Dealing with fires involving MDI and TDI

**General properties**

MDI and TDI are generic names for families of aromatic diisocyanates, which are a key component in the production of polyurethanes. MDI stands for methylene diphenyl diisocyanate; it is available in pure forms such as 4,4’-MDI, or as a mixture of isomers and different molecular weight oligomers in polymeric MDI or PMDI. TDI stands for toluene diisocyanate and is available in different mixtures of isomers.

MDI and TDI do not catch fire or burn easily, but they may be involved in a fire which is spread by other materials. These diisocyanates should be stored separately from combustible materials or other fire hazards, so that they will be protected in the event of a fire.

The flash points and autoignition temperatures of MDI and TDI are relatively high. The table underneath shows the flammability properties for some grades of MDI and TDI.

<table>
<thead>
<tr>
<th></th>
<th>4,4”-MDI</th>
<th>PMDI</th>
<th>80/20 TDI</th>
<th>65/35 TDI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting point</strong> °C</td>
<td>40</td>
<td>5</td>
<td>9.5 to 10</td>
<td>4</td>
</tr>
<tr>
<td><strong>Boiling range</strong> °C</td>
<td>&gt;300</td>
<td>&gt;300</td>
<td>252 to 254</td>
<td>253 to 255</td>
</tr>
<tr>
<td><strong>Autoignition</strong> °C</td>
<td>&gt;601</td>
<td>&gt;600</td>
<td>&gt;595</td>
<td>&gt;598</td>
</tr>
<tr>
<td><strong>Flash point</strong> °C</td>
<td>211</td>
<td>208</td>
<td>132.4</td>
<td>128.3</td>
</tr>
</tbody>
</table>

*Pensky-Martens closed cup method

Solvent grades of MDI exist. When MDI is formulated in a solvent, then the fire behaviour should be considered to be that of the solvent used rather than of MDI, and the appropriate storage safety measures should be taken. The safety data sheet of the solvent or the solvent grade MDI should be consulted.
Emergency actions if a fire occurs

1. **Evacuate the area**
As in any fire situation, all workers, except those dealing with the emergency, should be moved upwind of the fire to avoid inhaling the smoke and fumes.

2. **Inform management and emergency services**
Even if the fire does not involve the diisocyanate work or storage areas, the emergency services need to be informed that diisocyanates are present on the site.

3. **Use personal protective equipment**
Fire-fighters need to have fresh-air breathing equipment and full protective clothing when dealing with fires involving diisocyanates.

4. **Use fire-fighting foam or water to extinguish the blaze**
Small fires involving MDI or TDI should be extinguished using dry chemical or carbon dioxide appliances. If water is used it should only be applied from a safe distance and in large quantities, for example, using hoses. Small fires are preferably dealt with by those site staff who have been trained in dealing with emergencies.

Large fires involving MDI or TDI should be handled by fully trained and equipped emergency services. Water-based protein or other fire-fighting foams are effective in extinguishing such fires and also are useful in suppressing any release of diisocyanate vapour. However, it is preferable to use water immediately than to wait for foam to be obtained. If at all possible, the run-off water should be contained and disposed of suitably to prevent environmental contamination.

Metal drums of diisocyanate may rupture with great force if heated in a fire. If possible, any stored drums should be cooled with water, to prevent metal drums rupturing and combustible plastic containers degrading or melting.

5. **Test the area for diisocyanate residues**
After the fire is extinguished, and before work can be resumed, the air and surfaces must be tested to make sure there is no diisocyanate remaining.

**Actions after a fire incident**
A decision must be made on how to remove residual MDI or TDI. This may be very difficult if large quantities of material of unknown condition are left. Both the diisocyanate manufacturer and the fire service may need to be consulted. Small quantities of diisocyanates should be neutralized. Fire residues and contaminated extinguishing waters should be tested before disposal in accordance with local regulations.
All aspects of the involvement in the fire of the diisocyanate should be reviewed, to decide if further precautions could be put in place. Whenever there are significant changes to plant processes or to site lay-out the fire safety requirements should be reviewed. The local fire service should be given plans of the site showing the areas in which diisocyanates are used and stored.

Sources of information on MDI or TDI
Further information on the fire properties and behaviour of MDI and TDI can be obtained from the product suppliers. This text for this fact sheet has been provided by Global Isocyanates Limited (GIL). GIL is a UK based scientific consultancy with many years of experience in the diisocyanates industry.


The following websites contain relevant information:
- European Diisocyanate and Polyol Producers Association (ISOPA)  
  http://www.isopa.org
- American Chemistry Council Center for the Polyurethanes Industry  
  http://www.polyurethane.org/s_api/index.asp

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