does not fall within the definition of “manufacture” or “process.”

Recently, however, EPA created a subset of toxic chemicals, known as persistent and bioaccumulative toxic (PBT) chemicals that are subject to dioxin and dioxin-like compounds that are subject to a 0.1 gram threshold, these other PBTs are subject to either a 10 pounds or 100 pounds manufacturing, processing, or otherwise using threshold (*see* 40 CFR Section 372.28).

The 25,000 pounds manufacturing and processing and 10,000 pounds threshold, however, still applies to the diisocyanates category.

The 25,000 pound threshold will apply to most MDI and MDI/PMDI “users” since most applications, including polyurethane foam manufacturing and use in boat building, are considered to involve “processing” for purposes of section 313 reporting. EPA considers utilization of MDI-based products in making foundry molds that are used on-site and are not distributed in commerce as a “use” of MDI and MDI/PMDI mixtures for section 313 reporting. In such applications, the 10,000-pound reporting threshold applies.

Your purchases of section 313 listed chemicals may serve as a benchmark in determining what amounts you manufacture, process, or use; however, it is the actual amount of a substance that is manufactured, processed, or used in the reporting year that determines your reporting status. For example, a facility that purchased 30,000 pounds of MDI, a listed chemical, but processed only 24,000 pounds in the reporting year would not be required to report. Alternatively, a facility that purchased and processed 20,000 pounds of MDI and processed an additional 6,000 pounds from the previous year’s inventory, thereby processing a total of 26,000 pounds in one reporting year, would be required to report.

For chemicals like MDI and PMDI that are included in a category, the reporting threshold is based on the sum of all of the chemicals in the category processed or used in the reporting year. Thus, reporters must count all of the isocyanates manufactured, processed or used in the category in that reporting year in determining if a threshold is met.

MDI products containing “polymeric MDI,” may vary in their 4,4’-MDI content. Consult

3

The reporting threshold for Sections 311/312 of EPCRA should be distinguished from the Section 313 threshold. Under Sections 311/312, you are required to file an MSDS and annual inventory reports with state and local agencies if you store MDI on site in quantities greater than 10,000 pounds at any one time.

Material Safety Data Sheets from your supplier for this information as suppliers are required to disclose the identity and amount of section 313 listed chemicals on MSDS's.

If you have a mixture or trade name product that contains a toxic chemical, you must determine the amount of the toxic chemical in the mixture and combine that amount to the total quantity of the chemical processed or otherwise used at the facility in order to determine whether or not the reporting threshold has been reached.

EXAMPLE

Otherwise using:

Mixture 1:	10,000 pounds	Mixture 2:	12,000 lbs
Components:	50% water 50% MDI	Components:	50% water 50% Isophorone diisocyanate

Conclusion: Exceed the reporting threshold for the diisocyanates category.
You used 5000 lbs of MDI and 5000 lbs of Isophorone diisocyanate. Because the total amount of diisocyanates exceeds the 10,000 pound otherwise used threshold, you must file a TRI Report.

Are You Subject to State MDI Permit Reporting Obligations?

If a mixture of MDI and PMDI is processed or used (which is almost always the case), the combined emissions of both substances should be reported under section 313. (In contrast, state air permit officials may be particularly interested in MDI emissions alone, because MDI is a listed hazardous air pollutant (HAP). The estimation techniques in this book are directed primarily toward calculating emissions for the purpose of Section 313 reporting but may be useful in providing MDI emission estimates for state permitting purposes as well.

**Table 4
List of PBTs**

Chemical Name Limit	Cas No./ Category Code	Threshold
Benzo(g,h,l)perylene	00191-24-2	10 lbs.
Octachlorostyrene	29082-74-4	10 lbs.
Pentachlorobenzene	00608-93-5	10 lbs.
Tetrabromobisphenol A	00079-94-7	100 lbs.
Vanadium Compounds	N770	1 lb.
Aldrin	309-00-2	100 lbs.
Chlordane	57-74-9	10 lbs.
Dioxin and Dioxin-like Compounds gram	N150	0.1
Heptachlor	76-44-8	10 lbs.
Hexachlorobenzene	118-74-1	10 lbs.
Isodrin	465-73-6	10 lbs.
Lead	7439-92-1	100 lbs.
Lead Compounds	N420	100 lbs.
Mercury	7439-97-6	10 lbs.
Mercury Compounds	N458	10 lbs.
Methoxychlor	72-43-5	100 lbs.
Pendimethalin	40487-42-1	100 lbs.
Polychlorinated bisphenyls (PCBs)	1336-36-3	10 lbs.
Polycyclic Aromatic Compounds (PACs)	N590	100 lb.
Tetrabromobisphenol A	79-94-7	100 lbs.
Toxaphene	8001-35-2	10 lbs.
Trifluralin	1582-09-8	100 lbs.

Note:

For a complete listing of chemicals found in the listed categories consult EPA's "Section 313 of the Emergency Planning and Community Right-to Know Act Toxic Chemical Release Inventory Reporting Forms and Instructions Revised 2001 Version", United States Environmental Protection Agency, February 2002, Publication EPA 260-B-02-001

When, Where and How Should the TRI Reporting Data be Sent?

As specified in EPCRA Section 313, the report for any calendar year must be submitted on or before July 1 of the following year whether using Form R or Form A. If the reporting deadline falls on a Saturday or Sunday, EPA will accept reports that are postmarked on the following Monday. Any voluntary revision to a report can be submitted anytime during the calendar year for the current or any previous reporting year. However, voluntary revisions for the current reporting year should be submitted by July 31 in order to be included in that year's public data release.

Submissions must be sent to both EPA and the State or designated official of an Indian tribe. If a report is not received by both the EPA and the State or designated official of an Indian tribe, the submitter is considered out of compliance and subject to enforcement action. Send reports to EPA by regular mail to:

EPCRA Reporting Center
P.O. Box 3348
Merrifield, VA 22116-3348
Attention: Toxic Chemical Release Inventory

Certified mail, overnight, and hand-delivered submissions only should be addressed to:

EPCRA Reporting Center
C/o Titan Systems Corp.
Suite 300
4600 North Fairfax Drive
Arlington, VA 22203

Also send a copy of the report to the state in which the facility is located. Facilities located on Indian land should send a copy to the Chief Executive Officer of the applicable Indian tribe. Some tribes have entered into a cooperative agreement with states; in this case, a report submission should be sent to the entity designated in the cooperative agreement.

There are three ways in which the Toxic Release Inventory can be submitted:

- by magnetic media (floppy disk, Zip disk, CD-ROM)
- via the Internet, and
- by paper submittal.

The EPA has developed a package called “TRI Reporting Software”. This easy-to-use- CD-ROM includes ATRS and TRI-ME software and comes with complete instructions for its use. It also provides prompts and messages to help you report according to EPA instructions. Copies of the CD-ROM can be obtained by calling EPA at (202) 564-9554 or downloading from the EPA website located at <http://www.epa.gov/tri>.

If reports are being filed by magnetic media, you must enclose a cover letter signed by the official listed in Section 3 of Part 1 of the Form R or Form A (name and official title of owner/operator or senior management official) for each separate facility. If filing by magnetic media, DO NOT enclose a paper copy.

Private vendors offer software to assist facilities in producing magnetic media submissions or computer – generated facsimiles for EPCRA Section 313 reports. Every year and upon request, EPA makes available to vendors a copy of the Magnetic Media File Formats document for that specific reporting year. This document provides software vendors with details describing the appropriate output file format for processing in EPA’s TRI database.

It should be noted, however, that some States may not accept magnetic media or computer-generated facsimile reports.

Form R and /or Form A can also be submitted via the Internet to EPA’s Central Data Exchange. The TRI-ME software has the ability to directly submit your TRI submissions via the Internet. If you choose to submit your TRI Form R’s and /or Form A’s via the Internet, you must send a certification letter signed by the official listed in Section 3 of Part 1 of the Form R and /or Form A for each facility being reported. Once the submission has been successfully submitted via the Internet, TRI-ME will prompt you to print your certification letter. It is important to use the certification letter printed from the software because it will contain your CDX identification number, which is a unique identifier that matches your certification letter with the data that you submitted.

It should be clearly noted that submitting Form R’s and/or Form A’s to EPA via the Internet does not in any way satisfy your state reporting requirements. Separate submissions are to be made to the appropriate state offices. Be aware that not every state will accept electronic submittals.

What Kinds of Records Should be Maintained and for How Long?

Sound record keeping practices are essential for accurate and efficient TRI reporting. It is in the facility's interest, as well as, EPA's, to maintain records properly.

A partial list of records, organized by year, that a facility should maintain includes:

- Previous years' EPCRA Section 313 Reports
- EPCRA Section 313 Reporting Threshold Worksheet
- Engineering Calculations and other Notes
- Purchase Records from Suppliers
- Inventory Data
- EPA (NPDES) Permits and Monitoring Reports
- EPCRA Section 312 Tier II Reports
- Monitoring Reports
- Flowmeter Data
- RCRA Hazardous Waste Generator's Report
- Pretreatment Reports filed with Local Government
- Invoices from Waste Management Companies
- Manufacturer's Estimates of Treatment Efficiencies
- RCRA Manifests
- Process Diagrams that Indicates Emissions and other Releases
- Records for those EPCRA Section 313 Chemicals for which they did not file EPCRA Section 313 Reports

For at least 3 years from the date of submission, facilities must keep a copy of each report filed, along with the supporting documents. These reports will be helpful in completing future reports. They will also be required in the event that EPA requests documentation to support the data elements reported on a facility's Form A or Form R.

EPA may conduct data quality reviews of Form R or Form A submissions. An essential component of this process involves the reviewing a facility's records for accuracy and completeness.

How Do I Revise or Withdraw TRI Data?

Facilities that have filed a Form R and/or Form A Certification under EPCRA Section 313 may find it necessary to revise or withdraw TRI data. In order to have a submission in the TRI database **revised** a facility must submit a request to both EPA and the appropriate State Agency by submitting a 'Request for Revision' template and a copy of the Form R or Form A Certification that has to be revised. A copy of this template can be found in Appendix H-1 or in the TRI Reporting Forms and Instructions (2001 Version).

In order for the EPA to effectively process the request, EPA needs the following information:

- Facility Name and TRI Identification Number (TRIFID)
- Facility Mailing Address
- Reporting Year
- Chemical Name
- Technical Contact name and Telephone Number
- Name and Telephone Number of Requester
- Reason(s) for Revision
- Signature

Some of the key reasons for submitting a request for revision are:

- Revision of Facility Identification Information
- Revision of Chemical Identification Information
- Revision of Release and other Waste Management Activities Information
- Result of an EPA/State Inspection
- Result of Notice of Technical Error, Notice of Significant Error, or Notice on Noncompliance from EPA
- Result of Voluntary Disclosure or Audit Policy

Hardcopy revisions may be submitted using the most recent form available or the most recent version of the ATRS or TRI-ME software. Certify and date the form on page 1 or provide a cover letter with the software created data revision. Alternatively, you may also submit a photocopy of your original submission (from your file) with the corrections made in blue ink. Re-sign and date the certification statement on page 1. **Whenever you submit a diskette, do not submit a printout of what is on the diskette, because both the diskette and the printout will be processed as separate submissions, potentially resulting in duplicate records for your facility.**

Facilities that wish to request to the EPA to **withdraw** the Form R and/or Form A Certification submissions from EPA's database must submit a 'Request for Withdrawal' template to the EPA and the state agency along with a copy of the Form R or Form A certification they wish to have withdrawn. EPA will review each request and notify the requestor by letter whether or not the withdrawal request has been accepted. The information that needs to be submitted is similar to that listed above in "Request for Revision."

Some of the key reasons for requesting withdrawal are:

- The facility manufactures, processes or otherwise uses less than the threshold quantities
- Change in EPA's reporting requirements for a chemical
- The facility qualifies for EPCRA Section 313 exemptions
- The chemical reported is not an EPCRA Section 313 reportable chemical
- The chemical reported is not in the form listed on the EPCRA Section 313 Toxic Chemical List (i.e., aerosol, fume or dust, fibrous form, etc.)
- Activities involving the reported chemical do not meet EPA's definition of "manufacture, process or otherwise use"
- The facility qualifies for a Form A Certification Submission

Where do you Send Requests for Revision or Withdrawal of Data?

TRI Form R and/or Form A **revision requests** should be sent to the EPCRA Reporting Center.

If sending by regular U.S. mail, send to:

EPCRA Reporting Center
 P.O. Box 3348
 Merrifield, VA 22116-3348
Attention: TRI Revision Request

If sending by certified mail or overnight mail:

EPCRA Reporting Center
 C/o Titan Systems Corp.
 Suite 300
 4600 North Fairfax Drive

Arlington, VA 22203

Attention: TRI Revision Request

Withdrawal requests for TRI Form R and/or Form A Certification should be sent to the EPCRA reporting center.

If sending by regular U.S. mail, send to:

EPCRA Reporting Center

P.O. Box 3348

Merrifield, VA 22116-3348

Attention: TRI Withdrawal Request

If sending by certified mail or overnight:

EPCRA Reporting Center

C/o Titan Systems Corp.

Suite 300

4600 North Fairfax Drive

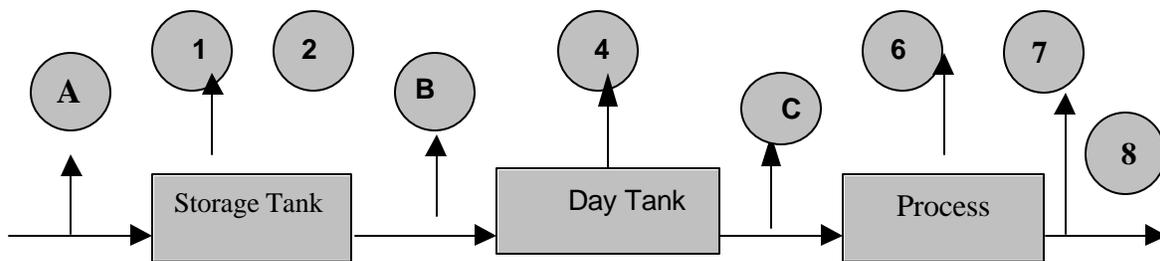
Arlington, VA 22203

Attention: TRI Withdrawal Request

Identifying Release Sources

The main goal and objective of this document is to provide information and guidance that will enable processors or users of MDI and MDI/PMDI mixtures to estimate releases of these chemicals in accordance with the Emergency Planning and Community Right to Know Act (EPCA) Section 313.

The first step in estimating the release of MDI and/or MDI/PMDI mixtures is to identify all possible emission sources. To do this, it may be helpful to develop a process flow diagram, outlining and depicting the activities in which MDI and MDI/PMDI emissions can be released. A general plant flow diagram presented below provides a broad overview of where emissions can occur and will be used to outline the general approach in calculating emissions throughout this document.



- | | | | |
|----------|---|----------|------------------------------|
| A | Transfer from Tanker or Railcar | 4 | Tank Breathing Losses |
| 1 | Working Losses | C | Transfer to Process |
| 2 | Breathing Losses | 6 | Process Stack Losses |
| 3 | Transfer from Storage Tank to Day Tank | 7 | Fugitive Emissions |
| 8 | Disposal and Treatment | | |

Once the activities have been identified for your facility, a systematic approach to calculating your overall emissions can be established. Each facility is unique and even though the regulation does not require you to generate a process flow diagram, preparation of a process flow diagram can and will demonstrate your efforts to responsibly comply with the EPCA reporting requirements

Estimating Releases of MDI and PMDI

Techniques:

Once all the possible release sources for MDI or MDI/PMDI mixtures have been identified, estimates of the quantity released from each source can be made.

Section 313 requires all releases to air, water, land, and transfers to off-site facilities for each toxic chemical meeting the threshold reporting requirements be reported.

In general, there are four basic techniques used to estimate emissions.

- Direct Measurement
- Mass Balance
- Emission Factors
- Engineering Calculations

The following section summarizes each basic technique that can be used to determine emissions. It may become necessary to employ a combination of all these techniques to obtain the total amount of emissions for your facility.

Direct Measurement:

The use of direct measurement or monitoring data to determine release measurement is based upon measured concentrations of a chemical in a waste stream and the flow rate/volume of that stream. Direct measurement gives you a more accurate account of what amounts of chemicals is being released. Even though this method is very costly than using other estimation techniques, this additional effort can be justified in instances where other estimation techniques may significantly overestimate releases. Direct data measurement consists of stack monitoring data, process equipment bagging studies, and waste stream contaminant analysis data. Industrial hygiene data is useful for evaluating worker exposure and estimating fugitive emissions, but should not be used in estimating process releases.

Mass Balance:

The use of mass balance to determine release estimates are based upon the assumption that the amount of chemical entering the process must be the same as the amount of chemical that leaves the process. If the input and output streams for a particular process are known, the difference would be the amount of material that is lost through waste streams, stacks, and as fugitives. However, using mass balance is inappropriate to use in situations where a chemical is consumed during a process where the chemical goes under a chemical reaction with another chemical to form a new compound. It is also inappropriate to use mass balance in situations where a chemical is destroyed by heat or combustion. Nearly all applications that use MDI and MDI/PMDI fall into this category. When a two part MDI-based polyurethane system is used, the MDI/PMDI is converted to a polyurethane polymer and is not present in the final product other than as a residual.

Emission Factors:

Emission factors express releases as a ratio of the amount of a substance released relative to process or equipment throughput. Emission factors are commonly used for air releases and are typically based upon the average measured emissions measured at several facilities in the same industry. The EPA has compiled a large number of emission factors for different chemicals used in many industries. However there is very little emission factor data available for MDI and MDI/PMDI mixtures. Consequently, use of EPA emission factors will result in significant over-reporting of releases.

Engineering Calculations:

Engineering calculations are assumptions and/or judgments used to estimate quantities of EPCA Section 313 chemicals and chemical categories released or otherwise managed as waste. The quantities are estimated by using physical and chemical properties and relationships (e.g., ideal gas law, Raoult's law, Henry's law) or by modifying an emission factor to reflect the chemical properties of the chemical in question. Engineering calculations rely on the process parameters; you must have a thorough knowledge of your facility operations to complete these calculations. For example, in estimating releases from closed mold-type processes, knowledge about the relationship between vapor pressure, temperature, and volume is used to calculate the maximum amount of MDI or MDI/PMDI that can be released from a single mold filling activity. Multiplying the amount that can be released or emitted per mold and multiplying by the number of molds fillings that occur in a given year provides a reasonable estimate of annual releases for that operation.

Engineering calculations can also include computer models. Several computer models are available for estimating emissions from stacks, landfills, wastewater treatment, water treatment and other processes.

Non-chemical-specific emission factors, Synthetic Organic Chemicals Manufacturing Industry (SOCMI) emission factors, industry-determined emission factors for processes or equipment, and site-specific emission factors also can be used, but must be classified as "Engineering Calculations" for EPCRA Section 313 reporting.

Simplified estimation techniques have been employed throughout the guideline document to make estimations of releases understandable. Adjustment factors are provided where MDI/PMDI mixtures are processed or used to calculate the combined emissions of both substances. The adjustment factors have been derived using actual measurement data on the vapor pressure for a range of MDI/PMDI mixtures. The emissions from processing or use of MDI/PMDI mixtures are always lower than emissions from the same activities where pure MDI is employed.

In estimating releases from facilities that use MDI/PMDI mixtures, emissions are first calculated as if MDI comprises 100 per cent of all mixtures and then an adjustment factor is used based upon the content of MDI in the mixture.

General equations and assumptions are used repeatedly throughout the guidebook. These assumptions are intended to provide conservative or reasonable worst-case assessments in estimating potential MDI and MDI/PMDI releases. Examples in the guidebook were selected to reflect major scenarios where releases are likely to occur. There may be release scenarios particular to your facility that is not described in this guidebook. The best judge of the use of any release source or release estimation technique is always an individual with knowledge of a specific operation at your facility. **Do not use the estimation techniques that follow if you feel that they are not based on assumptions that reflect your facility's operation.**

A more descriptive account of these techniques is provided in the U.S. EPA publication, "*Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Forms*" (1999 edition Reference 1).

U.S. EPA does not require you to conduct additional sampling or testing for EPCRA Section 313 reporting, however, you are required to use the best, readily available information to determine the method that will result in the most accurate estimate.

Tables I list the potential data source where available release and emission information may be obtained to help in determining accurate facility emissions.

Table I: Potential Data Sources for Release and Other Waste Management Calculations

Monitoring Data

- * Air Permits
- * Continuous Emission Monitoring
- * Effluent Limitations
- * Hazardous Waste Analysis
- * Industrial Hygiene Monitoring Data
- * NPDES Permits
- * Stack Monitoring Data

Engineering Calculations

- * Facility Non-specific Emission Factors
- * Henry's Law
- * Raoult's Law
- * Solubilities
- * Volatilization Rates

Mass Balance

- * Air Emissions Inventory
- * MSDS's
- * Pollution Prevention Reports
- * Spill Event Records
- * Supply Records
- * Hazardous Waste Manifests

Emission Factors

- * AP-42 Chemical Specific Emission Factors
- * Facility or Trade Association Derived Chemical Factors

General, Chemical-Specific, and Industry-Specific Guidance Documents

EPA has a number of EPCRA Section 313 documents that provide information and guidance to help assist one in completing and filing Form R and Form A Certification Documents. It is recommended that one obtain and read these documents before starting to fill out the forms. The Guidance Documents listed below can be obtained from the EPA by:

- Calling (202) 564-9554,
- Sending an e-mail request to TRIDOCES@epa.gov, or
- Visiting the TRI Home Page (<http://www.epa.gov/tri>).

I. General Guidance:

- **40 CFR 372, Toxic Chemical Release Reporting: Community Right-to-Know**
- **EPCRA Section 313 Questions and Answers-Revised 1998 Version**
December 1998 (EPA 745-B-98-012)
- **EPCRA Section 313 Releases and Other Waste Management Reporting Requirements,**
February 2001 (EPA 260/K-01-001)
- **Toxic Chemical Release Inventory Reporting Forms and Instructions Revised 2001 Version,** February 2002 (EPA 260-B-02-001)

II. Chemical-Specific Guidance

- **Emergency Planning and Community Right-to-Know Act-Section 313: Guidance for**

Reporting Releases and Other Waste Management Activities of Toxic Chemicals: Lead and Lead Compounds, November 2001 (EPA-260-B-01-027)

- **Mercury guidance document**

III. Industry-Specific Guidance

- **EPCRA Section 313: Guidance for Chemical Distribution Facilities,**
January 1999 (EPA 745-B-99-005)
- **Emergency Planning and Community Right-to-Know Act Section 313 reporting Guidance for the Presswood and Laminated Products Industry,**
August 2001 (EPA 260-B-01-013)
- **EPCRA Section 313 Reporting Guidance for Rubber and Plastics Manufacturing,**
May 2000 (EPA 745-B-00-017)
- **EPCRA section 313 Reporting Guidance for Spray Application and Electro deposition of Organic Coatings,**
December 1998 (EPA 745-R-98-014)

Tanks – Filling and Storage

Pure MDI is a solid at room temperature and even though MDI/PMDI is a liquid at room temperature, both have a very low vapor pressure. There will be minor to almost negligible releases occurring during filling or storage due to changes in temperature from day to night.

Working Losses:

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. A reasonable worst-case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The calculations that follow demonstrate that working losses of MDI/PMDI will be very low under most normal storage circumstances

The working losses can be estimated from the following expression:

$$L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_w * K_{mdi}$$

Where:

L_w represents the working losses in lb/year.

Q_w is the annual throughput of MDI pumped to the tank in ft³/year.

T_{amb} is the storage temperature in °K.

VP_{amb} is the vapor pressure of MDI at the storage temperature in mm Hg

M_w is the molecular weight of MDI (250.26)

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature.

Example 1: Working Losses:

A facility receives 1,000,000 gallons of MDI/PMDI annually. Material is stored in a 20,000-gallon storage tank at an average temperature of 77°F (298.2 °K). Calculate the working losses for the year.

The working losses can be estimated from the following expression:

$$L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_w * K_{mdi}$$

Where:

L_w represents the working losses in lb/year

Q_w is the annual throughput of MDI pumped to the tank in ft³/year

T_{amb} is the temperature of the stored material

VP_{amb} is the vapor pressure of MDI at the storage temperature in mm Hg

M_w is the molecular weight of MDI (250.26).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature

$$\begin{aligned}
Q_w &= 1,000,000 \text{ gallons/year. } \times 1 \text{ cu. ft./7.48 gal} \\
Q_w &= 133,690 \text{ cu. Ft.} \\
T_{\text{amb}} &= 298.2 \text{ }^\circ\text{K.} \\
VP_{\text{amb}} &= 1.0 \times 10^{-5} \text{ mm Hg @ } 298.2 \text{ }^\circ\text{K} \\
M_w &= \text{the molecular weight of MDI (250.26).} \\
K_{\text{mdi}} &= 0.55 \text{ for a 50/50 mixture of MDI/PMDI at } 298.2 \text{ }^\circ\text{K.} \\
&\text{(See Appendix B: Table II: MDI/PMDI Adjustment Factors)}
\end{aligned}$$

Therefore:

$$\begin{aligned}
L_w &= (133,690 \text{ cu. ft.})(1/359)(273.15/298.2)(1.0 \times 10^{-5}/760)(250.26)(.55) \\
L_w &= \mathbf{6.28 \times 10^{-4} \text{ lbs./yr.}}
\end{aligned}$$

Breathing Losses:

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with increasing temperature and decreases with a decreasing temperature. As outside temperature rises during the day, pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh airflows into the tank. MDI/PMDI mixtures are typically stored in temperature-controlled tanks, therefore losses for temperature controlled, refrigerated, or insulated tanks are assumed to be negligible.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42 (See Appendix C for development of formula). This modified method can only be used for materials that display very low vapor pressure characteristics.

The breathing losses can be determine using the following equations:

$$L_b = 365 * M_{\text{air}} * (VP_{\text{amb}} / 760) * M_w * K_{\text{mdi}}$$

$$M_{\text{air}} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{\text{amb}})$$

$$V_v = V_T * (100 - L_T) / 100$$

$$K_E = T_R / T_{\text{amb}}$$

Where:

L_b represents the breathing losses in lb/year.

M_{air} is the total air displaced per day in lb-mole/day.

VP_{amb} is the vapor pressure of MDI at the ambient temperature in mm Hg

M_w is the molecular weight of MDI .250.26.

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

T_{amb} is the average ambient temperature in $^\circ\text{K}$.

T_R is the average day-night temperature fluctuation in $^\circ\text{K}$.

K_E is the vapor expansion factor due to day-night temperature fluctuation.

Example 2: Breathing Losses

A fixed roof vertical tank contains MDI/PMDI. The tank has a volume of 12,000 gallons (10' D x 20' H) and is maintained at an average daily capacity of 50%. The tank is located in New York area. From meteorological data, the daily average ambient temperature is 54.55 °F (12.53 °C) and the daily average temperature range is 15.3 °F (8.5 °C). The MDI/PMDI vapor pressure at the daily average temperature is 1.945×10^{-6} mm Hg.

The breathing losses can be calculated from the following expression:

$$L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}$$

$$M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$$

$$V_v = V_T * (100 - L_T)$$

$$K_E = T_R / T_{amb}$$

Where:

L_b represents the breathing losses in lb/year.

M_{air} is the total air displaced per day in lb-mole/day.

VP_{amb} is the vapor pressure of MDI at the ambient temperature in mm Hg

M_w is the molecular weight of MDI (250.26)

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

T_{amb} is the average ambient temperature in °K.

T_R is the average day-night temperature fluctuation in °K.

K_E is the vapor expansion factor due to day-night temperature fluctuation.

$$V_v = V_T * (100 - L_T) = 12,000(100 - 50)/100 = 6,000 \text{ gallons}$$

$$K_E = T_R / T_{amb} = (8.5^\circ)/(12.53 + 273.15) = 0.02975$$

The total air displaced per day (M_{air} in lb-mole/day) is calculated from the following expression:

$$M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$$

$$M_{air} = (6,000/7.48) * (1/359) * (0.02975) * (273.15/285.68) = 0.0636 \text{ lb mole/day}$$

The breathing losses can now be estimated from the following expression:

$$L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}$$

$$L_b = 365 * (0.0636) * (1.945 \times 10^{-6} / 760) * (250.26) * (.54)$$

$$L_b = 8.16 \times 10^{-6} \text{ lbs/yr.}$$

Fugitive Emissions (Non-point Source):

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. *This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.*

The fugitive emissions can be estimated from the following expression:

$$L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f$$

Where:

L_{fg} is the fugitive emissions in lb/year.

C_{mdi} is the average MDI concentration, in ppmv, in the air within the building.

V_B is the volume of the workspace building in ft^3 .

N_{year} is the number of air exchanges per year.

T_{amb} is the ambient temperature in °K.

M_w is the molecular weight of MDI (250.26).

K_{fg} is the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Example 3: Fugitive Emissions

The average concentration of MDI throughout the year was measured at 0.001 ppm for a process area that measured 50 ft W x 100 ft L and 20 ft in height. There are an average of 5 air changes per hour and the plant operates 16 hours/day, 250 days/year. The average temperature of the facility is 77°F. Calculate the fugitive emissions.

The fugitive emissions can be estimated from the following expression:

$$L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f$$

L_{fg} is the fugitive emissions in lb/year.

C_{mdi} is the average MDI concentration, in ppmv, in the air within the building.

V_B is the volume of the workspace building in ft^3 .

N_{year} is the number of air exchanges per year.

T_{amb} is the ambient temperature in °K.

M_w is the molecular weight of MDI (250.26).

K_{fg} is the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Calculating:

$$C_{mdi} = 0.001 \text{ ppm} = 1.0 \times 10^{-9}$$

$$V_B = (50 \text{ ft} \times 100 \text{ ft} \times 20 \text{ ft}) = 100,000 \text{ ft}^3$$

N_{year} is the number of air exchanges per year.

$$N_{\text{year}} = (5 \text{ changes/hr} \times 16 \text{ hr/day} \times 250 \text{ days/yr}) = 20,000 \text{ changes/year}$$

$$T_{\text{amb}} = 298.2 \text{ }^\circ\text{K.}$$

M_w is the molecular weight of MDI (250.26).

K_{fg} is the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Therefore:

$$L_{fg} = (1.0 \times 10^{-9}) * (100,000 \text{ ft}^3/359) * (20,000) * (273.15/298.2) * (250.26) * (1.1)$$

$$L_{fg} = 1.43 \text{ lbs/year.}$$

Equipment Leaks

In cases where monitoring data are not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.
3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

$$SV = [1,315.8 \times 10^{[(10.902 - 4634.09/(266.15 + t))]}] \times 10^6$$

Where:

$$\begin{aligned} SV &= \text{Screening Value in ppmv and} \\ t &= \text{Temperature in } ^\circ\text{C.} \end{aligned}$$

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

Table V-6
Leak Rate/Screening Value Correlations

Equipment Type	Correlation Leak Rate (kg/hr) ($a \cdot (SV)^b$)
Gas Valve	$1.87 \times 10^{-06} \times (SV)^{0.873}$
Light Liquid Valve	$6.41 \times 10^{-06} \times (SV)^{0.787}$
Light Liquid Pump ^c	$1.90 \times 10^{-05} \times (SV)^{0.824}$
Connectors	$3.05 \times 10^{-06} \times (SV)^{0.885}$

^c This equation can be used for liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps.

The total emissions from equipment leaks will be equal to the emissions contributed from each gas valves, light liquid valves, light liquid pumps, and connectors.

For gas valves:

$$K_{\text{gas}} = 1.87 \times 10^{-6} * (C_{\text{mdi}})^{0.873}$$

For liquid valves:

$$K_{\text{liq}} = 6.41 \times 10^{-6} * (C_{\text{mdi}})^{0.787}$$

For liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps:

$$K_{\text{pump}} = 1.90 \times 10^{-5} * (C_{\text{mdi}})^{0.824}$$

For connectors:

$$K_{\text{con}} = 3.05 \times 10^{-6} * (C_{\text{mdi}})^{0.885}$$

Where:

K_{gas} represents the emission factor for gas valves in kg/year-item.

K_{liq} represents the emission factor for liquid valves in kg/year-item.

K_{pump} represents the emission factor for liquid pumps in kg/year-item.

K_{con} represents the emission factor for connectors in kg/year-item.

For Gas Valves the emissions can then be estimated from the following expression:

$$L_{\text{gv}} = K_{\text{gas}} * n_{\text{gv}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{gv} represents the annual losses from liquid valves in lb/yr.

n_{gv} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating.

For Liquid Valves the emissions can then be estimated from the following expression:

$$L_{\text{liq}} = K_{\text{liq}} * n_{\text{liq}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{liq} represents the annual losses from liquid valves in lb/yr.

n_{liq} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

For liquid Pumps the emissions can then be estimated from the following expression:

$$L_{\text{pump}} = K_{\text{pump}} * n_{\text{pump}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{pump} represents the annual losses from liquid valves in lb/yr.

n_{pump} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

For Connectors the emissions can then be estimated from the following expression:

$$L_{\text{con}} = K_{\text{con}} * n_{\text{con}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{con} represents the annual losses from liquid valves in lb/yr.

n_{con} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

Total Emissions can then be estimated from the following expression:

$$E_{\text{tot}} = L_{\text{gas}} * L_{\text{liq}} * L_{\text{pump}} * L_{\text{con}}$$

Table V-7: Equipment Leak Emission factors (lb./hr-component) @ 50 °C represents the emissions factors associated with each fitting in service at a temperature of 50 °C. If you know the number of fittings, multiply the emission factor by the number of fittings and add the total up to get the annual emissions from equipment leaks.

Table V-7
Equipment leak Emission Factors lbs/hr-component @ 50 °C

Equipment Type	Temp. °C	Vapor Pressure (mm Hg) ⁴	Screening Value (SV) ⁵ (ppmv) ²	Equation Constant (a)	Equation Constant (b)	Emission Factor ¹ (kg/hr) ³	Emission Factor ¹ (lb./hr) ³
Gas Valves	50	1.80x10 ⁻⁰⁴	2.37x10 ⁻⁰¹	1.87x10 ⁻⁰⁶	0.873	5.33x10 ⁻⁰⁷	1.18x10 ⁻⁰⁶
Light Liquid Valves	50	1.80x10 ⁻⁰⁴	2.37x10 ⁻⁰¹	6.41x10 ⁻⁰⁶	0.797	2.04x10 ⁻⁰⁶	4.49x10 ⁻⁰⁶
Light Liquid Pumps	50	1.80x10 ⁻⁰⁴	2.37x10 ⁻⁰¹	1.90x10 ⁻⁰⁵	0.824	5.81x10 ⁻⁰⁶	1.28x10 ⁻⁰⁵
Connectors	50	1.80x10 ⁻⁰⁴	2.37x10 ⁻⁰¹	3.05x10 ⁻⁰⁶	0.885	8.54x10 ⁻⁰⁷	1.88x10 ⁻⁰⁶

Illustrative example 1: Estimate MDI emissions from equipment leaks in a MDI manufacturing facility with the following equipment type counts:

- (1) 3000 valves in light liquid service
- (2) 4500 connectors.
- (3) 20 pump seals
- (4) 2 agitators

The MDI concentration in the stream is 12.7% and the air temperature is 50 °C.

The total emissions due to equipment leaks using the Modified Correlation Emission Factors are found in Table V-8.

**TableV-8
Equipment Leak Emissions Modified Correlation Screening Factors**

Equipment Type	Service	Number Components	Weight Fraction	Modified Corr. Factors	Emissions (lbs/hr)	Emissions (lbs./year)
Valves	Light Liquid	3000	0.127	4.49×10^{-06}	1.71×10^{-03}	15
Pumps	Light Liquid	20	0.127	1.28×10^{-05}	3.25×10^{-05}	0.285
Agitators	Light Liquid	2	0.127	1.28×10^{-05}	3.25×10^{-06}	0.0285
Connectors	All	4500	0.127	1.88×10^{-06}	1.07×10^{-03}	9.41
Total						24.7

Spills:

Section 313 of the Emergency Planning and Community Right-to-Know Act requires that you account for material lost because the chemical was spilled onto the ground, resulting in an air release. Evaporative releases from spills depend upon many factors including

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area
4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$Q_R = (0.003413) * (u)^{0.78} * A_{spill} * (VP_{MDI}/T_{spill}) * (MW)^{2/3} * K_{MDI}$$

Where:

- QR = the evaporation rate in lb/min.
- u = the airflow in m/sec. This is the airflow in the vicinity of the process.
- A_{spill} = the area of the spilled material in ft².
- VP_{MDI} = the vapor pressure of MDI in mm Hg. at the filling temperature
- T_{spill} = the average evaporation temperature in °K.
- MW = the molecular weight of MDI (250.26).
- K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (QR) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$L_{spill} = QR * t_{spill} * (60)$$

Where:

- L_{spill} = represents the evaporation losses resulting from the spill in lb.
- QR = represents the evaporation rate in lb/min.
- t_{spill} = represents the time that the spill is on the ground in hours.

A facility while transferring a 50% mixture of MDI/PMDI from the storage tank to the day tank develops a leak at a flange that results in a spill of 75 gallons of material. A liquid pool that has a surface area of 200 ft², remains on the floor for eight hours before a HAZMAT Team could be assembled. During that time, the wind speed remained at a constant 20 miles/hour (9 m/s). The temperature of the process area was a constant 70 °F (298.4 °K). Determine loss of material caused by evaporation.

Air emissions released because of the spill of MDI/PMDI can be calculated using EPA's proposed model:

$$Q_R = (0.003413) * (u)^{0.78} * A_{\text{spill}} * (VP_{\text{MDI}}/T_{\text{spill}}) * (MW)^{2/3} * K_{\text{MDI}}$$

Where:

- Q_R = the evaporation rate in lb/min.
- u = the airflow speed in m/sec. This is the airflow in the vicinity of the process
- A_{spill} = the area of the spilled material in ft².
- VP_{MDI} = the vapor pressure of MDI in mm Hg. at the filling temperature
- T_{spill} = the average evaporation temperature in °K.
- MW = the molecular weight of MDI (250.26).
- K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Therefore:

- QR = lb./minute
- u = 9.0 m/sec.
- A_{spill} = 200 ft².
- VP_{MDI} = 6.1 x 10⁻⁶ mm Hg
- T_{spill} = 298.4°K.
- MW = 250.26
- K_{MDI} = 0.54

Substituting the appropriate values into the equation, the emissions released due to the spill is equal to:

$$Q_R = (0.003413) * (9.0)^{0.78} * 200 * (6.1 \times 10^{-6}/298.4) * (250.26)^{2/3} * (0.54)$$

$$Q_R = 2.90 \times 10^{-6} \text{ lbs./min}$$

Using the equation:

$$L_{\text{spill}} = QR * t_{\text{spill}} * (60)$$

Where:

- L_{spill} = represents the evaporation losses resulting from the spill in lb.
- QR = represents the evaporation rate in lb/min.
- t_{spill} = represents the time that the spill is on the ground in hours

The total amount of MDI/PMDI from the spill is:

$$L_{\text{spill}} = (Q_R = 2.90 \times 10^{-6} \text{ lbs./min}) * (8 \text{ hours}) * (60 \text{ min/hr.})$$

$$L_{\text{spill}} = 1.40 \times 10^{-3} \text{ lbs.}$$

Disposal and Treatment:

Activities that involve the disposal and/or treatment of an EPCRA Section 313 chemical on-site or off-site must be reported. These activities are (but are not limited to):

- Discharges to surface waters
- Releases to land
- Releases to injection wells
- Surface impoundment
- On-site waste treatment, energy recovery, recycling
- Discharges to POTW
- Off-site waste disposal
- Transfer for energy recovery

Discharges to receiving streams or water bodies are usually accountable in the facilities NPDES permit. The permit lists the reported chemicals with limits on the quantity that can be discharged. Regulations require testing for amount of chemicals being discharged. You must also report releases contributed to storm water run-off.

On-site releases to land are accountable under histories and spill records, which are required under Section 304 of EPCRA and Section 112 (r)(7)(B)(ii) of the Clean Air Act. EPCRA chemicals sent to off-site RCRA landfills must be reported. Hazardous waste manifests contain description of waste and list waste composition that will aid you in calculating amount of Section 313 chemical being disposed.

Facilities that use surface impoundment, as a disposal method should keep records of waste stream composition. This can be used in determining the percentage of volatile chemicals that will be evaporated. This release determination will be reported under fugitive emissions.

Releases of EPCRA 313 chemicals that are discharged into publicly owned treatment works POTWs must be reported. If totals are less than a 1,000 pounds you may report that amount using a range, but if the quantity exceeds 1,000 pounds than you must report the exact estimate. Bases for determining the amount of EPCRA 313 chemical discharged is usually based upon stream analyses and monitoring data that is required by permit.

Transfers to off-site locations for the purposes of disposal, treatment, energy recovery or recycling must be reported. Estimates of quantities for these purposes are based upon chemical content contained in the overall waste. Materials that are shipped off-site for these purposes must be manifested. The manifest requires the listing of the chemical content. Analyses usually specify a range and judgment should be used in determining the amount. Transfers may also include any material that may include residuals in bags, totes, drums, tank trucks, and wasted product. Estimates of residual content can range from 0 to 3% depending upon viscosity of the material. MDI is a solid while a mixture of MDI/PMDI is a liquid at room temperature. If you properly decontaminate the containers, in accordance with recommended procedures, before disposal, the amount of MDI and MDI/PMDI can be considered negligible. However, if you decontaminate containers you must report this as treatment and the amount of material treated and its treatment efficiency must be reported.

The bases for determining all releases fall into one of four categories:

- Monitoring data and direct measurement
- Mass balance
- Emission factors derived from scientific studies and are chemical, equipment, through-put, and chemical specific
- Engineering calculations using published mathematical formulas or best engineering judgment

Judgment as to which method to use is critical. One has to weigh the validity of the data being presented along with the actual physical nature of the process and chemical to determine if the number calculated is correct. Over reporting has serious consequences as well as under reporting, so think and let sound judgment prevail when determining releases.

Stack Emissions (Point Source):

Stack emissions are releases of EPCRA Section 313 chemicals that are contained in confined air streams. Examples are emissions from stacks, vents, ducts, pipes and storage tanks from pollution control equipment are also included in this category. In the following section we will be looking at various applications where MDI and MDI/PMDI mixture are being used. Stack emissions will be calculated using sound engineering judgment.

The applications where MDI and MDI/PMDI are used fall into the following three areas:

1. Enclosed Process (Cavity and Foam Density)
2. Open Process
3. Specialty Process

The enclosed process estimation can be used for applications where the MDI-based products are introduced into a mold or cavity by injection, poured, or sprayed and will expand to fill the space. The MDI based resin may remain in the cavity in a final product or it may be released as a molded article. Examples of applications that can be considered as enclosed processes are:

- Reaction Injection Molding (RIM)
- Molded foam parts (automotive, furniture)
- Cast elastomers (shoe soles, packaging, furniture)
- Pout-in-place (appliance insulation, marine products,)
- Sandwich panels

The basic assumption used in calculating MDI and MDI/PMDI releases from closed mold/cavity processes is that MDI or MDI/PMDI saturated air first fills the volume of the mold cavity during the each use and is forced out into the environment as the chemicals are added.

The curing of an isocyanate-based product is almost accompanied by the generation of heat (exothermic reaction takes place). The concentration of MDI or MDI/PMDI in air depends on temperature. The higher the temperature the more material is volatilized and the saturated vapor concentration in air increases. Therefore, it is important to establish a maximum temperature at which the MDI or MDI/PMDI is likely to escape from a curing product. The relationship between vapor pressure and temperature is not linear but logarithmic; therefore the vapor pressure vs. temperature chart should be used to determine the correct vapor pressure for MDI or MDI/PMDI.

The open process estimation can be used for applications where the MDI-based products are introduced into a mold or cavity, but are cured with a significant fraction of the MDI containing product exposed to the atmosphere, or in which the MDI-base product is layered, sprayed or coated onto a surface. Examples of open process applications are:

- Slabstock/Bunstock
- Laminate boardstock
- Metal skin panels
- Carpet backing/flooring
- Bonded foam production
- Coatings
- Spray foaming
- Adhesives/sealants

The basic assumption used in calculating MDI and MDI/PMDI releases from open processes is that MDI and MDI/PMDI vapor will volatilize from all exposed surfaces of a curing foam, adhesive, coating, or other MDI-containing product. Evaporative releases from open processes (or spills) depend upon many factors including:

1. The volatility of the material
2. The surface area from which evaporation occurs
3. The temperature of the curing product
4. The airflow, and
5. The duration of the activity

To illustrate both enclosed and open processes, the guidebook will address the following applications:

1. Adhesive
2. Air Filters
3. Appliance
4. Appliance Truck
5. Automotive
6. Boardstock (open process)
7. Boats
8. Doors
9. Filling/Blending
10. Foundry
11. Laminator (cavity)
12. Mobile Homes/Motor Homes
13. Packaging
14. Rebond
15. Spandex
16. Spray Foam -Motor Home Roof Caps
17. Spray Booth Emissions
18. Water Heaters

A worst-case scenario will be presented for each application. The stack emissions will be presented in a step-by-step solution. The section on losses generated from storage tanks and fugitive emissions should be consulted for step-by-step description for calculating these emissions.

Illustrated Process Stack Emissions Examples

1.0 Adhesives/Coatings

Mixtures of methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) used as an adhesive are applied using a number of various ways. They can be rolled, sprayed, brushed, or applied using special applicators. These adhesives come in both two-component and one-component systems, and can be either water-based or solvent based. Depending on the formulation, they are applied at room temperature or as a hot melt. These adhesives usually have a set time and an open time ranging from 30 seconds to 4 minutes and a “tack-free” time of 5 to 30 seconds. Once applied, the adhesive is activated by air, heat, UV light, and/or by surface contact.

Process Description:

A 2 percent mixture of MDI is applied to both sides of a 4' x 8' wood panel using a special roller applicator system. Material, solid at room temperature, is pre-heated to 70°F to allow material to flow from the drum to applicator rollers. The rollers are heated and maintained at 275°F. Material is applied to both surfaces at a thickness of 1-2 mils and passed through an UV light. The wood paneling is placed over the wall and floor sections and pressure applied to sheeting. Set up time is 30 seconds. Tack time is 5 seconds. A blower operating at 550 CFM is used to carry off any emissions during application of adhesive. The length of the roller surface is 5' x 1'. The adhesive is applied at a rate of 11.5 grams/ft². Process covers at a rate of 2,465 ft²/hour. Plant operates 24 hours a day 365 days a year (8760 hours a year).

Calculating Stack Emissions:

MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the “tack-free” time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at “tack-free” temperature.
2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$W = 25.4 * VP_{MDI} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP _{MDI}	=	is the vapor pressure of MDI in atmospheres @ process temperature.
T _{proc}	=	is the process temperature in °K.
M _w	=	is the molecular weight of MDI
u	=	is the airflow speed in m/sec.
S _A	=	is the exposed surface area in M ² .
t _{TF}	=	is the “tack-free” time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Vapor Pressure of 2% MDI @ 275 °F in Atmospheres.

The vapor pressure of MDI @ 275 °F is 2.278×10^{-1} mm.
 Converting this to atmospheres and for a 2% mixture of MDI.

The vapor pressure (VP_{MDI}) of 2% MDI @ 275 °F is :

$$VP_{MDI} = (2.278 \times 10^{-1} \text{mm})(1 \text{ atm}/760 \text{mm}) \times (2 \text{ lbs. MDI} / 100 \text{ lbs. Mixture})$$

$$VP_{MDI} = \mathbf{5.99 \times 10^{-6} \text{ atmospheres}}$$

Step II: Determine Ventilation Rate in Meters/Second.

Ventilation rate (u)	=	Velocity @ STP/Surface Area
Roller Surface Area	=	1 foot by 5 feet = 5 ft^2
Velocity @ STP	=	$550 \text{ ACFM} \times 298^\circ\text{K}/308^\circ\text{K}$
Velocity	=	532SCFM
Ventilation rate (u)	=	Velocity/Surface Area
	=	$532 \text{SCFM} / 5 \text{ft}^2 \times \text{min.}/60 \text{ sec} \times .3048 \text{ m/ft.}$
Ventilation rate (u)	=	$5.41 \times 10^{-1} \text{ meters/second.}$

Step III: Determine Tack Time.

The problem states that the tack-free time is 5 seconds.

Step IV: Determine the Exposed Surface Area.

The exposed surface area is determined from the area of panel board processed.

The roller applicator coats $2465 \text{ ft}^2/\text{hr.}$

Based upon 24 hour production:

Total Exposed Surface Area (S_A)/day:

$$S_A = 2465 \text{ ft}^2 \times 24 \text{ hours/day}$$

$$S_A = 5.92 \times 10^4 \text{ ft}^2/\text{day}$$

Converting ft^2 to M^2 :

$$S_A = 5.92 \times 10^4 \text{ ft}^2/\text{day} \times \text{M}^2/10.76 \text{ Ft}^2$$

$$S_A = \mathbf{5.50 \times 10^3 \text{ M}^2 / \text{day}}$$

Therefore:

$$W = 25.4 * VP_{MDI} * (MW / T_{proc}) * (u)^{0.78} * S_A * t_{TF}$$

$$= (25.4)(5.99 \times 10^{-6} \text{atm})(250.26)/408(5.41 \times 10^{-1})^{0.78}$$

$$\text{m/sec}(5.50 \times 10^3 \text{ft}^2)(5) \text{sec}$$

$$W = \mathbf{1.61 \text{ grams./ day}}$$

Step V: Convert Grams per Day to Pounds per Year

$$W = 1.63 \text{ grams/day} \times 1 \text{ pound/454 grams} \times 365 \text{ days/year}$$

$$W = \mathbf{1.30 \text{ pounds / year}}$$

2.0 Air Filters

A mixture of methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) is reacted with a polyol blend to make a gasket or to become part of an air filter housing. The polyol and the diisocyanate are brought together and reacted in a customized piece of equipment which then dispenses the reacting mixture into a cavity. The cavity is then passed through a heated oven to cure the polyurethane formed by the diisocyanate/polyol reaction.

Process Description:

A polyurethane mixture with a ratio of 1.82 (polyol to MDI/PMDI) is dispersed into a mold cavity and then heated to 145°F in an oven. The dispenser dispenses through a customized nozzle head at a rate of 0.2579 lbs. Polyol/MDI/PMDI mixture per filter. The production lines produces 670 filters/hour. The diameter of the filter is 9 inches. Tack time is 2 seconds.

Calculating Stack Emissions:

To calculate the emissions for this process, the worst-case scenario will be presented. The MDI/PMDI emissions will be generated from two areas. are released as component A and Component B mixture is being dispensed into the cavity and as it is passed through the oven to be cured. Therefore, the total amount of MDI/PMDI emitted will equal the amount emitted while being dispersed plus the amount released during curing.

The total amount of emissions emitted during dispensing operations will correspond to the total volume of air displaced at the temperature of the process. A reasonable worst-case estimate of emissions can be made based upon the volume of the mold cavity, the number of pieces produced per year, and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_c	=	emissions from the enclosed process in lb./year.
V_{air}	=	the annual volume of displaced air in ft ³ /year.
T_{proc}	=	the temperature material is dispensed at in °K.
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at dispensed temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Determine Annual Volume Displaced (V_{air})

V_{air}	=	$N_f * M_{disp} * r *$
V_{air}	=	Annual Volume in Ft ³ /yr.
N_f	=	Annual Number of Filters Processed
M_{disp}	=	Amount of Material Dispensed/Filter
r	=	Density of Material lbs./ft ³

Therefore:

$$\begin{aligned}V_{\text{air}} &= (670 \text{ filters/hr.})(8760 \text{ hr./yr.})(0.26 \text{ lbs./filter})(1 \text{ gal/10lbs})1 \text{ ft}^3/7.48\text{gal} \\V_{\text{air}} &= 2.04 \times 10^4 \text{ ft}^3/\text{year}\end{aligned}$$

Step II: Convert Dispenser Temperature to °K

$$\begin{aligned}T_{\text{proc}} \text{ } ^\circ\text{K} &= (273^\circ + ^\circ\text{C}) \\T_{\text{proc}} \text{ } ^\circ\text{K} &= (273^\circ + 62.8^\circ\text{C}) \\T_{\text{proc}} \text{ } ^\circ\text{K} &= 335.8\end{aligned}$$

Step III: Determine the Vapor Pressure of MDI @ 335.8 °K

The vapor pressure of MDI @ 335.8^oK from chart is 6.663 x 10⁻⁴ mm

Step IV: Determine Adjustment Factor

The adjustment factor can be determined knowing that the ratio of polyol to MDI/PMDI mixture is 1.89.

Therefore:

$$\begin{aligned}\% \text{ MDI/PMDI} &= (1 / \text{ratio} + 1)(100) \\&= (1/1.89 + 1)100 \\ \% \text{ MDI/PMDI} &= 34.6\end{aligned}$$

From Chart:

$$K_{\text{MDI}} = 0.47$$

Therefore:

Losses due to cavity fill is:

$$\begin{aligned}L_c &= V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} \\&= V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} \\&= (2.04 \times 10^4 \text{ ft}^3/\text{year})(1/ 359)(273.15/335.8)(6.663 \times 10^{-4}\text{mm}/760)(254.38)(0.47) \\L_c &= 4.85 \times 10^{-3} \text{ lbs./year}\end{aligned}$$

Losses During the Curing Phase:

For this situation it is assumed that MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the “tack-free” time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at “tack-free” temperature.

2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$W = 25.4 * VP_{MDI} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP_{MDI}	=	is the vapor pressure of MDI in atmospheres @ process temperature.
T_{proc}	=	is the process temperature in °K.
M_w	=	is the molecular weight of MDI
u	=	is the airflow speed in m/sec.
S_A	=	is the exposed surface area in M^2 .
t_{TF}	=	is the “tack-free” time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Vapor Pressure of MDI @ 145 °F in Atmospheres.

The vapor pressure of MDI @ 145 °F is 6.682×10^{-4} mm.

Converting this to atmospheres:

The vapor pressure (VP_{MDI}) MDI @ 145 °F is :

$$VP_{MDI} = (6.682 \times 10^{-4} \text{mm}) (1 \text{ atm}/760 \text{mm})$$

$$VP_{MDI} = 8.792 \times 10^{-7} \text{ atmospheres}$$

Step II: Determine Ventilation Rate in Meters/Second.

Ventilation rate (u)	=	Velocity @ STP/Surface Area
Ventilation Area	=	$4' \times 3' = 12 \text{ft}^2$
Velocity @ STP	=	$990 \text{ acfm} \times 298^\circ \text{K}/336^\circ \text{K}$
Velocity	=	878 scfm
Ventilation rate (u)	=	Velocity/Surface Area
	=	$878 \text{ scfm}/12 \text{ft}^2 \times \text{min.}/60 \text{ sec} \times .3048 \text{ m/ft.}$
Ventilation rate (u)	=	3.72×10^{-1} meters/second.

Step III: Determine Tack Time.

The problem states that the tack-free time is 2 seconds.

Step IV: Determine the Exposed Surface Area.

The exposed surface area is determined from the area of exposed filter. Since the filter is conical in shape only the top surface is exposed.

$$\begin{aligned} \text{Exposed Surface Area} &= \pi r^2 = \pi(4.5/12)^2 = 0.44 \text{ Ft}^2 \\ \text{Based upon 24 hour production:} & \end{aligned}$$

$$\text{Total Exposed Surface Area (S}_A\text{)}/\text{day} = 0.44 \text{ ft}^2 / \text{filter} \times 670 \text{ filters/hr.} \times 24 \text{ hours/day}$$

$$\begin{aligned} S_A &= 7.08 \times 10^3 \text{ ft}^2/\text{day} \times 1 \text{ m}^2/10.77 \text{ ft}^2 \\ S_A &= \mathbf{658 \text{ m}^2} \end{aligned}$$

Therefore:

$$W = 25.4 * VP_{\text{MDI}} * (M_w / T_{\text{proc}}) * (u)^{0.78} * S_A * t_{\text{TF}}$$

$$W = (25.4)(8.8 \times 10^{-7}) \text{ ATM} (250.26/335.8)(3.72 \times 10^{-1})^{0.78} \text{ m/sec} (658 \text{ m}^2) (2) \text{ sec}$$

$$W = 0.0103 \text{ grams MDI/day}$$

We must multiply this by the KMDI correction factor to get pounds of MDI/PMDI emitted
KMDI is 0.47. Therefore,

$$W = \mathbf{0.00485 \text{ grams MDI/day}}$$

Step V: Convert Grams per Day to Pounds per Year

$$W = 0.00485 \text{ grams/day} \times 1 \text{ pound}/454 \text{ grams} \times 365 \text{ days/year}$$

$$W = \mathbf{0.004 \text{ pounds / year}}$$

Total Emissions:

$$T_T = L_C + W$$

$$T_T = 4.85 \times 10^{-3} \text{ lbs./yr.} + 4.0 \times 10^{-3} \text{ lbs./yr.}$$

$$T_T = \mathbf{8.85 \times 10^{-3} \text{ lbs./yr.}}$$

3.0 Appliances

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend to provide insulation inside the appliance frame. The two-component system will be injected through a spray nozzle inside the appliance frame after the appliance has been assembled and allow the polyurethane to expand filling the closed cavity. The two component system will also be injected into the cavity after the inner backing has been installed and a plate placed over outer backing allowing the polyurethane to expand to the contour of the framing while being passed through a curing stage. After the polyurethane has cured ,the appliance is assembled and the excess foam is removed.

Process:

The manufacturing process consists of four assembly lines that can be modified to accommodate different appliances. The system handles the manufacture of washers and dryers, refrigerators, and freezers. All processes are closed systems that use a two-component system where MDI and polyol are mixed in a specially designed spray head and the material is injected into the door of the side frame. The materials are transferred from storage tanks to day tanks when used. The equipment is set up where day tanks and pumps are in an enclosed system and have separate exhausts. The process equipment is also isolated and enclosed with separate exhausts.

Application I:

Door cavity is injected with MDI/polyol mix. Cover is placed over door cavity to form sealed compartment. System is then moved down conveyor. When doorframe gets to end of conveyor, system top plate is removed and excess foam is scrapped off.

Application II:

Carousel System allows for the injection of MDI/polyol Mixture into the door housing. The door housing is placed into chamber that contains exhaust system. Exhaust system is located on roof. Plate is placed over door housing and given cure time. System rotates in a carousel like fashion. (less space needed compared to conveyor system). Plate is removed and door removed from system.

Application III:

System consists of spray chamber where MDI/Polyol Mix is injected into appliance frame cavity. Plate is placed over frame and moved down conveyor system. At end of conveyor system plate is removed and excess material removed before frame is place on assembly line.

Application IV:

Three chambers process system consisting of three chambers being injected at the same time. System operates from one to three chambers depending upon product being run and number of units required.

The facility runs all four lines 24 hours a day 365 days a year. Line A and B produces at a rate of 100 doors per hour consuming an average of 123 lbs. MDI per hour. Line C produces 150 frames an hour consuming 12,226 lbs. MDI per hour. Line D produces 100 frames an hour consuming 1,343 lbs. MDI per hour. The annual amount of MDI consumed for each line is 1.08, 10.74, and 11.778 million pounds respectively. The process is run at 85°F. The size of the cavity changes but the density remains at 2.0 lbs/ft³

Calculating Stack Emissions

To estimate emissions from closed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression since the temperature of each line is the same:

$$L_{fd} = VT_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{fd}	=	emissions lb./year.
VT_{air}	=	total annual volume of displaced air in ft ³ /year by all lines.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air}) for each Line

$$V_{air} = (\text{Annual consumption of Polyol/MDI/PMDI}) / (\text{Foam Density})$$

$$\text{Line 1: } V_{air} = 1.08 \times 10^6 \text{ lbs/year} / 2.0 \text{ lbs/cu. ft.} = 5.4 \times 10^5 \text{ lbs/year}$$

$$\text{Line 2: } V_{air} = 1.08 \times 10^6 \text{ lbs/year} / 2.0 \text{ lbs/cu. ft.} = 5.4 \times 10^5 \text{ lbs/year}$$

$$\text{Line 3: } V_{air} = 10.74 \times 10^6 \text{ lbs/year} / 2.0 \text{ lbs/cu. ft.} = 5.37 \times 10^6 \text{ lbs/year}$$

$$\text{Line 4: } V_{air} = 11.78 \times 10^6 \text{ lbs/year} / 2.0 \text{ lbs/cu. ft.} = 5.89 \times 10^6 \text{ lbs/year}$$

Total volume displaced equals:

$$V_{tair} = \text{Line 1} + \text{Line 2} + \text{Line 3} + \text{Line 4}$$

$$V_{tair} = 123.4 \times 10^5 \text{ ft}^3/\text{year}$$

Step II: Determine vapor pressure of MDI @ 85°F

The vapor pressure of MDI @ 85 °F is 1.733×10^{-5} mm Hg

Step III: Determine Temperature of Process in °K

Converting 85 °F to °K:

$$^{\circ}\text{K} = (^{\circ}\text{F} - 32) / 1.8 + 273.15$$

$$^{\circ}\text{K} = 302.6$$

Step IV: Determine Adjustment Factor K_{MDI}

$$K_{\text{MDI}} = 0.56 @ 302.6 \text{ } ^{\circ}\text{K}$$

Therefore:

$$L_{\text{fd}} = V_{\text{Tair}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_{\text{w}} * K_{\text{MDI}}$$

$$L_{\text{fd}} = (1.234 \times 10^7 \text{ ft}^3/\text{year}) (1/359) (273.15/302.6) (1.733 \times 10^{-5} \text{ mm Hg}/760) (250.26) (0.56)$$

$$L_{\text{fd}} = \mathbf{0.10 \text{ lbs/year}}$$

4.0 Appliance – Truck

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture (Part A) is used in conjunction with a polyol blend (Part B) in the manufacture of truck trailers insulation. This mixture is injected into the cavity walls to form the insulation barrier between the inner and outer wall. The two parts are mixed in a customized system that mixes within the dispenser head and material dispersed into a cavity. The foam adheres to the wall cavity.

Process Description:

A two-component system, (consisting of a polyol to MDI/PMDI ratio of 93lbs. to 100 lbs.) is injected into the walls, floors, ceilings, and doors of tractor-trailer bodies to form insulation. The material is injected at a temperature of 78 °F. Amounts of material required for trailers of various lengths is as follows:

Trailer length	Amount of material required
28 ft.	565 lbs.
36 ft.	801 lbs.
45 ft.	802 lbs.
51 ft.	1,000 lbs.

The foam density is 2.25 lbs./ft³. The annual consumption of material used was 10.5 million pounds. The percent of MDI in component A is 52. The trailer to be injected is placed inside a containment area that has an individual exhaust system.

Calculating Stack Emissions

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{fd}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

$$V_{air} = (\text{Amount of material processed/year}) / \text{Foam Density}$$

$$V_{\text{air}} = (1.05 \times 10^7 \text{ lbs./year})(1/2.25 \text{ lbs./ft}^3)$$

$$V_{\text{air}} = 4.67 \times 10^6 \text{ ft}^3/\text{yr.}$$

Step II: Calculate Process Temperature in °K

The process temperature is 78 °F or;

$$T_{\text{proc}} = 298.7 \text{ °K}$$

Step III: Determine vapor Pressure of MDI @ 298.7 °K (VP_{MDI})

The vapor pressure @ 298.7 °K is 1.072×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}), the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 93/100. Therefore, the percentage of MDI/PMDI is:

$$\% \text{MDI/PMDI} = (100/(100 + 93)) * 100$$

$$\% \text{MDI/PMDI} = 51.8 \%$$

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

$$\% \text{MDI} = (51.8) * (52.0)$$

$$\% \text{MDI} = 26.9$$

Adjustment factor @ 298.7 °K and 26.9% MDI is 0.35

Therefore:

$$L_{\text{fd}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_{\text{fd}} = (4.67 \times 10^6 \text{ ft}^3/\text{yr.})(1/359)(273.15 \text{ °K} / 298.7 \text{ °K})(1.072 \times 10^{-5} \text{ mm}/760) (250.26)(0.35)$$

$$L_{\text{fd}} = 0.015 \text{ lbs. / year.}$$

5.0 Automotive

Releases of MDI/PMDI will be calculated for an automotive assembly facility that produces a variety of interior and exterior parts with MDI-based rigid foam. The facility uses a total of 1,500,000 pounds of feedstock that comprise a foam “system.” The “system” includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank. The storage tank is filled 25 times each year. MDI is transferred to a 1,500 lb. day tank as needed. The day tank is stored indoors. The MDI is pumped directly from the day tank to the foam mixer head. It may be difficult to estimate the cavity size of each part that is filled with the system. MDI releases can instead be estimated from the target foam density for the automotive part and the total quantity of foam feedstocks that are used in the year. The average density of the cured foam is 2.0 lbs./ft³ and the temperature of the cavity reaches 70°C.

Calculating Stack Emissions:

Estimating emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined if the following information is known:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}$$

Where:

L_{fd} represents the emissions from the enclosed process in lb/year.

V_{air} is the annual volume of displaced air in ft³/year.

T_{proc} is the process temperature in °K. This is the maximum temperature of MDI “tack free” time.

VP_{mdi} is the vapor pressure of MDI in mm Hg. at process temperature

$M_w = 250.26$ (this is the molecular weight of MDI).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate the Annual Volume of Displaced Air (V_{air})

$$V_{air} = \text{Annual material usage } (M_a) / \text{Foam Density } (F_d)$$

$$V_{air} = (1,500,000 \text{ lbs./year}) / 2.0 \text{ lbs/ft}^3$$

$$V_{air} = 750,000 \text{ ft}^3/\text{year}$$

Step II: Determine Process Temperature in °K

$$^{\circ}\text{K} = (^{\circ}\text{C} + 273.15)$$

$$^{\circ}\text{K} = (70 + 273.15)$$

$$^{\circ}\text{K} = 343.15$$

Step III: Determine Vapor Pressure of MDI @ 343.15 °K

MDI Vapor Pressure Chart ($V_{p_{mdi}}$) is 1.34×10^{-3} mm Hg

Step IV: Determine Adjustment Factor (K_{mdi})

A 50/50 mixture of MDI/PMDI from the Adjustment Factor Chart Table II K_{mdi} is 0.61.

Therefore:

$$\begin{aligned} L_{fd} &= V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi} \\ L_{fd} &= (750,000 \text{ ft}^3/\text{year})(1/359)(273.15/343.15)(1.34 \times 10^{-3} \text{ mmHg}/760 \text{ mmHg}) (250.26)(0.61) \\ L_{fd} &= \mathbf{0.455 \text{ lb/year}} \end{aligned}$$

6.0 Boardstock (Open Process)

Releases of MDI will be calculated for a laminate boardstock manufacturing facility that uses 1,300,000 pounds of MDI-based component of a rigid foam system each year. MDI/PMDI component is shipped to the facility in tank trucks and is transferred to a 5,000-gallon (rail car-larger producers) indoor storage tank that is temperature controlled. The MDI component product is transferred to 2,000 lb. capacity “day tanks” which are stored inside the producing facility. Both the storage tanks and day tanks are kept at a constant temperature of 77°F (25°C). The contents of the “day tanks” are pumped through a metered foam machine and then delivered, mixed with the polyol, additives, blowing agent and other ingredients of the rigid foam system, and applied to the bottom facer of the moving laminate conveyor line. The facility produces laminate boardstock that is on average 2” thick by 4’ wide at the rate of 72,000 to 100,800 linear feet per day. The facility operates 250 days each year. The building size is 11,300 M³ and the air concentration in the workplace shows a concentration of 0.001 ppm. The building experiences 5 air changes per hour, and the building operates 16 hours per day 250 days a year.

Calculating Stack Emissions:

Estimating emissions from open processes such as boardstock production, it is assumed that MDI will migrate from all exposed surfaces. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the “tack-free” time and the exposed surface area.

The calculation methodology involves four steps:

1. Determine partial pressure of MDI at “tack-free” time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF} * K_{mdi}$$

Where:

W represents the evaporation losses from the open process in gr/day.

VP_{mdi} is the vapor pressure of MDI in atm. at process temperature.

T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.

M_w = 250.26 (this is the molecular weight of MDI).

u is the airflow speed in m/sec. This is the airflow in the vicinity of the process.

S_A is the exposed surface area in M². (This is the exposed surface area per day. For boardstock production, the surface area can be determined from the dimensions of the board.)

t_{TF} is the “tack-free” time in seconds. The default value is 5 sec.

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Total Exposed Area

“A” will be the total exposed surface area of foam that is generated each day, including the area of foam that is exposed when the foam is cut at the end of the conveyor line. The foam is substantially cured when it is cut into

slabs at the end of the conveyor line. However, the cut end surface areas are included as a conservative measure to account for any small amount of unreacted MDI that may be trapped in the nearly cured foam cells and released when the foam is cut. Foam is produced 12 hours each day (6 pours x 2 hours/pour). The foam is produced at a rate of 6.1 feet/minute. Therefore;

$$\begin{aligned} \text{Total length of foam (ft) produce/day} &= (\text{Production time})(\text{Rate}) \\ \text{Length of foam (ft./day)} &= (12 \text{ hours/day}) (60 \text{ min./hour})(6.1 \text{ ft foam/Min.}) \\ \text{Length of foam (ft/day)} &= \mathbf{4,392 \text{ ft./day}} \end{aligned}$$

$$\begin{aligned} \text{Surface Area} &= \text{top surface} + \text{side surface} + \text{cut-end surface} \\ \text{Top surface} &= 4392 \text{ ft length} \times 4 \text{ ft width} \\ \text{Top Surface} &= \mathbf{17,568 \text{ ft}^2} \end{aligned}$$

$$\begin{aligned} \text{Side surface} &= 2 \times 4392 \text{ ft} \times 2 \text{ inch}/12 \text{ in/ft} \\ \text{Side surface} &= \mathbf{1,464 \text{ ft}^2} \end{aligned}$$

$$\begin{aligned} \text{Cut-end surface} &= 2 (4 \text{ ft by } 2 \text{ inch surfaces}) \text{ are produced for each } 8 \text{ ft board that is manufactured and cut} \\ \text{Cut-end surface} &= 2 \times [4 \text{ ft} \times (2 \text{ in width}/12 \text{ in/ft})](4392 \text{ ft}/8 \text{ ft}) \\ \text{Cut-end surface} &= \mathbf{732 \text{ ft}^2} \end{aligned}$$

Therefore, surface area is equal to:

$$\begin{aligned} \text{Surface area (A)} &= 17,568 \text{ ft}^2 + 1,464 \text{ ft}^2 + 732 \text{ ft}^2 \\ \text{Surface area (A)} &= \mathbf{19,764 \text{ ft}^2} \times \frac{\text{M}^3}{10.76 \text{ ft}^2} = \mathbf{1,837 \text{ M}^2} \end{aligned}$$

Step II: Determine Vapor Pressure in Atmospheres @ T_{pros}

$$\begin{aligned} \text{VP}_{\text{mdi}} &\text{ is the vapor pressure of MDI in atm. at process temperature.} \\ \text{VP}_{\text{mdi}} &= 4.361 \times 10^{-3} \text{ mm}/760 \text{ mm} \\ \text{VP}_{\text{mdi}} &= \mathbf{5.74 \times 10^{-6} \text{ atm.}} \end{aligned}$$

Step III: Determine the Process Temperature in °K

$$\begin{aligned} \text{T}_{\text{proc}} &= (^\circ\text{C} + 273.15) \\ \text{T}_{\text{proc}} &= \mathbf{(83 + 273.15) = 356.15 \text{ }^\circ\text{K}} \end{aligned}$$

Step IV: Determine Adjustment Factor K_{mdi}

From Adjustment Factor Chart K_{mdi} is 0.62 @ 356 °K

Therefore:

$$\mathbf{W = 25.4 * VP_{\text{mdi}} * (M_w / T_{\text{proc}}) * (u)^{0.78} * S_A * t_{\text{TF}} * K_{\text{mdi}}}$$

$$\mathbf{W = (25.4) (5.74 \times 10^{-6} \text{ atm.}) (250.26/356.15^\circ\text{K}) (5\text{m/sec})^{0.78} (1,837\text{M}^2)(5 \text{ sec}) (0.62)}$$

$$\mathbf{W = 2.08 \text{ lbs/year}}$$

7.0 Boats

Releases of MDI/PMDI will be calculated for a boat assembly that manufactures boats that are injected, through static mixing nozzles, a mixture of resin, PMDI, MDI, and blowing agent into the space between the inner and outer hulls by way of a hull-stiffening form. This produces rigid urethane foam that provides buoyancy and insulation for the craft. The foam mixture is supplied to the boat manufactures via 2500-pound totes and these totes are stored in-doors where the temperature remains constant. The foam mixture is injected at a “tack free” or “string” time temperature of 160°F (70°C). There are 18 different boat models manufactured ranging from 12-16ft. runabouts to 100-150ft. yachts. The majority of boat manufactures produce boats ranging from 25-30 ft. in length and anywhere from 25-30 boats per day. The typical production is a boat 25ft in length, 27 boats per day operating 24 hours a day, 250 days a year. The foam is 2” thick, has an average density of 1.8 lbs./cu.ft. and the surface area of the hull is 350 ft.². Fresh air is pulled across the work area and exhausted through hull-stiffening stack. The operation is performed in an area that is 100ft. by 100 ft. by 40 ft. and has a MDI concentration of 0.001 PPM. Calculate the stack emissions.

Calculating Stack Emissions

Estimating the emissions from closed processes, when the volume of the mold is known or can be determined by calculating the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_c	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air}	=	(Area/piece)(No. Pieces/year)(Thickness)
V_{air}	=	(350 ft ²)(27 pieces/day)(250 days/yr.)(2/12)ft
V_{air}	=	3.94⁺⁵ft³/yr.

Step II: Calculate Maximum Process Temperature in°K

The maximum temperature is the oven temperature of 70 °C or;

$$T_{\text{proc}} = (273.15 + 70^{\circ}\text{C})^{\circ}\text{K}$$

$$T_{\text{proc}} = 343.15^{\circ}\text{K}$$

Step III: Determine Vapor Pressure of MDI @ 341.15^oK (VP_{MDI})

The vapor pressure @ 343.15^oK is 1.340×10^{-3} mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 343.15^oK and 50% MDI is 0.61

Therefore:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_c = (3.94 \times 10^5 \text{ ft}^3/\text{yr.})(1/359)(273.15^{\circ}\text{K} / 343.15^{\circ}\text{K})(1.340 \times 10^{-3} \text{ mm}/760) (250.26)(0.61)$$

$$L_c = 0.2375 \text{ lbs. / year.}$$

8.0. Doors

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend to provide insulation inside a doorframe. There are two approaches used in industry. One application will inject the two-component system through a spray nozzle inside the doorframe after the door has been assembled and allows the polyurethane to expand filling the closed cavity. The second application is to inject the two component system into the door cavity after the inner backing has been installed, place the outer backing on the frame, allowing the polyurethane to expand to the contour of the door framing while being pass through a oven. Once polyurethane has cured the door assembly is finished. In both cases the application is a closed cavity system.

Process Description

An assembly line produces a standard door at a rate of 340 doors per hour. The size of the door is 7 feet high 36 inches wide and two inches thick. Each door is injected with 5.4 lbs. of a 1/1 resin to Diisocyanate blend. The temperature of the mixture is 80°F.

Calculating Stack Emissions

To estimate the emissions from closed processes, when the volume of the mold is known or can be determined, is calculated by determining the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_c	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

$$\begin{aligned} V_{air} &= (\text{Area/piece})(\text{No. Pieces/year})(\text{Thickness}) \\ V_{air} &= (21 \text{ ft}^2)(340 \text{ pieces/hr.})(24 \text{ hr./day})(365 \text{ days/yr.})(2/12)\text{ft} \\ V_{air} &= 1.04 \cdot 10^{+7} \text{ft}^3/\text{yr.} \end{aligned}$$

Step II: Calculate Maximum Process Temperature in °K

The maximum temperature is the oven temperature of 80°F or;

$$T_{\text{proc}} = 299.8^{\circ}\text{K}$$

Step III: Determine Vapor Pressure of MDI @ 299.8⁰K (VP_{MDI})

The vapor pressure @ 299.8⁰K is 1.23×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 299.8⁰K and 25% MDI is 0.34

Therefore:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_c = (1.04 \times 10^7 \text{ ft}^3/\text{yr.})(1/359)(273.15^{\circ}\text{K}/299.8^{\circ}\text{K})(1.23 \times 10^{-5} \text{ mm}/760)(250.26)(0.34)$$

$$L_c = .0365 \text{ lbs. / year.}$$

9.0. Filling/Blending

A company fills a blend consisting of 40% MDI/PMDI and 60% dioctylphthalate into half-gallon containers. The operation fills 5,000 containers a day. The facility operates 250 days/year. The material is mixed in a reactor-blend tank at 70 °F and packaged at a temperature of 70 °F. The percent MDI in the feedstock is 50%. Calculate annual emissions.

Calculating Stack Emissions

Estimating emissions from a mixing/blending operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst-case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI. Losses will be experienced when the reactor or blend tank is filled with the MDI/PMDI mixture and when the reactor/blend tank is emptied into containers. Losses will be based upon the volume of MDI/PMDI charged to the reactor/blend tank and the volume of containers filled with the blend.

The filling losses can be estimated from the following equation:

$$L_{\text{fill}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{fill}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} * C_{\text{blend}}$$

Where:

L_{fill} represents the emissions from the filling operation in lbs/year

V_{air} is the annual volume of displaced air in ft^3/year

T_{fill} is the temperature the material is charged or filled at in °K

VP_{MDI} is the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_w is the molecular weight of MDI (250.26)

K_{MDI} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blend} is the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blend} is 1.

To calculate the total emission we must determine what emission are contributed to the charging/filling of the reactor/blend tank and the emissions contributed from the discharge from the reactor/blend tank into the containers.

Step I: Determine Volume Displaced by MDI/PMDI During Charging/Filling of Reactor/Blend Tank

Assumption made is that the MDI/PMDI mixture is charged first and that the vapor space remains concentrated with MDI/PMDI during the charging of the dioctylphthalate (therefore presenting worst case scenario). The total volume of air displaced will be equal to the volume of containers filled.

Therefore:

$$\begin{aligned} V_{\text{Tair}} &= (\text{Number containers/year}) * (\text{Volume of container}) \\ &= (5,000 \text{ containers/day} \times 250 \text{ days/year}) * (1/5 \text{ gallon}) \\ &= (625,000 \text{ gallons/year}) / (7.48 \text{ gallons/ft}^3) \\ V_{\text{Tair}} &= 83,556 \text{ ft}^3 \end{aligned}$$

Total Volume of air displaced by MDI/PMDI is 40 % of total volume:

$$V_{\text{air}} = V_{\text{Tair}} \times \% \text{MDI/PMDI}$$

$$V_{\text{air}} = (83,556 \text{ ft}^3) (0.40)$$

$$V_{\text{air}} = 33,422 \text{ ft}^3$$

Step II: Determine Vapor Pressure at Charging/Blending Temperature VP_{MDI}

$$VP @ 70 \text{ }^\circ\text{F is } 6.09 \times 10^{-6} \text{ mm Hg}$$

Step III: Determine Charging/Filling Temperature (T_{fill}) in $^\circ\text{K}$

$$T_{\text{fill}} \text{ is equal to } 294.2 \text{ }^\circ\text{K}$$

Step IV: Determine Adjustment Factor K_{MDI}

The adjustment factor of 50% MDI/PMDI @ 294.2 $^\circ\text{K}$ is 0.54.

Step V: Determine C_{blnd}

$$C_{\text{blnd}} \text{ is equal to } 1.0.$$

Therefore:

$$L_{\text{fill}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{fill}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} * C_{\text{blnd}}$$

$$L_{\text{fill}} = (83556 \text{ ft}^3) (1/359) (273.15/294.2) (6.09 \times 10^{-6} \text{ mm Hg}/760) (250.26) (0.54) (1)$$

$$L_{\text{fill}} = 2.379 \times 10^{-4} \text{ lbs/year}$$

Part II: Determine Losses from the Filling of Containers

The losses from the filling of the containers can be found from the following equation:

$$L_{\text{fill}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{fill}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} * C_{\text{blnd}}$$

Where:

L_{fill} represents the emissions from the filling operation in lbs/year

V_{air} is the annual volume of displaced air in ft^3/year

T_{fill} is the temperature the material is charged or filled at in $^\circ\text{K}$

VP_{MDI} is the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_w is the molecular weight of MDI (250.26)

K_{MDI} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blnd} is the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blnd} is 1.

Step I: Determine Volume Displaced by the Filling of Containers

The total volume of air displaced will be equal to the volume of containers filled.

Therefore:

$$\begin{aligned} V_{Tair} &= (\text{Number containers/year}) * (\text{Volume of container}) \\ &= (5,000 \text{ containers/day} \times 250 \text{ days/year}) * (1/5 \text{ gallon}) \\ &= (625,000 \text{ gallons/year}) / (7.48 \text{ gallons/ft}^3) \\ V_{Tair} &= 83,556 \text{ ft}^3 \end{aligned}$$

Step II: Determine Vapor Pressure at Charging/Blending Temperature VP_{MDI}

$$VP @ 70 \text{ }^\circ\text{F is } 6.09 \times 10^{-6} \text{ mm Hg}$$

Step III: Determine Charging/Filling Temperature (T_{fill}) in $^\circ\text{K}$

$$T_{fill} \text{ is equal to } 294.2 \text{ }^\circ\text{K}$$

Step IV: Determine Adjustment Factor K_{MDI}

The adjustment factor of 50% MDI/PMDI @ 294.2 $^\circ\text{K}$ is 0.54.

Step V: Determine C_{blnd}

$$C_{blnd} \text{ is equal to } 0.40$$

Therefore:

$$\begin{aligned} L_{fill} &= V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd} \\ L_{fill} &= (83,556 \text{ ft}^3) (1/359) (273.15/294.2) (6.09 \times 10^{-6} \text{ mm Hg}/760) (250.26) (0.54) (.40) \\ L_{fill} &= 9.51 \times 10^{-5} \text{ lbs/year} \end{aligned}$$

Therefore total annual lost is equal to losses from charging/filling of the reactor/blend tank and the annual losses from filling the containers.

$$\begin{aligned} L_{fill} &= L_{f \text{ charging}} + L_{f \text{ filling}} \\ L_{fill} &= (2.379 \times 10^{-4} \text{ lbs/year}) + (9.51 \times 10^{-5} \text{ lbs/year}) \\ L_{fill} &= 3.33 \times 10^{-4} \text{ lbs/year} \end{aligned}$$

10.0 Foundry

TERMS:

% Reacted means:

The amount of this chemical that reacts during the curing process and no longer exists as this chemical after curing.

% Evaporated means:

The amount of this chemical that evaporates (becomes airborne) during the mold/core-making process.

% Remaining in Mold/Core Means:

The amount of this chemical that, even after curing/reacting, still remains in its original form in the finished product.

ASSUMPTIONS :

A phenolic urethane coldbox binder is used to make cores. This binder consists of two components; Part I and Part II. During the course of a year you have used 400,000 pounds of Part I and 325,000pounds of Part II. From the MSDS you know that

Part I consists of :

Phenol (6%),
Trimethylbenzene (2.08%),
Naphthalene (1.98%),
Xylene (0.44%),
Formaldehyde (0.3%),
Cumene (0.16%)
Biphenyl (0.08%)

Part II consists of:

MDI (39.95%)
Naphthalene (4.06%)
Xylene (0.2%)
Biphenyl (0.08%).

Since the percentages of Xylene, Cumene and Biphenyl in Part I and the percentages of Xylene and Biphenyl in Part II are below the SARA de minimis level (1% for non-carcinogens and 0.1% for carcinogens) no inventory or further calculations for these chemicals from this binder are necessary.

Step I: Calculate Inventory:

The amount of chemical in binder will equal the percentage amount times the amount of binder used.

Part I Chemicals:

<u>Chemical</u>	<u>%</u>	<u>Lbs. Used</u>	<u>Lbs. Chemical</u>
Phenol	6	400,000	24,000
Trimethylbenzene	2.08	400,000	8,320
Naphthalene	1.98	400,000	7,920
Formaldehyde	0.3	400,000	1,200

Part II Chemicals:

<u>Chemical</u>	<u>%</u>	<u>Lbs. Used</u>	<u>Lbs. Chemical</u>
MDI	39.95	325,000	29,838
Naphthalene	4.06	325,000	13,195

Step II: Determine Amount Reacted, Evaporated, Encapsulated in Core

Coldbox Process:

Part I Chemicals:

<u>Chemical</u>	<u>% Reacted</u>	<u>% Evaporated</u>	<u>% Remaining</u>
Phenol	90	0	10
Naphthalene	0	50	50

Part II

MDI	99.99	0	0.01
Naphthalene	0	50	50

Step III: Calculate amounts of chemical Reacted, Evaporated, and Remained in the Core

This is done by multiplying the pounds of the chemical by the percentage. Therefore:

<u>Chemical</u>	<u>Reacted</u>	<u>Evaporated</u>	<u>Remaining</u>
Phenol	21,600	0	2,400
MDI	129,825	0	13
Naphthalene	0	10,558	10,588

The amount of MDI lost due to emissions is 13 lbs.

Note: Most foundries vent the cold boxes to an acid scrubber. The unreacted MDI that can be lost due to core production would be hydrolyzed in the scrubber solution. The amount of MDI encapsulated in the core could only be lost during core and mold shakeout and amount of material that is vaporized would depend upon the shakeout temperature.

11.0 Laminator (Cavity)

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend in the manufacture of laminator boardstock. A two component system, using a polyol blend (Component A) is mixed with a MDI/PMDI mixture (Component B) through a special designed nozzle is dispersed onto laminator backing, enclosed between an upper and lower plate, and passed through an oven for curing. This produces rigid foam sheeting that is cut to desired length and width.

Process Description:

A two component system, (Component A: Polyol mixture; Component B: MDI/PMDI mixture), is dispersed onto a laminator boardstock backing, forming a polyurethane, at a rate of 52 lbs./min.. This is passed through an oven at an average temperature of 123°F. The line runs at a rate of 16 Ft²/piece with an average board thickness of 1.60 inches and produces 24 pieces/min.. The temperature of the ISO is 93°F containing a 1/1 ratio of MDI to PMDI.

The emissions from open processes can be estimated, when the volume of the mold is known or can be determined, by calculating the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

Where:

L_c	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

$$\text{Blend Consumed} = (52 \text{ lbs/min}) (60 \text{ min/hr}) (24 \text{ hr/day}) (365 \text{ days/year})$$

$$= 27,331,200 \text{ lbs/year}$$

$$V_{\text{air}} = (\text{Area/piece})(\text{No. Pieces/year})(\text{Thickness})$$

$$V_{\text{air}} = (16 \text{ ft}^2)(24 \text{ pieces/min})(60 \text{ min/hr})(24 \text{ hr./day})(365 \text{ days/yr.})(1.6/12)$$

$$V_{\text{air}} = 2.68 \times 10^7 \text{ ft}^3/\text{yr.}$$

Step II: Calculate Maximum Process Temperature in $^{\circ}\text{K}$

The maximum temperature is the oven temperature of 123 $^{\circ}\text{F}$ or;

$$T_{\text{proc}} = 323.7^{\circ}\text{K}$$

Step III: Determine vapor Pressure of MDI @ 323.7 $^{\circ}\text{K}$ (VP_{MDI})

The vapor pressure @ 323.7 $^{\circ}\text{K}$ is 1.92×10^{-4} mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 323.7 $^{\circ}\text{K}$ and 25% MDI is 0.38

Therefore:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_c = (2.68 \times 10^7 \text{ ft}^3/\text{yr.})(1/359)(273.15^{\circ}\text{K} / 323.7^{\circ}\text{K})(1.92 \times 10^{-4}\text{mm}/760)(250.26)(0.38)$$

$$L_c = 1.534 \text{ lbs. / year.}$$

12.0 Mobile Homes/Motor Homes

Releases of MDI/PMDI will be calculated for a mobile home assembly facility that produces mobile homes that are insulated with MDI-based rigid foam. The facility uses a total of 2,000,000 pounds of MDI/PMDI feedstock that comprise rigid foam “system.” The “system” includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank at 25°C. MDI is transferred to 550-lb. day tank as needed. The day tank is stored indoors. The MDI is pumped directly from the day tanks to the foam mixer head. It may be difficult to estimate the cavity size of each mobile home that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the insulation and the total quantity of foam feedstock that are used in the year.

Calculating Stack Emissions

To estimate the emissions from closed processes, when the volume of the mold is known or can be determined, is calculated by determining the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume of Polyol and MDI/PMDI used per year at the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

Where:

L_c	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

$$\begin{aligned} V_{\text{air}} &= (4,000,000 \text{ lbs./year}) / (10 \text{ lbs./gal.}) (1 \text{ gal}/7.48 \text{ ft}^3) \\ V_{\text{air}} &= 53,469 \text{ ft}^3 \end{aligned}$$

Step II: Calculate Maximum Process Temperature in °K

The maximum temperature is the oven temperature of 77 °F or;

$$T_{\text{proc}} = 298.2 \text{ °K}$$

Step III: Determine vapor Pressure of MDI @ 299.8 °K (VP_{MDI})

The vapor pressure @ 298.2°K is 1.00×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 298.2 °K and 25% MDI is 0.33

Therefore:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_c = (5.35 \times 10^4 \text{ ft}^3/\text{yr.})(1/359)(273.15^\circ\text{K}/298.2^\circ\text{K})(1.00 \times 10^{-5} \text{ mm}/760)(250.26)(0.33)$$

$$L_c = 1.51 \times 10^{-4} \text{ lbs. / year.}$$

13.0 Packaging

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend in the packaging of equipment, appliances, machine parts etc. to protect them from getting damaged. The system consist of two parts: Part A being polyol and Part B diisocyanate mixture. The two parts are mixed in a customized system that mixes within the dispenser head and material dispersed into a container or cavity containing the equipment, appliance, machine parts etc. The container is then placed on a conveyor and transported to the warehouse for storage.

A facility uses 10 million pounds of Polyol/MDI/PMDI blend for the packaging of machine parts to ship to Europe. The MDI/PMDI is stored in a 10,000-gallon storage tank and maintained at 25 °C. The Polyol/MDI/PMDI blend is injected into the containers inside an assembly room (50 ft. wide x 50 ft. long x 15 ft. high) that is vented through the roof. Since the container size varies, the targeted density of the foam is 1.5 lbs./ft³. Determine the stack emissions.

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process

The enclosed process losses can be estimated from the following expression:

$$L_{pk} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{pk}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air}	=	(Amount of material processed/year)/Foam Density
V_{air}	=	$(10.0 \times 10^{+6} \text{ lbs./year}) / (1.5 \text{ lbs./ft}^3)$
V_{air}	=	$6.6 \times 10^{+6} \text{ ft}^3/\text{yr.}$

Step II: Calculate Process Temperature in °K

The process temperature is of 25 °C or;

$$T_{proc} = 298.15^{\circ}\text{K}$$

Step III: Determine Vapor Pressure of MDI @ 298.15 °K (VP_{MDI})

The vapor pressure @ 298.15 °K is 1.072×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}), the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 1/1. Therefore, the percentage of MDI/PMDI is:

$$\begin{aligned}\% \text{MDI/PMDI} &= (1/(1+1)) * 100 \\ \% \text{MDI/PMDI} &= 50 \%\end{aligned}$$

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

$$\begin{aligned}\% \text{MDI} &= (51.8) * (50.0) \\ \% \text{MDI} &= 25.0\end{aligned}$$

Adjustment factor @ 298.7 °K and 25.0% MDI is 0.33

Therefore:

$$L_{pk} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

$$L_{pk} = (6.6 \times 10^6 \text{ ft}^3/\text{yr.})(1/359)(273.15^\circ\text{K} / 298.15^\circ\text{K})(1.072 \times 10^{-5} \text{ mm}/760)(250.26)(0.33)$$

$$L_{pk} = 0.0188 \text{ lbs. / year.}$$

14.0 Rebond

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate are used in a binder mixture that enables fabric and sponge-like material to bond into one solid flexible mass. This material can be cut to form carpet backing and underlay.

Process Description

A binder mixture containing polyol/MDI is added to a closed reactor system already charged with fluff (cut foam). Live steam is injected into the mixture at 60 psig for a period of 2.5 minutes. Steam is being exhausted from bottom and top of reactor through blower system. Binder mixture contains 40% MDI. Reactor produces a log that is 5' diameter and 10' high. System averages 10 logs per hour using 60 pounds of binder per log.

Calculating Stack Emissions

This is a unique process that combines the two-component system of Polyol and MDI and uses steam to produce the polyurethane foam. The amount of MDI lost can be calculated using the enclosed cavity equations.

The total amount of emissions emitted will correspond to the total volume of air displaced at the temperature of the process. A reasonable worst-case estimate of emissions can be made based upon the volume of the mold cavity, the number of pieces produced per year, and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_c	=	emissions from the enclosed process in lb./year.
V_{air}	=	the annual volume of displaced air in ft ³ /year.
T_{proc}	=	the temperature material is dispensed at in °K.
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at dispensed temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air}	=	Annual Consumption x Density
V_{air}	=	1,344,000 lbs/year / 10 lbs/gal/7.48 gal/ft ³
V_{air}	=	1.783 x 10⁴ ft³/year

Step II: Calculate Maximum Process Temperature in °K

The maximum temperature is the oven temperature will be the temperature of 60 psig steam. The temperature of 60 psig (75psi) is 425.9°K. Therefore:

$$T_{proc} = 425.9 \text{ °K}$$

Step III: Determine vapor Pressure of MDI @ 425.9°K (VP_{MDI})

The vapor pressure @ 425.9°K is 7.034×10^{-1} mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 425.9 °K and 40% MDI is 0.57

Therefore:

$$L_c = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_c = (1.783 \times 10^4 \text{ ft}^3/\text{yr}) (1/359) (273.15/425.9^\circ\text{K}) (7.034 \times 10^{-1} \text{ mm}/760 \text{ mm})(254.38) (0.57)$$

$$L_c = 4.27 \text{ lbs. per year}$$

Note: This presents worst-case scenario because it does not assume that any of the MDI/PMDI is hydrolyzed by the steam.

15.0 Spandex

One of the unique ways polyol and diisocyanate are used is in the manufacture of spandex. Polyol and a mixture of MDI/PMDI are reacted with amines to form a segmented polyurethane. Using a special technique a final product is obtained from a “dry-spinning” operation. To control emissions a scrubber system is installed to control emissions of silicon oils, various pre-polymers and other VOC's.

Process Description

A reactor system is charged with dimethylacetamide (DMAC), amines, methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture, and silicon oils. Reactor is heated to 150 °F and a blended polyol is added over a period of two hours. The reaction forms a segmented polyurethane which, through a “dry-spinning” process, produces a spandex material. The reactor is equipped with a water scrubber to remove VOC's including any unreacted MDI/PMDI. The scrubber has an exhaust blower and operates at a temperature between 20 – 40 °C. The blower operates at 8000 scfm. MDI is charged in 2% excess (total charge of MDI per batch is 600 lbs.). Two batches are run at the same time. Plant operates 24 hours a day 365 days a year. The facility process 5.7 million pounds of MDI.

Calculating Stack Emissions

The stack emissions are based upon the excess amount of MDI charged per batch and the efficiency of the scrubber. Most water scrubbers are 99 % efficient in hydrolyzing MDI. We will assume that the unreacted MDI will hydrolyze except 1%. The remaining unreacted MDI will volatilize according to the scrubber temperature.

The amount of MDI emitted to the atmosphere from the scrubber can be determined from the following equation:

$$L_s = V_{\text{air}} * (1/359) * (273.15/T_s) * (VP_{\text{MDI}}/760) * M_w$$

Where:

V_{air} is equal to annual volume of displaced air through the scrubber in ft³/year

T_s is equal to the maximum scrubber temperature

VP_{MDI} is the vapor pressure of MDI at maximum scrubber operating temperature °K

M_w is the molecular weight of MDI (250.26)

Step I: Calculate the Annual Displacement of Air by the Scrubber (V_{air})

Blower operates at 8000 cfm. Total air displaced per year is equal to the following:

$$V_{\text{air}} = (8000 \text{ ft}^3/\text{min}) (60 \text{ min/hr}) (8760 \text{ hr/year})$$

$$V_{\text{air}} = 4.20 \times 10^9 \text{ ft}^3/\text{year}$$

Step II: Determine Maximum Scrubber Temperature in °K (T_s)

$$^{\circ}\text{K} = (^{\circ}\text{C} + 273.15)$$

$$^{\circ}\text{K} = (40 + 273.15)$$

$$^{\circ}\text{K} = 313.15$$

Step III: Determine the Vapor Pressure of MDI @ 313.15 °K from Chart

The vapor pressure of MDI @ 313.15 is 8.76×10^{-4} mm

Step IV: Determine the partial pressure of MDI in air as it leaves the Scrubber

Conservatively we can assume that the mole fraction of MDI leaving the scrubber is 0.001.

Partial pressure of MDI is equal to 8.76×10^{-4} mm \times 0.001 or 8.76×10^{-7} mm

Therefore:

$$L_s = V_{\text{air}} * (1/359) * (273.15/T_s) * (VP_{\text{MDI}}/760) * M_w$$

$$L_s = (4.20 \times 10^9 \text{ ft}^3/\text{year}) (1/359) (273.15/313.15) (8.76 \times 10^{-7} \text{ mm}/760) (250.26)$$

$$L_s = 2.59 \text{ lbs/year}$$

16.0 Spray Foam

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend to provide insulation inside motor home roof caps. This mixture is injected into the cavity walls to form the insulation barrier between the inner and outer wall. Part A being polyol and Part B diisocyanate mixture. The two parts are mixing in a customized system that mixes within the dispenser head and material dispersed into a cavity or back of roof frame.

Process Description

A two component system, (Component A: Polyol mixture; Component B: MDI/PMDI mixture), is dispersed into the motor home roof cap forming a polyurethane foam insulation at a rate of 42 lbs./hr. The temperature of the ISO is 78 °F containing a 1/1 ratio of Polyol to MDI/PMDI. The targeted foam density is 2.0 lbs./ft³.

Calculating Stack Emissions

To estimate emissions from open processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{fd}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air}	=	(Amount of material processed/year)/Foam Density
V_{air}	=	(42 lbs./hr)(8760 hr./year)/(2.0 lbs./ft ³)
V_{air}	=	1.84 x 10 ⁵ ft ³ /yr.

Step II: Calculate Process Temperature in °K

The process temperature is 78°F or;

$$T_{\text{proc}} = 298.7^{\circ}\text{K}$$

Step III: Determine Vapor Pressure of MDI @ 298.7 °K (VP_{MDI})

The vapor pressure @ 298.7°K is 1.071×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

A Blend of 50/50 of MDI/PMDI at a ratio of 1/1 of Polyol to MDI/PMDI yields a composition of 25% MDI. Therefore,

Adjustment factor @ 298.7 °K and 25% MDI is 0.33

Therefore:

$$L_{\text{fd}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}}$$

$$L_{\text{fd}} = (1.81 \times 10^5 \text{ ft}^3/\text{yr.})(1/359)(273.15^{\circ}\text{K} / 298.7^{\circ}\text{K})(1.071 \times 10^{-5} \text{ mm}/760)(250.26)(0.33)$$

$$L_{\text{fd}} = 5.454 \times 10^{-4} \text{ lbs. / year.}$$

17.0 Spray Booth

A spray coating operation, carried out in the Specialty Products Section, spray coats automotive parts in a spray booth. The exhaust temperature is 90 °F and the blower air exhaust rate is 10,000 cfm. The percentage of MDI in the spray mix is 33%. The total annual spray time was 1000 hours.

The exhaust airflow rate and the temperature at which the spray coating is carried out will govern the emissions associated with a spray booth operation. If the concentration of the exit gas is not known, the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$L_{sp} = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * t_{sp}$$

Where:

L_{sp} represents the emissions in lb/year for spray coating operations.

V_{air} is the exhaust airflow rate in ft³/min.

T_{sp} is the spray temperature in °K.

C_{mdi} is the MDI concentration, in ppmv, in the exhaust air.

M_W is the molecular weight of MDI (250.26).

K_{MDI} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{sp} is the total time in hours/year that spray coating is occurring.

$$C_{mdi} = (VP_{MDI}/760) \times 10^6$$

$$VP_{MDI} = \text{MDI vapor pressure at exhaust temperature.}$$

Therefore:

$$L_{sp} = \text{emissions in lb/year.}$$

$$V_{air} = 10,000 \text{ ft}^3/\text{min.}$$

$$T_{sp} = 305.4 \text{ °K.}$$

$$C_{mdi} = 0.0319 \text{ ppmv}$$

$$M_W = 250.26.$$

$$K_{MDI} = 0.41$$

$$t_{sp} = 1000 \text{ hours/year that spray coating is occurring.}$$

Substituting the values into the equation:

$$L_{sp} = 4.94 \text{ lbs./year}$$

18.0 Water Heaters

A water heater assembly facility that produces water heaters insulated with MDI-based rigid foam uses a total of 6,000,000 pounds of feedstocks that comprise a rigid foam “system.” The “system” includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 60,000-gallon tank. The tanks are filled 65 times each year. The temperature of the MDI storage tank does not exceed 25°C and only drops 20° on an average a day. MDI is transferred to 400 lb. day tank as needed. The day tanks are stored indoors and temperature is maintained at 25°C. The MDI is pumped directly from the day tanks to the foam mixer head. The density of the foam is 1.9 lbs/ft³. It may be difficult to estimate the cavity size of each water heater that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the water heater insulation and the total quantity of foam feedstocks that are used in the year.

Calculating Stack Emissions

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{fd}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft ³ /year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

$$V_{air} = (\text{Amount of Material Processed/year}) / \text{Foam Density}$$

$$V_{air} = (6.0 \times 10^6 \text{ lbs./year}) / (1.9 \text{ lbs./ft}^3)$$

$$V_{air} = 3.2 \times 10^6 \text{ ft}^3/\text{yr.}$$

Step II: Calculate Process Temperature in °K

The process temperature is of 78 °F or;

$$T_{proc} = 298.7 \text{ °K}$$

Step III: Determine vapor Pressure of MDI @ 298.7 °K (VP_{MDI})

The vapor pressure @ 298.7 °K is 1.072×10^{-5} mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}), the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 1/1. Therefore, the percentage of MDI/PMDI is:

$$\% \text{MDI/PMDI} = (1/(1+1)) * 100$$

$$\% \text{MDI/PMDI} = 50 \%$$

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

$$\% \text{MDI} = (51.8) * (50.0)$$

$$\% \text{MDI} = 25.0$$

Adjustment factor @ 298.7 °K and 25.0% MDI is 0.33

Therefore:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

$$L_{fd} = (3.16 \times 10^{+6} \text{ ft}^3/\text{yr.}) (1/359) (273.15^\circ\text{K} / 298.7^\circ\text{K}) (1.072 \times 10^{-5} \text{ mm} / 760) (250.26) (0.33)$$

$$L_{fd} = 0.00953 \text{ lbs. / year.}$$

Overall Facility Example

The basic formulas presented in the preceding pages, can be used to estimate the amount of air emissions from a facility that handles an MDI and /or MDI/PMDI mixture, Typically the total air emissions will be the sum of the amounts emitted from the following:

- Storage and Day Tanks (working and breathing losses)
- Fugitive Emissions (non-point sources) Measured
- Fugitive Emissions(non-point Source) Equipment Leaks
- Stack Emissions from Enclosed Processes
- Stack Emissions from Open Processes
- Stack Emissions from Continuous Processes
- Stack Emissions from Saturated Air Stream

Although the above list represents the predominant sources of air emissions from most facilities, each facility and process is unique. One needs to consider whether there are other potential emission sources (both fugitive and point source emissions).

The example presented below utilizes the techniques described in the above-mentioned categories. In each case the worst-case scenario is used for illustration.

Example:

J & J Foam Products, Inc. operates a facility that processes 10 MMlb/yr of MDI/PMDI. Shipments are received by rail car and are off-loaded into a 40,000-gallon storage tank. Operations include:

1. Re-packaging of material from storage into 55-gallon drums,
2. Manufacture of automotive sun visors,
3. Manufacture of seat cushions,
4. Spray coating of bumpers and fenders, and
5. Manufacture of laminated boardstock used in the construction industry.

Fugitive emissions from the process area include measured air exhaust concentration and from equipment leaks located outside.

The facility had two spills during the year that resulted in a loss of 1000 gallons of material.

Process Details:

10 MM Lbs. of MDI/PMDI a year are received by rail car. The product is off-loaded into a 40,000-gallon storage tank located outdoors. Average annual air temperature is 68 °F with an average daily temperature range of 18 °F.

The total manufacturing area measures 200 ft. by 300 ft. by 30 ft. (1.8 million cu.ft.). The air exchange rate is 5 per hour. The operation manufactures 24 hours per day 365 days per year. The outside operation consists of a closed system that has 1000 connectors, 8 pumps, 25 light liquid valves, 4 agitators, and 4 safety relief valves. The annual average air temperature was reported to be 78 °F.

The facility makes sun visors for the automotive industry. The average size sun visor is 2 ft. long by 6 inches wide and 2 inches thick (0.17 cu.ft.). The company produces 1.5 million parts using a closed mold two-component system of MDI/PMDI and polyol resin (1:1 ratio). The process is carried out at a temperature of 85 °F.

2 MM lbs. of MDI/PMDI are used to produce seat cushions. The polyol and isocyanate are mixed through a

special head at 85 °F at a ratio of 1:1. The foam density of the cushion is 2.0 lbs./cu.ft.

Laminated boardstock 8 feet long by 4 feet wide and 2 inches thick is produced at a rate of 17 ft/min. The temperature of the exit air is 85 °F. The wind velocity across the surface of the board was measured at 3 ft/sec. Tack time is one minute. The line operates 24 hours per day 7 days per week.

MDI/PMDI is repackaged at 75 °F into 55 gallon drums each one weighing 500 pounds net. Total pounds re-packaged 1 MM lbs.

Shipping cartons are assembled using an adhesive mixture containing 2% MDI. The adhesive is applied using a special roller applicator that covers 20,000 sq.ft./day. The plant operates 5 days/week (250 days/year). The material is applied at 275 °F and the exposed area is subject to an airflow velocity of 5 meters/second. Tack-time is 10 seconds.

A spray coating operation, carried out in the Specialty Products Section, spray coats automotive parts in a spray booth. The exhaust temperature is 90 °F and the blower air exhaust rate is 10,000 cfm. The percentage of MDI in the spray mix is 33%. The total annual spray time was 1000 hours.

During the course of the year the facility had a number of spills. Total amount of material spilled was 1000 gallons that resulted in exposed area 1000 sq.ft. for 20 hours. The evaporation temperature was 85 °F and the airflow velocity was 20 miles/hour. The percent of MDI in the material was 50.

Estimate the total emissions of MDI/PMDI.

To estimate the total emissions will require calculating the emission from the following:

1. Storage: Working and Breathing Loses
2. Fugitive: Measured and Equipment Leaks
3. Process: Closed Cavity, Foam Density, and Continuous
4. Filling/Blending Operation
5. Adhesives
6. Spray Coating
7. Spill

1. Storage: Working and Breathing Loses

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. Reasonable worst case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The working losses can be estimated from the following expression:

$$L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (V_{pamb} / 760) * M_w * K_{mdi}$$

Where:

L_w represents the working losses in lb/year.

Q_w is the annual throughput of MDI pumped to the tank in ft³/year.

T_{amb} is the storage temperature in °K.

V_{pamb} is the vapor pressure of MDI at the storage temperature in mm Hg

M_w is the molecular weight of MDI (250.26).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature.

Substituting the following values into the equation:

$$\begin{aligned}L_w &= \text{lbs./year} \\Q_w &= 1,000,000 \text{ gallons/yr.} = 133,681 \text{ ft}^3/\text{year.} \\T_{amb} &= 68 \text{ }^\circ\text{F} = 293.2 \text{ }^\circ\text{K.} \\VP_{amb} &= 5.2 \times 10^{-6} \text{ mm Hg} \\M_w &= 250.26 \\K_{mdi} &= 0.54 \text{ @ } 293.2 \text{ }^\circ\text{K, 50\% MDI} \\L_w &= \mathbf{3.256 \times 10^{-4} \text{ lb./yr.}}\end{aligned}$$

The breathing losses can be estimated from the following expression:

$$\begin{aligned}L_B &= 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi} \\M_{air} &= (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb}) \\V_v &= V_T * (100 - L_T) \\K_E &= T_R / T_{amb}\end{aligned}$$

Where:

L_B represents the breathing losses in lb/year.
 M_{air} is the total air displaced per day in lb-mole/day.
 VP_{amb} is the vapor pressure of MDI at the ambient temperature in mm Hg
 M_w is the molecular weight of MDI (250.26).
 K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
 V_v is the daily average vapor space of the storage tank in gallons
 V_T is the capacity of the storage tank.
 T_{amb} is the average ambient temperature in $^\circ\text{K}$.
 T_R is the average day-night temperature fluctuation in $^\circ\text{K}$.
 K_E is the vapor expansion factor due to day-night temperature fluctuation.

Substituting the following values into the equations:

$$\begin{aligned}L_B &= \text{breathing losses in lb/year.} \\VP_{amb} \text{ mm Hg} &= 5.2 \times 10^{-6} \text{ mm Hg} \\M_w &= 250.26 \\K_{mdi} &= 0.54. \\V_v &= 20,000 \text{ gallons} \\V_T &= 40,000 \text{ gallons.}\end{aligned}$$

$$\begin{aligned}
T_{\text{amb}} &= 293.2 \text{ }^\circ\text{K.} \\
T_{\text{R}} &= 10 \text{ }^\circ\text{K.} \\
K_{\text{E}} &= 10 \text{ }^\circ\text{K}/293.2 \text{ }^\circ\text{K} = 0.0341.
\end{aligned}$$

$$\begin{aligned}
V_{\text{V}} &= V_{\text{T}} * (100 - L_{\text{T}}) = 20,000 \text{ gallons} \\
K_{\text{E}} &= T_{\text{R}} / T_{\text{amb}} = 0.0341 \\
M_{\text{air}} &= (V_{\text{V}} / 7.48) * (1 / 359) * K_{\text{E}} * (273.15 / T_{\text{amb}}) = 3.33 \times 10^{-3} \text{ lb-mole/day} \\
L_{\text{B}} &= 365 * M_{\text{air}} * (VP_{\text{amb}} / 760) * M_{\text{w}} * K_{\text{mdi}} \\
L_{\text{B}} &= 8.0 \times 10^{-7} \text{ lb./yr.}
\end{aligned}$$

Therefore;

$$\begin{aligned}
L_{\text{T}} &= L_{\text{W}} + L_{\text{B}} \\
L_{\text{T}} &= 3.256 \times 10^{-4} \text{ lb./yr.} + 8.0 \times 10^{-7} \text{ lb./yr.} \\
L_{\text{T}} &= 3.26 \times 10^{-4} \text{ lb./yr}
\end{aligned}$$

2. Fugitive Emissions: Measured and Equipment Leaks

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.

Measured Fugitive Emissions:

The fugitive emissions can be estimated from the following expression:

$$L_{\text{fg}} = C_{\text{mdi}} * (V_{\text{B}} / 359) * N_{\text{year}} * (273.15 / T_{\text{amb}}) * M_{\text{w}} * K_{\text{f}}$$

Where:

L_{fg} represents the fugitive emissions in lb/year.

C_{mdi} is the average MDI concentration, in ppmv, in the air within the building.

V_{B} is the volume of the workspace building in ft^3 .

N_{year} is the number of air exchanges per year.

T_{amb} is the ambient temperature in $^\circ\text{K}$.

M_{w} is the molecular weight of MDI (250.26).

K_{f} is an adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Therefore:

$$C_{\text{mdi}} = 0.001 \text{ ppm} = 1.0 \times 10^{-9}$$

$$\begin{aligned}
V_B &= 1,800,000 \text{ ft}^3 \\
N_{\text{year}} &= 43,800 \text{ per year} \\
T_{\text{amb}} &= 298.2 \text{ }^\circ\text{K.} \\
M_w &= 250.26. \\
K_f &= 1.10
\end{aligned}$$

Therefore:

$$L_{fg} = (1.0 \times 10^{-9}) * (1,800,000 \text{ ft}^3/359) * (43,800) * (273.15/298.2) * (250.26) * (1.1)$$

$$L_{fg} = 56.33 \text{ lbs/year.}$$

Fugitive Emissions: Equipment Leaks

In cases where monitoring data is not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.
3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

$$SV = 1,315.8 \times 10^{[(10.902 - 4634.09/(266.15 + t))]}$$

Where:

$$\begin{aligned}
SV &= \text{Screening Value in ppmv and} \\
t &= \text{Temperature in } ^\circ\text{C.}
\end{aligned}$$

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

Table V-6
Leak Rate/Screening Value Correlations

Equipment Type	Correlation Leak Rate (kg/hr) (a*(SV) ^b)
Gas Valve	$1.87 \times 10^{-06} \times (SV)^{0.873}$
Light Liquid Valve	$6.41 \times 10^{-06} \times (SV)^{0.787}$
Light Liquid Pump ^c	$1.90 \times 10^{-05} \times (SV)^{0.824}$
Connectors	$3.05 \times 10^{-06} \times (SV)^{0.885}$

**Table V-7
Equipment leak Emission Factors lbs/hr-component @ 78 °F**

Equipment Type	Temp. °F	Vapor Pressure (mm Hg)	Screening Value (SV) (ppmv)	Equation Constant (a)	Equation Constant (b)	Emission Factor ¹ (lb./hr) ³
Gas Valves	78	1.0720x10 ⁻⁰⁴	1.41x10 ⁻⁰²	1.87x10 ⁻⁰⁶	0.873	9.992x10 ⁻⁰⁸
Light Liquid Valves	78	1.0720x10 ⁻⁰⁴	1.41x10 ⁻⁰²	6.41x10 ⁻⁰⁶	0.797	4.941x10 ⁻⁰⁷
Light Liquid Pumps	78	1.0720x10 ⁻⁰⁴	1.41x10 ⁻⁰²	1.90x10 ⁻⁰⁵	0.824	1.251x10 ⁻⁰⁶
Connectors	78	1.0720x10 ⁻⁰⁴	1.41x10 ⁻⁰²	3.05x10 ⁻⁰⁶	0.885	1.548x10 ⁻⁰⁷

Equipment Type	Service	Number Components	Adjustment Factor	Emissions (lbs/hr)	Emissions (lbs./year)
Valves	Light Liquid	25	0.55	4.941x10 ⁻⁰⁷	0.0593
Pumps	Light Liquid	16	0.55	1.251x10 ⁻⁰⁶	0.09608
Connectors	All	1000	0.55	1.548x10 ⁻⁰⁷	0.7433
Total				0.8987	

Total Fugitive emissions due to emissions from process area and outside:

$$L_{fg} = 56.33 \text{ lbs/year} + 0.8987 \text{ lbs./year} = 57.23 \text{ lbs./year}$$

3. Process: Closed Cavity

The manufacture of sun visors represents a closed system. Since the cavity size and the number of parts manufactured in a year are known, the emissions can be estimated using the following equation:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

- L_c = emissions lb./year.
- V_{air} = annual volume of displaced air in ft³/year.
- T_{proc} = process temperature in °K. (maximum temperature of the MDI).
- VP_{MDI} = vapor pressure of MDI in mm Hg. at process temperature.
- M_w = 250.26 (this is the molecular weight of MDI).
- K_{MDI} = adjustment factor
- $V_{air} = V_{pc} \times N_{pc}$
- V_{pc} = volume displaced per piece
- N_{pc} = number of pieces

Therefore:

$$V_{air} = \text{annual volume of displaced air in ft}^3\text{/year.}$$

$$\begin{aligned}
T_{\text{proc}} &= 302.6^{\circ}\text{K.} \\
VP_{\text{MDI}} &= 1.733 \times 10^{-5} \text{ mm Hg. at process temperature.} \\
M_{\text{w}} &= 250.26 \text{ (this is the molecular weight of MDI).} \\
K_{\text{MDI}} &= 0.56 \\
\dot{V}_{\text{air}} &= V_{\text{pc}} \times N_{\text{pc}} \\
V_{\text{pc}} &= 0.17 \text{ ft.}^3 \\
N_{\text{pc}} &= 1,500,000 \text{ pieces} \\
L_{\text{c}} &= 2.031 \times 10^{-3} \text{ lb./year}
\end{aligned}$$

Process: Closed Foam Density

To estimate the emissions for the manufacture of seat cushions, the formula to estimate emissions for a closed system given the foam density is used. The equation is:

$$L_{\text{fd}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{mdi}} / 760) * MW * K_{\text{mdi}}$$

Where

L_{fd} represents the emissions from the enclosed process in lb/year.
 V_{air} is the annual volume of displaced air in ft³/year.
 T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.
 VP_{mdi} is the vapor pressure of MDI in mm Hg. at process temperature.
 $M_{\text{w}} = 250.26$ (this is the molecular weight of MDI).
 K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Therefore:

$$L_{\text{fd}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{proc}}) * (VP_{\text{mdi}} / 760) * MW * K_{\text{mdi}}$$

Where

$$\begin{aligned}
L_{\text{fd}} &= \text{lbs./year} \\
V_{\text{air}} &= 4,000,000 \text{ lbs.} / 2.0 \text{ lbs./ft}^3 = 2,000,000 \text{ ft}^3 \text{ /year.} \\
T_{\text{proc}} &= 302.6^{\circ}\text{K.} \\
VP_{\text{mdi}} &= 1.733 \times 10^{-5} \text{ mm Hg.} \\
M_{\text{w}} &= 250.26 \\
K_{\text{mdi}} &= 0.34 \\
L_{\text{fd}} &= 9.759 \times 10^{-3} \text{ lb./year}
\end{aligned}$$

Process: Open Process(continuous):

To estimate the emissions from the laminated boardstock process, the formula for the Open Process (continuous) can be used.

The calculation methodology involves four steps:

1. Determine partial pressure of MDI at “tack-free” time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u^{0.78}) * SA * t_{TF} * K_{mdi}$$

Where

W represents the evaporation losses from the open process in gr/day.

VP_{mdi} is the vapor pressure of MDI in atm. at process temperature.

T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.

$M_w = 250.26$ (this is the molecular weight of MDI).

u is the airflow speed in m/sec. This is the airflow in the vicinity of the process.

SA is the total exposed surface area in M^2/day . This includes top and all sides.

t_{TF} is the “tack-free” time in seconds..

K_{mdi} is the adjustment factor.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Therefore:

VP_{mdi}	=	2.281×10^{-8} atm.
T_{proc}	=	302.6°K
M_w	=	250.26 (this is the molecular weight of MDI).
u	=	0.91m/sec.
SA	=	10,234 M^2 .(This includes top and all sides).
t_{TF}	=	60 seconds..
K_{mdi}	=	0.56.

Substituting the values into the equation:

$$\begin{aligned} W &= \mathbf{0.152 \text{ grams/day}} \\ W &= \mathbf{(0.152 \text{ grms./day})(365 \text{ days/year}) (1 \text{ lb./454 grms.})} \\ W &= \mathbf{0.125 \text{ lb./year}} \end{aligned}$$

4. Calculating Emissions from Mixing/Blending/Filling Process

Estimating emissions from a filling operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst-case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI.

The filling losses can be estimated from the following equation:

$$L_{\text{fill}} = V_{\text{air}} * (1 / 359) * (273.15 / T_{\text{fill}}) * (VP_{\text{MDI}} / 760) * M_w * K_{\text{MDI}} * C_{\text{blend}}$$

Where:

L_{fill} represents the emissions from the filling operation in lbs/year

V_{air} is the annual volume of displaced air in ft^3/year

T_{fill} is the temperature the material is charged or filled at in $^{\circ}\text{K}$

VP_{MDI} is the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_w is the molecular weight of MDI (250.26)

K_{MDI} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blend} is the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blend} is 1.

Therefore:

L_{fill}	=	emissions lbs/year
V_{air}	=	13,368 ft^3/year
T_{fill}	=	297 $^{\circ}\text{K}$
VP_{MDI}	=	8.692×10^{-6} mm Hg.
M_w	=	254.38
K_{MDI}	=	0.55
C_{blend}	=	1.0

Substituting the values into the equation, the estimated emissions from the filling operation is:

$$L_{\text{fill}} = 5.34 \times 10^{-5} \text{ lb./year}$$

5. Process: Adhesive

MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the “tack-free” time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at “tack-free” temperature.
2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$W = 25.4 * VP_{\text{MDI}} * (M_w / T_{\text{proc}}) * (u)^{0.78} * S_A * t_{\text{TF}}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP_{MDI}	=	is the vapor pressure of MDI in atmo spheres @ process temperature.

T_{proc}	=	is the process temperature in °K.
M_{W}	=	is the molecular weight of MDI
u	=	is the airflow speed in m/sec.
S_{A}	=	is the exposed surface area in M^2 .
t_{TF}	=	is the “tack-free” time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Therefore:

W	=	losses in gr./day.
VP_{MDI}	=	4.155×10^{-5} atmospheres
T_{proc}	=	380.4 °K.
M_{W}	=	250.26
u	=	5 m/sec.
S_{A}	=	1858 m^2 .
t_{TF}	=	5 seconds.

Substituting the values into the equation, the estimated emissions from applying the adhesive is:

W	=	0.906 grms./day
W	=	(0906grms./day)(250days/year) (1 lb./454 grms.)
W	=	0.499 lb./year

6. Process: Spray Coating

The exhaust airflow rate and the temperature at which the spray coating is carried out will govern the emissions associated with a spray booth operation. If the concentration of the exit gas is not known, the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$L_{\text{sp}} = (V_{\text{air}}/359) * (273.15/T_{\text{sp}}) * 60 * (C_{\text{mdi}}/1000000) * M_{\text{W}} * k_{\text{MDI}} * t_{\text{sp}}$$

Where:

- L_{sp} represents the emissions in lb/year for spray coating operations.
- V_{air} is the exhaust airflow rate in ft³/min.
- T_{sp} is the spray temperature in °K.
- C_{mdi} is the MDI concentration, in ppmv, in the exhaust air.
- M_{W} is the molecular weight of MDI (250.26).
- K_{MDI} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
- t_{sp} is the total time in hours/year that spray coating is occurring.

$$C_{\text{mdi}} = (VP_{\text{MDI}}/760) \times 10^6$$

VP_{MDI} = MDI vapor pressure at exhaust temperature.

Therefore:

L_{sp} = emissions in lb/year.
 V_{air} = 10,000 ft³/min.
 T_{sp} = 305.4 °K.
 C_{mdi} = 0.0319 ppmv
 M_w = 250.26.
 K_{MDI} = 0.41
 t_{sp} = 1000 hours/year that spray coating is occurring.

Substituting the values into the equation:

$$L_{sp} = 4.94 \text{ lbs./year}$$

7. Spills:

A liquid chemical accidentally spilled onto the ground may spread out over an area, vaporize and cause an air emission. Such accidental releases must be reported under section 313. Evaporative losses from spills (and other open processes) depend on a number of factors including:

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area
4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$Q_R = (0.284/82.05) * (u)^{0.78} * A_{spill} * (VP_{MDI}/T_{spill}) * (M_w)^{2/3} * K_{mdi}$$

Where:

Q_R represents the evaporation rate in lb/min.

u is the airflow speed in m/sec. This is the airflow in the vicinity of the process.

A_{spill} is the area of the spilled material in ft²

VP_{mdi} is the vapor pressure of MDI in mm Hg. at the spill temperature.

T_{spill} is the average evaporation temperature in °K.

M_w is the molecular weight of MDI (250.26).

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (Q_R) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$L_{spill} = Q_R * t_{spill} * (60)$$

Where:

L_{spill} represents the evaporation losses resulting from the spill in lb.

Q_R represents the evaporation rate in lb/min.

t_{spill} represents the time that the spill is on the ground in hours.

Therefore:

Q_R = represents the evaporation rate in lb/min.

u = 8.94 m/sec

A_{spill} = 1,000 ft²

VP_{mdi} = 1.733×10^{-5} mm Hg.

T_{spill} = 302.6 °K.

M_W = 250.26

K_{MDI} = 0.56.

Substituting the values into the equation:

$$Q_R = 2.413 \times 10^{-5} \text{ lb./min}$$

Therefore:

$$L_{\text{spill}} = Q_R * t_{\text{spill}} * (60)$$

Where:

$$t_{\text{spill}} = 20 \text{ hours}$$

$$L_{\text{spill}} = 2.896 \times 10^{-2} \text{ lb./year}$$

8. Summary: Total Emissions

The total estimated MDI Emissions are:

Step No.	Process	MDI Emissions (lbs./year)
1	Storage	3.264×10^{-4}
2	Fugitive (Measured)	5.633×10^{-1}
3	Fugitive (Equipment Leaks)	8.987×10^{-1}
4	Process (Cavity)	2.031×10^{-3}
5	Process (Foam Density)	9.759×10^{-3}
6	Process (Continuous)	1.225×10^{-1}
7	Process (Filling)	5.314×10^{-5}
8	Process (Adhesive)	4.99×10^{-1}
9	Process (Spray Coating)	4.94×10^0
10	Spill	<u>2.896×10^{-2}</u>
	Total	6.283×10^{-1}

The total estimated emissions for the year is 62.83 lbs.

Appendix A

MDI Vapor Pressure/Temperature Chart³

Table I: MDI Vapor Pressure Chart is a table that lists the Vapor Pressure of 4,4'-MDI vapor pressure (VP) at temperature from 20 °C to 207 °C.

To determine the vapor pressure of 4,4'-MDI at a temperature not listed or if the temperature range is outside the range of values listed, you may use the following equation:

$$\text{Log (MDI VP in mm mercury)} = 11.15 - 4809.8 / \text{Temperature in } ^\circ\text{K}$$

Where:

$$\text{Temp in } ^\circ\text{K} = 273 + \text{Temp in } ^\circ\text{C}$$

$$\text{Temp in } ^\circ\text{C} = 5/9 \times (\text{temp in } ^\circ\text{F} - 32)$$

³ Chakrabarti, A., *Vapor Pressure of Diphenylmethane Diisocyanate (MDI) Formulations*, The Dow Chemical Company, Midland, Michigan.

Table I: MDI Vapor Pressure Chart

Temperature (°Fahrenheit)	Temperature (°Celsius)	Vapor Pressure (mm Hg)
68.0	20	5.424E-06
69.8	21	6.168E-06
71.6	22	7.008E-06
73.4	23	7.956E-06
75.2	24	9.024E-06
77.0	25	1.023E-05
78.8	26	1.158E-05
80.6	27	1.310E-05
82.4	28	1.481E-05
84.2	29	1.673E-05
86.0	30	1.888E-05
87.8	31	2.130E-05
89.6	32	2.400E-05
91.4	33	2.702E-05
93.2	34	3.040E-05
95.0	35	3.418E-05
96.8	36	3.840E-05
98.6	37	4.310E-05
100.4	38	4.835E-05
102.2	39	5.420E-05
104.0	40	6.071E-05
105.8	41	6.795E-05
107.6	42	7.600E-05
109.4	43	8.494E-05
111.2	44	9.487E-05
113.0	45	1.06E-04
114.8	46	1.181E-04
116.6	47	1.316E-04
118.4	48	1.466E-04
120.2	49	1.632E-04
122.0	50	1.815E-04
123.8	51	2.018E-04
125.6	52	2.242E-04
127.4	53	2.489E-04
129.2	54	2.761E-04
131.0	55	3.062E-04
132.8	56	3.393E-04
134.6	57	3.757E-04
136.4	58	4.158E-04
138.2	59	4.599E-04
140.0	60	5.083E-04
141.8	61	5.616E-04
143.6	62	6.200E-04
145.4	63	6.841E-04
147.2	64	7.544E-04
149.0	65	8.314E-04
150.8	66	9.158E-04

Temperature (°Fahrenheit)	Temperature (°Celsius)	Vapor Pressure (mm Hg)
152.6	67	1.008E-03
154.4	68	1.109E-03
156.2	69	1.220E-03
158.0	70	1.340E-03
159.8	71	1.472E-03
161.6	72	1.616E-03
163.4	73	1.774E-03
165.2	74	1.945E-03
167.0	75	2.132E-03
168.8	76	2.335E-03
170.6	77	2.557E-03
172.4	78	2.798E-03
174.2	79	3.061E-03
176.0	80	3.346E-03
177.8	81	3.656E-03
179.6	82	3.993E-03
181.4	83	4.358E-03
183.2	84	4.755E-03
185.0	85	5.186E-03
186.8	86	5.652E-03
188.6	87	6.158E-03
190.4	88	6.706E-03
192.2	89	7.299E-03
194.0	90	7.941E-03
195.8	91	8.635E-03
197.6	92	9.386E-03
199.4	93	1.020E-02
201.2	94	1.107E-02
203.0	95	1.202E-02
204.8	96	1.304E-02
206.6	97	1.414E-02
208.4	98	1.533E-02
210.2	99	1.661E-02
212.0	100	1.799E-02
213.8	101	1.948E-02
215.6	102	2.108E-02
217.4	103	2.280E-02
219.2	104	2.466E-02
221.0	105	2.665E-02
222.8	106	2.879E-02
224.6	107	3.109E-02
226.4	108	3.356E-02
228.2	109	3.622E-02
230.0	110	3.906E-02
231.8	111	4.212E-02
233.6	112	4.540E-02
235.4	113	4.891E-02

Table I: MDI Vapor Pressure Chart (continued)

Temperature (°Fahrenheit)	Temperature (°Celsius)	Vapor Pressure (mm Hg)
237.2	114	5.267E-02
239.0	115	5.670E-02
240.8	116	1.168E+00
242.6	117	1.239E+00
244.4	118	1.313E+00
246.2	119	1.392E+00
248.0	120	1.475E+00
249.8	121	1.562E+00
251.6	122	1.654E+00
253.4	123	1.752E+00
255.2	124	1.854E+00
257.0	125	1.962E+00
258.8	126	2.075E+00
260.6	127	2.195E+00
262.4	128	2.321E+00
264.2	129	2.454E+00
266.0	130	2.593E+00
267.8	131	2.740E+00
269.6	132	2.894E+00
271.4	133	3.057E+00
273.2	134	3.227E+00
275.0	135	3.407E+00
276.8	136	3.595E+00
278.6	137	3.793E+00
280.4	138	4.001E+00
282.2	139	4.220E+00
284.0	140	4.449E+00
285.8	141	4.690E+00
287.6	142	4.942E+00
289.4	143	5.207E+00
291.2	144	5.485E+00
293.0	145	5.776E+00
294.8	146	6.082E+00
296.6	147	6.402E+00
298.4	148	6.738E+00
300.2	149	7.090E+00
302.0	150	7.458E+00
303.8	151	7.844E+00
305.6	152	8.249E+00
307.4	153	8.672E+00
309.2	154	9.115E+00
311.0	155	9.578E+00
312.8	156	1.006E+01
314.6	157	1.057E+01
316.4	158	1.110E+01
318.2	159	1.166E+01
320.0	160	1.224E+01

Temperature (°Fahrenheit)	Temperature (°Celsius)	Vapor Pressure (mm Hg)
321.8	16er1	1.168E+00
323.6	162	1.239E+00
325.4	163	1.313E+00
327.2	164	1.392E+00
329.0	165	1.475E+00
330.8	166	1.562E+00
332.6	167	1.654E+00
334.4	168	1.752E+00
336.2	169	1.854E+00
338.0	170	1.962E+00
339.8	171	2.075E+00
341.6	172	2.195E+00
343.4	173	2.321E+00
345.2	174	2.454E+00
347.0	175	2.593E+00
348.8	176	2.740E+00
350.6	177	2.894E+00
352.4	178	3.057E+00
354.2	179	3.227E+00
356.0	180	3.407E+00
357.8	181	3.595E+00
359.6	182	3.793E+00
361.4	183	4.001E+00
363.2	184	4.220E+00
365.0	185	4.449E+00
366.8	186	4.690E+00
368.6	187	4.942E+00
370.4	188	5.207E+00
372.2	189	5.485E+00
374.0	190	5.776E+00
375.8	191	6.082E+00
377.6	192	6.402E+00
379.4	193	6.738E+00
381.2	194	7.090E+00
383.0	195	7.458E+00
384.8	196	7.844E+00
386.6	197	8.249E+00
388.4	198	8.672E+00
390.2	199	9.115E+00
392.0	200	9.578E+00
393.8	201	1.006E+01
395.6	202	1.057E+01
397.4	203	1.110E+01
399.2	204	1.166E+01
401.0	205	1.224E+01
402.8	206	1.284E+01
404.6	207	1.348E+01

Appendix C

Breathing Losses From Storage Tanks

The objective of this analysis is to present a simplified method to estimate breathing losses from fixed roof storage tanks and compare the estimated losses with results obtained from the conventional EPA methodology.

1. Description of simplified procedure

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with an increasing temperature and decreases with a decreasing temperature. As the outside temperature rises during the day, the pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh airflows into the tank.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42 (Supplement E of AP-42 – October 1992).

Consider a tank with a volume of V_T (gallons). Assume that the liquid level in the tank is L_T . The vapor space V_v (gallons) of the tank is:

$$V_v = V_T \times (100 - L_T) / 100$$

Assume that the average ambient temperature is T_{amb} (in °K). Assume also that the day-night temperature fluctuation is T_R (in °K).

The vapor expansion factor K_E due to day-night temperature fluctuation is defined as:

$$K_E = T_R / T_{amb}$$

The total air displaced per day (M_{air} in lbmole/day) is calculated from the following expression:

$$M_{air} = (V_v / 7.48) \times (1 / 359) \times K_E \times (273.15 / T_{amb})$$

The breathing losses can now be estimated from the following expression:

$$L_b = 365 \times M_{air} \times (VP_{amb} / 760) \times M_w \times K_{mdi}$$

Where:

L_b = Breathing losses in lb/year

M_{air} = Total air displaced per day in lb-mole/day

VP_{amb} = Vapor pressure of MDI at the ambient temperature in mm Hg

M_w = Molecular weight of MDI (250.26)

K_{mdi} = Adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature

365 = days/year

2. Conventional EPA methodology

a. Old EPA method

The original method to estimate breathing losses was first proposed in July 1962 by the American Petroleum Institute. The methodology was reaffirmed in August 1987 in API Bulletin 2518. EPA adopted the method and incorporated it in Appendix C of AP-42 (4th Edition, September 1985)

The empirical equation presented in AP-42 is applicable to tanks with vertical cylindrical shells and fixed roofs. The tanks must be substantially liquid and vapor tight and must operate approximately at atmospheric pressure. Under these conditions, breathing losses can be estimated from:

$$L_B = 2.26 \times 10^{-2} \times M_v (P/P_A - P)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_p \times C \times K_c$$

Where:

L_B = Fixed roof breathing loss in lbs./yr.

M_v = Molecular weight of vapor in storage.

P_A = Average atmospheric pressure at tank location in psia

P = Vapor pressure of compound at bulk liquid conditions in psia

D = Tank Diameter in ft

H = Average vapor space height, including roof volume correction in ft

ΔT = Average ambient diurnal temperature change in °F

F_p = Paint factor

C = Adjustment factor for small diameter tanks

K_c = Product factor. For crude oil $K_c = 0.65$. For all other organic liquids $K_c = 1.0$.

b. New EPA method

The EPA adopted a new method to estimate breathing losses (often referred to as standing loss) from storage tanks and incorporated it in Supplement E of AP-42 (October 1992).

The new method is applicable to vertical tanks and can be used to estimate breathing losses from tanks equipped with a conservation vent. The method can also be adapted to estimate breathing losses from horizontal tanks.

The operating equation is given below:

$$L_s = 365 \times V_v \times W_v \times K_E \times K_s$$

Where:

L_s = Standing storage loss in lbs.yr

V_v = Vapor space volume in ft³

W_v = Vapor density in lbs.ft³

K_E = Vapor space expansion factor, dimensionless

K_s = Vented vapor saturation factor, dimensionless

365 = days/year

The EPA publication provides detailed guidelines for evaluating each of the above terms.

- The vapor space volume (V_v) is the vapor space above the liquid. For a cylindrical tank, V_v is equal to the cross sectional area of the tank times the tank outage. Specific instructions are given to evaluate the vapor space volume for vertical tanks equipped with a dome or a cone and for horizontal tanks.
- The vapor density of the vapor (W_v) is calculated from the molecular weight of the liquid (M_v), the daily average liquid surface

liquid temperature (T_{LA}) and the vapor pressure of the liquid (P_{VA}) at the daily average liquid surface temperature using the ideal gas equation. The daily average liquid surface temperature (T_{LA}) is a function of the daily ambient temperature ambient (ΔT_{AA}), the liquid bulk temperature (T_B), the tank paint absorptance (α) and the total daily insulation factor (I).

- The vapor space expansion factor (K_E) is determined from the increase in volume due to the change in the daily vapor temperature and the change in vapor pressure of the liquid at the liquid surface temperature. Specific instructions are given to determine the vapor space expansion factor. The daily vapor temperature range (ΔT_v) is a function of the daily average ambient temperature (ΔT_A), the tank paint absorptance (α) and the total daily insulation factor (I).
- The vented vapor saturation factor (K_s) can be viewed as the approach to saturation of the liquid in the vapor space. It is a function of the vapor pressure at the daily average liquid temperature and tank outage. The saturation factor approaches 1.0 when the vapor pressure is low or the tank outage is small.

As noted above the new EPA method recognizes that the temperature of the liquid and the temperature of the vapor space may be different from the ambient temperature. Empirical formulas are provided to determine the required temperatures if the ambient temperature and the daily range are given.

Determination of the breathing losses through the new EPA method is quite tedious. A software program to evaluate storage tank losses (working losses and breathing losses) was developed by the EPA. The software (Tanks 4.0) is available for downloading from the EPA home page on the Internet.

3. Comparison of results

The simplified method used for the MDI Emissions Estimator is an adaptation of the new EPA method. In developing the simplified method the following assumptions are made:

- The pressure term in the vapor space expansion factor is ignored. It can be shown that for liquids having a low vapor pressure the pressure term is negligible relative to the temperature term and can thus be ignored.
- The vented vapor saturation factor is 1.0. It can be shown that for liquids having a low vapor pressure the vented vapor saturation factor approaches 1.0.
- The average liquid surface temperature and the vapor temperature are the same as the ambient temperature.

Under these circumstances, the simplified method will yield identical results to the new EPA method.

Table 1 provides a side-by-side comparison of the working losses and breathing losses for the three methods discussed above.

COMPARATIVE EXAMPLE

The following illustrative example demonstrates the equivalency between the simplified method and the new EPA method when simplifying assumptions are made:

A fixed roof vertical tank contains MDI. The tank has a volume of 11,750 gallons (10' D x 20" H) and is half full. The tank is located in New York. From meteorological data, the daily average ambient temperature is 54.55 °F (12.53 °C) and the daily average temperature range is 15.3 °F (8.5 °C). The MDI vapor pressure at the daily average temperature is 1.945×10^{-6} mm Hg.

Simplified method

$$V_v = 11,750 \times 0.5 = 5,875 \text{ gallons}$$

$$K_E = 8.5 / (12.53 + 273.15) = 0.02975$$

$$M_{\text{air}} = 5,875 / 7.48 \times (1 / 359) \times 0.02975 \times (273.15 / 285.68) = 0.06229 \text{ lb-mole/day}$$

$$L_b = 365 \times 0.06229 \times (1.945 \times 10^6) / 760 \times 254.38$$

$$L_b = 1.480 \times 10^5 \text{ lbs.yr}$$

1. New EPA method using simplifying assumptions

The operating equation is given below:

$$L_s = 365 \times V_v \times W_v \times K_E \times K_s$$

$$V_v = 5,875 / 7.48 = 785.40 \text{ ft}^3$$

$$W_v = \frac{254.38 \times (1.945 \times 10^6 \times 14.7 / 760)}{10.73 \times (54.55 + 460)} = 1.733 \times 10^9 \text{ lbs.ft}^3$$

$$K_E = 15.3 / (54.55 + 460) = 0.02973$$

$$K_s = 1.0$$

$$L_s = 365 \times 785.40 \times 1.733 \times 10^9 \times 0.02973 \times 1.0$$

$$L_s = 1.474 \times 10^5 \text{ lbs.yr}$$

2. New EPA method without simplifying assumptions

The operating equation is given below:

$$L_s = 365 \times V_v \times W_v \times K_E \times K_s$$

$$V_v = 5,875 / 7.48 = 785.40 \text{ ft}^3$$

$$W_v = \frac{254.38 \times (2.194 \times 10^6 \times 14.7 / 760)}{10.73 \times (56.13 + 460)} = 1.949 \times 10^9 \text{ lbs.ft}^3$$

$$K_E = 0.03214 \text{ (from Table 1)}$$

$$K_s = 1.0 \text{ (from Table 1)}$$

$$L_s = 365 \times 785.40 \times 1.949 \times 10^9 \times 0.03214 \times 1.0$$

$$L_s = 1.796 \times 10^5 \text{ lbs.yr}$$

TABLE 1
MDI LOSSES FROM STORAGE TANKS
Comparison of results with EPA methods

Tank No.	T-501		Tank type	Vertical fixed roof	Date	3/15/00	
Material stored	MDI		Company	National Coatings	Performed by	Dennis Miller	
City	New York		State	NY			
Description	Outdoor storage tank						
	INPUT DATA				CALCULATIONS		
		Symbol	Units			Symbol	Units
Vapor pressure Antoine constants				New EPA method (AP-42) *			
Constant A			10.902				
Constant B			4634.09	Breathing losses			
Constant C			266.415	Tank vapor space volume	Vv	785.4	ft3
Molecular weight	Mv		254.38	Lb/lb-mole	Vapor density	Wv	1.949E-09 lb/ft3
					Vapor space expansion factor	KE	3.214E-02
Tank design data					Vented vapor saturation factor	Ks	1.000E+00 ft2
Shell height	Hs		20	ft			
Diameter	D		10	ft	Breathing losses	LB	1.796E-05 lb/yr
Liquid height			20	ft			
Avg. Liquid height	HL		10	ft	Working losses	Lw	3.020E-05 lb/yr
Tank volume			11749.584	gallons			
Tutnovers	N		10		Total losses	LT	4.815E-05 lb/yr
Net throughput	Q		117495.84	gallons/yr			
Meteorological data				Simplified method **			
Daily ave. ambient temp.	TAA		54.55	°F			
Daily max. ambient temp.	TAX		62.2	°F	Breathing losses		
Daily min. ambient temp.	TAN		46.9	°F	Temperature expansion factor		2.977E-02
Daily ambient temp. range	DTA		15.3	°F	Air displaced per day		6.227E-02 lbmole/day
Tank paint solar absorptance	a		0.17				
Daily total insolation factor	I		1171	Btu/ft2-day	Breathing losses	LB	1.480E-05 lb/yr
Liquid bulk temperature	TB		54.57	°F	Working losses	Lw	2.724E-05 lb/yr
Daily vapor temp. range	DTv		16.58996	°F			
					Total losses	LT	4.203E-05 lb/yr
Daily ave. liquid surface temp.	TLA		56.133853	°F			
Daily max. liquid surface temp.	TLX		60.281343	°F			
Daily min. liquid surface temp.	TIN		51.986363	°F	Old EPA method ***		
VP @ daily ave. liquid surf. temp.	PvA		2.194E-06	mm Hg	Breathing losses *	LB	5.336E-03 lb/yr
VP @ daily max. liquid surf. temp.	PvX		2.995E-06	mm Hg			
VP @ daily min. liquid surf. temp.	PvN		1.598E-06	mm Hg	Working losses	Lw	3.020E-05 lb/yr
VP @ daily ave. ambient temp.	Pamb		1.945E-06	mm Hg	Total losses	LT	0.005366 lb/yr
Daily vapor pressure range	DPv		1.397E-06	mm Hg			
Breather vent pressure setting range			0	psia	For old EPA method		
Breather vent pressure setting range	DPB		0	mm Hg	Paint factor (white - good condition)	Fp	1
					Adjustment for small diameter tanks	C	0.95

* New EPA methc(Source AP-42 - Supplement E - October 1992)

$$LS = 365 * Vv * Wv * Ke * Ks$$

** Simplified method (Adaptation of the new EPA method)

*** Old EPA metho (Source AP-42 - Appendix C - September 1985)

$$LB = 0.0226 * MV * ((Pamb/(760-Pamb))^0.68 * D^1.73 * (Hs-HL)^0.51 * (DTA)^0.50 * Fp * C$$

Appendix D – Basic Formulas

The following are the basic formulas used to calculate the emissions for the various applications.

1.0 Calculating Working Losses from Storage Tanks

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. A reasonable worst case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The working losses can be estimated from the following expression:

$$L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_w * K_{mdi}$$

Where:

L_w represents the working losses in lb/year.

Q_w is the annual throughput of MDI pumped to the tank in ft³/year.

T_{amb} is the ambient temperature in °K.

VP_{amb} is the vapor pressure of MDI at the ambient temperature in mm Hg.

M_w is the molecular weight of MDI (250.26).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

2.0 Calculating Breathing Losses from Storage Tanks

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with increasing temperature and decreases with a decreasing temperature. As outside temperature rises during the day, pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh airflows into the tank.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42.

The breathing losses can be calculated from the following expression:

$$L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}$$
$$M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$$
$$V_v = V_T * (100 - L_T)$$
$$K_E = T_R / T_{amb}$$

Where:

- L_b represents the breathing losses in lb/year.
- M_{air} is the total air displaced per day in lb-mole/day.
- VP_{amb} is the vapor pressure of MDI at the ambient temperature in mm Hg
- M_w is the molecular weight of MDI (250.26).
- K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
- T_{amb} is the average ambient temperature in °K.
- T_R is the average day-night temperature fluctuation in °K.
- K_E is the vapor expansion factor due to day-night temperature fluctuation.

3.0 Calculating Fugitive Emissions from Process Areas

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions whenever possible. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.

The fugitive emissions can be estimated from the following expression:

$$L_{fg} = C_{mdi} * (VB / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f$$

Where:

- L_{fg} represents the fugitive emissions in lb/year.
- C_{mdi} is the average MDI concentration, in ppmv, in the air within the building.
- VB is the volume of the workspace building in ft³.
- N_{year} is the number of air exchanges per year.
- T_{amb} is the ambient temperature in °K.
- M_w is the molecular weight of MDI (250.26).
- K_f is an adjustment factor to the MDI concentration in the building air. A value of 1.10 is used.

4.0 Calculating Fugitive Emissions from Equipment Leaks

In cases where monitoring data is not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-

95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.
3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

$$SV = 1,315.8 \times 10^{[(10.902 - 4634.09)/(266.15 + t)]}$$

Where:

$$\begin{aligned} SV &= \text{Screening Value in ppmv and} \\ t &= \text{Temperature in } ^\circ\text{C.} \end{aligned}$$

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

**Table V-6
Leak Rate/Screening Value Correlations**

Equipment Type	Correlation Leak Rate (kg/hr) (a*(SV) ^b)
Gas Valve	1.87x10⁻⁰⁶ x (SV) 0.873
Light Liquid Valve	6.41x10⁻⁰⁶ x (SV) 0.787
Light Liquid Pump ^c	1.90x10⁻⁰⁵ x (SV) 0.824
Connectors	3.05x10⁻⁰⁶ x (SV) 0.885

^c This equation can be used for liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps

The total emissions from equipment leaks will be equal to the emissions contributed from each gas valves, light liquid valves, light liquid pumps, and connectors.

The emissions factors can be estimated from the following expressions:

For gas valves:

$$K_{\text{gas}} = 1.87 \times 10^{-6} * (C_{\text{mdi}})^{0.873}$$

For liquid valves:

$$K_{\text{liq}} = 6.41 \times 10^{-6} * (C_{\text{mdi}})^{0.787}$$

For liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps:

$$K_{\text{pump}} = 1.90 \times 10^{-5} * (C_{\text{mdi}})^{0.824}$$

For connectors:

$$K_{\text{con}} = 3.05 \times 10^{-6} * (C_{\text{mdi}})^{0.885}$$

Where:

K_{gas} represents the emission factor for gas valves in kg/year-item.

K_{liq} represents the emission factor for liquid valves in kg/year-item.

K_{pump} represents the emission factor for liquid pumps in kg/year-item.

K_{con} represents the emission factor for connectors in kg/year-item.

For Gas Valves the emissions can then be estimated from the following expression:

$$L_{\text{gv}} = K_{\text{gas}} * n_{\text{gv}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{gv} represents the annual losses from liquid valves in lb/yr.

n_{gv} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating.

For Liquid Valves the emissions can then be estimated from the following expression:

$$L_{\text{liq}} = K_{\text{liq}} * n_{\text{liq}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{liq} represents the annual losses from liquid valves in lb/yr.

n_{liq} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

For liquid Pumps the emissions can then be estimated from the following expression:

$$L_{\text{pump}} = K_{\text{pump}} * n_{\text{pump}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{pump} represents the annual losses from liquid valves in lb/yr.

n_{pump} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

For Connectors the emissions can then be estimated from the following expression:

$$L_{\text{con}} = K_{\text{con}} * n_{\text{con}} * K_{\text{mdi}} * t_{\text{pr}}$$

L_{con} represents the annual losses from liquid valves in lb/yr.

n_{con} represents the number of liquid valves.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{pr} is the total time in hours/year that the process is operating

Total Emissions can then be estimated from the following expression:

$$E_{tot} = L_{gas} * L_{liq} * L_{pump} * L_{con}$$

5.0 Calculating Emissions from Enclosed Processes (Based on Cavity Size)

To estimate emissions from enclosed processes when the volume of the mold is known or can be determined. The emissions from the process will correspond to the total volume of air displaced from the molding operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume of the mold cavity, the number of pieces produced per year and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}$$

Where:

L_C represents the emissions from the enclosed process in lb/year.

V_{air} is the annual volume of displaced air in ft³/year.

T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.

VP_{mdi} is the vapor pressure of MDI in mm Hg. at process temperature.

$M_w = 250.26$ (this is the molecular weight of MDI).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

6.0 Calculating Emissions from Enclosed Processes (Based on Foam Density)

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year. For this situation the emissions can be estimated from:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}$$

Where

L_{fd} represents the emissions from the enclosed process in lb/year.

V_{air} is the annual volume of displaced air in ft³/year.

T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.

VP_{mdi} is the vapor pressure of MDI in mm Hg. at process temperature.

$M_w = 250.26$ (this is the molecular weight of MDI).

K_{mdi} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

7.0 Calculating Emissions from Open Processes (Continuous Processes)

To estimate emissions from open processes such as boardstock production. For this situation it is assumed that MDI will migrate from all exposed surfaces. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the “tack-free” time and the exposed surface area.

The calculation methodology involves four steps:

1. Determine partial pressure of MDI at “tack-free” time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u^{0.78}) * SA * t_{TF} * K_{mdi}$$

Where

W represents the evaporation losses from the open process in gr/day.

VP_{mdi} is the vapor pressure of MDI in atm. at process temperature.

T_{proc} is the process temperature in °K. This is the maximum temperature of the MDI “tack free” time.

$M_w = 250.26$ (this is the molecular weight of MDI).

u is the airflow speed in m/sec. This is the airflow in the vicinity of the process.

SA is the exposed surface area in M². This is the exposed surface area per day. For boardstock production, the surface area can be determined from the dimensions of the board.

t_{TF} is the “tack-free” time in seconds. The default value is 5 sec.

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

8.0 Calculating Emissions from Mixing/Blending/Filling Process

Calculating Stack Emissions

Estimating emissions from a mixing/blending operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst-case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI. Loses will be experienced when the reactor or blend tank is filled with the MDI/PMDI mixture and when the reactor/blend tank is emptied into containers. Loses will be based upon the volume of MDI/PMDI charged to the reactor/blend tank and the volume of containers filled with the blend.

The filling losses can be estimated from the following equation:

$$L_{fill} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blend}$$

Where:

L_{fill} represents the emissions from the filling operation in lbs/year

V_{air} is the annual volume of displaced air in $ft^3/year$

T_{fill} is the temperature the material is charged or filled at in $^{\circ}K$

VP_{MDI} is the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_w is the molecular weight of MDI (250.26)

K_{MDI} is the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blend} is the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blend} is 1.

9.0 Calculating Emissions from a Spray Booth Operation

The exhaust airflow rate and the temperature at which the spray coating is carried out will govern the emissions associated with a spray booth operation. If the concentration of the exit gas is not known, the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$L_{sp} = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_w * k_{MDI} * t_{sp}$$

Where:

L_{sp} represents the emissions in lb/year for spray coating operations.

V_{air} is the exhaust airflow rate in ft^3/min .

T_{sp} is the spray temperature in $^{\circ}K$.

C_{mdi} is the MDI concentration, in ppmv, in the exhaust air.

M_w is the molecular weight of MDI (250.26).

K_{MDI} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{sp} is the total time in hours/year that spray coating is occurring.

$$C_{mdi} = (VP_{MDI}/760) \times 10^6$$

$$VP_{MDI} = \text{MDI vapor pressure at exhaust temperature.}$$

9. Spills:

A liquid chemical accidentally spilled onto the ground may spread out over an area, vaporize and cause an air emission. Such accidental releases must be reported under section 313. Evaporative losses from spills (and other open processes) depend on a number of factors including:

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area
4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$Q_R = (0.284/82.05) * (u)^{0.78} * A_{\text{spill}} * (VP_{\text{MDI}}/T_{\text{spill}}) * (M_W)^{2/3} * K_{\text{mdi}}$$

Where:

Q_R represents the evaporation rate in lb/min.

u is the airflow speed in m/sec. This is the airflow in the vicinity of the process.

A_{spill} is the area of the spilled material in ft^2

VP_{mdi} is the vapor pressure of MDI in mm Hg . at the spill temperature.

T_{spill} is the average evaporation temperature in $^{\circ}\text{K}$.

M_W is the molecular weight of MDI (250.26).

K_{mdi} is an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (Q_R) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$L_{\text{spill}} = Q_R * t_{\text{spill}} * (60)$$

Where:

L_{spill} represents the evaporation losses resulting from the spill in lb.

Q_R represents the evaporation rate in lb/min.

t_{spill} represents the time that the spill is on the ground in hours.

Appendix E – SIC Codes

Who Will Report to TRI Starting in the 1998 Reporting Year?

Metal mining (SIC code 10, except for SIC codes 1011,1081, and 1094)
Coal mining (SIC code 12, except for 1241 and extraction activities)
Electrical utilities that combust coal and/or oil (SIC codes 4911, 4931, and 4939) Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous waste treatment and disposal facilities (SIC code 4953)
Chemicals and allied products wholesale distributors (SIC code 5169)
Petroleum bulk plants and terminals (SIC code 5171)
Solvent recovery services (SIC code 7389)

SIC Industry Group:

10	Metal Mining (except 1011,1081, and 1094)
12	Coal Mining (except 1241)
20	Food
21	Tobacco
22	Textiles
23	Apparel
24	Lumber and Wood
25	Furniture
26	Paper
27	Printing and Publishing
28	Chemicals
29	Petroleum and Coal
30	Rubber and Plastics
31	Leather
32	Stone, Clay, and Glass
33	Primary Metals
34	Fabricated Metals
35	Machinery (excluding electrical)
36	Electrical and Electronic Equipment
37	Transportation Equipment
38	Instruments
39	Miscellaneous Manufacturing

1000 Metal Mining

1021	Copper Ores
1031	Lead and Zinc Ores
1041	Gold Ores
1044	Silver Ores
1061	Ferroalloy Ores Except Vanadium
1099	Miscellaneous Metal Ores, n.e.c.

1200 Coal Mining (Except 1241)

1221	Bituminous Coal and Lignite Surface Mining
1222	Bituminous Coal Underground Mining
1231	Anthracite Mining

2000 Food and Kindred Products

- 2011 Meat packing plants.
- 2013 Sausages and other prepared meat products.
- 2015 Poultry slaughtering and processing.
- 2021 Creamery products.
- 2022 Natural, processed, and imitation cheese
- 2023 Dry, condensed, and evaporated dairy products.
- 2024 Ice cream and frozen desserts.
- 2026 Fluid milk.
- 2035 Pickled fruits and vegetables, vegetable sauces and seasonings, and salad dressings
- 2037 Frozen fruits, fruit juices, and vegetables.
- 2038 Frozen specialties, not elsewhere classified.

- 2041 Flour and other grain mill products.
- 2043 Cereal breakfast foods.
- 2044 Rice milling.
- 2045 Prepared flour mixes and doughs.
- 2046 Wet corn milling.
- 2047 Dog and cat food
- 2048 Prepared feeds and feed ingredients for animals and fowls except dogs and cats
- 2051 Bread and other bakery products, except cookies and crackers.
- 2052 Cookies and crackers .
- 2053 Frozen bakery products except bread.

- 2061 Cane sugar, except refining.
- 2062 Cane sugar refining.
- 2063 Beet sugar
- 2064 Candy and other confectionery products
- 2066 Chocolate and cocoa products.
- 2067 Chewing gum
- 2068 Salted and roasted nuts
- 2074 Cottonseed oil mills
- 2075 Soybean oil mills
- 2076 Vegetable oil mills, n.e.c.
- 2077 Animal and marine fats and oils
- 2079 Shortening, table oils, margarine, and other edible fats and oils, n.e.c.
- 2082 Malt beverages.
- 2084 Wines, brandy, and brandy spirits.
- 2085 Distilled and blended liquors
- 2086 Bottled and canned soft drinks and carbonated waters
- 2087 Flavoring extracts and flavoring syrups, not elsewhere classified.
- 2091 Canned and cured seafoods.
- 2092 Prepared fresh or frozen fish or seafoods
- 2095 Roasted coffee.
- 2096 Potato chips, corn chips, and similar.
- 2097 Manufactured ice.
- 2098 Macaroni, spaghetti vermicelli, and noodles
- 2099 Food preparations, not elsewhere classified.

2100 Tobacco products.

- 2111 Cigarettes.

- 2121 Cigars.
- 2131 Chewing and smoking tobacco and snuff.
- 2141 Tobacco stemming and redrying.

2200 Textile Mill Products.

- 2211 Broadwoven fabric mills, cotton.
- 2221 Broadwoven fabric mills, manmade fiber, and silk
- 2231 Broadwoven fabric mills, wool (including dyeing and finishing)
- 2241 Narrow fabric and other small wares mills: cotton, wool, silk, and manmade fiber.
- 2251 Women's full-length and knee-length hosiery, except socks.
- 2252 Hosiery, n.e.c.
- 2253 Knit outerwear mills.
- 2254 Knit underwear and nightwear mills
- 2257 Weft knit fabric mills
- 2258 Lace and warp knit fabric mills
- 2259 Knitting mills, n.e.c.
- 2261 Finishers of broadwoven fabrics of cotton
- 2262 Finishers of broadwoven fabrics of manmade fiber and silk.
- 2269 Finishers of textiles, n.e.c.
- 2273 Carpets and rugs.
- 2281 Yarn spinning mills.
- 2282 Yarn texturizing, throwing, twisting, and winding mills
- 2284 Thread mills
- 2295 Coated fabrics, not rubberized
- 2296 Tire cord and fabrics
- 2297 Nonwoven fabrics
- 2298 Cordage and twine
- 2299 Textile goods, n.e.c.

2300 Apparel and other Finished Products Made from Fabrics and Similar Materials

- 2311 Men's and boys' suits coats, and overcoats.
- 2321 Men's and boys' shirts except work shirts.
- 2322 Men's and boys' underwear and nightwear.
- 2323 Men's and boys' neckwear.
- 2325 Men's and boys' separate trousers and slacks.
- 2326 Men's and boys' work clothing.
- 2329 Men's and boys' clothing, not elsewhere classified.
- 2331 Women's, misses', and juniors' blouses and shirts.
- 2335 Women's, misses', and juniors' dresses.
- 2337 Women's, misses', and juniors' suits, skirts, and coats.
- 2339 Women's, misses', and juniors' outerwear, not elsewhere classified.
- 2341 Women's, misses', children's, and infants' underwear and nightwear.
- 2342 Brassieres, girdles, and allied garments.
- 2353 Hats, caps, and millinery.
- 2361 Girls', children's, and infants' dresses, blouses, and shirts.
- 2369 Girls', children's, and infants' outerwear, not elsewhere classified.
- 2385 Waterproof outerwear.
- 2386 Leather and sheep lined clothing
- 2387 Apparel belts.
- 2389 Apparel and accessories, not elsewhere classified.
- 2391 Curtains and draperies.
- 2392 House furnishings, except curtains and draperies.

- 2393 Textile bags.
- 2394 Canvas and related products
- 2395 Pleating, decorative and novelty stitching, and tucking for the trade.
- 2396 Automotive trimmings, apparel findings, and related products.
- 2397 Schiffi machine embroideries
- 2399 Fabricated textile products, not elsewhere classified.

2400 Lumber and Wood Products, Except Furniture

- 2411 Logging
- 2421 Sawmills and planing mills, general.
- 2426 Hardwood dimension and flooring
- 2429 Special product sawmills, n.e.c.
- 2431 Millwork.
- 2434 Wood kitchen cabinets.
- 2435 Hardwood veneer and plywood.
- 2436 Softwood veneer and plywood
- 2439 Structural wood members
- 2441 Nailed and lock corner wood boxes and shooks
- 2448 Wood pallets and skids.
- 2449 Wood containers
- 2451 Mobile homes.
- 2452 Prefabricated wood buildings and components
- 2491 Wood preserving.
- 2493 Reconstituted wood products
- 2499 Wood products, not elsewhere classified.

2500 Furniture and fixtures

- 2511 Wood household furniture, except upholstered.
- 2512 Wood household furniture, upholstered.
- 2514 Metal household furniture.
- 2515 Mattresses foundations, and convertible beds.
- 2517 Wood television, radio, phonograph, and sewing machine cabinets.
- 2519 Household furniture, not elsewhere classified.
- 2521 Wood office furniture.
- 2522 Office furniture except wood.
- 2531 Public building and related furniture.
- 2541 Wood office and store fixtures, partitions, shelving, and lockers.
- 2542 Office and store fixtures, partitions, shelving, and lockers, except wood.
- 2591 Drapery hardware and window blinds and shades.
- 2599 Furniture and fixtures, not elsewhere classified.

2600 Paper and Allied Products.

- 2611 Pulp mills.
- 2621 Paper mills.
- 2631 Paperboard mills.
- 2652 Setup paperboard boxes.
- 2653 Corrugated and solid fiber boxes.
- 2655 Fiber cans, tubes drums, and similar products.
- 2656 Sanitary food containers, except folding
- 2657 Folding paperboard boxes, including sanitary.

- 2671 Packaging paper and plastics film, coated and laminated.
- 2672 Coated and laminated paper, not elsewhere classified.
- 2673 Plastics, foil, and coated paper bags.
- 2674 Uncoated paper and multi-wall bags.
- 2676 Sanitary paper products.
- 2677 Envelopes.
- 2678 Stationery, tablets, and related products.
- 2679 Converted paper and paperboard products, not elsewhere classified.

2700 Printing, Publishing, and Allied Industries.

- 2711 Newspapers: publishing, or publishing and printing.
- 2731 Books: publishing, or publishing and printing.
- 2732 Book printing.
- 2741 Miscellaneous publishing.
- 2752 Commercial printing, lithographic.
- 2754 Commercial printing, gravure.
- 2759 Commercial printing, not elsewhere classified.
- 2761 Manifold business forms.
- 2771 Greeting cards
- 2782 Blank books, loose-leaf binders and devices.
- 2789 Bookbinding and related work
- 2291 Typesetting
- 2796 Plate making and related services.

2800 Chemicals and Allied Products.

- 2812 Alkalies and chlorine
- 2813 Industrial gases.
- 2816 Inorganic gases
- 2819 Industrial inorganic chemicals, not elsewhere classified.
- 2821 Plastics materials, synthetic resins, and non-vulcanizable elastomers.
- 2822 Synthetic rubber (vulcanizable elastomers).
- 2823 Cellulosic manmade fibers
- 2824 Manmade organic fibers, except cellulosic
- 2833 Medicinal chemicals and botanical products.
- 2834 Pharmaceutical preparations.
- 2835 In vitro and in vivo diagnostic substances.
- 2836 Biological products, except diagnostic substances.
- 2841 Soap and other detergents, except specialty cleaners.
- 2842 Specialty cleaning, polishing, and sanitation preparations.
- 2843 Surface active agents, finishing agents, sulfonated oils, and assistants
- 2844 Perfumes, cosmetics, and other toilet preparations.
- 2851 Paints, varnishes, lacquers, enamels, and allied products.
- 2860 Industrial organic chemicals.
- 2861 Gum and wood chemicals
- 2865 Cyclic organic crudes and intermediates, and organic dyes and pigments.
- 2869 Industrial organic chemicals, not elsewhere classified.
- 2873 Nitrogenous fertilizers.
- 2874 Phosphatic fertilizers
- 2875 Fertilizers, mixing only
- 2879 Pesticides and agricultural chemicals, not elsewhere classified.

2891 Adhesives and sealants.
2892 Explosives
2893 Printing ink
2894 Carbon black
2899 Chemicals and chemical preparations, not elsewhere classified.

2900 Petroleum Refining and Related Industries.

2911 Petroleum refining.
2951 Asphalt paving mixtures and blocks.
2952 Asphalt felts and coatings.
2992 Lubricating oils and greases.
2999 Products of petroleum and coal, n.e.c.

3000 Rubber and Miscellaneous Plastics Products.

3011 Tires and inner tubes
3021 Rubber and plastic footwear
3052 Rubber and plastics hose and belting
3053 Gaskets, packing, and sealing devices.
3061 Molded, extruded and lathe cut mechanical rubber products
3069 Fabricated rubber products, not elsewhere classified.
3081 Unsupported plastics film and sheet.
3082 Unsupported plastics profile shapes.
3083 Laminated plastics plate, sheet, and profile shapes.
3084 Plastics pipe.
3085 Plastics bottles.
3086 Plastics foam products.
3087 Custom compounding of purchased plastics resin.
3088 Plastics plumbing fixtures.
3089 Plastics products, not elsewhere classified.

3100 Leather and Leather Products.

3111 Leather tanning and finishing
3131 Boot and shoe cut stock and findings.
3142 House slippers.
3143 Men's footwear, except athletic.
3144 Women's footwear, except athletic.
3149 Footwear, except rubber, not elsewhere classified.
3151 Leather gloves and mittens.
3161 Luggage.
3171 Women's handbags and purses.
3172 Personal leather goods, except women's handbags and purses.
3199 Leather goods, n.e.c.

3200 Stone, Clay, Glass, and Concrete Products.

3211 Flat glass.
3221 Glass containers
3229 Pressed and blown glass and glassware, n.e.c.
3231 Glass products, made of purchased glass.
3241 Cement, hydraulic.

- 3251 Brick and structural clay tile
- 3253 Ceramic wall and floor tile
- 3255 Clay refractories
- 3261 Vitreous china plumbing fixtures and china and earthenware fittings and bathroom accessories.
- 3262 Vitreous china table and kitchen articles
- 3263 Fine earthenware (white ware) table and kitchen articles
- 3264 Porcelain electrical supplies
- 3269 Pottery products, not elsewhere classified.

- 3271 Concrete block and brick.
- 3272 Concrete products, except block and brick.
- 3273 Ready-mixed concrete.
- 3274 Lime.
- 3275 Gypsum products.
- 3281 Cut stone and stone products.

- 3291 Abrasive products
- 3292 Asbestos products
- 3295 Minerals and earths, ground or otherwise treated.
- 3296 Mineral wool.
- 3297 Non-clay refractories
- 3299 Nonmetallic mineral products, n.e.c.

3300 Primary Metal Industries.

- 3312 Steel works, blast furnaces (including coke ovens), and rolling mills.
- 3313 Electrometallurgical products, except steel
- 3315 Steel wiredrawing and steel nails and spikes
- 3317 Steel pipe and tubes.
- 3321 Gray and ductile iron foundries
- 3322 Malleable iron foundries
- 3324 Steel investment foundries
- 3325 Steel foundries, n.e.c.
- 3331 Primary smelting and refining of copper
- 3334 Primary production of aluminum
- 3339 Primary smelting and refining of nonferrous, except copper and aluminum
- 3341 Secondary smelting and refining of nonferrous metals.
- 3351 Rolling, drawing, and extruding of nonferrous metals.
- 3353 Aluminum sheet, plate, and foil.
- 3354 Aluminum extruded products.
- 3355 Aluminum rolling and drawing, n.e.c.
- 3356 Rolling, drawing, and extruding of nonferrous metal, except copper and aluminum
- 3357 Drawing and insulating of nonferrous wire
- 3363 Aluminum die-casting
- 3364 Nonferrous die-casting, except aluminum
- 3365 Aluminum foundries.
- 3366 Copper foundries
- 3369 Nonferrous foundries, except aluminum and copper.
- 3398 Metal heat-treating.
- 3399 Primary metal products, not elsewhere classified.

3400 Fabricated Metal Products, Except Machinery and Transportation Equipment.

3411 Metal cans.
3412 Metal shipping barrels, drums, kegs, and pails.
3421 Cutlery.
3423 Hand and edge tools, except machine tools and handsaws.
3425 Handsaw and saw blades
3429 Hardware, not elsewhere classified.
3431 Enameled iron and metal sanitary ware
3432 Plumbing fixture fittings and trim
3433 Heating equipment, except electric and warm air furnaces.
3441 Fabricated structural metal.
3442 Metal doors, sash, frames, molding, and trim.
3443 Fabricated plate work (boiler shops).
3444 Sheet metal work.
3446 Architectural and ornamental metal work.
3448 Prefabricated metal buildings and components
3449 Miscellaneous structural metal work.
3450 Screw machine products, and bolts, nuts, screws, rivets, and washers.
3451 Screw machine products
3452 Bolts, nuts, screws, rivets, and washers.
3462 Iron and iron forgings
3463 Nonferrous forgings
3465 Automotive stampings
3468 Crown and closures
3469 Metal stampings, not elsewhere classified.
3471 Electroplating, plating, polish anodizing and coloring.
3479 Coating, engraving and allied services, n.e.c.
3482 Small arms ammunition
3483 Ammunition, except for small arms
3484 Small arms
3489 Ordnance and accessories, n.e.c.

3491 Industrial valves
3492 Fluid power valves and hose fittings
3493 Steel springs, except wire
3494 Valves and pipe, fittings, not else where classified.
3495 Wire springs.
3496 Miscellaneous fabricated wire products.
3497 Metal foil and leaf
3498 Fabricated pipe and pipefittings.
3499 Fabricated metal products, not elsewhere classified.

3500 Industrial and Commercial Machinery and Computer Equipment.

3511 Steam, gas and hydraulic turbines, and turbine generator set units
3519 Internal combustion engines, n.e.c.
3523 Farm machinery and equipment
3524 Lawn and garden tractors and home lawn and garden equipment
3531 Construction machinery and equipment.
3532 Mining machinery and equipment, except oil and gas field machinery and equipment.
3534 Elevators and moving stairways.
3535 Conveyors and conveying equipment.
3536 Overhead traveling cranes, hoists, and monorail systems

3537 Industrial trucks, tractors, trailers, and stackers
3541 Machine tools, metal-cutting types.
3542 Machine tools, metal-forming types
3543 Industrial patterns
3544 Industrial Patterns
3544 Special dies and tools, die sets, jigs and fixtures, and industrial molds.
3545 Cutting tools, machine tool accessories, and machinists' precision measuring devices.
3546 Power driven hand tools.
3547 Rolling mill machinery and equipment.
3548 Electric and gas welding and soldering equipment
3549 Metal working machinery, n.e.c.
3552 Textile machinery
3553 Woodworking machinery
3554 Paper industry machinery
3555 Printing trades machinery and equipment.
3556 Food products machinery
3559 Special industrial machinery, n.e.c.
3561 Pumps and pumping equipment
3562 Ball and roller bearings.
3563 Air and gas compressors.
3564 Industrial and commercial fans and blowers and air purification equipment.
3565 Packaging equipment
3566 Speed changers, industrial high speed drives, and gears
3567 Industrial process furnaces and ovens
3568 Mechanical power transmission equipment, not elsewhere classified.
3569 General industrial machinery and equipment, not elsewhere classified.
3571 Electronic computers.
3572 Computer storage devices.
3575 Computer terminals
3577 Computer peripheral equipment, not elsewhere classified.
3578 Calculating and accounting machines, except computers
3579 Office machines, not elsewhere classified.
3581 Automatic vending machines
3582 Commercial laundry, dry cleaning, and pressing machines
3585 Air-conditioning and warm air heating equipment and commercial and industrial refrigeration equipment.
3586 Measuring and dispensing pumps
3589 Service industry machinery, not elsewhere classified.
3592 Carburetors, pistons, piston rings, and valves.
3593 Fluid power cylinders and actuators
3594 Fluid power pumps and motors
3596 Scales and balances, except laboratory.
3599 Industrial and commercial machinery and equipment, elsewhere classified.

3600 Electronic and other Electrical Equipment and Components, Except Computer Equipment.

3612 Power, distribution, and specialty transformers.
3613 Switchgear and switchboard apparatus.

3621 Motors and generators.
3624 Carbon and graphite products.
3625 Relays and industrial controls.
3629 Electrical industrial apparatus, not elsewhere classified.

- 3630 Household appliances.
- 3631 Household cooking equipment
- 3632 Household refrigerators and home and farm freezers
- 3633 Household laundry equipment
- 3634 Electrical house wares and fans
- 3635 Household vacuum cleaners
- 3639 Household appliances, not elsewhere classified.

- 3641 Electric lamp bulbs and tubes.
- 3643 Current-carrying wiring devices.
- 3644 Non-current-carrying wiring devices.
- 3645 Residential electric lighting fixtures.
- 3646 Commercial, industrial, and institutional electric lighting fixtures.
- 3647 Vehicular lighting equipment
- 3648 Lighting equipment, not elsewhere classified.
- .
- 3651 Household audio and video equipment.
- 3652 Phonograph records and pre-recorded audiotapes and disks.
- 3661 Telephone and telegraph apparatus.
- 3663 Radio and television broadcasting and communications equipment.
- 3669 Communications equipment, not elsewhere classified.
- 3671 Electron tubes
- 3672 Printed circuit boards.
- 3674 Semiconductors and related devices.
- 3675 Electronic capacitors
- 3677 Electronic coils, transformers and other inductors.
- 3678 Electronic connectors.
- 3679 Electronic components, not elsewhere classified.
- 3691 Storage batteries
- 3692 Primary batteries, dry and wet.
- 3694 Electrical equipment for internal combustion engines.
- 3695 Magnetic and optical recording media
- 3699 Electrical machinery, equipment, and supplies, n.e.c.

- 3700 Transportation Equipment.**

- 3711 Motor vehicles and motor vehicle equipment.
- 3713 Truck and bus bodies.
- 3714 Motor vehicle parts and accessories.
- 3715 Truck trailers
- 3716 Motor homes
- 3721 Aircraft.
- 3724 Aircraft engines and parts
- 3728 Aircraft parts and auxiliary equipment, not elsewhere classified.
- 3731 Ship building and repairing.
- 3732 Boat building and repairing.
- 3743 Railroad equipment
- 3751 Motorcycles, bicycles and parts
- 3761 Guided missiles and space vehicle
- 3764 Guided missile and space vehicle propulsion units and propulsion parts
- 3769 Guided missile and space vehicle parts and auxiliary equipment, n.e.c.
- 3792 Travel trailers and campers.
- 3795 Tanks and tank components

3799 Transportation Equipment, n.e.c.

3800 Measuring, Analyzing, and Controlling Instruments; Photographic, Medical, and Optical Goods, Watches and Clocks.

3812 Search, detection, navigation, guidance, aeronautical, and nautical systems instruments, and equipment.
3821 Laboratory apparatus and furniture.
3822 Automatic controls for regulating residential and commercial environments and appliances.
3823 Industrial instruments for measurement, display, and control of process variables; and related products.
3824 Totalizing fluid meters and counting devices.
3825 Instruments for measuring and testing of electricity and electrical signals.
3826 Laboratory analytical instruments
3827 Optical instruments and lenses
3829 Measuring and controlling devices not elsewhere classified.
3841 Surgical and medical instruments and apparatus.
3842 Orthopedic, prosthetic, and surgical appliances and supplies.
3843 Dental equipment and supplies.
3844 X-ray apparatus and tubes and related irradiation apparatus.
3845 Electro medical and electrotherapeutic apparatus.
3851 Ophthalmic goods.
3861 Photographic equipment and supplies.
3873 Watches, clocks, clockwork operated devices, and parts.

3900 Miscellaneous Manufacturing Industries.

3911 Jewelry, precious metal.
3914 Silverware, plated ware, and stainless steel ware.
3915 Jewelers' findings and materials, and lapidary work.
3931 Musical instruments.
3942 Dolls and stuffed toys.
3944 Games, toys and children's vehicles; except dolls and bicycles
3949 Sporting and athletic goods, not elsewhere classified.
3951 Pens, mechanical pencils, and parts.
3952 Lead pencils, crayons, and artists' materials.
3953 Marking devices.
3955 Carbon paper and ink ribbons
3961 Costume jewelry and costume novelties, except precious metal.
3965 Fasteners, buttons, needles, and pins.
3991 Brooms and brushes.
3993 Signs and advertising specialties.
3995 Burial caskets.
3999 Manufacturing industries not elsewhere classified.

4900 Electric, Gas, and Sanitary Services (limited to 4911, 4931, 4939, and 4953)

4911 Electric Services (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)
4931 Electric and Other Services Combined (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)
4939 Combination utilities, n.e.c. (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)
4953 Refuse Systems (limited to facilities regulated under the RCRA Subtitle C, 42 U.S.C. section

6921 *et seq.*)

5100 Wholesale Trade -Nondurable Goods(Limited to 5169 and 5171)

5169 Chemical and allied Products, n.e.c.

5171 Petroleum Terminals and bulk stations

7300 Business Services (limited to 7389)

7389 Business services, n.e.c. (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis)

Appendix F – Computer Printouts

A software package “**MDI Emissions Estimator**”, developed by the Alliance for the Polyurethane Industry (API), calculates emissions for the following applications:

1. Working Losses from Storage Tanks
2. Breathing Losses from Storage Tank
3. Fugitive Emissions from Process Area
4. Enclosed Processes Based on Cavity Size
5. Enclosed Processes Based on Foam Density
6. Open Processes Based on a Continuous Process

The processes presented using the “MDI EMISSIONS ESTIMATOR” are:

1. Appliance-Refrigerator
2. Appliance-Truck
3. Automotive
4. Boardstock
5. Boats
6. Door Insulation
7. Doors
8. Laminator Boardstock
9. Mobile Homes
10. Packaging
11. Rebond
12. Water Heater

Application: Appliances

Frozen Frig Inc. operates four lines 24 hours a day 365 days a year. Line I and Line II produce at a rate of 100 doors per hour, each consuming an average of 123 lbs. MDI/PMDI per hour. Line III produces 150 frames per hour, consuming 12,226 lbs. MDI/PMDI per hour. Line IV produces 100 frames per hour, consuming 1,343 lbs. MDI/PMDI per hour. The amounts of MDI/PMDI consumed annually for each line are 1.08, 1.08, 10.74, and 11.8 million pounds respectively. The MDI/PMDI is stored in a 50,000-gallon storage tank that is maintained at 68 °F.

The process is run at 85 °F. The size of the cavity changes but the density remains at 2.0 lbs/ft³. Each Line has its own handling system that is enclosed in a 2,000 ft³ room that undergoes 5 air exchanges/hour. Measured concentration of MDI was 1 ppb. Calculate the total emission for the facility.

Application: Appliance – Truck

Fleetwood Truck manufactures tractor trailer bodies. It uses a MDI/PMDI mixture along with a polyol to inject into the ceiling, floor and wall cavities to form insulation. The facility receives 5.440 million pounds of MDI/PMDI (52% MDI) annually and stores it in a 10,000 gallon storage tank that is maintained at 78 °F. The trailer bodies are worked on in a closed area. Total consumption of blend is 10.5 million pounds with a targeted foam density of 2.25 lbs./cu.ft. The temperature of the blend injected into the cavities is 78 °F. Calculate total emissions for a facility that operates 16 hours a day 250 days a year.

Application: Automotive

Allied Motors produces bumpers from economy -size to full-size vehicles. It uses 1.5 million pounds of MDI/PMDI that is stored in a 6,000 gallons storage tank maintained at 77 °F. The material is transferred to a 1,500 gallons Day Tank and is mixed with a polyol blend to produce bumpers with a foam density of 2.0 lbs./cu.ft. The process is carried out in an area that is 20-ft. wide 50-ft. long and 20-ft. high. Monitoring data showed an annual concentration of 3ppb for MDI. Calculate total emissions for a facility that operates 16 hours a day 250 days a year.

Application: Boardstock

General Paper operates a facility that produces laminated boardstock at a rate of 6.1 ft./min. The annual consumption of MDI/PMDI is 1.3 million pounds a year that is stored in a 5,000 gallon storage tank at 77 °F. The material is transferred to a 200 gallon Day Tank where it is then mixed in a mixing head with a polyol bend and applied onto a boardstock backing. The boardstock is processed at 83°C with a “tack-time” of 5 seconds. The board is cut into 4 ft. x 8 ft. sections that are 2 inches thick. The air flow is kept constant at 5 M/second. size of the operating area is 11,300 M³ and tests indicate 1 ppb of MDI average annual concentration. Calculate the total emissions for the facility that operates 16 hours/day 250 days/year.

Application: Boats

Vacation Boat manufactures boats that are injected, through static mixing nozzles, a mixture of resin, PMDI, MDI, and blowing agent into the space between the inner and outer hulls by way of a hull-stiffening forms. This produces rigid urethane foam that provides buoyancy and insulation for the craft. The foam mixture is supplied to the boat manufactures via 2500-pound totes and these totes are stored in-doors where the temperature remains constant. The foam mixture is injected at a “tack free” or “string” time temperature of 160°F (70°C). There are 18 different boat models manufactured ranging from 12-16ft. “runabouts” to 100-150ft. yachts. The majority of boat manufactures produce boats ranging from 25-30 ft. in length and anywhere from 25-30 boats per day. The typical production is a boat 25ft in length, 27 boats per day operating 24 hours a day, 250 days a year. The foam is 2” thick, has an average density of 1.8 lbs./cu.ft. and the surface area of the hull is 350 ft.². Fresh air is pulled across the work area and exhausted through hull-stiffening stack. The operation is performed in an area that is 100ft. by 100 ft. by 40 ft. and has a MDI concentration of 0.001 PPM. Calculate the stack emissions.

Application: Door Insulation

Garage Doors Inc. produces a standard door at a rate of 340 doors per hour. The size of the door is 7 feet high 36 inches wide and two inches thick. Each door is injected with 5.4 lbs. of a 1/1 resin to MDI/PMDI mixture. The temperature of the mixture is 80°F. The facility receives 2.7 million pounds a year that is stored in an outdoor tank at 77°F. The storage tank is exposed to an average daily temperature range of 18 °F. Material before being processed is transferred to a 50 gallon Day Tank at 77 °F. The process is carried out in an area that measures 2,800 M³. Calculate the total emissions for the facility that operates 16 hours/day 250 days/year.

Application: Doors

The TRUE DOORS, Inc. manufactures insulated doors. They receive a 50% mixture of MDI/PMDI by rail-car. The MDI/PMDI is stored in a 60,000 gallon storage tank that is subject to daily temperature changes of 10 °K, while the average daily temperature for the year is 55.55 °F (12.53 °C). The storage tank is filled 45 times a year. The production line produces at a rate of 340 doors per hour. The size of the door is 7 feet high 36 inches wide and two inches thick. Each door is injected with 5.4 lbs. of a 1/1 resin to Diisocyanate blend. The MDI/PMDI mixture is transferred from storage to 500 gallon Day Tank. The temperature of the foam inside the door is 80 °F. process area is approximately 98,870-ft³ Calculate the facility’s emissions.

Application: Laminator Board

The Perfect Products Company produces laminated boardstock 24 hours a day 365 days a year. It has in operation two lines: Line A uses 52 lbs./min (27,331,200 lbs./yr.) and Line B uses 16.7 lbs./min (8,760,00 lbs./yr.) which is stored at a constant 75 °F in a 2-5,000 gallon storage tanks. The mixture is a ratio of 1/1 Polyol to ISO and the isocyanate is 50% MDI/MDI mixture. Line A produces 24 pieces/min, each piece has covers an area of 16 ft² with a thickness of 2 inches and a foam density of 1.0015 lbs./ft³. Line B produces 8 pieces/min. Each piece covers an area of 16 ft², 2 inches thick, and a foam density of 0.781 lbs./ft³. Both lines operate at a temperature of 140 °K. Line A and line B are each located in an area that is 16 ft wide x 50ft long x 15 ft high (12,000ft³). Calculate total emissions.

Application: Mobile Homes

Home-On-Wheels produces mobile homes that are insulated with MDI-based rigid foam. The facility uses a total of 2,000,000 pounds of MDI/PMDI feedstock that comprise a rigid foam “system.” The “system” includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank at 25°C. MDI is transferred to 550-lb. day tank as needed. The day tank is stored indoors. MDI is pumped directly from the day tanks to the foam mixer head where the blend is injected in the ceiling, floor, and wall cavities. The MDI/PMDI mixture is combined in a 1/1 ratio with a polyol blend at 25°C. The operation is carried out in a n area that is 30 ft wide x 50 ft. long x 20 ft. high that average annual monitoring measured 3 ppb of MDI concentration. It may be difficult to estimate the cavity size of each mobile home that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the insulation and the total quantity of foam feedstock that are used in the year. Calculate total emissions for the facility that operates 8 hours/day 250 days/year.

Application: Packaging

Shipment Express uses 10 million pounds of Polyol/MDI/PMDI blend for the packaging of machine parts to ship to Europe. The MDI/PMDI is stored in a 10,000 gallon storage tank and maintained at 25 °C. Polyol/MDI/PMDI blend in injected into the containers inside a assembly room (50 ft. wide x 50 ft. long x 15 ft. high) that is vented through the roof. Since the container size varies, the targeted density of the foam is 1.5 lbs./ ft³. Calculate total emissions for a facility that operates 8 hours/day 250 days/year.

Application: Rebond

A & S Carpet produces a carpet under-lay using a binder mixture containing polyol/MDI that is added to a closed reactor system already charged with fluff (cut foam). Live steam is injected into the mixture at 60 psig for a period of 2.5 minutes. Steam is being exhausted from bottom and top of reactor through blower system. Binder mixture contains 40% MDI. Reactor produces a log that is 5' diameter and 10' high. System averages 10 logs per hour using 60 pounds of binder per log. The facility receives 1.334 million pounds of a MDI/PMDI mixture (40% MDI) that is stored in a 10,000 gallon storage tank that is exposed to a 18 °F daily temperature range. Calculate the total emission for the facility that operates 24 hours/day 250 days/year.

Application: Water Heaters

Edison Heaters produces water heaters that are insulated with MDI-based rigid foam. The facility uses a total of 6,000,000 pounds of feedstocks that comprise of a rigid foam “system.” The “system” includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank. The tanks are filled 50 times each year. The temperature of the

MDI storage tank does not exceed 25°C and is exposed to a daily temperature that drops 20 °F a day. MDI is transferred to a 400lb. day tank as needed. The day tanks are stored indoors and temperature is maintained at 25°C. The MDI is pumped directly from the day tanks to the foam mixer head. The density of the foam is 1.9 lbs./ft³. The process is carried out in an area that measures 25 ft. wide x 40 ft. long x 20 high with an average daily monitoring measuring 1 ppb concentration of MDI. It may be difficult to estimate the cavity size of each water heater that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the water heater insulation and the total quantity of foam feedstock that was used in the year. Calculate total emissions for the facility that operates 16 hours/day 250 days/year.

Appendix G – Glossary

AP-42	the EPA document, <u>Compilation of Air Pollutant Emission Factors</u> , which contains information on over 200 stationary source categories. This information includes brief descriptions of processes used, potential sources of air emissions from the processes, and in many cases, common methods used to control these air emissions.
Covered Facility	a facility defined in 40 CFR Section 372.3 that has 10 or more full-time employees, is in a covered SIC code and meets the activity threshold for manufacturing, processing, or otherwise using a listed toxic chemical.
Covered SIC Code	prior to 1/1/1998 SIC code 20 through 39. Beginning 1/1/1998 SIC Code 10 (except 1011, 1081, and 1094), 12 (except 1241), or 20-39; industry codes 4911, 4931, or 4939 (limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); or 4953 (limited to facilities regulated under the RCRA, subtitle C, 42 U.S.C. Section 6921 et seq.) or 5169, or 5171, or 7389 (limited to facilities primarily engaged in solvent recovery).
Disposal	any underground injection, placement in landfills/surface impoundments, land treatment, or other intentional land disposal (40 CFR Section 372.3).
Environment	includes water, air, and land and the interrelationship that exists among and between water, air, and land and all living things (EPCRA Section 329(2)).
Facility	all buildings, equipment, structures and other stationary items which are located on a single site or contiguous or adjacent sites and which are owned or operated by the same person (or by any person which controls, is controlled by or under common control with such person).
Full-time Employee	a person who works 2,000 hours per year of full time equivalent employment. A facility would calculate the number of full-time employees by totaling the hours worked during the calendar year by all employees, including contract employees, and dividing the total by 2,000 hours (40 CFR Section 372.3)
Manufacture	to produce, prepare, import, or compound a toxic chemical. Manufacture also applies to a toxic chemical that is produced coincidentally during the manufacture, processing, use, or disposal of another chemical or mixture of chemicals, including a toxic chemical that is separated from that other chemical or mixture of chemicals as a byproduct, and a toxic chemical that remains in that other chemical or mixture of chemicals as an impurity (40 CFR Section 372.3).
Mixture	any combination of two or more chemicals if the combination is not, in whole or in part, the result of a chemical reaction. However, if the combination was produced by a chemical reaction, but could have been produced without a chemical reaction, it is also treated as a mixture. A mixture also includes any combination that consists of a chemical and associated impurities (40 CFR Section 372.3). A waste is not considered a mixture for EPCRA Section 313 reporting purposes.
Otherwise Use	any use of a toxic chemical that is not covered by the terms manufacture or process, and includes use of a toxic chemical contained in a mixture or trade name product. Relabeling or redistributing a container of a toxic chemical where no repackaging of the toxic chemical occurs does not constitute use or processing of the toxic chemical. Otherwise use of a toxic chemical does not include disposal, stabilization (without

subsequent distribution in commerce), or treatment for destruction unless the toxic chemical that was disposed, stabilized or treated for destruction was received from off-site for the purposes of further waste management or it was disposed, stabilized, or treated for destruction as a result of waste management activities on materials received from off-site for the purposes of further waste management activities.

Release

any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles) of any toxic chemicals (40 CFR Section 372.2).

Total Annual Reportable Amount

a facility's total reportable amount is equal to the combined total quantities released at the facility (including disposal), treated at the facility (as represented by amounts destroyed or converted by treatment processes), recovered at the facility as a result of recycle operations, combusted for the purpose of energy recovery at the facility, and the amounts transferred from the facility to off-site locations for the purpose of recycling, energy recovery, treatment, and/or disposal.

Toxic Chemical

a chemical or chemical category listed in 40 CFR Section 372.65 (40 CFR Section 372.3).

Appendix H – Sample Revision and Withdrawal Letters

Request for Withdrawal

Facility Name
Facility Mailing Address

Date:

EPCRA Reporting Center
P.O. Box 3348
Merrifield, VA 22116-3348
Attention: TRI Withdrawal Request

To whom it may concern:

(Fill in your facility name and TRIFID here) is requesting a withdrawal for the following submissions filed under EPCRA Section 313 from EPA's database (i.e. the Toxic Release Inventory System (TRIS)):

Chemical Name Reported:
CAS Number/Category Code:
Report Type (please check one): Form R * * Form A Certification * *
Reporting Year:
Reason (s) for Withdrawal:

The technical contact is: (Insert name here) and may be reached at: (Insert telephone number here).

Requester's Name:
Requester's Signature:
Address: (If different from facility address or facility mailing address)

**Make certain that a copy of Form R or Form A Certification that you want to withdraw is sent along with the request for withdrawal
Please submit a copy of the request to the appropriate state agency, if required.**

Request For Revision

Facility Name
Facility Mailing Address

Date:

EPCRA Reporting Center
P.O. Box 3348
Merrifield, VA 22116-3348
Attention: TRI Revision Request

To whom it may concern:

(Fill in your facility name and TRIFID here) is requesting a revision for the following submissions filed under EPCRA Section 313 from EPA's database (i.e. the Toxic Release Inventory System (TRIS)):

Chemical Name Reported:
CAS Number/Category Code:
Report Type (please check one): **Form R * * Form A Certification * ***
Reporting Year:
Reason (s0 for Withdrawal:

The technical contact is: (Insert name here) and may be reached at: (Insert telephone number here).

Requester's Name:
Requester's Signature:
Address: (If different from facility address or facility mailing address)

Please include a copy of Form R or Form A Certification (revision box checked) you want to revise.

Please submit a copy of the request to the appropriate state agency, if required.

Appendix I – References

1. U.S. EPA, December 1987, *Estimating Releases and Waste Treatment Efficiencies for the Toxic Release Inventory Form*, EPA Office of Pollution Prevention and Toxics, EPA Publication No. 560/4-88-002.
2. Power, R.W., 1984, “*Estimating Worker Exposure to Gases and Vapors Leaking from Pumps and Valves*,” American Industrial Hygiene Association Journal, 45, A7-A-15.
3. Chakrabarti, A., *Vapor Pressure of Diphenylmethane Diisocyanate (MDI) Formulations*, The Dow Chemical Company, Midland, Michigan.
4. *Compilation of Air Pollutant Emission Factors*, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources, Chapter 7 Liquid Storage Tanks.
5. *Form R: Reporting of Binder Chemicals Used in Foundries*, 2nd Edition, 1998, American Foundrymen’s Society, Inc. and Casting Industry Suppliers Association
6. U.S. EPA Toxic Chemical Release Inventory Reporting Forms and Instructions, Revised 2001 Version, Section 313 of the Emergency Planning and Community Right-to Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986).
7. MDI Emissions Estimator, Version 2.0, May 2002, Alliance for the Polyurethanes Industry

