MDI Emissions Reporting Guidelines for the Polyurethane Industry

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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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Center for the Polyurethanes Industry
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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 reporting 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 (N-120) for which reports must be filed.

EPCRA 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 is reported on the Annual Toxic Chemical Release Form R. In certain circumstances, however, facilities may be able to report using the 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. Review definitions of “source reduction,” “treatment,” “recycling” and your activities, which are required to be 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 by EPA.
Use of TRI Database

When Congress passed the EPCRA in 1986, EPA were mandated to promote contingency planning for chemical releases and provide the public with previously unavailable information about toxic and hazardous chemicals in their communities.

Under Section 313(h) of EPCRA, Congress provides for the wide distribution of the industry information gathered. The release forms required under this section are intended to provide information to federal, state and local governments and the public. This includes citizens of communities surrounding the covered facilities. These forms provide information about chemical releases to the environment to enable government agencies, researchers, and other individuals conducting research and data gathering to develop appropriate regulations, guidelines, and standards. Since the TRI data has become available, it has become a useful resource for many different organizations:

- Federal, state and local governments use TRI data to set the priorities and allocate environmental protection resources.
- Regulators use TRI data to set permit limits, measure compliance with those limits, and target facilities for enforcement activities.
- Governments use TRI data to assess or modify taxes and fees based on toxic emissions or overall environmental performance.
- Communities use TRI data to begin dialogues with local facilities and to encourage them to reduce their emissions, develop pollution prevention plans, and address safety measures.
- Industry uses TRI data to identify pollution prevention opportunities, set goals for toxic chemical release reductions, and demonstrate its commitment to and progress in reducing emissions.
- Public interest groups use TRI data to identify the potential need for new environmental regulations or improved implementation and enforcement of existing regulations.
- Consultants and others use TRI data to identify business opportunities, such as marketing pollution prevention and control technologies to TRI reporting facilities.

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 can risk enforcement action by the Agency.
EPCRA Requirements

To put the EPCRA Section 313 requirements in perspective, this chapter very briefly reviews the provisions of the EPCRA and the PPA. Additional materials addressing EPCRA requirements are available from the Center for the Polyurethanes Industry (CPI).

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 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 EPA’s 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 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 (SDS) must be maintained under Occupational Safety and Health Act (OSHA). Under EPCRA Section 311, such facilities must prepare or have available SDS’s and submit either copies of the SDS’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 (see 40 CFR Sections 370.20-.28).

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 hazardous 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.

EPCRA 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 (see 40 CFR Sections 370.40-.41).

Section 313: Toxic Chemical Release Reporting/Emissions Inventory

As noted above, EPCRA Section 313 (TRI) 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.

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. See 40 CFR Section 372.22.

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 the equivalent of 10 or more full-time employees;
- The facility is included in a listed North American Industry Classification System (NAICS) code; and
- The facility manufactures (defined to include importing), processes, or otherwise uses any EPCRA Section 313 (TRI) chemical in quantities greater than the established threshold in the course of a calendar year.
See 40 CFR Section 372.22 for further explanation of when a facility falls within a listed NAICS code. Reporting documents, including the Form R and Form A, may be accessed at http://www.epa.gov/tri/report/index.htm.

**Form R Toxic Release Inventory Reporting Form**

Facilities that are subject to the requirements of Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 are required to file a Form R for each EPCRA chemical for which the applicable threshold limits are exceeded. (An exception is that, if certain low use/low emission criteria are met, the facility may be able to submit a Form A rather than a Form R - see below).

Form R consists of two parts:

- Part I: Facility Identification Information
- Part II: Chemical-Specific Information

The Facility Identification Information that must be provided in Part I of Form R includes five sections:

- Section 1: Reporting Year
- Section 2: Trade Secret Information
- Section 3: Certification
- Section 4: Facility Identification
- Section 5: Parent Company Information

The Chemical-Specific Information that must be provided in Part II of Form R includes eight sections that must be completed for each listed EPCRA chemical that meets the reporting criteria. The sections are:

- Section 1: Toxic Chemical Identity
- Section 2: Mixture Component Identity
- Section 3: Activities and Uses of the Toxic Chemical at the Facility
- Section 5: Quantity of the Toxic Chemical Entering Each Environmental Medium Onsite
- Section 6: Transfers of the Toxic Chemical in Wastes to Off-Site Locations
- Section 7: On-Site Waste Treatment Methods - Energy Recovery Processes - Recycling Process
- Section 8: Source Reduction and Recycling Activities
This document is intended to provide guidance that will enable processors or users of MDI and MDI/PMDI mixtures to estimate air releases of these chemicals for purposes of completing Part II, Section 5 of Form R. Information regarding the filing of Form R, frequently asked questions, filing software, forms, etc. can be obtained on the TRI Home Page (http://www.epa.gov/tri) or the TRI Guidance Documents Page (http://www.epa.gov/tri/guide_docs/index.htm).

Form A Certification Statement

EPA established the Form A Certification Statement, known as Form A, to simplify and reduce the compliance burden associated with EPCRA Section 313 (TRI). Like the Form R, 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).

The 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. Reporting documents, including the Form A, may be accessed at http://www.epa.gov/tri/report/index.htm.
Are You Subject to EPCRA Reporting Obligations?

This section of the booklet summarizes the general steps to determine if you must report releases of MDI, MDI and polymeric MDI mixtures and other EPCRA Section 313 (TRI) chemicals that you manufacture, process, or use.

Is Your Facility Subject to Section 313 Reporting?

EPCRA Section 313 (TRI) reporting requirements apply to facilities in specified North American Industry Classification System (NAICS) codes. The full list of codes is available at www.epa.gov/tri. These codes correspond to Standard Industrial Classification (SIC) Codes 20-39, among others, and include chemical manufacturers, coating manufacturers, plastic resin, foam, and other plastic product manufacturers, foundries, boat builders, and automotive and recreational vehicle manufacturers.

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 aggregate reported with other isocyanates in Category N120. Synonyms for MDI are provided in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Synonyms for MDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1’-methylenebis [4-isocyanato benzene]</td>
<td>4,4’-diisocyanatodiphenylmethane</td>
</tr>
<tr>
<td>bis(4-isocyanatophenyl) methane</td>
<td>methylenebis(p-phenylene isocyanate)</td>
</tr>
<tr>
<td>diphenylmethane 4,4’-diisocyanate</td>
<td>methylenebis (p-phenyl isocyanate)</td>
</tr>
<tr>
<td>methylenebis (4-isocyanatobenzene)</td>
<td>bis (1,4-isocyanatophenyl) methane</td>
</tr>
<tr>
<td>MBI</td>
<td>methylenebis-p-phenylene diisocyanate</td>
</tr>
<tr>
<td>4,4’-MBI</td>
<td>4,4’-methylenebiphenylene isocyanate</td>
</tr>
<tr>
<td>isocyanic acid, methylenedi-p-phenylene ester</td>
<td>4,4’-diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>bis(p-isocyanatophenyl) methane</td>
<td>p,p’-diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>p,p’-methyleneb (phenyl isocyanate)</td>
<td>4,4’-methylenebiphenylene diisocyanate</td>
</tr>
<tr>
<td>4,4’-methyleneb (phenyl cyanate)</td>
<td>diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>methylenebis (4-phenyl isocyanate)</td>
<td>di(4-isocyanatophenyl) methane</td>
</tr>
<tr>
<td>methylenedi-p-phenylene isocyanate</td>
<td>4,4’-methyleneb(isocyanatobenzene)</td>
</tr>
<tr>
<td>4,4’-diisocyanatodiphenylmethane</td>
<td>methylenebisphenylene diisocyanate</td>
</tr>
<tr>
<td></td>
<td>isocyanic acid, diphenylmethane ester</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.\(^1\) 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 according to EPA.

Users and processors are required by EPA to report releases of all chemicals in any listed category listing as a single number. \textit{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. \textit{Please note} that TDI is not a member of the diisocyanates category, and that the

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
\textbf{Chemical Name} & \textbf{CASRN} \\
\hline
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 \\
Diethylidiocyanatobenzene & 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-Methylidiphenylmethane-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 \\
\hline
\end{tabular}
\caption{Isocyanates in the EPCRA Section 313 Diisocyanates Reporting Category Category Code N120}
\end{table}

\(^1\) 59 Fed. Reg. 61,432 (November 30, 1994).
Center for the Polyurethanes Industry (CPI) has developed a separate guidance document and emissions tool for estimating releases of TDI. There are other EPCRA Section 313 (TRI) chemicals that may also be used in your process as blowing agents, catalysts, polyols, and additives. A list of other EPCRA Section 313 (TRI) chemicals 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 EPCRA Section 313 (TRI) reporting may be required. The TRI reporting list may be accessed at [http://www.epa.gov/tri/report/index.htm](http://www.epa.gov/tri/report/index.htm). The list of TRI reportable chemicals is also in the Code of Federal Regulations at 40 C.F.R. § 372.65.

<table>
<thead>
<tr>
<th>Additive Type/Chemical Name</th>
<th>CASRN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diisocyanates</strong></td>
<td></td>
</tr>
<tr>
<td>Toluene-2,4-diisocyanate</td>
<td>584-84-9</td>
</tr>
<tr>
<td>Toluene-2,6-diisocyanate</td>
<td>91-08-7</td>
</tr>
<tr>
<td>Toluene diisocyanate (mixed isomers)</td>
<td>26471-62-5</td>
</tr>
<tr>
<td><strong>Curing Agents</strong></td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>107-21-1</td>
</tr>
<tr>
<td>Certain glycol ethers</td>
<td>category</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>111-42-2</td>
</tr>
<tr>
<td><strong>Catalysts</strong></td>
<td></td>
</tr>
<tr>
<td>Lead compounds</td>
<td>category</td>
</tr>
<tr>
<td>Mercury compounds*</td>
<td>category</td>
</tr>
<tr>
<td><strong>Fillers</strong></td>
<td></td>
</tr>
<tr>
<td>Barium compounds (except barium sulfate)</td>
<td>category</td>
</tr>
<tr>
<td><strong>Colorants</strong></td>
<td></td>
</tr>
<tr>
<td>Cadmium compounds*</td>
<td>category</td>
</tr>
<tr>
<td>Cobalt compounds*</td>
<td>category</td>
</tr>
<tr>
<td>Copper compounds (excluding certain phthalocyanine-based pigments)*</td>
<td>category</td>
</tr>
<tr>
<td><strong>Solvents</strong></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
</tbody>
</table>
| *Usage of these compounds as a processing aid for the manufacture of polyurethanes has declined in recent years.
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 listed 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) otherwise used more than 10,000 pounds of a listed chemical or chemical category, you had to comply with the EPCRA Section 313 (TRI) reporting requirements.2

In 1999, however, EPA created a subset of listed chemicals, known as persistent and bioaccumulative toxic (PBT) chemicals that are subject to lower thresholds. Dioxin and dioxin-like compounds that are subject to a 0.1 gram threshold; other listed PBTs are subject to either a 10 pound or 100 pound threshold for amounts manufactured, processed or otherwise used (see 40 CFR Section 372.28).

The 25,000 pounds manufacturing and processing and 10,000 pounds otherwise use thresholds, however, still apply to the diisocyanates category.

The 25,000 pound threshold will likely apply to most MDI and MDI/PMDI “users” since most applications, including polyurethane foam manufacturing and use in boat building and use as a packing material for fragile products shipped to customers, 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 an “otherwise use” of MDI and MDI/PMDI mixtures for Section 313 reporting. In such applications, the 10,000-pound reporting threshold applies.

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2 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 SDS 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.
Your purchases of Section 313 listed chemicals may serve as a benchmark in determining what amounts you manufacture, process, or “otherwise use”; however, it is the actual amount of a substance that is manufactured, processed, or “otherwise 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, EPA requires reporters to count all of the isocyanates manufactured, processed or “otherwise used” in the category in that reporting year in determining if a threshold is met.

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 pounds |
| Components: | 50% water     | Components: | 50% water     |
|            | 50% MDI       |            | 50% Isophorone diisocyanate |

Conclusion: Exceeds the reporting threshold for the diisocyanates category. You used 5,000 lbs of MDI and 6,000 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?**

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. State air permit officials may be particularly interested in MDI emissions, because MDI is a listed hazardous air pollutant (HAP). You should refer to your state and local regulations for more information.
Identifying Release Sources

The main goal and objective of this document is to provide information and guidance that will help processors or users of MDI and MDI/PMDI mixtures to estimate releases of these chemicals in accordance with the EPRCA 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.

![Process Flow Diagram](image)

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 EPCRA 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.

EPCRA Section 313(TRI) 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 estimated 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 are being released. Even though this method is more 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, EPA stated that using mass balance is inappropriate to use in situations where a chemical is consumed during a process were 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 could result in inaccurate reporting.

Engineering Calculations

Engineering calculations are assumptions and/or judgments used to estimate quantities of EPCRA Section 313 (TRI) 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(TRI) 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 percent 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 these guidelines. 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 these guidelines. 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. Consider using 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 (TRI) reporting; however, you are required to use the best, readily available information to determine the method that will result in the most accurate estimate.
Table 4 lists the potential data sources where available release and emission information may be obtained to help in determining accurate facility emissions.

<table>
<thead>
<tr>
<th>Monitoring Data</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Air Permits</td>
<td>* Air Emissions Inventory</td>
</tr>
<tr>
<td>* Continuous Emission Monitoring</td>
<td>* SDS’s</td>
</tr>
<tr>
<td>* Effluent Limitations</td>
<td>* Pollution Prevention Reports</td>
</tr>
<tr>
<td>* Hazardous Waste Analysis</td>
<td>* Spill Event Records</td>
</tr>
<tr>
<td>* Industrial Hygiene Monitoring Data</td>
<td>* Supply Records</td>
</tr>
<tr>
<td>* NPDES Permits</td>
<td>* Hazardous Waste Manifests</td>
</tr>
<tr>
<td>* Stack Monitoring Data</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Engineering Calculations</th>
<th>Emission Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Facility Non-specific Emission Factors</td>
<td>* AP-42 Chemical Specific Emission Factors</td>
</tr>
<tr>
<td>* Henry’s Law</td>
<td>* Facility or Trade Association Derived Chemical Factors</td>
</tr>
<tr>
<td>* Raoult’s Law</td>
<td></td>
</tr>
<tr>
<td>* Solubilities</td>
<td></td>
</tr>
<tr>
<td>* Volatilization Rates</td>
<td></td>
</tr>
</tbody>
</table>

**Guidance Documents**

EPA has a number of EPCRA Section 313 (TRI) 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 EPA by downloading from: [http://www.epa.gov/tri/guide_docs/index.htm](http://www.epa.gov/tri/guide_docs/index.htm)

**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 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:

\[ L_w = Q_w \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{amb}} \right) \times \left( \frac{V_{P_{amb}}}{760} \right) \times M_w \times K_{mdi} \]

Where:

- \( L_w \) = the working losses in lb/yr
- \( Q_w \) = the annual throughput of MDI pumped to the tank in ft\(^3\)/yr
- \( T_{amb} \) = the storage temperature in K
- \( V_{P_{amb}} \) = the vapor pressure of MDI at the storage temperature in mm Hg
- \( M_w \) = 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 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:

\[
L_w = Q_w \times \frac{1}{359} \times \frac{273.15}{T_{amb}} \times \frac{V_{Pamb}}{760} \times M_w \times K_{mdi}
\]

Where:

- \(L_w\) = the working losses in lb/yr
- \(Q_w\) = the annual throughput of MDI pumped to the tank in ft\(^3\)/yr
- \(T_{amb}\) = the temperature of the stored material
- \(V_{Pamb}\) = the vapor pressure of MDI at the storage temperature in mm Hg
- \(M_w\) = 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 storage temperature

\(Q_w = 1,000,000 \text{ gal/yr} \times \frac{1 \text{ cu. ft}}{7.48 \text{ gal}}\)
\(Q_w = 133,690 \text{ cu ft}\)
\(T_{amb} = 298.2 \text{ K}\)
\(V_{Pamb} = 1.0 \times 10^{-5} \text{ mm Hg @ 298.2 K}\)
\(M_w = \text{the molecular weight of MDI (250.26)}\)
\(K_{mdi} = 0.55\) for a 50/50 mixture of MDI/PMDI at 298.2 K

(See Appendix B: Table II: MDI/PMDI Adjustment Factors)

Therefore:

\[
L_w = (133,690 \text{ cu. ft.})(1/359)(273.15/298.2)(1.0 \times 10^{-5}/760)(250.26)(.55)
\]
\[L_w = 6.28 \times 10^{-4} \text{ lbs/yr}\]
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 determined using the following equations:

\[ L_b = 365 \times M_{\text{air}} \times \left( \frac{V_{\text{amb}}}{760} \right) \times M_w \times K_{\text{mdi}} \]

\[ M_{\text{air}} = \frac{V_v}{7.48} \times \left( \frac{1}{359} \right) \times K_E \times \left( \frac{273.15}{T_{\text{amb}}} \right) \]

\[ V_v = V_T \times \frac{(100-L_T)}{100} \]

\[ K_E = \frac{T_R}{T_{\text{amb}}} \]

Where:

- \( L_b \) = the breathing losses in lb/yr
- \( M_{\text{air}} \) = the total air displaced per day in lb-mole/day
- \( V_{\text{amb}} \) = the vapor pressure of MDI at the ambient temperature in mm Hg
- \( M_w \) = the molecular weight of MDI (250.26)
- \( K_{\text{mdi}} \) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- \( T_{\text{amb}} \) = the average ambient temperature in K
- \( T_R \) = the average day-night temperature fluctuation in K
- \( K_E \) = 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 x 10^{-6} mm Hg.

The breathing losses can be calculated from the following expression:

\[ L_b = 365 \cdot M_{air} \cdot \left( \frac{V_{amb}}{760} \right) \cdot M_w \cdot K_{mdi} \]

\[ M_{air} = \left( \frac{V_v}{7.48} \right) \cdot \frac{1}{359} \cdot K_E \cdot \frac{273.15}{T_{amb}} \]

\[ V_v = V_T \cdot (100-L_T) \]

\[ K_E = \frac{T_R}{T_{amb}} \]

Where:

\[ L_b = \text{the breathing losses in lb/yr} \]

\[ M_{air} = \text{the total air displaced per day in lb-mole/day} \]

\[ V_{amb} = \text{the vapor pressure of MDI at the ambient temperature in mm Hg} \]

\[ M_w = \text{the molecular weight of MDI (250.26)} \]

\[ K_{mdi} = \text{the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature} \]

\[ T_{amb} = \text{the average ambient temperature in K} \]

\[ T_R = \text{the average day-night temperature fluctuation in K} \]

\[ K_E = \text{the vapor expansion factor due to day-night temperature fluctuation} \]

\[ V_v = V_T \cdot (100-L_T) = 12,000(100-50)/100 = 6,000 \text{ gal} \]

\[ K_E = \frac{T_R}{T_{amb}} = \frac{8.5}{12.53+273.15} = 0.02975 \]

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

\[ M_{air} = \left( \frac{V_v}{7.48} \right) \cdot \frac{1}{359} \cdot K_E \cdot \frac{273.15}{T_{amb}} \]

\[ M_{air} = \left( 6,000/7.48 \right) \cdot \frac{1}{359} \cdot (0.02975) \cdot \frac{273.15}{285.68} \]

\[ M_{air} = 0.0636 \text{ lb mole/day} \]

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

\[ L_b = 365 \cdot M_{air} \cdot \left( \frac{V_{amb}}{760} \right) \cdot M_w \cdot K_{mdi} \]

\[ L_b = 365 \cdot (0.0636) \cdot \left( 1.945 \times 10^{-6} / 760 \right) \cdot (250.26) \cdot (0.54) \]

\[ L_b = 8.16 \times 10^{-6} \text{ lbs/yr} \]
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:

\[
L_{fg} = C_{mdi} \times \left(\frac{V_B}{359}\right) \times N_{year} \times \frac{273.15}{T_{amb}} \times M_w \times K_{fg}
\]

Where:

- \(L_{fg}\) = the fugitive emissions in lb/yr
- \(C_{mdi}\) = the average MDI concentration, in ppmv, in the air within the building
- \(V_B\) = the volume of the workspace building in ft\(^3\)
- \(N_{year}\) = the number of air exchanges per year
- \(T_{amb}\) = the ambient temperature in K
- \(M_w\) = the molecular weight of MDI (250.26)
- \(K_{fg}\) = the adjustment factor to the MDI concentration in the building air. CPI 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 is 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:

\[ L_{fg} = C_{mdi} \times \left( \frac{V_B}{359} \right) \times N_{year} \times \left( \frac{273.15}{T_{amb}} \right) \times M_w \times K_{fg} \]

- \( L_{fg} \): the fugitive emissions in lb/yr
- \( C_{mdi} \): the average MDI concentration, in ppmv, in the air within the building
- \( V_B \): the volume of the workspace building in ft\(^3\)
- \( N_{year} \): the number of air exchanges per year
- \( T_{amb} \): the ambient temperature in K
- \( M_w \): the molecular weight of MDI (250.26)
- \( K_{fg} \): the adjustment factor to the MDI concentration in the building air. CPI uses a value of 1.10

Calculating:

\[ C_{mdi} = 0.001 \text{ppm} = 1.0 \times 10^{-9} \]
\[ V_B = (50 \text{ ft} \times 100 \text{ ft} \times 20 \text{ ft}) = 100,000 \text{ ft}^3 \]
\[ N_{year} = (5 \text{ changes/hr} \times 16 \text{ hr/day} \times 250 \text{ days/yr}) = 20,000 \text{ changes/yr} \]
\[ T_{amb} = 298.2 \text{ K} \]
\[ M_w = \text{the molecular weight of MDI (250.26)} \]
\[ K_{fg} = \text{the adjustment factor to the MDI concentration in the building air. CPI uses a value of 1.10} \]

Therefore:

\[ L_{fg} = (1.0 \times 10^{-9}) \times (100,000 \text{ ft}^3/359) \times (20,000) \times (273.15/298.2) \times (250.26)^* (1.1) \]
\[ L_{fg} = 1.40 \text{ lbs/yr} \]
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:

\[
SV = 1315.8 \times 10^{-0.873} \left[10.902 - \frac{4634.09}{266.15 + t}\right]
\]

Where:

- \(SV\) = Screening Value in ppmv and
- \(t\) = Temperature in °C

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table 5) and the leakage rate is determined.

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Correlation Leak Rate (kg/hr) ((a\times(SV)^b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Valve</td>
<td>1.87x10^06 x (SV) 0.873</td>
</tr>
<tr>
<td>Light Liquid Valve</td>
<td>6.41x10^06 x (SV) 0.787</td>
</tr>
<tr>
<td>Light Liquid Pump Seal(^c)</td>
<td>1.90x10^05 x (SV) 0.824</td>
</tr>
<tr>
<td>Connectors</td>
<td>3.05x10^06 x (SV) 0.885</td>
</tr>
</tbody>
</table>

\(^c\) This equation can be used for liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pump seals.
The total emissions from equipment leaks will be equal to the emissions contributed from each gas valves, light liquid valves, light liquid pump seals, and connectors.

For gas valves:

\[ K_{gas} = 1.87 \times 10^{-6} \cdot (C_{mdi})^{0.873} \]

For liquid valves:

\[ K_{liq} = 6.41 \times 10^{-6} \cdot (C_{mdi})^{0.787} \]

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

\[ K_{pump} = 1.90 \times 10^{-5} \cdot (C_{mdi})^{0.824} \]

For connectors:

\[ K_{con} = 3.05 \times 10^{-6} \cdot (C_{mdi})^{0.885} \]

Where:

- \( K_{gas} \) = the emission factor for gas valves in kg/year-item
- \( K_{liq} \) = the emission factor for liquid valves in kg/year-item
- \( K_{pump} \) = the emission factor for liquid pump seals in kg/year-item
- \( K_{con} \) = the emission factor for connectors in kg/year-item

For gas valves the emissions can then be estimated from the following expression:

\[ L_{gas} = K_{gas} \cdot n_{gas} \cdot K_{mdi} \cdot t_{pr} \cdot 2.205 \text{ lb/kg} \]

- \( L_{gas} \) = the annual losses from gas valves in lb/yr
- \( n_{gas} \) = the number of gas valves
- \( K_{mdi} \) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- \( t_{pr} \) = the total time in hours/year that the process is operating

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

\[ L_{liq} = K_{liq} \cdot n_{liq} \cdot K_{mdi} \cdot t_{pr} \cdot 2.205 \text{ lb/kg} \]

- \( L_{liq} \) = the annual losses from liquid valves in lb/yr
- \( n_{liq} \) = the number of liquid valves
- \( K_{mdi} \) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
The total time in hours/year that the process is operating.

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

\[ L_{pump} = K_{pump} \times n_{pump} \times K_{mdi} \times t_{pr} \]

\[ L_{pump} \] = the annual losses from liquid pump seals in lb/yr
\[ n_{pump} \] = the number of liquid pump seals
\[ K_{mdi} \] = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
\[ t_{pr} \] = the total time in hours/year that the process is operating

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

\[ L_{con} = K_{con} \times n_{con} \times K_{mdi} \times t_{pr} \times 2.205 \text{ lb/kg} \]

\[ L_{con} \] = the annual losses from connectors in lb/yr
\[ n_{con} \] = the number of connectors
\[ K_{mdi} \] = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
\[ t_{pr} \] = the total time in hours/year that the process is operating

Total emissions can then be estimated from the following expression:

\[ E_{tot} = L_{gas} + L_{liq} + L_{pump} + L_{con} \]

Table 6: 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>
<thead>
<tr>
<th>Equipment Type</th>
<th>Temp. °C</th>
<th>Vapor Pressure (mm Hg)(^d)</th>
<th>Screening Value (SV)(^5) (ppmv)(^2)</th>
<th>Equation Constant (a)</th>
<th>Equation Constant (b)</th>
<th>Emission Factor(^1) (kg/hr)(^3)</th>
<th>Emission Factor(^1) (lb./hr)(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Valves</td>
<td>50</td>
<td>1.80x10(^{-04})</td>
<td>2.37x10(^{-01})</td>
<td>1.87x10(^{-06})</td>
<td>0.873</td>
<td>5.33x10(^{-07})</td>
<td>1.18x10(^{-06})</td>
</tr>
<tr>
<td>Light Liquid Valves</td>
<td>50</td>
<td>1.80x10(^{-04})</td>
<td>2.37x10(^{-01})</td>
<td>6.41x10(^{-06})</td>
<td>0.787</td>
<td>2.04x10(^{-06})</td>
<td>4.49x10(^{-06})</td>
</tr>
<tr>
<td>Light Liquid Pump Seals</td>
<td>50</td>
<td>1.80x10(^{-04})</td>
<td>2.37x10(^{-01})</td>
<td>1.90x10(^{-05})</td>
<td>0.824</td>
<td>5.81x10(^{-06})</td>
<td>1.28x10(^{-05})</td>
</tr>
<tr>
<td>Connectors</td>
<td>50</td>
<td>1.80x10(^{-04})</td>
<td>2.37x10(^{-01})</td>
<td>3.05x10(^{-06})</td>
<td>0.885</td>
<td>8.54x10(^{-07})</td>
<td>1.88x10(^{-06})</td>
</tr>
</tbody>
</table>
**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 7.

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Service</th>
<th>Number Components</th>
<th>Weight Fraction</th>
<th>Modified Corr. Factors</th>
<th>Emissions (lbs/hr)</th>
<th>Emissions (lbs./year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>Light Liquid</td>
<td>3000</td>
<td>0.127</td>
<td>4.49x10^-06</td>
<td>1.71x10^-03</td>
<td>15</td>
</tr>
<tr>
<td>Pump Seals</td>
<td>Light Liquid</td>
<td>20</td>
<td>0.127</td>
<td>1.28x10^-05</td>
<td>3.25x10^-05</td>
<td>0.285</td>
</tr>
<tr>
<td>Agitators</td>
<td>Light Liquid</td>
<td>2</td>
<td>0.127</td>
<td>1.28x10^-05</td>
<td>3.25x10^-06</td>
<td>0.0285</td>
</tr>
<tr>
<td>Connectors</td>
<td>All</td>
<td>4500</td>
<td>0.127</td>
<td>1.88x10^-06</td>
<td>1.07x10^-03</td>
<td>9.41</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>24.7</strong></td>
</tr>
</tbody>
</table>

**Spills**

Section 313 of the EPCRA 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:

$$ Q_R = \frac{0.284}{82.05} \times u^{0.78} \times A_{spill} \times (V_{P,MDI}/T_{spill}) \times (MW)^{2/3} \times K_{MDI} $$

Where:

- $Q_R$ = 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 ft$^2$
- $V_{P,MDI}$ = 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:

$$ L_{spill} = QR \times t_{spill} \times 60 $$

Where:

- $L_{spill}$ = the evaporation losses resulting from the spill in lb
- $QR$ = the evaporation rate in lb/min
- $t_{spill}$ = 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 ft$^2$, 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 (294.1 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:

\[
QR = \frac{0.284}{82.05} \times (u)^{0.78} \times A_{\text{spill}} \times \frac{VP_{\text{MDI}}}{T_{\text{spill}}} \times (MW)^{2/3} \times K_{\text{MDI}}
\]

Where:
- \(QR\) = the evaporation rate in lb/min
- \(u\) = the airflow speed in m/sec. This is the airflow in the vicinity of the process
- \(A_{\text{spill}}\) = the area of the spilled material in ft\(^2\)
- \(VP_{\text{MDI}}\) = the vapor pressure of MDI in mm Hg at the filling temperature
- \(T_{\text{spill}}\) = the average evaporation temperature in K
- \(MW\) = the molecular weight of MDI (250.26)
- \(K_{\text{MDI}}\) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature

Therefore:

\[
QR = \text{lb/minute}
\]

\[
u = 8.94 \text{ m/sec}
\]

\[
A_{\text{spill}} = 200 \text{ ft}^2
\]

\[
VP_{\text{MDI}} = 6.26 \times 10^{-6} \text{ mm Hg}
\]

\[
T_{\text{spill}} = 294.1 \text{ K}
\]

\[
MW = 250.26
\]

\[
K_{\text{MDI}} = 0.54
\]

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

\[
QR = \left(\frac{0.284}{82.05}\right) \times (8.94)^{0.78} \times 200 \times \frac{6.26 \times 10^{-6}}{294.1} \times (250.26)^{2/3} \times 0.54
\]

\[
QR = 1.74 \times 10^{-6} \text{ lbs/min}
\]

Using the equation:

\[
L_{\text{spill}} = QR \times t_{\text{spill}} \times 60
\]

Where:
- \(L_{\text{spill}}\) = the evaporation losses resulting from the spill in lb
- \(QR\) = the evaporation rate in lb/min
- \(t_{\text{spill}}\) = the time that the spill is on the ground in hours

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

\[
L_{\text{spill}} = (QR = 1.74 \times 10^{-6} \text{ lbs/min}) \times (8 \text{ hours}) \times (60 \text{ min/hr})
\]

\[
L_{\text{spill}} = 8.38 \times 10^{-4} \text{ lbs}
\]
Disposal and Treatment

Activities that involve the disposal and/or treatment of an EPCRA Section 313 (TRI) chemical on-site or off-site are required by EPA to 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 facility’s 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 are also required to report releases contributed to storm water run-off.

On-site releases to land are accountable under histories and spill records. EPCRA Section 313 (TRI) chemicals sent to off-site RCRA landfills must be reported according to EPA. Hazardous waste manifests contain description of waste and list waste composition that will aid you in calculating amount of EPCRA Section 313 (TRI) chemical being disposed.

Facilities that use surface impoundment as a disposal method 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 Section 313 (TRI) chemicals that are discharged into publicly owned treatment works (POTWs) must be reported to EPA. 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 Section 313 (TRI) 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 procedure, before disposal, the amount of MDI and MDI/PMDI can be considered negligible. However, if you decontaminate containers you are required to report this as treatment and the amount of material treated and its treatment efficiency must also 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

Use your 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 or under reporting have serious consequences so think and use your personal judgment when determining releases.

**Stack Emissions (Point Source)**

Stack emissions are releases of EPCRA Section 313 (TRI) chemicals that are contained in confined air streams. Examples are emissions from stacks, vents, ducts, pipes and storage tanks. Emissions 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 mixtures 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)
- Pour-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 each use and is forced out into the environment as the chemicals are added.

The curing of an isocyanate-based product is almost always 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 will evaporate 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, these guidelines will address the following applications:

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

A worst-case scenario will be presented for each application. The stack emissions will be presented in a step-by-step solution. Consult the section on losses generated from storage tanks and fugitive emissions for step-by-step guidance describing 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 ft. x 8 ft. 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 the sheeting. Set up time is 30 seconds. Tack-free time is 5 seconds. A blower operating at 550 CFM is used to carry off any emissions during application of the adhesive. The length of the roller surface is 5 ft. x 1 ft. 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 of 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:

\[ W = 25.4 \times V_{P_{MDI}} \times \left( \frac{M_w}{T_{proc}} \right) \times (u)^{0.78} \times S_A \times t_{TF} \]

Where:

- \( W \) = the evaporation losses from the open process in gram/day
- \( V_{P_{MDI}} \) = the vapor pressure of MDI in atmospheres @ process temperature
- \( T_{proc} \) = the process temperature in K
- \( M_w \) = the molecular weight of MDI
- \( u \) = the airflow speed in m/sec
- \( S_A \) = the exposed surface area in M²
- \( t_{TF} \) = 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 2.298 x 10 \(^{-1}\) mm.

Converting this to atmospheres and for a 2% mixture of MDI.

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

\[ V_{P_{MDI}} = \left( 2.298 \times 10^{-1}\text{mm} \right) \times \left( \frac{1 \text{ atm}}{760 \text{mm}} \right) \times \left( \frac{2 \text{ lbs. MDI}}{100 \text{ lbs. Mixture}} \right) = 6.05 \times 10^{-6} \text{ atmospheres} \]

**Step II: Determine Ventilation Rate in Meters/Second**

<table>
<thead>
<tr>
<th>Ventilation rate (( u ))</th>
<th>Flow Rate/Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roller Surface Area</td>
<td>1 foot by 5 feet = 5 ft(^2)</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>550 ACFM</td>
</tr>
<tr>
<td>Ventilation rate (( u ))</td>
<td>Flow Rate/Surface Area</td>
</tr>
<tr>
<td></td>
<td>550 ACFM/ 5ft(^2) x min./60 sec x .3048 m/ft</td>
</tr>
<tr>
<td>Ventilation rate (( u ))</td>
<td>5.59 x 10(^{-1}) meters/second</td>
</tr>
</tbody>
</table>
Step III: **Determine Tack-Free 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 ft\(^2\)/hr. Based upon 24 hour production:

Total Exposed Surface Area (\(S_A\))/day:

\[
S_A = 2465 \text{ ft}^2 \times 24 \text{ hrs/day}
\]

\[
S_A = 5.92 \times 10^{-4} \text{ ft}^2/\text{day}
\]

Converting ft\(^2\) to M\(^2\):

\[
S_A = 5.92 \times 10^{-4} \text{ ft}^2/\text{day} \times 10.76 \text{ ft}^2/\text{M}^2
\]

\[
S_A = 5.50 \times 10^{-3} \text{ M}^2/\text{day}
\]

Therefore:

\[
W = 25.4 \times VP_{MDI} \times (MW / T_{proc}) \times (u)^{0.78} \times S_A \times t_{TF}
\]

\[
W = (25.4)(6.05 \times 10^{-6}) \text{ atm}(250.26)(5.59 \times 10^{-1})^{0.78} \text{ m/sec}(5.50 \times 10^{-3})\text{ft}^2\text{m/sec}
\]

\[
W = 1.63 \text{ grams/day}
\]

**Step V: Convert Grams per Day to Pounds per Year**

\[
W = 1.63 \text{ grams/day} \times 1 \text{ pound/454 grams} \times 365 \text{ days/yr}
\]

\[
W = 1.31 \text{ lbs/yr}
\]

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 disperses through a customized nozzle head at a rate of 0.2579 pounds. Polyol/MDI/PMDI mixture per filter. The production lines produce 670 filters/hour. The diameter of the filter is 9 inches. Tack-free 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. Emissions are released as (1) component A and Component B mixture is being dispensed into the cavity and (2) 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:

\[ L_c = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{P_{MDI}}}{760} \right) \times M_w \times K_{MDI} \]

Where:

- \( L_c \): emissions from the enclosed process in lb/yr
- \( V_{air} \): the annual volume of displaced air in ft\(^3\)/yr
- \( T_{proc} \): the temperature material is dispensed at in K
- \( V_{P_{MDI}} \): 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
- 359: the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere

**Step I: Determine Annual Volume Displaced (V\(_{air}\))**

\[ V_{air} = N_f \times M_{disp} \times \rho \times \left( \frac{1}{7.48} \right) \]

Where:

- \( V_{air} \): Annual Volume in ft\(^3\)/yr
- \( N_f \): Annual Number of Filters Processed
- \( M_{disp} \): Amount of Material Dispensed/Filter
- \( \rho \): Density of Material lbs/ft\(^3\)

Therefore:

\[ V_{air} = (670 \text{ filters/hr})(8760 \text{ hr/yr})(0.26 \text{ lbs/filter})(1 \text{ gal/10lbs})(1 \text{ ft}^3/7.48\text{gal}) \]

\[ V_{air} = 2.04 \times 10^{+4} \text{ ft}^3/\text{yr} \]
Step II: Convert Dispenser Temperature to K

\[ T_{\text{proc}} \, K = (273 + 62.8 \, ^{\circ}C) \]
\[ T_{\text{proc}} \, K = 335.8 \]

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

The vapor pressure of MDI @ 335.8 K from the table in Appendix A 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:

\[ \% \, \text{MDI/PMDI} = \frac{1}{\text{ratio} + 1}(100) \]
\[ \% \, \text{MDI/PMDI} = \frac{1}{1.89 + 1}100 \]
\[ \% \, \text{MDI/PMDI} = 34.6 \]

From Chart:

\[ K_{\text{MDI}} = 0.47 \]

Therefore, losses due to cavity fill are:

\[ L_c = V_{\text{air}} \cdot \frac{1}{359} \cdot \frac{273.15}{T_{\text{proc}}} \cdot \frac{V_{P_{\text{MDI}}}}{760} \cdot M_w \cdot K_{\text{MDI}} \]
\[ L_c = \frac{2.04 \times 10^4 \, \text{ft}^3/\text{yr}}{359} \cdot \frac{273.15}{335.8} \cdot \frac{6.663 \times 10^{-4} \, \text{mm}}{760} \cdot 254.38 \cdot 0.47 \]
\[ L_c = 4.85 \times 10^{-3} \, \text{lbs/yr} \]

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:
\[
W = 25.4 \times VP_{MDI} \times \left(\frac{M_W}{T_{proc}}\right) \times u^{0.78} \times S_A \times t_{TF}
\]

Where:

- \(W\) = the evaporation losses from the open process in gram/day
- \(VP_{MDI}\) = the vapor pressure of MDI in atmospheres @ process temperature
- \(T_{proc}\) = the process temperature in K
- \(M_W\) = the molecular weight of MDI
- \(u\) = the airflow speed in m/sec
- \(S_A\) = the exposed surface area in M\(^2\)
- \(t_{TF}\) = 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 \times 10^{-4} mm

Converting this to atmospheres:

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

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

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

**Step II: Determine Ventilation Rate in Meters/Second**

- Ventilation rate \((u)\) = Velocity @ STP/Surface Area
- Ventilation Area = 4 ft. \times 3 ft = 12 ft\(^2\)
- Velocity @ STP = 990 acfm \times \frac{298 \text{ K}}{336 \text{ K}}
- Velocity = 878 scfm
- Ventilation rate \((u)\) = Velocity/Surface Area
- Ventilation rate \((u)\) = \frac{878 \text{ scfm}}{12 \text{ft}^2} \times \frac{\text{min/60 sec}}{0.3048 \text{ m/ft}}

\[
Ventilation \ rate \ (u) = 3.72 \times 10^{-1} \text{ meters/second}
\]

**Step III: Determine Tack-Free 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.

\[
Exposed \ Surface \ Area = \frac{\pi r^2}{\pi(4.5/12)^2} = 0.44 \text{ ft}^2
\]
Based upon 24 hour production:

Total Exposed Surface Area (\(S_A\))/day = 0.44 ft\(^2\) /filter \(\times\) 670 filters/hr. \(\times\) 24 hours/day

\[
S_A = 7.08 \times 10^3 \text{ ft}^2/\text{day} \times 1 \text{ m}^2/10.77 \text{ ft}^2 \\
S_A = 658 \text{ m}^2
\]

Therefore:

\[
W = 25.4 \times V_{P_{MDI}} \times (M_w / T_{proc}) \times (u)^{0.78} \times S_A \times t_{TF}
\]

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

\[
W = 0.0103 \text{ grams MDI/day}
\]

We must multiply this by the \(K_{MDI}\) correction factor to get pounds of MDI/PMDI emitted

\(K_{MDI}\) is 0.47. Therefore:

\[
W = 0.00485 \text{ grams MDI/day}
\]

**Step V: Convert Grams per Day to Pounds per Year**

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

\[
W = 0.004 \text{ pounds/year}
\]

**Total Emissions:**

\[
T_T = L_c + W
\]

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

\[
T_T = 8.85 \times 10^{-3} \text{ lbs/yr}
\]

**3.0 Appliances**

Methylenebis (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol resin 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, dryers, refrigerators, and freezers. All processes are closed systems that use a two-component system where MDI and polyol resin are fed from day tanks and are mixed together in a specially designed spray head and the material is injected into the door frame and/or of the side frames. The process is set up where all equipment is isolated and contained in enclosed areas with separate exhaust systems.

**Application I:**

Door cavity is injected with MDI/polyol resin 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 resin mixture into the door housing. The door housing is placed into a chamber with a self-contained 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 resin mixture 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:**

The process system, consisting of three chambers, is 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 pounds of MDI per hour. Line C produces 150 frames an hour consuming 12,226 pounds of MDI per hour. Line D produces 100 frames an hour consuming 1,343 pounds of 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 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:

\[
L_{fd} = V_{Tair} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{VP_{MDI}}{760} \right) \times M_w \times K_{MDI}
\]

Where:

- \(L_{fd}\) = emissions lb/yr
- \(V_{Tair}\) = total annual volume of displaced air in ft³/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
- 359 = the molar volume of an ideal gas in ft³/lb-mole @ 0 °C and 1-atmosphere

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

\[
V_{air} = \frac{\text{Annual consumption of Polyol/MDI/PMDI}}{\text{Foam Density}}
\]

Line 1: \(V_{air} = 1.08 \times 10^6\) lbs/year / 2.0 lbs/cu. ft. = 5.4 x10⁵ lbs/year
Line 2: \(V_{air} = 1.08 \times 10^6\) lbs/year / 2.0 lbs/cu. ft. = 5.4 x10⁵ lbs/year
Line 3: \(V_{air} = 10.74 \times 10^6\) lbs/year / 2.0 lbs/cu. ft. = 5.37 x10⁶ lbs/year
Line 4: \(V_{air} = 11.78 \times 10^6\) lbs/year / 2.0 lbs/cu. ft. = 5.89 x10⁶ lbs/year

Total volume displaced equals:

\[
V_{Tair} = \text{Line 1 } + \text{ Line 2 } + \text{ Line 3 } + \text{ Line 4}
\]

\[
V_{Tair} = 123.4 \times 10^5\text{ ft}^3/\text{yr}
\]

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

The vapor pressure of MDI @ 85 °F is 1.733 x 10⁻⁵ mm Hg

**Step III: Determine Temperature of Process in K**

Converting 85 °F to K:

\[
K = 273.15 + (F - 32) \times \frac{5}{9}
\]

\[
K = 302.6
\]

**Step IV: Determine Adjustment Factor K_{MDI}**
MDI Emissions Reporting Guidelines for the Polyurethanes Industry

\[ K_{\text{MDI}} = 0.56 \text{ @ } 302.6 \text{ K} \]

Therefore:

\[ L_{\text{fd}} = V T_{\text{air}} \left( \frac{1}{359} \right) \left( \frac{273.15}{T_{\text{proc}}} \right) \left( \frac{V P_{\text{MDI}}}{760} \right) M_w K_{\text{MDI}} \]

\[ L_{\text{fd}} = (1.234 \times 10^{-7} \text{ ft}^3/\text{yr}) \left( \frac{1}{359} \right) \left( \frac{273.15}{302.6} \right) \left( 1.733 \times 10^{-5} \text{ mm Hg}/760 \right) (250.26) (0.56) \]

\[ L_{\text{fd}} = 0.10 \text{ lbs/yr} \]

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 materials 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 93 lbs. 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. Amount of material required for trailers of various lengths is as follows:

<table>
<thead>
<tr>
<th>Trailer Length</th>
<th>Amount of Material Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 ft.</td>
<td>565 lbs.</td>
</tr>
<tr>
<td>36 ft.</td>
<td>801 lbs.</td>
</tr>
<tr>
<td>45 ft.</td>
<td>802 lbs.</td>
</tr>
<tr>
<td>51 ft.</td>
<td>1,000 lbs.</td>
</tr>
</tbody>
</table>

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 time during the curing process.

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

\[ L_{\text{fd}} = V_{\text{air}} \left( \frac{1}{359} \right) \left( \frac{273.15}{T_{\text{proc}}} \right) \left( \frac{V P_{\text{MDI}}}{760} \right) M_w K_{\text{MDI}} \]
Where:

- \( L_{fd} \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft\(^3\)/year
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{PMDI} \) = 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
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere

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

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

\[
V_{air} = (1.05 \times 10^{-7} \text{ lbs/yr})(1/2.25 \text{ lbs/ft}^3)
\]

\[
V_{air} = 4.67 \times 10^{-6} \text{ ft}^3/\text{yr}
\]

**Step II: Calculate Process Temperature in K**

The process temperature is 78 °F or;

\[
T_{proc} = 298.7 \text{ K}
\]

**Step III: Determine vapor Pressure of MDI @ 298.7 K (\( V_{PMDI} \))**

The vapor pressure @ 298.7 K is 1.072 \times 10^{-5} \text{ 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:

\[
\%_{MDI/PMDI} = \left(\frac{100}{100 + 93}\right) \times 100 = 51.8 \%
\]

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

\[
\%_{MDI} = (51.8) \times (52.0) = 26.9
\]

Adjustment factor @ 298.7 K and 26.9% MDI is 0.35

Therefore:

\[
L_{fd} = V_{air} \times \left(\frac{1}{359}\right) \times \left(\frac{T_{proc}}{273.15}\right) \times \left(\frac{V_{PMDI}}{760}\right) \times M_w \times K_{MDI}
\]

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

\[
L_{fd} = 0.015 \text{ lbs/yr}
\]
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 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 feedstock that is used in the year. The average density of the cured foam is 2.0 pounds/ft$^3$ 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 time during the curing process.

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

$$L_{fd} = V_{air} \times \frac{1}{359} \times \frac{273.15}{T_{proc}} \times \frac{V_{Pmdi}}{760} \times M_w \times K_{mdi}$$

Where:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{fd}$</td>
<td>emissions from the enclosed process in lb/yr</td>
</tr>
<tr>
<td>$V_{air}$</td>
<td>annual volume of displaced air in ft$^3$/yr</td>
</tr>
<tr>
<td>$T_{proc}$</td>
<td>process temperature in K. This is the maximum temperature of MDI tack-free time</td>
</tr>
<tr>
<td>$V_{Pmdi}$</td>
<td>vapor pressure of MDI in mm Hg. at process temperature</td>
</tr>
<tr>
<td>$M_w$</td>
<td>250.26 (this is the molecular weight of MDI)</td>
</tr>
<tr>
<td>$K_{mdi}$</td>
<td>adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature</td>
</tr>
<tr>
<td>359</td>
<td>the molar volume of an ideal gas in ft$^3$/lb-mole @ 0 °C and 1-atmosphere</td>
</tr>
</tbody>
</table>

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

$$V_{air} = \frac{\text{Annual material usage (M$_a$)}}{\text{Foam Density (F$_d$)}}$$

$$V_{air} = \frac{(1,500,000 \text{ lbs/yr} \times 2.0 \text{ lbs/ft}^3) \times 750,000 \text{ ft}^3/\text{yr}}$$
Step II: **Determine Process Temperature in K**

\[
K = (°C + 273.15)
\]

\[
K = (70 + 273.15)
\]

\[
K = 343.15
\]

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

MDI Vapor Pressure Chart \((V_{p_{mdi}})\) is \(1.34 \times 10^{-3}\) 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:

\[
L_{fd} = V_{air} \times \left(\frac{1}{359}\right) \times \left(\frac{273.15}{T_{proc}}\right) \times \left(\frac{V_{p_{mdi}}}{760}\right) \times M_w \times K_{mdi}
\]

\[
L_{fd} = (750,000 \text{ ft}^3/\text{year})\left(\frac{1}{359}\right)\left(\frac{273.15}{343.15}\right)\left(\frac{1.34 \times 10^{-3}\text{ mmHg}}{760\text{ mmHg}}\right) (250.26)(0.61)
\]

\[
L_{fd} = 0.455 \text{ lb/year}
\]

### 6.0 Belt & Tire Cord Manufactures

A MDI/PMDI mixture is used in belt manufacturing as a hardener. In the manufacture of belts, part of the process is to run synthetic cords through a vat solution containing a MDI/PMDI and toluene mixture and then pass it through an oven to activate the bonding process between the synthetic cord and isocyanate and dry the cord coating. The off-gases from the oven are passed through an incinerator or combustion device for destruction. Depending upon the process, the synthetic cord then goes through a number of various mixture dips and oven treatments. Once the cords have been treated, they are wound on spools for use in the belt building process.

The typical process consists of synthetic cords (60 -100 strands) averaging between 1/16 inch to ¼ inch) are passed through a vat solution containing a 15% solution of MDI/PMDI and toluene. The cords then pass through an oven that is heated to 250-280 °F. The length of the oven is 30 feet in length. While the cords are being processed in the oven, the MDI/PMDI impregnates the cords and reactivity bonds with the cord fibers. The excess solution of toluene and MDI/PMDI is evaporated off. The off gas of the oven is passed through a combustion device to destroy excess solvent and MDI/PMDI mixture or vented to the atmosphere. The cords pass through another vat solution containing a hardener and toluene. The cords then passed through another oven at 450-480 °F. The off gas from the oven is used as makeup air for the first oven with the excess air being diverted through a combustion device. Once the cords have been treated and cooled, they are wound on spools for use in the belt building process. The cords are processed at a rate of 175 feet/hour and can go through a number of dipping solutions. The process runs for 24 hours a day, 5 days a week.
The estimated MDI emissions can be calculated by taking the actual operating conditions for the application into consideration.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is saturated with all the MDI that is available. Actual operating conditions showed that the exit temperature of the stack was 250 °F and 8500 cfm and the cords were fed at a rate of 175 feet/hour. The length of the oven is 30 feet. The amount of MDI/PMDI in the feed is 15% with the actual concentration of MDI in the MDI/PMDI feedstock being 50%. The MDI emissions can be calculated using the following formula:

\[
L = \frac{V_{\text{air}}}{359} \times \frac{273.15}{T_{\text{sp}}} \times 60 \times \frac{C_{\text{mdi}}}{1000000} \times M_W \times k_{\text{MDI}} \times C_f \times R_{\text{MDI}}
\]

Where:
- \( L \) = the emissions in lb/hr
- \( V_{\text{air}} \) = the exhaust airflow rate in ft³/min
- \( T_{\text{sp}} \) = the exhaust temperature in K
- \( C_{\text{mdi}} \) = the MDI concentration, in ppmv, in the exhaust air
- \( M_W \) = the molecular weight of MDI (250.26)
- \( k_{\text{MDI}} \) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- \( C_f \) = per cent MDI/PMDI in solution
- 359 = the molar volume of an ideal gas in ft³/lb-mole @ 0 °C and 1-atmosphere
- \( C_{\text{mdi}} \) = \( \frac{\text{VP}_{\text{MDI}}}{760} \times 10^6 \)
- \( \text{VP}_{\text{MDI}} \) = MDI vapor pressure at exhaust temperature
- \( R_{\text{MDI}} \) = Unreacted fraction of MDI

Where:
- \( R_{\text{MDI}} = e^{-k \times t_R} \)

Where:
- \( R_{\text{MDI}} \) = the unreacted fraction of MDI
- \( k \) = the first order reaction rate constant in min⁻¹
- \( t_R \) = the reaction time in minutes

Therefore:

\[
L = \frac{8500}{359} \times \frac{273.15}{394.3} \times 60 \times \frac{0.15}{1000000} \times 250.26 \times 1 \times 0.15 \times e^{-1 \times t_R}
\]

Where:
- \( L \) = the emissions in lb/hr
- \( V_{\text{air}} \) = 8500 ft³/min
- \( T_{\text{sp}} \) = 250 °F = 394.3 K
- \( M_W \) = 250.26
5-15

\[ \text{Cf} = 15\% \]

359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 \(^\circ\)C and 1-atmosphere

\[ \text{VP}_{\text{MDI}} = 0.08788 \text{ mm} \]

\[ \text{Cmdi} = \frac{(0.08788/760) \times 10^{-6}}{115.6 \text{ ppmv}} \]

\[ \text{R}_{\text{MDI}} = e^{(-k \times t_R)} \]

\( k \) = the first order reaction rate constant in min\(^{-1}\)

\( t_R \) = the reaction time in minutes. (Total residence time in oven)

The cord passes through 30 feet of oven at a temperature of 280 \(^\circ\)F and then another 30 feet where the cords are cooled before going through a second vat solution. Though the reaction is complete after 30 feet, a worst-case scenario is to assume completion is done after the cord exits the oven:

\[ t_R = \frac{(30 \text{ ft} \times 2)/175 \text{ ft/hr}}{0.34 \text{ hr} = 21 \text{ min}} \]

\[ \text{R}_{\text{MDI}} = 0.001 \text{ (assuming complete reaction is 99.9\%)} \]

Solving for \( k \):

\[ k = 0.329 \text{ min}^{-1} \]

If we substitute the \( k \) constant in the equation, we will find the free amount of MDI at the midpoint of the reaction is 0.0316 or that the reaction is 96.84\% complete.

Substituting the values into the equation the emissions per hour are:

\[ L = \frac{V_{\text{air}}}{359} \times \frac{(273.15/T_{\text{sp}})}{60} \times \frac{\text{Cmdi}}{1000000} \times M_W \times k_{\text{MDI}} \times C_f \times R_{\text{MDI}} \]

\[ L = \frac{8500/359}{(273.15/394.3)} \times (60) \times \frac{115.6}{1000000} \times (250.26) \times (0.69) \times (0.15) \times (0.0316) \]

\[ L = 0.093 \text{ lbs/hr} \]

This represents the maximum emission rate at steady state conditions prior to the exhaust stream being treated.

The entire concentration profile of the free MDI can be calculated and plotted assuming a first order reaction mechanism. Plotting the un-reacted profile and taking the area under the curve, we find that the effective unreacted fraction is 0.146 or 85.4\% completion. Therefore:

\[ L = \text{the emissions in lb/hr} \]

\[ V_{\text{air}} = 8500 \text{ ft}^3/\text{min} \]

\[ T_{\text{sp}} = 250 \text{ \(^\circ\)F} = 394.3 \text{ K} \]

\[ M_W = 250.26 \]

\[ k_{\text{MDI}} = 0.69 \]

\[ C_f = 15\% \]
VP_{MDI} = 0.08788 mm

C_{mdi} = (0.08788/760) \times 10^6 = 115.6 \text{ ppmv}

R_{MDI} = e^{-k \cdot t_R}

k = \text{the first order reaction rate constant in min}^{-1}

t_R = \text{the reaction in minutes. (Total resonance time in oven)}

\begin{align*}
t_R &= \frac{(30 \text{ ft} \times 2)}{175 \text{ ft/hr}} = 0.34 \text{ hr} = 21 \text{ min} \\
R_{MDI} &= 0.146
\end{align*}

Substituting the values into the equation the emissions per hour are:

\begin{align*}
L &= \frac{V_{air}}{359} \times \frac{(273.15)}{T_{sp}} \times 60 \times \frac{(C_{mdi}/1000000)}{M_w} \times k_{MDI} \times C_f \times R_{MDI} \\
L &= \frac{8500}{359} \times \frac{(273.15)}{394.3} \times 60 \times \frac{(115.6/1000000)}{250.26} \times (0.69) \times (0.15) \times (0.146) \\
L &= 0.426 \text{ lbs/hr (before control)} \\
L &= 0.426 \text{ lbs/hr} \times 24 \text{ hrs/day} \times 5 \text{ days/wk} \times 52 \text{ wks/yr} \\
L &= 2658 \text{ lbs/yr before control and reaction completion of 84.4%}
\end{align*}

The value above represents the emission rate before control. The standard control method in the Belt & Tire Cord Industry is incineration. If we assume a worst case scenario of only 85% control efficiency, the emission rate after control will be:

\begin{align*}
L_y &= 0.426 \text{ lbs/hr} \times 0.15 = 0.064 \text{ lbs/hr} \\
L_y &= 0.064 \text{ lbs/yr} \times 24 \text{ hrs/day} \times 5 \text{ days/wk} \times 52 \text{ wks/yr} \\
L_y &= 399 \text{ lbs/yr (This assumes no excess of MDI in Solution)}
\end{align*}

If we assume that the MDI present in the vat solution does not react with the cord, fibers the maximum emission rate can be calculated with the formula:

\begin{align*}
L &= \frac{V_{air}}{359} \times \frac{(273.15)}{T_{sp}} \times 60 \times \frac{(C_{mdi}/1000000)}{M_w} \times k_{MDI} \times C_f \times R_{MDI} \\
\text{Where:}
L &= \text{the emissions in lb/hr} \\
V_{air} &= \text{the exhaust airflow rate in ft}^3/\text{min} \\
T_{sp} &= \text{the exhaust temperature in K} \\
C_{mdi} &= \text{the MDI concentration, in ppmv, in the exhaust air} \\
M_w &= \text{the molecular weight of MDI (250.26)} \\
k_{MDI} &= \text{the adjustment factor to the vapor pressure that is a function of MDI} \\
C_f &= \text{per cent MDI/PMDI in solution} \\
359 &= \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ 0 °C and 1-atmosphere}
\end{align*}
\[ C_{\text{mdi}} = \left( \frac{\text{VP}_{\text{MDI}}}{760} \right) \times 10^6 \]
\[ \text{VP}_{\text{MDI}} = \text{MDI vapor pressure at exhaust temperature} \]
\[ R_{\text{MDI}} = \text{unreacted fraction of MDI} \]

Therefore:

\[
L = \text{the emissions in lb/hr} \\
V_{\text{air}} = 8500 \text{ ft}^3/\text{min} \\
T_{sp} = 250 \degree F = 394.2 \text{ K} \\
M_W = 250.26 \\
K_{\text{MDI}} = .69 \\
C_f = 15% \\
359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole} @ 0 \degree C \text{ and 1-atmosphere} \\
\text{VP}_{\text{MDI}} = 0.08788 \text{ mm} \\
C_{\text{mdi}} = \left( \frac{0.08788}{760} \right) \times 10^6 = 115.6 \text{ ppmv} \\
R_{\text{MDI}} = 1.0 \\
L = \left( \frac{V_{\text{air}}}{359} \right) \times (273.15/T_{sp}) \times 60 \times (C_{\text{mdi}}/1000000) \times M_W \times k_{\text{MDI}} \times C_f \\
L = \left( \frac{8500}{359} \right) \times (273.15/394.2) \times (115.6/1000000) \times (250.26) \times (.69) \times (.15) \times (60) \times (1) \\
L = 2.94 \text{ lbs/hr (Worst case: No reaction/No control)}
\]

If the amount of excess of MDI present in the vat solution is known, then this can be factored into the equation. However, based upon the above set of conditions the maximum emission rate cannot exceed 2.94 lbs/hr.

### 7.0 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 indoor storage tank that is temperature controlled. The MDI component product is transferred to 2,000 pound 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 \degree F (25 \degree 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 laminate conveyor passes through a heated oven where the temperature is kept at a constant 180 \degree F. The tack-free time is 5 seconds. Assume that the hot air in the oven passes over the laminate surface once at a rate of 5 meters/second. The facility produces laminate boardstock that is on average 2 inch thick by 4 feet wide at the rate of 10 linear feet per minute. The operation takes place in an area that measures 150 feet long x 25 feet wide x 20 high (100,000 ft.\(^3\)). The air concentration in the workplace shows 0.001 ppm MDI. The building under goes 5 air changes per
hour, and production operates 16 hours per day 250 days a year.

**Calculating Stack Emissions**

To estimate 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 gram/day) is determined from the following expression:

\[
W = 25.4 \times V_{P_{mdi}} \times \left(\frac{M_w}{T_{proc}}\right) \times (u)^{0.78} \times S_A \times t_{TF} \times K_{mdi}
\]

Where:

- \(W\) = the evaporation losses from the open process in gram/day
- \(V_{P_{mdi}}\) = the vapor pressure of MDI in atm. at process temperature
- \(T_{proc}\) = 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)
- \(u\) = the airflow speed in m/sec. This is the airflow in the vicinity of the process
- \(S_A\) = the exposed surface area in \(M^2\). This is the exposed surface area per day. For boardstock production, the surface area can be determined from the dimensions of the board
- \(t_{TF}\) = the tack-free time in seconds. The default value is 5 sec
- \(K_{mdi}\) = 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**

The total exposed surface area \((S_A)\) 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. The laminate conveyor passes through a heated oven where the temperature is kept at a constant temperature of 180°F. The tack-free time is 5 seconds. Assume that the hot air in the oven passes over the laminate surface once at a rate of 5 meters/second. The facility produces laminate boardstock that is on average 2 inch thick by 4 feet wide at the rate of 10 linear feet per minute.

Total length of foam (ft) produce/day = (Production time)( Rate)
Length of foam (ft/day) = (16 hours/day) (60 min/hour)(10 ft foam/Min)
Length of foam (ft/day) = 9,600

Surface Area = top surface + side surface + cut-end surface
Top surface = 9,600 ft length x 4 ft width
Top Surface = 38,400 ft²
Side surface = 2 x 9,600 ft x (2 inch/12 in)/ft
Side surface = 3,200 ft²
Cut-end surface = 2(4-ft by 2-inch surfaces) are produced for each 8-ft board that is manufactured and cut
Cut-end surface = 2 x [4 ft x (2 in width/12 in/ft)](9,600 ft/8 ft)
Cut-end surface = 1,600 ft²

Therefore, surface area is equal to:

Surface area (A) = 38,400 ft² + 3,200 ft² + 1,600 ft²

Step II: Determine Vapor Pressure in Atmospheres @ Tₚᵣᵒˢ

VPmdi = the vapor pressure of MDI in atm. at process temperature
VPmdi = 4.361 x 10⁻³ mm/760mm
VPmdi = 5.74 x 10⁻⁶ atm

Step III: Determine the Process Temperature in K

Tₚᵣₒᶜ = (° C + 273.15)
Tₚᵣₒᶜ = 355.4 K

Step IV: Determine Adjustment Factor Kmdi

From Adjustment Factor Chart Kmdi is 0.62 @ 356 K

Therefore:
8.0 Boats

Releases of MDI/PMDI will be calculated for a boat assembly that injects, through a static mixing nozzle, 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 manufacturers via 2,500-pound totes and these totes are stored in-doors where the temperature remains constant. The foam mixture is injected at a temperature of 160 °F (70 °C). There are 18 different boat models manufactured ranging from 12-16 feet runabouts to 100-150 feet yachts. The majority of boat manufacturers produce boats ranging from 25-30 feet 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 inches thick, has an average density of 1.8 pounds/cubic feet, and the surface area of the hull is 350 ft². Fresh air is pulled across the work area and exhausted through hull-stiffening stack. The operation is performed in an area that is 100 feet by 100 feet by 40 feet and has a MDI concentration of 0.001ppm. Calculate the stack emissions.

Calculating Stack Emissions

Emissions from closed processes can be estimated when the volume of the mold is known and the number of pieces produced are known, which can be used to calculate the total volume of air displaced from the operations. 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:

\[ L_c = V_{air} \times \frac{1}{359} \times \frac{273.15}{T_{proc}} \times \frac{V_{P_{MDI}}}{760} \times \frac{M_w}{K_{MDI}} \]

Where:

- \( L_c \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft³/yr
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{P_{MDI}} \) = vapor pressure of MDI in mm Hg at process temperature
\( M_w = 250.26 \) (this is the molecular weight of MDI)
\( K_{\text{MDI}} = \) adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
359 = the molar volume of an ideal gas in \( \text{ft}^3/\text{lb-mole} @ 0^\circ \text{C} \) and 1-atmosphere

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

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

\[
V_{\text{air}} = (350 \text{ ft}^2)(27 \text{ pieces/day})(250 \text{ days/yr})(2/12)\text{ft}
\]

\[
V_{\text{air}} = 3.94 \times 10^5 \text{ ft}^3/\text{yr}
\]

**Step II: Calculate Maximum Process Temperature in K**

The maximum temperature is the oven temperature of 70 \(^\circ\text{C}\) or;

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

\[
T_{\text{proc}} = 343.15 \text{ K}
\]

**Step III: Determine Vapor Pressure of MDI @ 341.15 K \( (V_{\text{PMDI}}) \)**

The vapor pressure @ 343.15 K is 1.340 \( \times 10^{-3} \) mm

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

Adjustment factor @ 343.15 K and 50% MDI is 0.61

Therefore:

\[
L_c = V_{\text{air}} \times \frac{1}{359} \times \frac{273.15}{T_{\text{proc}}} \times \frac{(V_{\text{PMDI}})}{760} \times M_w \times K_{\text{MDI}}
\]

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

\[
L_c = 0.2375 \text{ lbs/ year}
\]

**9.0 Carpet & Rug Underlay**

The Carpet and Rug Industry incorporates isocyanate into the production process to enhance the quality and performance of the final product. The isocyanate feed, consisting of methylenebis (phenyl Isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI), is reacted with a blend of polyol and inorganic filler. This formulation is continuously applied to the carpet substrate on a moving conveyer belt. Upon curing, the polyurethane that is formed imparts elasticity, strength, and resistance to the carpet.
There are two basic process configurations for coating carpets with polyurethane formulations. The flow-on method is generally used to apply laminate adhesives or cushion formulations to carpet floor coverings and reactively binding yarn and fabric. The process consists of pre-mixing a polyol and inorganic filler and delivering it as a liquid stream to a mixing and frothing device where it is combined with MDI/PMDI. The formed polyurethane is distributed across the width of the backside of the textile fabric by a traversing positioning device. A reservoir of the mixture is maintained in contact with the backside of the fabric and a “doctoring” blade scraps onto the fabric the desired amount of the polymerizing mixture. The “doctoring” blade also gauges and controls the gap of the desired thickness of the laminating layer. Once applied, the carpet is then passed through a heated oven for curing, cooled and collected on take-up rolls for storage.

The second method takes the pre-mixed polyol/filler and mixes it with MDI in a specially designed low-pressure mixing head. A reservoir of the mixture is maintained on the belt and the newly formed polyurethane is spread across the width of a Teflon-impregnated conveyor belt with the use of a traversing positioning device. The carpet is then continuously laid onto the polymerizing mixture and conveyed over heated plates where the carpet is heated until the polymerization is complete. The carpet is the cooled and collected on take-up rolls for further processing.

**Process Description**

A two-component system is used to produce a carpet backing which is applied to a substrate surface. Part A, representing 84% of the total formulation, is a mixture of polyol and inorganic filler. Part B, representing 16% of the total formulation, is a 50% MDI/PMDI isocyanate mixture. The mixture is continuously applied on a conveyor belt having a width of 8 feet and moving at a speed of 30 feet/minute. The application rate of the formulation is 2 lb/yd². The carpet production rate is 345,600 ft²/day, corresponding to a consumption rate of 76,800 lb/day of total formulation (12,288 pound/day of MDI/PMDI). The process temperature is 200 °F and the air gap above the conveyor belt is 6 inches. An air blower with a capacity of 20,000 ft³/minute discharges air at a temperature of 130 °F. The unit operates 6,000 hours/year (250 days/year). Estimate the annual emissions of MDI using the proposed methods.

The methodology developed assumes that the application of the MDI formulation occurs on a conveyor belt that is essentially enclosed. An air blower maintains a slight negative pressure in the conveyor belt area by continuously exhausting air from the process area through a stack. The MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the reaction rate between the isocyanate and polyol resin, and the "effective" MDI concentration in the gas stream. A block diagram of the carpet coating operation is shown in Figure 2. As a worst-case scenario, it can be assumed that the air leaving the application area will be in thermodynamic equilibrium with the MDI present on the carpet. This approach can usually be applied irrespective of how the polyurethane is applied to the carpet substrate.
The emissions from carpet coating operation can be estimated from the following expression:

\[
L_{cc} = \frac{V_{air}}{359} \left(60 \cdot \frac{ppmv}{1000000} \cdot MW \cdot K_{MDI} \cdot C_{iso}/100 \cdot t_{cc} \cdot R_{MDI}\right) \quad (1)
\]

Where:

- \(L_{cc}\) = the emissions in lb/year for carpet coating operations
- \(V_{air}\) = the exhaust airflow rate in ft\(^3\)/min (at 32 °F = 0 °C)
- \(ppmv\) = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T\(_{st}\)). It is directly determined from the vapor pressure
- \(T_{st}\) = the temperature of the air leaving the stack in K
- \(MW\) = the molecular weight of MDI (250.26)
- \(K_{MDI}\) = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of \(K_{MDI}\) is 1.00 for pure MDI
- \(C_{iso}\) = the % of isocyanate feedstock in the total formulation
- \(R_{MDI}\) = the unreacted fraction of MDI on the conveyor belt relative to the MDI initially present in the formulation. This value reflects the unreacted fraction of MDI present at the midpoint of the application process and is based upon a first-order reaction
- \(t_{cc}\) = the total time of operation in hours/year
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere
- 60 = time, minutes/hr

A first order reaction can be expressed by the following reaction:

\[
R_{mdi} = e^{-k(t_R)} \quad (2)
\]

Where:

- \(R_{MDI}\) = the unreacted fraction of MDI
- \(k\) = the first order reaction rate constant in min\(^{-1}\)
- \(t_R\) = the reaction time in minutes

Solution:

\[
\begin{align*}
V_{air} & = 20,000 \text{ ft}^3/\text{min (at 130 °F)} = 16,676 \text{ ft}^3/\text{min (at 32 °F)} = 327.6 \\
T_{st} & = 130 °F = 54.4 °C = 327.6 K \\
V_P_{mdi} & = 2.879 \times 10^{-1} \text{ mm Hg} \\
ppmv & = 2.879 \times 10^{-1}/760 = 0.3788 \text{ ppmv} \\
MW & = 250.26 \\
\% \text{ MDI} & = 50 \\
K_{MDI} & = 0.59 \\
C_{iso} & = 16 \% \\
t_{cc} & = 6000 \text{ hr/yr}
\end{align*}
\]

To determine the value of \(R_{mdi}\) the expression for the first-order reaction is used:

\[
R_{mdi} = e^{-k(t_R)} \quad (2)
\]

Where:

- \(R_{mdi}\) = the unreacted fraction of MDI
\[ k = \text{the first order reaction rate constant in } \text{min}^{-1} \]
\[ t_R = \text{the reaction time in minutes} \]

For a conversion of 99.9 %, \( R_{\text{mdi}} = 0.001 \) and \( t_R = 4.0 \text{ min} \)

Substituting the appropriate values into Equation 2:
\[ 0.001 = e^{-k(4.0)} \]
\[ k = 1.727 \text{ min}^{-1} \]

For \( t_R = 2.0 \text{ min} \)
\[ R_{\text{mdi}} = e^{-1.727(2.0)} = 0.0316 \]

This value means that after 2 minutes (half the reaction time) about 97% of the “free” MDI has polymerized and no longer contributes to the MDI emission.

\[ R_{\text{mdi}} = 0.03 \text{ (this value represents a typical unreacted fraction of MDI at the midpoint of the application process)} \]

Substituting the appropriate values into Equation 1:
\[ L_{cc} = (16,676 \text{ ft}^3/\text{min}/359\text{ ft}^3/\text{lbf-mole}) (60\text{min/hr}) (0.3788\text{ppmv}/1000000) \]
\[ (250.26 \text{lbf/lb-mole}) (0.59) (16\text{ parts MDI/100parts mixture}) (6000\text{hrs/yr}) (0.0316) \]
\[ L_{cc} = 4.73 \text{ lbf/yr} \]

The annual consumption of MDI/PMDI = \( (12,288\text{ lbf/day}) (250\text{ days/yr}) \)
\[ = 3,072,000 \text{ lbf/yr isocyanate feedstock} \]

\[
\text{Emission factor} = \frac{\text{MDI Emitted}}{\text{lbs MDI Processed}}
\]
\[ = \frac{4.73}{3,072,000} \]

\[
\text{Emission factor} = 1.54 \times 10^{-6} \text{ lb MDI emission/lb isocyanate}
\]
Methylenediphenyl diisocyanate (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 an 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 pounds of a 1/1 ratio resin to Diisocyanate blend. The temperature of the mixture is 80 °F.
Calculating Stack Emissions

To estimate the emissions from closed process 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:

\[ L_c = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{MDI}}{760} \right) \times M_w \times K_{MDI} \]

Where:

\[ L_c = \text{emissions lb/yr} \]
\[ V_{air} = \text{annual volume of displaced air in ft}^3/\text{yr} \]
\[ T_{proc} = \text{process temperature in K (maximum temperature of the MDI)} \]
\[ V_{MDI} = \text{vapor pressure of MDI in mm Hg at process temperature} \]
\[ M_w = 250.26 \text{ (this is the molecular weight of MDI)} \]
\[ K_{MDI} = \text{adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ 0 }{^\circ}\text{C and 1-atmosphere} \]

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

\[ V_{air} = \text{(Area/piece)(No. Pieces/year)(Thickness)} \]
\[ V_{air} = (21 \text{ ft}^2)(340 \text{ pieces/hr.})(24 \text{ hr/day})(365 \text{ days/yr})(2/12)\text{ft} \]
\[ V_{air} = 1.04 \times 10^7 \text{ft}^3/\text{yr} \]

Step II: Calculate Maximum Process Temperature in K

The maximum temperature is the oven temperature of 80 \(^\circ\)F or;

\[ T_{proc} = 299.8 \text{ K} \]

Step III: Determine Vapor Pressure of MDI @ 299.8 K \((V_{MDI})\)

The vapor pressure @ 299.8 K is \(1.23 \times 10^{-5}\)mm

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

Adjustment factor @ 299.8 K and 25% MDI is 0.34
Therefore:

\[ L_c = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{P_{MDI}}}{760} \right) \times M_w \times K_{MDI} \]

\[ L_c = (1.04 \times 10^{-7} \text{ ft}^3/\text{yr})(1/359)(273.15 \text{ K } / 299.8 \text{ K})(1.23 \times 10^{-5} \text{ mm Hg } / 760) \]

\[ L_c = (250.26)(0.34) \]

\[ L_c = 0.0365 \text{ lbs/yr} \]

11.0 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:

\[ L_{fill} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{fill}} \right) \times \left( \frac{V_{P_{MDI}}}{760} \right) \times M_w \times K_{MDI} \times C_{blnd} \]

Where:

- \( L_{fill} \) = the emissions from the filling operation in lbs/yr
- \( V_{air} \) = the annual volume of displaced air in \( \text{ft}^3/\text{yr} \)
- \( T_{fill} \) = the temperature the material is charged or filled at in K
- \( V_{P_{MDI}} \) = the vapor pressure of MDI in mm Hg at the charging/filling temperature
- \( M_w \) = the 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/or blend and at the blending/filling temperature.
- \( C_{blnd} \) = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then \( C_{blnd} \) is 1
- \( 359 \) = the molar volume of an ideal gas in \( \text{ft}^3/\text{lb-mole} @ 0^\circ \text{C and 1-atmosphere} \)
To calculate the total emissions, determine what emissions 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**

The 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:

\[
V_{\text{air}} = (\text{Number containers/year}) \times (\text{Volume of container})
\]

\[
= (5,000 \text{ containers/day} \times 250 \text{ days/yr}) \times (1/2 \text{ gallon})
\]

\[
= (625,000 \text{ gallons/year})/(7.48 \text{ gallons/ft}^3)
\]

\[
V_{\text{air}} = 83,556 \text{ ft}^3
\]

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

\[
V_{\text{air}} = V_{\text{air}} \times \%\text{MDI/PMDI}
\]

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

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

**Step II: Determine Vapor Pressure at Charging/Blending Temperature \(V_{P_{\text{MDI}}}\)**

\(V_P \ @ \ 70^\circ\text{F} \text{ is } 6.09 \times 10^{-6} \text{ mm Hg}\)

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

\(T_{\text{fill}} \text{ is equal to } 294.2 \text{ K}\)

**Step IV: Determine Adjustment Factor \(K_{\text{MDI}}\)**

The adjustment factor of 50% MDI/PMDI @ 294.2 K is 0.54

**Step V: Determine \(C_{\text{blnd}}\)**

\(C_{\text{blnd}} \text{ is equal to } 1\)
Therefore:

\[ L_{\text{fill}} = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{\text{fill}}} \right) \times \left( \frac{V_P \text{MDI}}{760} \right) \times M_w \times K_{\text{MDI}} \times C_{\text{blend}} \]

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

\[ L_{\text{fill}} = 2.379 \times 10^{-4} \text{ lbs/yr} \]

**Part II: Determine Losses from the Filling of Containers**

This step is nearly identical to Part I above with the exception of \( C_{\text{blend}} \), which from the example is 40% or 0.4. The losses from the filling of the containers can be found from the following equation:

\[ L_{\text{fill}} = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{\text{fill}}} \right) \times \left( \frac{V_P \text{MDI}}{760} \right) \times M_w \times K_{\text{MDI}} \times C_{\text{blend}} \]

Where:

- \( L_{\text{fill}} \) = the emissions from the filling operation in lbs/yr
- \( V_{\text{air}} \) = the annual volume of displaced air in ft\(^3\)/yr
- \( T_{\text{fill}} \) = the temperature the material is charged or filled at in K
- \( V_P \text{MDI} \) = the vapor pressure of MDI in mm Hg at the charging/filling temperature
- \( M_w \) = the molecular weight of MDI (250.26)
- \( K_{\text{MDI}} \) = 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
- \( C_{\text{blend}} \) = the proportion of MDI/PMDI in the blend

**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:

\[ V_{\text{Tair}} = (\text{Number containers/year}) \times (\text{Volume of container}) \]
\[ = (5,000 \text{ containers/day x 250 days/year}) \times (1/2 \text{ gallon}) \]
\[ = (625,000 \text{ gallons/year})/(7.48 \text{ gallons/ft}^3) \]

\[ V_{\text{Tair}} = 83,556 \text{ ft}^3 \]

**Step II: Determine Vapor Pressure at Charging/Blending Temperature \( V_P \text{MDI} \)**

\( V_P @ 70^\circ F \) is \( 6.09 \times 10^{-6} \text{ mm Hg} \)
Step III: **Determine Charging/Filling Temperature (T_{fill}) in K**

\[ T_{fill} \text{ is equal to } 294.2 \text{ K} \]

Step IV: **Determine Adjustment Factor K_{MDI}**

The adjustment factor of 50% MDI/PMDI @ 294.2 K is 0.54

Step V: **Determine C_{blnd}**

\[ C_{blnd} \text{ is equal to } 0.40 \]

Therefore:

\[
L_{fill} = \frac{V_{air}}{359} \times \frac{273.15}{T_{fill}} \times \frac{V_{P_{MDI}}}{760} \times M_{w} \times K_{MDI} \times C_{blnd}
\]

\[
L_{fill} = \frac{(83,556 \text{ ft}^3)}{(1/359)} \times \frac{(273.15/294.2)}{(6.09 \times 10^{-6} \text{ mm Hg}/760)} \times (250.26) \times (0.54) \\
L_{fill} = 9.51 \times 10^{-5} \text{ lbs/yr}
\]

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

\[
L_{fill} = L_{f \text{ charging}} + L_{f \text{ filling}}
\]

\[
L_{fill} = (2.379 \times 10^{-4} \text{ lbs/yr}) + (9.51 \times 10^{-5} \text{ lbs/yr})
\]

\[
L_{fill} = 3.33 \times 10^{-4} \text{ lbs/yr}
\]

12.0 **Foundry & Casters**

Stack emissions from the process used by foundries & casters can be estimated using (1) material balance or (2) engineering calculations.

**Material Balance**

**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 cold box 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 325,000 pounds of Part II. The two-component system is injected into the mold at ambient temperature (20 °C) and the exhaust temperatures of the hot ore pour and shakedown systems are 110 °C and 22 °C, respectively. The exhaust blowers are rated at 20,000 cfm and 50,000 cfm respectively. The reaction goes to 99.99% completion. The (Material) Safety Data Sheets (SDS) shows the each component consists of the following:

Part I consists of:

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

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:**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>%</th>
<th>Lbs. Used</th>
<th>Lbs. Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>6</td>
<td>400,000</td>
<td>24,000</td>
</tr>
<tr>
<td>Trimethylbenzene</td>
<td>2.08</td>
<td>400,000</td>
<td>8,320</td>
</tr>
</tbody>
</table>
Naphthalene 1.98 400,000 7,920
Formaldehyde 0.3 400,000 1,200

Part II Chemicals:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>%</th>
<th>Lbs. Used</th>
<th>Lbs. Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI</td>
<td>39.95</td>
<td>325,000</td>
<td>29,838</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>4.06</td>
<td>325,000</td>
<td>13,195</td>
</tr>
</tbody>
</table>

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

Cold box Process:

Part I Chemicals:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% Reacted</th>
<th>% Evaporated</th>
<th>% Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Part II

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% Reacted</th>
<th>% Evaporated</th>
<th>% Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI</td>
<td>99.99</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Reacted</th>
<th>Evaporated</th>
<th>Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>21,600</td>
<td>0</td>
<td>2,400</td>
</tr>
<tr>
<td>MDI</td>
<td>129,825</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0</td>
<td>10,558</td>
<td>10,588</td>
</tr>
</tbody>
</table>

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.
Engineering Calculations

Core Box Step:

During this step, the MDI formulation is injected into the mold at ambient temperature. The losses will correspond to the total volume of air displaced from the molds at the filling temperature. A reasonable worst-case estimate of filling losses can be made based on the total volume of MDI formulation consumed, the composition of the MDI formulation and the injection temperature.

The core box losses can be estimated from the following expression:

\[ L_{cb} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{cb}} \right) \times \left( \frac{VP_{mdi}}{760} \right) \times MW \times K_{mdi} \times C_{iso}/100 \]

Where:

- \( L_{cb} \) = the emissions from the core box step in lb/yr
- \( V_{air} \) = the annual volume of displaced air in ft\(^3\)/yr (at the filling temperature)
- \( T_{cb} \) = the filling temperature in K
- \( VP_{mdi} \) = the vapor pressure of MDI in mm Hg at the filling temperature
- \( MW \) = the molecular weight of MDI (250.26)
- \( K_{mdi} \) = an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- \( C_{iso} \) = the % of isocyanate feedstock in the total formulation. If only MDI/PMDI material is filled then \( C_{iso} = 100\% \)

Therefore:

\[ L_{cb} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{cb}} \right) \times \left( \frac{VP_{mdi}}{760} \right) \times MW \times K_{mdi} \times C_{iso}/100 \]

\[ V_{air} = 400,000 \text{ lbs Part 1} + 325,000 \text{ lbs Part 2} = 725,000 \text{ lbs} \times 1 \text{ gal/10 lbs} \times 1 \text{ ft}^3/7.45 \text{ gal} \]

\[ V_{air} = 9692 \text{ ft}^3/\text{yr} \]

\[ T_{cb} = \text{ the filling temperature in K} = 20 \degree \text{C} + 273.15 \degree \text{K} = 293.15 \degree \text{K} \]

\[ VP_{mdi} = \text{ the vapor pressure of MDI in mm Hg @20 \degree \text{C}} = 5.28 \times 10^{-6} \text{ mm Hg} \]

\[ MW = \text{ the molecular weight of MDI (250.26)} \]

\[ K_{mdi} = \text{ an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature. 100 pure MDI is used in the feedstock K =1.0} \]

\[ C_{iso} = \text{ the % of isocyanate in the total formulation. 325,000 lbs x 39% / 725,000 lbs} \]

\[ C_{iso} = 0.04 \]

\[ L_{cb} = (9692 \text{ ft}^3/\text{yr}) \times (1/359) \times (273.15/293.15) \times (5.28 \times 10^{-6}/760) \times (250.26) \times (1) \times (0.04) \]

\[ L_{cb} = 1.80 \times 10^{-6} \text{ lbs/yr} \]
Mold Pour and Shakeout Step

During the mold pour and shakeout step, exhaust air blowers are used to maintain a slight negative pressure in the process area by continuously drawing air and exhausting it to the atmosphere through a series of exhaust stacks. Residual MDI is thus removed from the mold and the sand. For this situation the MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the residual free MDI in the mold, and the “effective” MDI concentration in the gas stream. As a worst-case scenario, it can be assumed that the air leaving the process area will be in thermodynamic equilibrium with the free MDI remaining in the mold.

The losses from the mold pour and shakeout step can be estimated from the following expression:

\[ L_{so} = \left( \frac{V_{air}}{359} \right) \times (60) \times \left( \frac{ppmv}{1000000} \right) \times (MW) \times (K_{mdi}) \times \left( \frac{C_{iso}}{100} \right) \times (t_{so}) \times (F_{mdi}) \]

Where:

- \( L_{so} \) = the emissions in lb/year from the shakeout and mold pour step
- \( V_{air} \) = the exhaust airflow rate in ft\(^3\)/min (at stack temperature)
- \( ppmv \) = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (\( T_{st} \)). It is directly determined from the vapor pressure
- \( MW \) = the molecular weight of MDI (250.26)
- \( K_{mdi} \) = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanates feedstock and the temperature, the value of \( K_{mdi} \) is 1.00 for pure MDI
- \( C_{iso} \) = the % of isocyanate feedstock in the total formulation
- \( F_{mdi} \) = the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01 (1% of the initial MDI remains unreacted during this step)
- \( T_{so} \) = the total time of operation in hours/year
- \( 359 \) = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 \( ^\circ \)C and 1-atmosphere
- \( 60 \) = time, minutes/hour

Mold Pour:

- \( L_{mp} \) = the emissions in lb/year from the mold pour step
- \( V_{air} \) = the exhaust airflow rate in ft\(^3\)/min (at stack temperature)
- \( ppmv \) = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (\( T_{st} \)). It is directly determined from the vapor pressure
- \( MW \) = the molecular weight of MDI (250.26)
- \( K_{mdi} \) = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of \( K_{mdi} \) is 1.00 for pure MDI
MDI Emissions Reporting Guidelines for the Polyurethanes Industry

\[ C_{iso} = \text{the } \% \text{ of isocyanate feedstock in the total formulation} \]
\[ F_{mdi} = \text{the fraction of free MDI remaining in the mold. The free MDI is assumed to be } 0.01 \%(1\% \text{ of the initial MDI remains unreacted during this step}) \]
\[ T_{so} = \text{the total time of operation in hrs/yr} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ } 0 \, ^\circ \text{C and 1-atmosphere} \]
\[ 60 = \text{time, minutes/hr} \]

Where:

\[ V_{air} = 20,000 \text{ cfm} \times (273.15 \, ^\circ \text{K} / 383.15 \, ^\circ \text{K}) = 14,258 \text{ acfm} \]
\[ ppmv = (0.03898/760) \times (1,000,000) = 51.3 \text{ ppmv} \]
\[ MW = 250.26 \]
\[ K_{mdi} = 1.0 \]
\[ C_{iso} = (29,838 \text{ lbs MDI}/725,000 \text{ lbs Total feed}) = .04 \]
\[ F_{mdi} = 0.0001 \]
\[ T_{so} = 8760 \text{ hrs/yr} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ } 0 \, ^\circ \text{C and 1-atmosphere} \]
\[ 60 = \text{time, minutes/hour} \]

Therefore:

\[ L_{mp} = (14,258 \text{ acfm}) \times (60\text{min/hr}) \times (51.3\text{ppmv}/1000000) \times (250.26) \times (0.04) \times (1.0) \times (8760) \times (0.0001) \]
\[ L_{mp} = 1.07 \text{ lbs/yr} \]

Using the same approach for the shakeout step, the estimated emissions are:

\[ L_{so} = \text{the emissions in lb/year from the shakeout and mold pour step} \]
\[ V_{air} = \text{the exhaust airflow rate in ft}^3/\text{min (at stack temperature)} \]
\[ ppmv = \text{the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure} \]
\[ MW = \text{the molecular weight of MDI (250.26)} \]
\[ K_{mdi} = \text{adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of } K_{mdi} \text{ is 1.00 for pure MDI} \]
\[ C_{iso} = \text{the } \% \text{ of isocyanate feedstock in the total formulation} \]
\[ F_{mdi} = \text{the fraction of free MDI remaining in the mold. The free MDI is assumed to be } 0.01 \%(1\% \text{ of the initial MDI remains unreacted during this step}) \]
\[ T_{so} = \text{the total time of operation in hrs/yr} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ } 0 \, ^\circ \text{C and 1-atmosphere} \]
\[ 60 = \text{time, mins/hr} \]
Where:

\[ V_{\text{air}} = 50,000 \text{ cfm} \times (273.15 \text{ K } / 295.15 \text{ K}) = 46,273 \text{ acfm} \]
\[ \text{ppmv} = (0.00000682 / 760) \times (1,000,000) = 0.0090 \text{ ppmv} \]
\[ MW = 250.26 \]
\[ K_{\text{mdi}} = 1.0 \]
\[ C_{\text{iso}} = (29,838 \text{ lbs MDI} / 725,000 \text{ lbs Total feed}) = 0.04 \]
\[ F_{\text{mdi}} = 0.0001 \]
\[ T_{\text{so}} = 8760 \text{ hrs/yr} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole} @ 0 \text{ } ^\circ\text{C and 1-atmosphere} \]
\[ 60 = \text{time, minutes/hr} \]

Therefore:

\[ L_{\text{so}} = (46,273 \text{ acfm}) \times (60 \text{ min/hr}) \times (0.009 \text{ ppmv/1000000}) \times (250.26) \times (0.04) \times (1.0) \times (8760) \times (0.0001) \]

\[ L_{\text{so}} = 6.12 \times 10^{-4} \text{ lbs/yr} \]

Total Emissions = \( L_{\text{cb}} + L_{\text{mp}} + L_{\text{so}} \)

Total Emissions = 1.80 \times 10^{-6} \text{ lbs/yr} + 1.07 \text{ lbs/yr} + 6.12 \times 10^{-4} \text{ lbs/yr}

Total Emissions = 1.07 \text{ lbs/yr}

13.0 Laminator (Cavity)

Methylenedis (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 by 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 pounds/minute. This is passed through an oven at an average temperature of 123 \(^\circ\text{F}\). The line runs at a rate of 16 ft\(^2\)/piece with an average board thickness of 1.60 inches and produces 24 pieces/minute.

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:

$$L_c = V_{air} \times \left(\frac{1}{359}\right) \times \frac{273.15}{T_{proc}} \times \frac{V_{P_{MDI}}}{760} \times M_w \times K_{MDI}$$

Where:

- $L_c$ = emissions lb/yr
- $V_{air}$ = annual volume of displaced air in ft$^3$/yr
- $T_{proc}$ = process temperature in K (maximum temperature of the MDI)
- $V_{P_{MDI}}$ = 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
- 359 = the molar volume of an ideal gas in ft$^3$/lb-mole @ 0 $^\circ$C and 1-atmosphere

**Step I: Calculate Annual Volume of Displaced Air (Vair)**

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

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

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

**Step II: Calculate Maximum Process Temperature in K**

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

$$T_{proc} = 323.7 \ K$$

**Step III: Determine vapor Pressure of MDI @ 323.7 K (V_{P_{MDI}})**

The vapor pressure @ 323.7 K is 1.92 x 10$^{-4}$mm

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

Adjustment factor @ 323.7 K and 25% MDI is 0.38

Therefore:

$$L_c = V_{air} \times \left(\frac{1}{359}\right) \times \frac{273.15}{T_{proc}} \times \frac{V_{P_{MDI}}}{760} \times M_w \times K_{MDI}$$

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

$$L_c = 1.534 \ lbs/yr$$
14.0 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:

\[
L_c = \frac{V_{air}}{359} \times \frac{273.15}{T_{proc}} \times \frac{V_{P_{MDI}}}{760} \times M_w \times K_{MDI}
\]

Where:

- \( L_c \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft\(^3\)/yr
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{P_{MDI}} \) = 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
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere

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

\[
V_{air} = \frac{(4,000,000 \text{ lbs/yr})/(10 \text{ lbs/gal})}{(1 \text{ gal/7.48 ft}^3)} = 53,469 \text{ ft}^3
\]
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 (} V_{P,\text{MDI}})\)

The vapor pressure @ 298.2 K is \(1.00 \times 10^{-5}\text{mm}\)

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

Adjustment factor @ 298.2 K and 25% MDI is 0.33

Therefore:

\[
L_c = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \frac{(273.15 / T_{\text{proc}})}{760} \times \frac{M_w}{V_{P,\text{MDI}}} \times K_{\text{MDI}}
\]

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

\[
L_c = 1.51 \times 10^{-4} \text{ lbs/ yr}
\]

15.0 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 is polyol and Part B is diisocyanate mixture. The two parts are mixed in a customized system that mixes within the dispenser head and the material is 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 in 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 pounds/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 time during the curing process.

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

\[ L_{pk} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{P_{MDI}}}{760} \right) \times M_w \times K_{MDI} \]

Where:
- \( L_{pk} \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft^3/yr
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{P_{MDI}} \) = 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
- 359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere

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

\[ V_{air} = \frac{\text{(Amount of material processed/yr)}}{\text{Foam Density}} \]

\[ V_{air} = \frac{(10.0 \times 10^6 \text{ lbs/yr})}{(1.5 \text{ lbs./ft}^3)} \]

\[ V_{air} = 6.6 \times 10^6 \text{ ft}^3/\text{yr} \]

Step II: **Calculate Process Temperature in K**

The process temperature is of 25°C or;

\[ T_{proc} = 298.15 \text{ K} \]

Step III: **Determine Vapor Pressure of MDI @ 298.15 K (\( V_{P_{MDI}} \))**

The vapor pressure @ 298.15 K is 1.072 x 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:

\[ \%\text{MDI/PMDI} = \frac{1}{(1+1)} \times 100 \]

\[ \%\text{MDI/PMDI} = 50 \% \]
The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

\[
\%\text{MDI} = (51.8) \times (50.0)
\]

\[
\%\text{MDI} = 25.0
\]

Adjustment factor @ 298.7 K and 25.0% MDI is 0.33

Therefore:

\[
L_{pk} = V_{\text{air}} \times \left(\frac{1}{359}\right) \times \left(\frac{273.15}{T_{\text{proc}}}\right) \times \left(\frac{V_{P_{\text{MDI}}}}{760}\right) \times M_w \times K_{\text{MDI}}
\]

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

\[
L_{pk} = 0.0188 \text{ lbs / yr}
\]

16.0 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 exhausted from bottom and top of reactor through blower system. Binder mixture contains 40% MDI. The reactor produces a log that is 5’ diameter and 10’ high. The 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:
\[ L_C = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{MDI}}{760} \right) \times M_w \times K_{MDI} \]

Where:
- \( L_C \) = emissions from the enclosed process in lb/yr
- \( V_{air} \) = the annual volume of displaced air in ft³/yr
- \( T_{proc} \) = the temperature material is dispensed at in K
- \( V_{MDI} \) = 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
- 359 = the molar volume of an ideal gas in ft³/lb-mole @ 0°C and 1-atmosphere

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

\[ V_{air} = \text{Annual Consumption} \times \text{Density} \]

\[ V_{air} = 1,344,000 \text{ lbs/yr} / 10 \text{ lbs/gal/7.48 gal/ft}^3 \]

\[ V_{air} = 1.783 \times 10^4 \text{ ft}^3/\text{yr} \]

**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 \( (V_{MDI}) \)**

The vapor pressure @ 425.9 K is \( 7.034 \times 10^{-1} \)mm

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

Adjustment factor @ 425.9 K and 40% MDI is 0.57

Therefore:

\[ L_C = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{MDI}}{760} \right) \times M_w \times K_{MDI} \]

\[ L_C = (1.783^{4\text{ft}^3/\text{yr}}) \left( \frac{1}{359} \right) \left( \frac{273.15}{425.9} \right) \text{ K} \left( 7.034 \times 10^{-1} \text{mm/760 mm}(254.38) \right) (0.57) \]

\[ L_C = 4.27 \text{ lbs. per yr} \]

**Note:** This presents worst-case scenario because it does not assume that the steam hydrolyzes any of the MDI/PMDI.
17.0 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 VOCs.

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 VOCs 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. The 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:

\[ L_s = V_{air} \times \frac{1}{359} \times \frac{273.15}{T_s} \times \frac{VP_{MDI}}{760} \times M_w \]

Where:

- \( V_{air} \) = the annual volume of displaced air through the scrubber in \( ft^3/yr \)
- \( T_s \) = the maximum scrubber temperature
- \( VP_{MDI} \) = the vapor pressure of MDI at maximum scrubber operating temperature K
- \( M_w \) = the molecular weight of MDI (250.26)
- 359 = the molar volume of an ideal gas in \( ft^3/lb\)-mole @ 0 °C and 1-atmosphere
Step I: Calculate the Annual Displacement of Air by the Scrubber \( V_{\text{air}} \)

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

\[
V_{\text{air}} = (8000 \text{ ft}^3/\text{min}) (60 \text{ min/hr}) (8760 \text{ hr/yr})
\]

\[
V_{\text{air}} = 4.20 \times 10^{+9} \text{ ft}^3/\text{yr}
\]

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

\[
K = (^0 \text{ C} + 273.15)
\]

\[
K = (40 + 273.15)
\]

\[
K = 313.15
\]

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

The vapor pressure of MDI @ 313.15 is 8.76 x 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 x 10\(^{-4}\) mm \( \times \) 0.001 or 8.76 x 10\(^{-7}\) mm

Therefore:

\[
L_s = V_{\text{air}} \times \frac{1}{359} \times \frac{273.15}{T_s} \times \left( \frac{\text{VP}_{\text{MDI}}}{760} \right) \times M_w
\]

\[
L_s = (4.20 \times 10^{-9} \text{ ft}^3/\text{yr}) \times \frac{1}{359} \times \frac{273.15}{313.15} \times \left( \frac{8.76 \times 10^{-7} \text{ mm}}{760} \right) \times 250.26
\]

\[
L_s = 2.59 \text{ lbs/yr}
\]

18.0 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 is a polyol and Part B is a diisocyanate mixture. The two parts are mixing in a 1/1 ratio 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 pounds/hour. The temperature of the process is 78 °F. The targeted foam density is 2.0 pounds/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 time during the curing process.

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

\[ L_{fd} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{P_{MDI}}}{760} \right) \times M_w \times K_{MDI} \]

Where:

- \( L_{fd} \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft³/yr
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{P_{MDI}} \) = 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
- 359 = the molar volume of an ideal gas in ft³/lb-mole @ 0 °C and 1-atmosphere

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

\[ V_{air} = \frac{(Amount\ of\ material\ processed/\ year)}{Foam\ Density} \]

- \( V_{air} = \frac{(42\ lbs/hr)(8760\ hr./year)(1/2.0\ lbs/ft^3)}{2.0\ ft^3/yr} \)
- \( V_{air} = 1.84 \times 10^{-5} \) ft³/yr

Step II: Calculate Process Temperature in K

The process temperature is 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 $1.071 \times 10^{-5}$ 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:

$$L_{fd} = \frac{V_{air}}{359} \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{VP_{MDI}}{760} \right) \times M_w \times K_{MDI}$$

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

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

19.0 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 1,000 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:

$$L_{sp} = \left( \frac{V_{air}}{359} \right) \times \left( \frac{273.15}{T_{sp}} \right) \times 60 \times \left( \frac{C_{mdr}}{1000000} \right) \times M_w \times K_{MDI} \times t_{sp}$$

Where:

$$L_{sp} = \text{the emissions in lb/year for spray coating operations}$$

$$V_{air} = \text{the exhaust airflow rate in ft}^3/\text{min}$$

$$T_{sp} = \text{the spray temperature in K}$$
\[ C_{\text{mdi}} = \text{the MDI concentration, in ppmv, in the exhaust air} \]
\[ M_W = \text{the molecular weight of MDI (250.26)} \]
\[ K_{\text{MDI}} = \text{the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature} \]
\[ t_{\text{sp}} = \text{is the total time in hours/year that spray coating is occurring} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ 0 }^\circ\text{C and 1-atmosphere} \]
\[ C_{\text{mdi}} = (V_{\text{PM}}/760) \times 10^6 \]
\[ V_{\text{PM}} = \text{MDI vapor pressure at exhaust temperature} \]

Therefore:
\[ L_{\text{sp}} = \text{emissions in lb/yr} \]
\[ V_{\text{air}} = 10,000 \text{ ft}^3/\text{min} \]
\[ T_{\text{sp}} = 305.4 \text{ K.} \]
\[ C_{\text{mdi}} = 0.0319 \text{ ppmv} \]
\[ M_W = 250.26 \]
\[ K_{\text{MDI}} = 0.41 \]
\[ t_{\text{sp}} = 1000 \text{ hrs/yr that spray coating is occurring} \]

**Substituting the values into the equation:**

\[ L_{\text{sp}} = 4.94 \text{ lbs/yr} \]

### 20.0 Oriented Strand Board (OSB) Manufactures

Methylenebis (phenyl isocyanate) (MDI) is used as a binder in the production of particleboard. The process consists of four steps:

**Step I:** Wood chips, straw, wheat, hays, or other grains are grounded up and conveyed into moisturizing chamber. Water is added to produce moisture content of 10-13%.

**Step II:** The mixture of woodchips, straw, wheat, hays, and other grains and water is transferred into second chamber where a 50/50 mix of MDI/PMDI is added at a weight equivalent to 3.9 %. The chamber is a closed system with no vent.

**Step III:** The combination of wood, water and MDI is mixed and then spread over a “cold plate” frame that forms an 8-inch matting. The “cold plate” moves along a
A conveyor system where between 5-6 frames are loaded onto a press where a hydraulic system compresses the mixture to a desired thickness between 1/4" to 5/8", while heating the "cold plate" to a temperature of 175 - 180 °C. During this step, the MDI reacts with the water to form a polyurethane bond with the fiber. The press is open and the trapped carbon dioxide is released. The press is equipped with a blower system that vents to the roof. The temperature of the exit gases range between 90-140 °F.

**Step IV:** The formed boards are removed from the press, checked for quality, trimmed to 4x8' sheets, and stacked for shipping.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is saturated with MDI. Actual operating conditions showed that the exit temperature of the stack was 140 °F and 8,400 cfm. The amount of MDI/PMDI in the feed is 3.9%, and MDI accounts for 50% of the MDI/PMDI mix. The facility operates 24/7.

The estimated MDI emission can be calculated using the following formula:

\[
L = \left( \frac{V_{\text{air}}}{359} \right) \times \left( \frac{273.15}{T_{\text{sp}}} \right) \times 60 \times \left( \frac{C_{\text{mdi}}}{1000000} \right) \times M_W \times k_{\text{MDI}} \times C_f
\]

Where:

- \( L \): the emissions in lb/hr
- \( V_{\text{air}} \): the exhaust airflow rate in ft\(^3\)/min
- \( T_{\text{sp}} \): the exhaust temperature in K
- \( C_{\text{mdi}} \): the MDI concentration, in ppmv, in the exhaust air
- \( M_W \): the molecular weight of MDI (250.26)
- \( k_{\text{MDI}} \): the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- \( C_f \): per cent MDI/PMDI in solution
- \( 359 \): the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere

\[
C_{\text{mdi}} = \left( \frac{VP_{\text{MDI}}}{760} \right) \times 10^6
\]

\[
VP_{\text{MDI}} \quad \text{MDI vapor pressure at exhaust temperature}
\]

Therefore:

\[
L = \text{the emissions in lb/hr}
V_{\text{air}} = 8400 \text{ ft}^3/\text{min}
T_{\text{sp}} = 140 \circ \text{F} = 333.2 \text{ K}
\]
\[
\begin{align*}
M_W &= 250.26 \\
K_{\text{MDI}} &= 0.60 \\
C_f &= 3.9\% \\
359 &= \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole} @ 0^\circ \text{C and 1-atmosphere} \\
V_{P_{\text{MDI}}} &= 0.00005071 \text{ mm} \\
C_{\text{rdi}} &= (0.00005071/760) \times 10^6 = 0.6672 \text{ ppmv} \\
L &= \left(\frac{V_{\text{air}}}{359}\right) \times \left(\frac{273.15}{T_{\text{sp}}}\right) \times 60 \times \left(\frac{C_{\text{rdi}}}{1000000}\right) \times M_W \times K_{\text{MDI}} \times C_f \\
L &= \left(\frac{8400}{359}\right) \times \left(\frac{273.15}{333.2}\right) \times \left(\frac{0.6672}{1000000}\right) \times \left(250.26\right) \times \left(0.60\right) \times \left(0.039\right) \times \left(60\right) \\
L &= 0.0045 \text{ lbs/hr} \\
L &= 0.0045 \text{ lbs/hr} \times 8760 \text{ hrs/yr} \\
L &= 40 \text{ lbs/yr}
\end{align*}
\]

**21.0 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 \( \circ \text{C} \) and only drops 20 \( \circ \text{C} \) on an average a day. MDI is transferred to 400 pound day tank as needed. The day tanks are stored indoors and temperature is maintained at 25 \( \circ \text{C} \). The MDI is pumped directly from the day tanks to the foam mixer head. The density of the foam is 1.9 pounds/ft\(^3\). 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 time during the curing process.
The enclosed process losses can be estimated from the following expression:

\[
L_{fd} = V_{air} \times \left(\frac{1}{359}\right) \times \left(\frac{273.15}{T_{proc}}\right) \times \left(\frac{V_{P_{MDI}}}{760}\right) \times M_w \times K_{MDI}
\]

Where:
- \( L_{fd} \) = emissions lb/yr
- \( V_{air} \) = annual volume of displaced air in ft\(^3\)/yr
- \( T_{proc} \) = process temperature in K (maximum temperature of the MDI)
- \( V_{P_{MDI}} \) = 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
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0\(^\circ\)C and 1-atmosphere

**Step I: Calculate Annual Volume of Displaced Air (Vair)**

\[
V_{air} = \frac{\text{Amount of Material Processed/year}}{\text{Foam Density}}
\]

\[
V_{air} = \frac{6.0 \times 10^6 \text{lbs/yr}}{1.9 \text{ lbs./ft}^3} = 3.2 \times 10^6 \text{ ft}^3/\text{yr}
\]

**Step II: Calculate Process Temperature in K**

The process temperature is of 78\(^\circ\)F or;

\[
T_{proc} = 298.7 \text{ K}
\]

**Step III: Determine vapor Pressure of MDI @ 298.7 K (V_{P_{MDI}})**

The vapor pressure @ 298.7 K is 1.072 \times 10^{-5}\text{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:

\[
\%\text{MDI/PMDI} = 1/(1+1) \times 100 = 50\%
\]

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

\[
\%\text{MDI} = (51.8) \times (50.0)
\]
%MDI = 25.0

Adjustment factor @ 298.7 K and 25.0% MDI is 0.33

Therefore:

\[
L_{fd} = V_{air} \times \left(\frac{1}{359}\right) \times \left(\frac{273.15}{T_{proc}}\right) \times \left(\frac{V_{P_{MDI}}}{760}\right) \times M_w \times K_{MDI}
\]

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

\[
L_{fd} = 0.00953 \text{ lbs/yr}
\]
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 10,000,000 pound/year 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. Manufacturing 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 1,000 gallons of material.
Process Details:

10,000,000 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 feet by 300 feet by 30 feet (1.8 million cu.ft.). The air exchange rate is 5 air changes 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 (with 2 seals per pump), 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 feet 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. 2,000,000 pounds 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 pounds/cubic feet.

Laminated boardstock 8 feet long by 4 feet wide and 2 inches thick is produced at a rate of 17 feet/minuet. 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-free 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 1,000,000 pounds.

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-free 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 1,000 hours.
During the course of the year, the facility had a number of spills. The total amount of material spilled was 1,000 gallons that resulted in exposed area 1,000 square feet 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 Losses
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 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. 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:

\[ L_w = Q_w \times \left( \frac{1}{359} \right) \times \frac{273.15}{T_{amb}} \times \frac{V_{pamb}}{760} \times M_w \times K_{mdi} \]

Where:

- \( L_w \) = the working losses in lb/yr
- \( Q_w \) = the annual throughput of MDI pumped to the tank in ft\(^3\)/yr
- \( T_{amb} \) = the storage temperature in K
- \( V_{pamb} \) = the vapor pressure of MDI at the storage temperature in mm Hg
- \( M_w \) = 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
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere

Substituting the following values into the equation:
MDI Emissions Reporting Guidelines for the Polyurethanes Industry

$L_w = \text{lbs/yr}$

$Q_w = 1,000,000 \text{ gallons/yr.} = 133,681 \text{ ft}^3/\text{yr}$

$T_{amb} = 68^\circ\text{F} = 293.2 \text{ K}$

$V_{P_{amb}} = 5.2 \times 10^{-6} \text{ mm Hg}$

$M_w = 250.26$

$K_{mdi} = 0.54 @ 293.2 \text{ K, 50\% MDI}$

$L_w = 3.256 \times 10^{-4} \text{ lb/yr}$

The breathing losses can be estimated from the following expression:

$L_B = 365 * M_{air} * (V_{P_{amb}} / 760) * M_w * K_{mdi}$

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

$V_v = V_T * (100 - L_T)$

$K_E = T_R / T_{amb}$

Where:

$L_B = \text{the breathing losses in lb/yr}$

$M_{air} = \text{the total air displaced per day in lb-mole/day}$

$V_{P_{amb}} = \text{the vapor pressure of MDI at the ambient temperature in mm Hg}$

$M_w = \text{the molecular weight of MDI (250.26)}$

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

$V_v = \text{the daily average vapor space of the storage tank in gallons}$

$V_T = \text{the capacity of the storage tank}$

$T_{amb} = \text{the average ambient temperature in K}$

$T_R = \text{the average day-night temperature fluctuation in K}$

$K_E = \text{the vapor expansion factor due to day-night temperature fluctuation}$

Substituting the following values into the equations:

$L_B = \text{breathing losses in lb/yr}$

$V_{P_{amb}} = 5.2 \times 10^{-6} \text{ mm Hg}$

$M_w = 250.26$

$K_{mdi} = 0.54$

$V_v = 20,000 \text{ gallons}$

$V_T = 40,000 \text{ gallons}$

$T_{amb} = 293.2 \text{ K}$

$T_R = 10 \text{ K}$

$K_E = 10 \text{ K} / 293.2 \text{ K} = 0.0341$

$V_v = V_T * (100 - L_T) = 20,000 \text{ gallons}$

$K_E = T_R / T_{amb} = 0.0341$
\[ M_{\text{air}} = \frac{(V_v}{7.48} \times \frac{1}{359} \times K_E \times \frac{273.15}{T_{\text{amb}}}) = 3.33 \times 10^{-3} \text{ lb-mole/day} \]
\[ L_B = 365 \times M_{\text{air}} \times \left( \frac{V_{\text{amb}}}{760} \right) \times M_w \times K_{\text{mdi}} \]
\[ L_B = 8.0 \times 10^{-7} \text{ lb/yr} \]

Therefore:
\[ LT = L_W + L_B \]
\[ LT = 3.256 \times 10^{-4} \text{ lb/yr} + 8.0 \times 10^{-7} \text{ lb/yr} \]
\[ LT = 3.26 \times 10^{-4} \text{ lb/yr} \]

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:

\[ L_{fg} = C_{\text{mdi}} \times \left( \frac{V_B}{359} \right) \times N_{\text{year}} \times \left( \frac{273.15}{T_{\text{amb}}} \right) \times M_w \times K_f \]

Where:

- \( L_{fg} \) = the fugitive emissions in lb/yr
- \( C_{\text{mdi}} \) = the average MDI concentration, in ppmv, in the air within the building
- \( V_B \) = the volume of the workspace building in ft\(^3\)
- \( N_{\text{year}} \) = the number of air exchanges per year
- \( T_{\text{amb}} \) = the ambient temperature in K
- \( M_w \) = the molecular weight of MDI (250.26)
- \( K_f \) = an adjustment factor to the MDI concentration in the building air. CPI uses a value of 1.10
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0°C and 1-atmosphere

Therefore:
\[
C_{\text{mdii}} = 0.001\text{ppm} = 1.0 \times 10^{-9}
\]
\[
V_B = 1,800,000\text{ ft}^3
\]
\[
N_{\text{year}} = 43,800\text{ per year}
\]
\[
T_{\text{amb}} = 298.2\text{ K}
\]
\[
M_W = 250.26
\]
\[
K_f = 1.10
\]

Therefore:
\[
L_{\text{fg}} = (1.0 \times 10^{-9}) \times (1,800,000\text{ ft}^3/359) \times (43,800) \times (273.15/298.2) \times (250.26) \times (1.1)
\]
\[
L_{\text{fg}} = 56.33\text{ lbs/yr}
\]

**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:

\[
SV = \text{Screening Value in ppmv and}
\]
\[
t = \text{Temperature in }^\circ\text{C.}
\]

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table 8.10) and the leakage rate is determined.
### Table 8
Leak Rate/Screening Value Correlations

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Correlation Leak Rate (kg/hr) (a*(SV)^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Valve</td>
<td>1.87x10^-06 x (SV) 0.873</td>
</tr>
<tr>
<td>Light Liquid Valve</td>
<td>6.41x10^-06 x (SV) 0.787</td>
</tr>
<tr>
<td>Light Liquid Pump Seal</td>
<td>1.90x10^-05 x (SV) 0.824</td>
</tr>
<tr>
<td>Connectors</td>
<td>3.05x10^-06 x (SV) 0.885</td>
</tr>
</tbody>
</table>

### Table 9
Equipment Leak Emission Factors lbs/hr-component @ 78 °F

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Temp. °F</th>
<th>Vapor Pressure (mm Hg)</th>
<th>Screening Value (SV) (ppmv)</th>
<th>Equation Constant (a)</th>
<th>Equation Constant (b)</th>
<th>Emission Factor 1 (lb./hr)^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Valves</td>
<td>78</td>
<td>1.0720x10^-04</td>
<td>1.41x10^-02</td>
<td>1.87x10^-06</td>
<td>0.873</td>
<td>9.992x10^-08</td>
</tr>
<tr>
<td>Light Liquid Valves</td>
<td>78</td>
<td>1.0720x10^-04</td>
<td>1.41x10^-02</td>
<td>6.41x10^-06</td>
<td>0.787</td>
<td>4.941x10^-07</td>
</tr>
<tr>
<td>Light Liquid Pump Seals</td>
<td>78</td>
<td>1.0720x10^-04</td>
<td>1.41x10^-02</td>
<td>1.90x10^-05</td>
<td>0.824</td>
<td>1.251x10^-06</td>
</tr>
<tr>
<td>Connectors</td>
<td>78</td>
<td>1.0720x10^-04</td>
<td>1.41x10^-02</td>
<td>3.05x10^-06</td>
<td>0.885</td>
<td>1.548x10^-07</td>
</tr>
</tbody>
</table>

### Table 10
Total Emissions

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Service</th>
<th>Number Components</th>
<th>Adjustment Factor</th>
<th>Emissions (lbs/hr)</th>
<th>Emissions (lbs./year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>Light Liquid</td>
<td>25</td>
<td>0.55</td>
<td>4.941x10^-07</td>
<td>0.0593</td>
</tr>
<tr>
<td>Pump Seals</td>
<td>Light Liquid</td>
<td>16</td>
<td>0.55</td>
<td>1.251x10^-06</td>
<td>0.09608</td>
</tr>
<tr>
<td>Connectors</td>
<td>All</td>
<td>1000</td>
<td>0.55</td>
<td>1.548x10^-07</td>
<td>0.7433</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8987</td>
</tr>
</tbody>
</table>

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

\[ L_{fg} = 56.33 \text{ lbs/year} + 0.8987 \text{ lbs/yr} = 57.23 \text{ lbs/yr} \]

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:
\[ L_C = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{\text{proc}}} \right) \times \left( \frac{\nu_{\text{MDI}}}{760} \right) \times M_w \times K_{\text{MDI}} \]

Where:

- \( L_C \) = emissions lb/yr
- \( V_{\text{air}} \) = annual volume of displaced air in ft\(^3\)/yr
- \( T_{\text{proc}} \) = process temperature in K. (maximum temperature of the MDI)
- \( \nu_{\text{MDI}} \) = vapor pressure of MDI in mm Hg at process temperature
- \( M_w \) = 250.26 (this is the molecular weight of MDI)
- \( K_{\text{MDI}} \) = adjustment factor
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0\(^\circ\)C and 1-atmosphere
- \( V_{\text{air}} \) = \( V_{\text{pc}} \times N_{\text{pc}} \)
- \( V_{\text{pc}} \) = volume displaced per piece
- \( N_{\text{pc}} \) = number of pieces

Therefore:

\[ V_{\text{air}} = \text{annual volume of displaced air in ft}^3/\text{year} \]
\[ T_{\text{proc}} = 302.6K \]
\[ \nu_{\text{MDI}} = 1.733 \times 10^{-5} \text{ mm Hg at process temperature} \]
\[ M_w = 250.26 \text{ (this is the molecular weight of MDI)} \]
\[ K_{\text{MDI}} = 0.56 \]
\[ V_{\text{air}} = V_{\text{pc}} \times N_{\text{pc}} \]
\[ V_{\text{pc}} = 0.17 \text{ ft.}^3 \]
\[ N_{\text{pc}} = 1,500,000 \text{ pieces} \]

\[ L_C = 2.031 \times 10^{-3} \text{ lb/yr} \]

**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:

\[ L_{\text{fd}} = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{\text{proc}}} \right) \times \left( \frac{\nu_{\text{MDI}}}{760} \right) \times M_w \times K_{\text{MDI}} \]

Where:

- \( L_{\text{fd}} \) = the emissions from the enclosed process in lb/yr
- \( V_{\text{air}} \) = the annual volume of displaced air in ft\(^3\)/year
- \( T_{\text{proc}} \) = the process temperature in K. This is the maximum temperature of the MDI tack-free time
VP_{mdi} = \text{the vapor pressure of MDI in mm Hg. at process temperature}
M_w = 250.26 \text{ (this is the molecular weight of MDI)}
K_{mdi} = \text{the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature}
359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ 0 °C and 1-atmosphere}

Therefore:

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

Where:

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

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 gram/day) is determined from the following expression:

\[ W = 25.4 \times VP_{mdi} \times (M_w / T_{proc}) \times (u)^{0.78} \times SA \times t_{TF} \times K_{mdi} \]

Where:

\begin{align*}
W & = \text{the evaporation losses from the open process in gram/day} \\
VP_{mdi} & = \text{the vapor pressure of MDI in atm. at process temperature} \\
T_{proc} & = \text{the process temperature in K. This is the maximum temperature of the MDI} \\
M_w & = 250.26 \text{ (this is the molecular weight of MDI)} \\
u & = \text{the airflow speed in m/sec. This is the airflow in the vicinity of the process}
\end{align*}
\[
S_A = \text{the total exposed surface area in } M^2/\text{day. This includes top and all sides.}
\]
\[
\tau_{TF} = \text{the tack-free time in seconds}
\]
\[
K_{\text{mdi}} = \text{the adjustment factor}
\]

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

Therefore:

\[
VP_{\text{mdi}} = 2.281 \times 10^{-8} \text{ atm}
\]
\[
T_{\text{proc}} = 302.6 \text{K}
\]
\[
M_w = 250.26 \text{ (this is the molecular weight of MDI)}
\]
\[
u = 0.91 \text{ m/sec}
\]
\[
S_A = 10,234 M^2 \text{ (This includes top and all sides)}
\]
\[
\tau_{TF} = 60 \text{ seconds}
\]
\[
K_{\text{mdi}} = 0.56
\]

Substituting the values into the equation:

\[
W = 0.152 \text{ grams/day}
\]
\[
W = (0.152 \text{ grams/day})(365 \text{ days/year})(1 \text{ lb./454 grams})
\]
\[
W = 0.125 \text{ lb/yr}
\]

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:

\[
L_{\text{fill}} = V_{\text{air}} \times \left(\frac{1}{359}\right) \times \frac{273.15}{T_{\text{fill}}} \times \frac{VP_{\text{MDI}}}{760} \times M_w \times K_{\text{MDI}} \times C_{\text{blnd}}
\]

Where:

\[
L_{\text{fill}} = \text{the emissions from the filling operation in lbs/yr}
\]
\[
V_{\text{air}} = \text{the annual volume of displaced air in ft}^3/\text{yr}
\]
\[
T_{\text{fill}} = \text{the temperature the material is charged or filled at in K}
\]
\[
VP_{\text{MDI}} = \text{the vapor pressure of MDI in mm Hg at the charging/filling temperature.}
\]
\[
M_w = \text{the molecular weight of MDI (250.26)}
\]
**KMDI** = 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

**Cblnd** = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then **Cblnd** is 1

359 = the molar volume of an ideal gas in ft³/lb-mole @ 0°C and 1-atmosphere

Therefore:

\[ L_{fll} = \text{emissions lbs/yr} \]
\[ V_{air} = 13,368 \text{ ft}^3/\text{yr} \]
\[ T_{fill} = 297 \text{ K} \]
\[ V_{PMDI} = 8.692 \times 10^{-6} \text{ mm Hg} \]
\[ M_w = 254.38 \]
\[ K_{MDI} = 0.55 \]
\[ C_{blnd} = 1.0 \]

Substituting the values into the equation, the estimated emissions from the filling operation is:

\[ L_{fll} = 5.34 \times 10^{-5} \text{ lb/yr} \]

**5. Process: Adhesive**

MDI will migrate from all exposed surfaces and all losses will be the result of 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:

\[ W = 25.4 * V_{PMDI} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF} \]

Where:

\[ W = \text{the evaporation losses from the open process in gr/day} \]
\[ V_{PMDI} = \text{the vapor pressure of MDI in atmospheres @ process temperature} \]
The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Therefore:

\[
W = \text{losses in gram/day}
\]

\[
VP_{\text{MDI}} = 4.155 \times 10^{-5} \text{ atmospheres}
\]

\[
T_{\text{proc}} = 380.4 \text{ K}
\]

\[
M_w = 250.26
\]

\[
U = 5 \text{ m/sec}
\]

\[
S_A = 1858 \text{ m}^2
\]

\[
t_{\text{TF}} = 5 \text{ seconds}
\]

Substituting the values into the equation, the estimated emissions from applying the adhesive is:

\[
W = 22.7 \text{ gram/day}
\]

\[
W = (22.7 \text{ gram/day})(250\text{days/yr}) (1 \text{ lb./454 grams})
\]

\[
W = 12.5 \text{ lb/yr}
\]

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:

\[
L_{\text{sp}} = \left( \frac{V_{\text{air}}}{359} \right) \times \left( \frac{273.15}{T_{\text{sp}}} \right) \times 60 \times \frac{C_{\text{mdl}}}{1000000} \times M_w \times k_{\text{MDI}} \times t_{\text{sp}}
\]

Where:

\[
L_{\text{sp}} = \text{the emissions in lb/year for spray coating operations}
\]

\[
V_{\text{air}} = \text{the exhaust airflow rate in ft}^3/\text{min}
\]

\[
T_{\text{sp}} = \text{the spray temperature in K}
\]
**MDI Emissions Reporting Guidelines for the Polyurethanes Industry**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{mdi}}$</td>
<td>the MDI concentration, in ppmv, in the exhaust air</td>
</tr>
<tr>
<td>$M_W$</td>
<td>the molecular weight of MDI (250.26)</td>
</tr>
<tr>
<td>$K_{\text{MDI}}$</td>
<td>an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature</td>
</tr>
<tr>
<td>$t_{\text{sp}}$</td>
<td>the total time in hours/year that spray coating is occurring</td>
</tr>
<tr>
<td>$359$</td>
<td>the molar volume of an ideal gas in ft$^3$/lb-mole @ 0 °C and 1-atmosphere</td>
</tr>
</tbody>
</table>

\[ C_{\text{mdi}} = \frac{\text{VP}_{\text{MDI}}}{760} \times 10^6 \]

\[ \text{VP}_{\text{MDI}} \] is MDI vapor pressure at exhaust temperature

Therefore:

\[ L_{\text{sp}} = \text{emissions in lb/yr} \]

\[ V_{\text{air}} = 10,000 \text{ ft}^3/\text{min} \]

\[ T_{\text{sp}} = 305.4 \text{ K} \]

\[ C_{\text{mdi}} = 0.0319 \text{ ppmv} \]

\[ M_W = 250.26 \]

\[ K_{\text{MDI}} = 0.41 \]

\[ t_{\text{sp}} = 1000 \text{ hrs/yr that spray coating is occurring} \]

Substituting the values into the equation:

\[ L_{\text{sp}} = 4.94 \text{ lbs/yr} \]

### 7. Spills:

A liquid chemical accidentally spilled onto the ground and may spread out over an area, vaporize and cause an air emission. Such accidental releases must be reported under EPCRA Section 313 (TRI). 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:

\[ Q_R = (0.284/82.05) \times (u)^{0.78} \times A_{\text{spill}} \times \left( \frac{\text{VP}_{\text{MDI}}}{T_{\text{spill}}} \right) \times (M_W)^{2/3} \times K_{\text{mdi}} \]
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 ft\(^2\)
- \( V_{P_{\text{mdi}}} \) = the vapor pressure of MDI in mm Hg at the spill temperature
- \( T_{spill} \) = the average evaporation temperature in K
- \( M_W \) = 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 (\( Q_R \)) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

\[
L_{spill} = Q_R \times t_{spill} \times (60)
\]

Where:

- \( L_{spill} \) = the evaporation losses resulting from the spill in lb
- \( Q_R \) = the evaporation rate in lb/min
- \( t_{spill} \) = 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 ft\(^2\)
- \( V_{P_{\text{mdi}}} \) = \( 1.733 \times 10^{-5} \) 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:

\[
L_{spill} = Q_R \times t_{spill} \times (60)
\]

Where:

- \( t_{spill} \) = 20 hours
- \( L_{spill} \) = \( 2.896 \times 10^{-2} \) lb/yr
8. **Summary: Total Emissions**

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Process</th>
<th>MDI Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Storage</td>
<td>$3.264 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>Fugitive (Measured)</td>
<td>$5.633 \times 10^{+1}$</td>
</tr>
<tr>
<td>3</td>
<td>Fugitive (Equipment Leaks)</td>
<td>$8.987 \times 10^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>Process (Cavity)</td>
<td>$2.031 \times 10^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>Process (Foam Density)</td>
<td>$9.759 \times 10^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>Process (Continuous)</td>
<td>$1.225 \times 10^{-1}$</td>
</tr>
<tr>
<td>7</td>
<td>Process (Filling)</td>
<td>$5.314 \times 10^{-5}$</td>
</tr>
<tr>
<td>8</td>
<td>Process (Adhesive)</td>
<td>$4.99 \times 10^{-1}$</td>
</tr>
<tr>
<td>9</td>
<td>Process (Spray Coating)</td>
<td>$4.94 \times 10^{0}$</td>
</tr>
<tr>
<td>10</td>
<td>Spill</td>
<td>$2.896 \times 10^{-2}$</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>$6.283 \times 10^{+1}$</td>
</tr>
</tbody>
</table>

The total estimated emissions for the year is 62.83 lbs.
## Appendix A - Vapor Pressure/Temperature Chart

**MDI Vapor Pressure/Temperature Chart**

Table A-1: 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:

\[
\text{Log (MDI VP in mm mercury)} = 11.15 - \frac{4809.8}{\text{Temperature in K}}
\]

Where:

\[
\text{Temp in K} = 273 + \text{Temp in °C}
\]

\[
\text{Temp in °C} = \frac{5}{9} \times (\text{temp in °F} - 32)
\]

### Table A-1: MDI Vapor Pressure Chart

<table>
<thead>
<tr>
<th>Temperature (°Fahrenheit)</th>
<th>Temperature (°Celsius)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0</td>
<td>20</td>
<td>5.424E-06</td>
</tr>
<tr>
<td>69.8</td>
<td>21</td>
<td>6.168E-06</td>
</tr>
<tr>
<td>71.6</td>
<td>22</td>
<td>7.008E-06</td>
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<td>1.057E+01</td>
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<tr>
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<td>1.110E+01</td>
</tr>
<tr>
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</tr>
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<td>1.284E+01</td>
</tr>
<tr>
<td>404.6</td>
<td>207</td>
<td>1.348E+01</td>
</tr>
</tbody>
</table>
Appendix B - Vapor Pressure Adjustment Factors for MDI/PMDI Mixtures

PMDI is considerably less volatile than MDI and, as a consequence, mixtures of MDI/PMDI have a lower vapor pressure than pure MDI. Engineering estimates that are based on the vapor pressure of pure MDI may significantly overestimate the reportable emissions of a facility, therefore, an adjustment factor will have to be used. The adjustment factors are a ratio of the ratio of the vapor pressure of MDI/PMDI mixtures and the vapor pressure of pure MDI. Your release estimates, calculated assuming pure MDI, should be corrected for the presence of PMDI by multiplying your estimates by the appropriate factor. The table in this appendix shows the adjustment factor as it relates to the percent MDI in the mixture at a specific temperature.

Table B-1: MDI/PMDI Adjustment Factors Chart

<table>
<thead>
<tr>
<th>Temperature Fahrenheit</th>
<th>Percentage MDI 0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
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<td>0.37</td>
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<td>0.83</td>
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<td>0.55</td>
<td>0.65</td>
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<td>0.56</td>
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<td>0.83</td>
<td>0.92</td>
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<td>0.40</td>
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<td>0.66</td>
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<td>0.85</td>
<td>0.93</td>
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<td>0.61</td>
<td>0.69</td>
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<td>0.85</td>
<td>0.93</td>
<td>1.00</td>
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</tr>
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<td>0.39</td>
<td>0.47</td>
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<td>0.96</td>
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</table>
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 air flows 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:

$$V_v = V_T \times \frac{(100-L_T)}{100}$$

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:

$$K_E = \frac{T_R}{T_{amb}}$$

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

$$M_{air} = \left( \frac{V_v}{7.48} \right) \times \left( \frac{1}{359} \right) \times K_E \times \left( \frac{273.15}{T_{amb}} \right)$$

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

$$L_b = 365 \times M_{air} \times \left( \frac{VP_{amb}}{760} \right) \times M_w \times K_{mdi}$$

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
MDI Emissions Reporting Guidelines for the Polyurethanes Industry

\[ M_v = \text{Molecular weight of MDI 250.26) } \\
K_{mdi} = \text{Adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature } \\
365 = \text{days/year} \\
359 = \text{The molar volume of an ideal gas in } \text{ft}^3/\text{lb-mole} @ 0 \degree \text{C and 1-atmosphere} \\

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 (API). 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:

\[ L_B = 2.26 \times 10^{-2} \times M_v \left( \frac{P}{P_A-P} \right)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_P \times C \times K_c \]

Where:

\[ L_B = \text{Fixed roof breathing loss in lbs/yr} \]
\[ M_v = \text{Molecular weight of vapor in storage} \]
\[ P_A = \text{Average atmospheric pressure at tank location in psia} \]
\[ P = \text{Vapor pressure of compound at bulk liquid conditions in psia} \]
\[ D = \text{Tank Diameter in ft} \]
\[ H = \text{Average vapor space height, including roof volume correction in ft} \]
\[ \Delta T = \text{Average ambient diurnal temperature change in } \degree \text{F} \]
\[ F_P = \text{Paint factor} \]
\[ C = \text{Adjustment factor for small diameter tanks} \]
\[ K_c = \text{Product factor. For crude oil } K_c = 0.65. \text{ For all other organic liquids } K_c = 1.0 \]

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:
Ls = 365 x Vv x Wv x KE x Ks

Where:

Ls = Standing storage loss in lbs/yr
Vv = Vapor space volume in ft³
Wv = Vapor density in lbs.ft³
KE = Vapor space expansion factor, dimensionless
Ks = 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 (Vv) is the vapor space above the liquid. For a cylindrical tank, Vv 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 (Wv) is calculated from the molecular weight of the liquid (Mv), the daily average liquid surface liquid temperature (TLA) and the vapor pressure of the liquid (PvA) at the daily average liquid surface temperature using the ideal gas equation. The daily average liquid surface temperature (TLA) is a function of the daily ambient temperature ambient (∆TAA), the liquid bulk temperature (TB), the tank paint absorptance (α) and the total daily insulation factor (I).

• The vapor space expansion factor (KE) 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 (∆Tv) is a function of the daily average ambient temperature (∆TAA), the tank paint absorptance (α) and the total daily insulation factor (I).

• The vented vapor saturation factor (Ks) 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) is available for downloading from the EPA at http://www.epa.gov/ttnchie1/software/tanks/.

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 C-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 $1.945 \times 10^{-6}$ mm Hg.

**Simplified method**

\[
\begin{align*}
V_v &= 11,750 \times 0.5 = 5,875 \text{ gallons} \\
K_E &= 8.5 / (12.53 + 273.15) = 0.02975 \\
M_{air} &= 5,875 / 7.48 \times (1 / 359) \times 0.02975 \times (273.15 / 285.68) = 0.06229 \text{ lb-mole/day} \\
L_b &= 365 \times 0.06229 \times (1.945 \times 10^{-6}) / 760 \times 254.38 \\
L_b &= 1.480 \times 10^{-5} \text{ lbs/yr}
\end{align*}
\]

1. **New EPA method using simplifying assumptions**

The operating equation is given below:

\[
\begin{align*}
L_s &= 365 \times V_v \times W_v \times K_E \times K_s \\
V_v &= 5,875 / 7.48 = 785.40 \text{ ft}^3 \\
W_v &= 254.38 \times (1.945 \times 10^{-6} \times 14.7 / 760) = 1.733 \times 10^{-9} \text{ lbs.ft}^3 \\
&\quad \times 10.73 \times (56.13 + 460) \\
K_E &= 15.3 / (54.55 + 460) = 0.02973 \\
K_s &= 1.0 \\
L_s &= 365 \times 785.40 \times 1.733 \times 10^{-9} \times 0.02973 \times 1.0 \\
L_s &= 1.474 \times 10^{-5} \text{ lbs/yr}
\end{align*}
\]

2. **New EPA method without simplifying assumptions**

The operating equation is given below:

\[
\begin{align*}
L_s &= 365 \times V_v \times W_v \times K_E \times K_s \\
V_v &= 5,875 / 7.48 = 785.40 \text{ ft}^3 \\
W_v &= 254.38 \times (2.194 \times 10^{-6} \times 14.7 / 760) = 1.949 \times 10^{-9} \text{ lbs.ft}^3 \\
&\quad \times 10.73 \times (56.13 + 460) \\
K_E &= 0.03214 \text{ (from Table 1)} \\
K_s &= 1.0 \text{ (from Table 1)} \\
L_s &= 365 \times 785.40 \times 1.949 \times 10^{-9} \times 0.03214 \times 1.0 \\
L_s &= 1.796 \times 10^{-5} \text{ lbs/yr}
\end{align*}
\]
Table C-1: MDI Losses from Storage Tanks Comparison of Results with EPA’s Methods

<table>
<thead>
<tr>
<th>Tank No.</th>
<th>Material stored</th>
<th>Description</th>
<th>Date</th>
<th>Material Emitted</th>
<th>Symbol</th>
<th>Units</th>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Vapor pressure Antoine constants**

| Constant A | 16.502 |
| Constant B | 4034.09 |
| Constant C | 206.415 |

**Molecular weight**

| Molecular weight | 264.38 lb/mol |

**Tank design data**

| Shelf height | 29 ft |
| Diameter     | 13 ft |
| Liquid height| 29 ft |
| Avg. Liquid height | 13 ft |
| Tank volume  | 11749.82 galons |
| No. of Tubs  | 10 |
| Total losses | 4815E-05 b/yr |

**Meteorological data**

| Liquid bulk temperature | 54.57 °F |
| Daily max. ambient temp. | 62.2 °F |
| Daily min. ambient temp. | 48.9 °F |
| Daily max. liquid surface temp. | 60.28 °F |

**Old EPA method (Source: AP-42 - Appendix C - September 1985)**

| VP @ daily max. liquid surface temp. | 38.9 mm Hg |
| VP @ daily max. liquid surface temp. | 1.8E+06 mm Hg |
| VP @ daily min. liquid surface temp. | 1.4E+06 mm Hg |
| VP @ daily min. liquid surface temp. | 3.5E+06 mm Hg |
| VP @ daily avg. liquid surface temp. | 1.8E+06 mm Hg |
| Daily vapor pressure range | 1.4E+06 mm Hg |
| Breather vent pressure setting range | 3 psi |
| Breather vent pressure range setting | 0 mm Hg |
| Paint factor (white - good condition) | 1 |

**New EPA method (Source: AP-42 - Supplement E - October 1992)**

| LS | 365 °Vv + Wv * Ke |

**Simplified method (Adaptation of the new EPA method)**

| LT | 4.203E-05 b/yr |

---

* New EPA met (Source: AP-42 - Supplement E - October 1992)

** Simplified method (Adaptation of the new EPA method)

*** Old EPA method (Source: AP-42 - Appendix C - September 1985)
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:

\[ L_w = \frac{Q_w}{359} \times \frac{(273.15)}{T_{amb}} \times \frac{VP_{amb}}{760} \times M_w \times K_{mdi} \]

Where:
- \( L_w \) = the working losses in lb/yr
- \( Q_w \) = the annual throughput of MDI pumped to the tank in ft\(^3\)/yr
- \( T_{amb} \) = the ambient temperature in K
- \( VP_{amb} \) = the vapor pressure of MDI at the ambient temperature in mm Hg
- \( M_w \) = 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

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 air flows 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:

\[ L_b = 365 \times \frac{M_{air}}{7.48} \times \frac{(VP_{amb})}{760} \times M_w \times K_{mdi} \]

\[ M_{air} = \frac{(V_v)}{(100-L_T)} \times \frac{(VP_{amb})}{760} \times M_w \times K_{ansi} \times \frac{(273.15)}{T_{amb}} \]

\[ V_v = V_T \times (100-L_T) \]
KE = TR / Tamb

Where:

Lb = the breathing losses in lb/year
Mair = the total air displaced per day in lb-mole/day
VPamb = the vapor pressure of MDI at the ambient temperature in mm Hg
Mw = the molecular weight of MDI (250.26)
Kmdi = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
Tamb = the average ambient temperature in K
TR = the average day-night temperature fluctuation in K
KE = 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:

Lfg = Cmdi * (VB / 359) * Nyear * (273.15 / Tamb) * Mw * Kf

Where:

Lfg = the fugitive emissions in lb/yr
Cmdi = the average MDI concentration, in ppmv, in the air within the building
VB = the volume of the workspace building in ft³
Nyear = the number of air exchanges per year
Tamb = the ambient temperature in K
Mw = the molecular weight of MDI (250.26)
Kf = the adjustment factor to the MDI concentration in the building air. A value of 1.10 is used
359 = the molar volume of an ideal gas in ft³/lb-mole @ 0 °C and 1-atmosphere

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:

- \(SV\): Screening Value in ppmv
- \(t\): Temperature in °C

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table D-1) and the leakage rate is determined.

<table>
<thead>
<tr>
<th>Equipment Type</th>
<th>Correlation Leak Rate (kg/hr) ((a \times (SV)^b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Valve</td>
<td>(1.87 \times 10^{-06} \times (SV)^{0.873})</td>
</tr>
<tr>
<td>Light Liquid Valve</td>
<td>(6.41 \times 10^{-06} \times (SV)^{0.787})</td>
</tr>
<tr>
<td>Light Liquid Pump Seal(^\text{C})</td>
<td>(1.90 \times 10^{-05} \times (SV)^{0.824})</td>
</tr>
<tr>
<td>Connectors</td>
<td>(3.05 \times 10^{-06} \times (SV)^{0.885})</td>
</tr>
</tbody>
</table>

\(^\text{C}\) 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:

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

For liquid valves:

\[K_{\text{liq}} = 6.41 \times 10^{-6} \times (C_{\text{mdi}})^{0.787}\]
For liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps:

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

For connectors:

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

Where:

- \( K_{\text{gas}} \) = the emission factor for gas valves in kg/year-item
- \( K_{\text{liq}} \) = the emission factor for liquid valves in kg/year-item
- \( K_{\text{pump}} \) = the emission factor for liquid pumps in kg/year-item
- \( K_{\text{con}} \) = the emission factor for connectors in kg/year-item

For gas valves the emissions can then be estimated from the following expression:

\[ L_{\text{gas}} = K_{\text{gas}} \times n_{\text{gas}} \times K_{\text{mdi}} \times t_{\text{pr}} \times 2.205 \text{ lb/kg} \]

\( L_{\text{gas}} \) = the annual losses from gas valves in lb/yr
\( n_{\text{gas}} \) = the number of gas valves
\( K_{\text{mdi}} \) = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
\( t_{\text{pr}} \) = the total time in hours/year that the process is operating

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

\[ L_{\text{liq}} = K_{\text{liq}} \times n_{\text{liq}} \times K_{\text{mdi}} \times t_{\text{pr}} \times 2.205 \text{ lb/kg} \]

\( L_{\text{liq}} \) = the annual losses from liquid valves in lb/yr
\( n_{\text{liq}} \) = the number of liquid valves
\( K_{\text{mdi}} \) = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
\( t_{\text{pr}} \) = the total time in hours/year that the process is operating

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

\[ L_{\text{pump}} = K_{\text{pump}} \times n_{\text{pump}} \times K_{\text{mdi}} \times t_{\text{pr}} \]

\( L_{\text{pump}} \) = the annual losses from liquid pump seals in lb/yr
\( n_{\text{pump}} \) = the number of liquid pump seals
\( K_{\text{mdi}} \) = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
\( t_{\text{pr}} \) = the total time in hours/year that the process is operating

For connectors the emissions can then be estimated from the following expression:
\[ L_{\text{con}} = K_{\text{con}} \cdot n_{\text{con}} \cdot K_{\text{mdi}} \cdot t_{\text{pr}} \cdot 2.205 \text{ lb/kg} \]

\[ L_{\text{con}} \] is the annual losses from connectors in lb/yr

\[ n_{\text{con}} \] is the number of connectors

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

\[ t_{\text{pr}} \] is the total time in hours/year that the process is operating

Total emissions can then be estimated from the following expression:

\[ E_{\text{tot}} = L_{\text{gas}} + L_{\text{liq}} + L_{\text{pump}} + L_{\text{con}} \]

### 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:

\[ L_{\text{c}} = \frac{V_{\text{air}}}{359} \cdot \frac{273.15}{T_{\text{proc}}} \cdot \frac{\text{VP}_{\text{mdi}}}{760} \cdot M_{w} \cdot K_{\text{mdi}} \]

Where:

\[ L_{\text{c}} \] is the emissions from the enclosed process in lb/yr

\[ V_{\text{air}} \] is the annual volume of displaced air in ft³/yr

\[ T_{\text{proc}} \] is the process temperature in K. This is the maximum temperature of the MDI tack-free time

\[ \text{VP}_{\text{mdi}} \] is the vapor pressure of MDI in mm Hg at process temperature

\[ M_{w} = 250.26 \text{ (this is the molecular weight of MDI)} \]

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

\[ 359 \] is the molar volume of an ideal gas in ft³/lb-mole @ 0°C and 1-atmosphere

### 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 time during the curing process.

The enclosed process losses can be estimated from the following expression:
\[ L_{fd} = V_{air} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{proc}} \right) \times \left( \frac{V_{Pmdi}}{760} \right) \times M_w \times K_{mdi} \]

Where

- \( L_{fd} \) is the emissions from the enclosed process in lb/yr
- \( V_{air} \) is the annual volume of displaced air in ft³/yr
- \( T_{proc} \) is the process temperature in K. This is the maximum temperature of the MDI tack-free time
- \( V_{Pmdi} \) 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
- 359 is the molar volume of an ideal gas in ft³/lb-mole @ 0°C and 1-atmosphere

7.0 Calculating Emissions from Open Processes (Continuous Processes)

To estimate emissions from open processes such as boardstock production, it is assumed that MDI will evaporate 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 gram/day) is determined from the following expression:

\[ W = 25.4 \times V_{Pmdi} \times \left( \frac{M_w}{T_{proc}} \right) \times u^{0.78} \times SA \times t_{TF} \times K_{mdi} \]

Where

- \( W \) is the evaporation losses from the open process in gram/day
- \( V_{Pmdi} \) 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 air flow speed in m/sec. This is the air flow 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 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.

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. 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:

\[
L_{\text{fill}} = V_{\text{air}} \times \left( \frac{1}{359} \right) \times \left( \frac{273.15}{T_{\text{fill}}} \right) \times \left( \frac{V_{P_{\text{MDI}}}}{760} \right) \times M_w \times K_{\text{MDI}} \times C_{\text{blnd}}
\]

Where:

- \( L_{\text{fill}} \) = the emissions from the filling operation in lbs/yr
- \( V_{\text{air}} \) = the annual volume of displaced air in ft\(^3\)/yr
- \( T_{\text{fill}} \) = the temperature the material is charged or filled at in K
- \( V_{P_{\text{MDI}}} \) = the vapor pressure of MDI in mm Hg at the charging/filling temperature.
- \( M_w \) = the molecular weight of MDI (250.26)
- \( K_{\text{MDI}} \) = 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
- \( C_{\text{blnd}} \) = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then \( C_{\text{blnd}} \) is 1

9.0 Calculating Emissions from a Spray Booth Operation

The emissions associated with a spray booth operation will be governed by the exhaust air flow rate and the temperature at which the spray coating is carried out. 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:

\[
L_{\text{sp}} = \left( \frac{V_{\text{air}}}{359} \right) \times \left( \frac{273.15}{T_{\text{sp}}} \right) \times 60 \times \left( \frac{C_{\text{mdi}}}{1000000} \right) \times M_w \times K_{\text{MDI}} \times t_{\text{sp}}
\]

Where:

- \( L_{\text{sp}} \) = the emissions in lb/year for spray coating operations
- \( V_{\text{air}} \) = the exhaust air flow rate in ft\(^3\)/min
The spray temperature in K
the MDI concentration, in ppmv, in the exhaust air
the molecular weight of MDI (250.26)
the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
the total time in hours/year that spray coating is occurring
the molar volume of an ideal gas in ft³/lb-mole @ 0 °C and 1-atmosphere

\[ C_{mdi} = \left( \frac{VP_{MDI}}{760} \right) \times 10^6 \]

MDI vapor pressure at exhaust temperature

10.0 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 EPCRA Section 313 (TRI). 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:

\[ QR = \frac{0.284}{82.05} \times (u^{0.78}) \times A_{spill} \times \left( \frac{VP_{MDI}}{T_{spill}} \right) \times (M_W)^{2/3} \times K_{mdi} \]

Where:

- \( QR \) = the evaporation rate in lb/min
- \( u \) = the air flow speed in m/sec. This is the air flow 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 spill temperature
- \( T_{spill} \) = the average evaporation temperature in K
- \( M_W \) = 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:

\[ L_{spill} = QR \times t_{spill} \times (60) \]
Where:

\[ L_{\text{spill}} = \text{the evaporation losses resulting from the spill in lb} \]
\[ Q_R = \text{the evaporation rate in lb/min} \]
\[ t_{\text{spill}} = \text{the time that the spill is on the ground in hours} \]

**11.0 Calculation Emissions from Continuous Process (Carpet & Rug Application)**

The emissions from carpet coating operation can be estimated from the following expression:

\[ L_{cc} = \left( \frac{V_{\text{air}}}{359} \right) (60) \frac{\text{ppmv}}{1000000} (\text{MW}) (K_{\text{MDI}}) \left( \frac{C_{\text{iso}}}{100} \right) (t_{cc}) (R_{MDI}) \]

Where:

\[ L_{cc} = \text{the emissions in lb/year for carpet coating operations} \]
\[ V_{\text{air}} = \text{the exhaust airflow rate in ft}^3/\text{min (at 32°F = 0°C)} \]
\[ \text{ppmv} = \text{the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure} \]
\[ T_{st} = \text{the temperature of the air leaving the stack in K} \]
\[ \text{MW} = \text{the molecular weight of MDI (250.26)} \]
\[ K_{\text{MDI}} = \text{adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of } K_{\text{MDI}} \text{ is 1.00 for pure MDI} \]
\[ C_{\text{iso}} = \text{the % of isocyanate feedstock in the total formulation} \]
\[ R_{MDI} = \text{represents the unreacted fraction of MDI on the conveyor belt relative to the MDI initially present in the formulation. This value reflects the unreacted fraction of MDI present at the midpoint of the application process and is based upon a first-order reaction} \]
\[ t_{cc} = \text{the total time of operation in hours/year} \]
\[ 359 = \text{the molar volume of an ideal gas in ft}^3/\text{lb-mole @ 0°C and 1-atmosphere} \]
\[ 60 = \text{time, minutes/hour} \]

A first order reaction can be expressed by the following reaction:

\[ R_{\text{MDI}} = e^{-(k) (t_R)} \]

Where:

\[ R_{MDI} = \text{the unreacted fraction of MDI} \]
\[ k = \text{the first order reaction rate constant in min}^{-1} \]
\[ t_R = \text{the reaction time in minutes} \]

**12. Foundry & Casters**

The emissions from the foundry/casters can be estimated using the following equations:
A. Core Box Step:

During this step the MDI formulation is injected into the mold at ambient temperature. The losses will correspond to the total volume of air displaced from the molds at the filling temperature. A reasonable worst-case estimate of filling losses can be made based on the total volume of MDI formulation consumed, the composition of the MDI formulation and the injection temperature.

The core box losses can be estimated from the following expression:

$$L_{cb} = \frac{V_{air}}{359} \times \left(273.15 / T_{cb}\right) \times \left(\frac{VP_{mdi}}{760}\right) \times MW \times K_{mdi} \times C_{iso}/100$$

Where:

- $L_{cb}$ = the emissions from the core box step in lb/yr
- $V_{air}$ = the annual volume of displaced air in ft$^3$/year (at the filling temperature)
- $T_{cb}$ = the filling temperature in K
- $VP_{mdi}$ = the vapor pressure of MDI in mm Hg. at the filling temperature
- $MW$ = the molecular weight of MDI (250.26)
- $K_{mdi}$ = an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
- $C_{iso}$ = the % of isocyanate feedstock in the total formulation. If only MDI/PMDI material is filled then $C_{iso} = 100$
- $359$ = the molar volume of an ideal gas in ft$^3$/lb-mole @ 0°C and 1-atmosphere

B. Mold Pour and Shakeout Step:

During the ore pour and shakeout step, exhaust air blowers are used to maintain a slight negative pressure in the process area by continuously drawing air and exhausting it to the atmosphere through a series of exhaust stacks. Residual MDI is thus removed from the mold and the sand. For this situation, the MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the residual free MDI in the mold, and the "effective" MDI concentration in the gas stream. As a worst-case scenario, it can be assumed that the air leaving the process area will be in thermodynamic equilibrium with the free MDI remaining in the mold.

The losses from the mold pour and shakeout step can be estimated from the following expression:

$$L_{so} = \left(\frac{V_{air}}{359}\right) \times (60) \times \left(\frac{ppmv}{1000000}\right) \times MW \times K_{mdi} \times C_{iso}/100 \times (t_{so}) \times (F_{mdi})$$

Where:

- $L_{so}$ = the emissions in lb/year from the shakeout and mold pour step
- $V_{air}$ = the exhaust airflow rate in ft$^3$/min (at stack temperature)
- ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature ($T_{st}$), it is directly determined from the vapor pressure
- $MW$ = the molecular weight of MDI (250.26)
K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI

C_{iso} = the % of isocyanate feedstock in the total formulation

F_{mdi} = the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01

T_{so} = the total time of operation in hours/yr

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere

60 = time, minutes/hour

Mold Pour:

L_{mp} = the emissions in lb/yr from the mold pour step

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature)

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}), it is directly determined from the vapor pressure

MW = the molecular weight of MDI (250.26)

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI

C_{iso} = the % of isocyanate feedstock in the total formulation

F_{mdi} = the fraction of free MDI remaining in the mold

T_{so} = the total time of operation in hrs/yr

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere

60 = time, mins/hr

Shakeout:

L_{so} = the emissions in lb/yr from the shakeout step

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature)

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure

MW = the molecular weight of MDI (250.26)

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI

C_{iso} = the % of isocyanate feedstock in the total formulation

F_{mdi} = the fraction of free MDI remaining in the mold

T_{so} = the total time of operation in hours/year

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere

60 = time, minutes/hour
13. Oriented Strand Board (OSB)

Methylenebis (phenyl isocyanate) (MDI) is used as a binder in the production of particleboard. The process consists of four steps:

**Step I:** Wood chips, straw, wheat, hays, or other grains are grounded up and conveyed into moisturizing chamber. Water is either added or removed to a specific moisture content.

**Step II:** The mixture of woodchips and water is transferred into second chamber where MDI is added to a specific weight equivalent. Chamber is a closed system with no vent.

**Step III:** The combination of wood, water and MDI is mixed and then spread over a "cold plate" frame that forms an 8-inch matting. The “cold plate” moves along a conveyor system where 5-6 frames are loaded onto a press where a hydraulic system compresses the mixture to a desired thickness between 1/4” to 5/8”, the “cold plate” is heated to a design temperature. During this step the MDI reacts with the water to form a polyurethane bond with the fiber. The press is open and the trapped carbon dioxide is released. The press is equipped with a blower system that vents to the roof. The press blower is also used to exhaust the air from other parts of the process.

**Step IV:** The formed boards are removed from the press, checked for quality, trimmed to the designed length and width.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is saturated with MDI.

The estimated MDI emission can be calculated using the following formula:

\[
L = \frac{V_{\text{air}}}{359} \times \frac{273.15}{T_{\text{sp}}} \times 60 \times \frac{C_{\text{mdi}}}{1000000} \times M_W \times k_{\text{MDI}} \times C_f
\]

Where:
- \(L\) = the emissions in lb/hr
- \(V_{\text{air}}\) = the exhaust airflow rate in ft\(^3\)/min
- \(T_{\text{sp}}\) = the exhaust temperature in K
- \(C_{\text{mdi}}\) = the MDI concentration, in ppmv, in the exhaust air
- \(M_W\) = the molecular weight of MDI (250.26)
- \(k_{\text{MDI}}\) = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
- \(C_f\) = per cent MDI/PMDI in solution
- 359 = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0\(^\circ\)C and 1-atmosphere.
- \(C_{\text{mdi}}\) = \((V_{\text{PMDI}}/760) \times 10^6\)
- \(VP_{\text{MDI}}\) = MDI vapor pressure at exhaust temperature
14. Belts and Tire Cord

A MDI/PMDI mixture is used in belt manufacturing as a hardener. In the manufacture of belts, part of the process is to run synthetic cords through a vat solution containing a MDI/PMDI and toluene mixture and then passed it through an oven to activate the bonding process between the synthetic cord and isocyanate and dry the cord coating. The off-gases from the oven are passed through an incinerator or combustion device for destruction. Depending upon the process, the synthetic cord then goes through a number of various mixture dips and oven treatments. Once the cords have been treated, they are wound on spools for use in the belt building process.

The controlling parameters that influence the emission rate are the temperature, flow rate, concentration of the exit gas stream, reaction rate, and the unreacted fraction of MDI. The worst-case scenario is that the exit gas stream is saturated with all the MDI that is available. The MDI emissions can be calculated using the following formula:

\[
L = \frac{(V_{air}/359) \times (273.15/T_{sp}) \times 60 \times (C_{mdi}/1000000) \times M_W \times k_{MDI} \times C_f \times R_{MDI}}{359}
\]

Where:
- \(L\) = the emissions in lb/hr
- \(V_{air}\) = the exhaust airflow rate in ft\(^3\)/min
- \(T_{sp}\) = the exhaust temperature in K
- \(C_{mdi}\) = the MDI concentration, in ppmv, in the exhaust air
- \(M_W\) = 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
- \(C_f\) = per cent MDI/PMDI in solution
- \(359\) = the molar volume of an ideal gas in ft\(^3\)/lb-mole @ 0 °C and 1-atmosphere
- \(C_{mdi}\) = \((V_{MDI}/760) \times 10^6\)
- \(V_{MDI}\) = MDI vapor pressure at exhaust temperature
- \(R_{MDI}\) = Unreacted fraction of MDI

Where:

\[
R_{MDI} = e^{(-k \times t_R)}
\]

Where:
- \(R_{MDI}\) = the unreacted fraction of MDI
- \(k\) = the first order reaction rate constant in min\(^{-1}\)
- \(t_R\) = the reaction time in minute
Appendix E - Glossary

AP-42
The EPA document, Compilation of Air Pollutant Emission Factors, 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 NAICS code and meets the activity threshold for manufacturing, processing, or otherwise using a listed toxic chemical (40 CFR Section 372.22).

Covered NAICS Code
You can determine whether a NAICS code is covered by TRI (EPCRA Section 313) by going to http://www.epa.gov/tri/lawsandregs/naic/ncodes.htm.

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) (40 CFR Section 372.3).

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 (40CFR Section 372.3). A waste is not considered a mixture for EPCRA Section 313 (TRI) 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. 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 (40 CFR Section 372.3).

Process

The preparation of a toxic chemical, after its manufacture, for distribution in commerce: (1) In the same form or physical state as, or in a different form or physical state from, that in which it was received by the person so preparing such substance, or (2) As part of an article containing the toxic chemical. Process also applies to the processing of a toxic chemical contained in a mixture or trade name product (40 CFR Section 372.3).

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 (40 CFR372.27).
Toxic Chemical  A chemical or chemical category listed in 40 CFR Section 372.65 (40 CFR Section 372.3).
## Appendix F - List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACFM</td>
<td>Actual cubic feet per minute</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts Service</td>
</tr>
<tr>
<td>CERCLA</td>
<td>Comprehensive Environmental Response, Compensation, and Liability Act (1990)</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
<tr>
<td>EHS</td>
<td>Extremely Hazardous Substance</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Act</td>
</tr>
<tr>
<td>EPCRA</td>
<td>Emergency Preparedness and Community Right-to-Know Act (1986)</td>
</tr>
<tr>
<td>HAP</td>
<td>Hazardous Air Pollutant</td>
</tr>
<tr>
<td>LEPC</td>
<td>Local Emergency Planning Committee</td>
</tr>
<tr>
<td>LEPD</td>
<td>Local Emergency Planning District</td>
</tr>
<tr>
<td>MDI</td>
<td>4,4’-methylene diphenyl diisocyanate (MDI)</td>
</tr>
<tr>
<td>NAICS</td>
<td>North American Industrial Classification System</td>
</tr>
<tr>
<td>NPDES</td>
<td>National Pollutant Discharge Elimination System</td>
</tr>
<tr>
<td>NRC</td>
<td>National Response Commission</td>
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<tr>
<td>OSB</td>
<td>Oriented Strand Board</td>
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<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration</td>
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<tr>
<td>PMDI</td>
<td>Polymeric diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>POTW</td>
<td>Publicly Owned Treatment Works</td>
</tr>
<tr>
<td>PPA</td>
<td>Pollution Prevention Act of 1990</td>
</tr>
<tr>
<td>PSIA</td>
<td>Pounds per Square Inch Absolute</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act (1976)</td>
</tr>
<tr>
<td>RIM</td>
<td>Reaction Injection Molding</td>
</tr>
<tr>
<td>RQ</td>
<td>Reportable Quantity</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>SARA</td>
<td>Superfund Amendments and Reauthorization Act of 1986</td>
</tr>
<tr>
<td>SCFM</td>
<td>Standard cubic feet per minute</td>
</tr>
<tr>
<td>SDS</td>
<td>Safety Data Sheet (formally known as Material Safety Data Sheet or MSDS)</td>
</tr>
<tr>
<td>SERC</td>
<td>State Emergency Response Commission</td>
</tr>
<tr>
<td>TPQ</td>
<td>Threshold Planning Quantity</td>
</tr>
<tr>
<td>TRI</td>
<td>Toxic Release Inventory</td>
</tr>
</tbody>
</table>
Appendix G - References


