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Subject: 8EHQ-0700-14714

This is in response to your August 31, 2000 letter on the above subject requesting additional information on the feasibility study.

1. The measured or estimated levels of monomeric, dimeric and trimeric MDI in the generated aerosol: Information from CTL on the possible distribution of MDI oligomers:

"Polymeric MDI is comprised typically of 40-50% 4,4'-MDI ("monomeric MDI"), 20-25% trimer, and the remainder higher molecular weight oligomers. The sample used in the feasibility study was commercially available MDI that was consistent with this specification. With respect to the experimentally generated aerosols, no chemical analysis was conducted, concentrations were based entirely on gravimetric analysis. However, results in these laboratories when assessing the sub-acute inhalation toxicity of polymeric MDI aerosols (III ref. 11362: *Polymeric MDI. 28 day inhalation toxicity study in female rats with post-exposure observation periods up to 30 days*)* in which these aerosols were analysed chemically, has shown a similar proportion of 4,4'-MDI and trimer in the generated aerosols compared with the supplied test material. It is expected, therefore, that in the feasibility study the generated aerosols had a chemical composition similar to the test sample supplied."

*His report was submitted to the EPA 8 (c) coordinator in a letter dated January 19, 2000 and was assigned reference 8EHQ-00-14645.

- 2. Measured or estimated viscosity of the MDI used to generate the aerosol: this information is in section 2 (Test Substance) of the report, Viscosity (mPas) 220 approx (at 25° C).
- 3. Molecular weights to calculate vapor pressures: enclosed is a III report 28268. "MDI and TDI, vapour pressures and saturated vapour concentrations.



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4. Your final question, regarding types of commercial spray applications and range of dilution factors needed to generate these types of sprays, is difficult to answer. Atomization of MDI is not a normal procedure. The study in question was a feasibility study to determine if you could artificially produce small particles that would then be used to determine an LD₅₀ which was requested by the U.S. Fire Marshals for a NFPA report.

The largest application for MDI spray foams is in tank and roof insulation. The MDI is not sprayed by itself but is mixed with a polyol in a nozzle, producing a mixture that reacts as it is being delivered and in some applications produces a froth.

Sincerely,



M.J. Blankenship

cc: J. Chapman
D. Gilbert
J. Jadlocki
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GIL Report

III ref. 28268

MDI and TDI: vapour pressures and saturated vapour concentrations

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D Pemberton
Gilbert International Limited

Report Number 2000/B

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1. MDI

Nomenclature

The term PMDI is used to represent polymeric MDI. PMDI usually contains about 50% monomeric MDI.

Review of experimental studies

Vapour pressure over liquid MDI

In Table 1 are listed the results of those studies on MDI for which a method is given, and in which there are no obvious errors. Values at 20°C, extrapolated where necessary, are quoted for comparison. For the high-temperature study such extrapolation is likely to lead to error, so a value at 150°C is quoted for comparison with TDI (Table 3).

Table 1
MDI: Experimental values of vapour pressure.

Material	Method	Temperature range (°C)	Vapour pressure (Pa) at:		Study	Reference
			20°C	150°C		
2,4'-MDI	Static *	24/41	0.0014		Shell	Kelly, 1997
4,4'-MDI	Effusion *	38/85	0.0007		Dow	Chakrabarti, 1989
	Gas saturation*	20/70	0.0005		Bayer	Brochhagen, 1986
	Effusion	65/89	0.0008		Upjohn	de Kruif, 1981
	Static	160/210		45	Upjohn	de Kruif, 1981
PMDI (ca 50% 4,4'-MDI)	Effusion *	15/73	0.0003		Dow	Chakrabarti, 1989
	Static *	23/56	0.0009		Shell	Kelly, 1997

* Experimental data are recorded in the reference

In assessing the relative merits of the above studies, it is important to understand the difficulties inherent in the measurements, particularly at ambient temperatures. The vapour pressure of MDI

at ambient temperature is extremely low, below the satisfactory range of most static methods. Further, MDI may contain trace impurities of significantly higher volatility; also it will react with traces of water to produce carbon dioxide. Consequently, static procedures, where the pressure of vapour in equilibrium with liquid is measured, can seriously overestimate the vapour pressure unless adequate precautions are taken.

The Chakrabarti data are probably the most reliable for MDI. However, all the data for 4,4'-MDI in the table (as well the boiling points) are well represented by the Antoine equation of best-fit:

$$\text{Log}_{10} P = 10.25 - 2961 / (t + 200)$$

where the vapour pressure (P) is in pascals (Pa) and the temperature (t) is in °C.

The vapour pressures calculated from the above best-fit equation are given in Table 2. Also included in the table are the saturated vapour concentrations at the corresponding temperatures, as calculated from the vapour pressures using the conventional equation of state.

Vapour pressure over solid 4,4'- MDI

The calculated values in Table 2 relate to the pressures of vapour above liquid, which will be higher than those above the solid. The ratio of these pressures can be predicted from the melting point of the substance. For 4,4'-MDI, melting point 40°C, the pressure above the solid is calculated to be 63% of that above liquid at 20°C, and 80% at 30°C. The difference is unlikely to have practical significance considering the very low pressures involved.

Vapour pressure over polymeric MDI

For polymeric (or 'modified') MDI, the experimental data, mainly from the Chakrabarti study, show a reasonably linear correlation of vapour pressure with the weight proportion of monomeric MDI in the sample. There is also evidence, from the de Kruif study, that the vapour above PMDI is composed predominantly of 4,4'-MDI.

In the absence of volatile impurities the vapour above polymeric MDI is essentially monomeric MDI, at a pressure roughly proportional to its concentration in the sample. As an example, a sample of polymeric MDI containing 40% monomer should have a vapour pressure, due to monomer, of about 2.5×10^{-4} Pa (40% of 6.2×10^{-4} Pa) at 20°C.

Table 2

4,4'-MDI: vapour pressures and saturated vapour concentrations. Best-fit values.

TEMPERATURE	VAPOUR PRESSURE	SATURATED VAPOUR
-------------	-----------------	------------------

(°C)	(Pa)	CONCENTRATION ($\mu\text{g}/\text{m}^3$)*
-10	4.6×10^{-6}	0.5
-5	1.2×10^{-5}	1.3
0	2.8×10^{-5}	3.1
5	6.6×10^{-5}	6.9
10	1.4×10^{-4}	15
15	3.0×10^{-4}	31
20	6.2×10^{-4}	64
25	1.2×10^{-3}	120
30	2.4×10^{-3}	240
35	4.5×10^{-3}	440
40	8.2×10^{-3}	790
50	2.5×10^{-2}	2.4×10^3
100	2.4	2.0×10^5
150	62	4.5×10^6
200	700	4.5×10^7

These calculated values relate to the pressures of vapour above liquid 4,4'-MDI, which will be higher than those above the solid. The values can be used without appreciable error for polymeric MDI and, probably, for 2,4'-MDI. See the text for comment.

*Note: TDI values (page 8) are expressed as mg/m^3 units.

2. TDI

Review of experimental studies

In Table 3 are listed the results of those studies on TDI for which a method is given, and in which there are no obvious errors. Values at 20°C or 150°C (extrapolated where necessary), dependent upon the temperature range of the measurement, are quoted for comparison.

Table 3
TDI: Experimental values of vapour pressure.

Material	Method	Temperature range (°C)	Vapour pressure (Pa) at:		Reference
			20°C	150°C	
2,4-TDI	Gas saturation*	20/40	1.4		Frensdorff, 1975
	Static *	50/86	2.1		Kelly, 1997
	Static *	103/170		4600	Frensdorff, 1975 Cole, 1958
	Static *	150/250		4700	Daubert, 1990
	Static	120/190		4200	Molard, 1964
	Static *	135/181		4300	Pelloux, 1994
2,6-TDI	Effusion *	-9/18	1.4		Bayer, 1996
	Static	100/180		4900	Cole, 1958
	Static *	140/250		5200	Daubert, 1990
	Static	120/190		4500	Molard, 1964
80/20 TDI	Effusion *	-9/18	0.8		Bayer, 1996
	Gas saturation*	20	1.2		Wu, 1996
65/35 TDI	Static *	134/163		4300	Pelloux, 1994

*Experimental data are recorded in the reference.

When the relative merits of these studies are being assessed, the difficulties inherent in the measurements, particularly at ambient temperatures, must be understood. The ambient vapour pressure of TDI is low, and falls inconveniently around the upper limit of most flow methods and the lower limit of most static methods. In addition, TDI can contain trace impurities having significantly higher volatility: it will also react readily with traces of water to produce carbon

dioxide. Consequently, static procedures, where the pressure of vapour in equilibrium with liquid is measured, can seriously overestimate the vapour pressure unless adequate precautions are taken.

The Frensdorff/Cole data for TDI are probably the most reliable. However all the data for 2,4-TDI in the table (and also the boiling points) are well represented by the Antoine equation of best-fit:

$$\text{Log}_{10} P = 9.66 - 2120 / (t + 203)$$

where the vapour pressure (P) is in pascals (Pa) and the temperature (t) is in °C.

The vapour pressures calculated from the above best-fit equation are given in Table 4. Also included in the table are the saturated vapour concentrations at the corresponding temperatures, as calculated from the vapour pressures using the conventional equation of state.

Vapour pressure of 2,6-TDI and its mixtures with 2,4-TDI

The vapour pressures of 2,6-TDI and its mixtures with 2,4-TDI appear to be very similar to those of 2,4-TDI, and predicted values for the latter can be used for all without appreciable error.

Table 4
2,4-TDI: vapour pressure and saturated vapour concentrations. Best-fit values

TEMPERATURE (°C)	VAPOUR PRESSURE (Pa)	SATURATED VAPOUR CONCENTRATION (mg/m ³)*
---------------------	-------------------------	--

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-10	0.047	3.7
-5	0.090	7.0
0	0.16	13
5	0.29	22
10	0.51	38
15	0.86	63
20	1.4	100
25	2.3	160
30	3.6	250
35	5.7	380
40	8.6	580
50	19	1.2×10^3
100	460	2.6×10^4
150	4,500	2.3×10^5
200	25,000	1.1×10^6

These values can also be used for 2,6-TDI and mixtures of 2,4- and 2,6-TDI, without appreciable error.

*Note: MDI values (page 5) are expressed as $\mu\text{g}/\text{m}^3$ units.

3. CONVERSION OF UNITS

Pressure relationships

The relationship between pressure units is straightforward in that:

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1 standard atmosphere = 760mmHg = 1013mbar = 101325 Pa

This leads to the following conversion factors.

Table 5
Pressure relationships

Pa	mmHg (Torr)	mbar
1	0.0075	0.01
133	1	1.33
100	0.75	1

For example: 5 Pa = 5 x 0.01mbar = 0.05 mbar

Concentration relationships

For conversion to gravimetric units the equation state of an ideal gas is used:

1 mole of MDI is 250.3g

1 mole of TDI is 174.2g

1 mole occupies $(22.414 \times T/273.2)$ litres at 1 standard atmosphere and temperature T (K)

This leads to the following conversion factors.

Table 6
Concentration Relationships

ppm (volumetric)	mg/m ³ (20°C)	
	MDI	TDI
1	10.4	7.2
0.096	1	
0.138		1

Pressure/Concentration Relationships

Since 10⁶ppm is equivalent to 1 standard atmosphere, Tables 5 and 6 can be combined to give the more detailed Table 7 below.

Table 7
Pressure/Concentration Relationships

Pa	mmHg (Torr)	mbar	ppm	mg/m ³ (20°C)	
				MDI	TDI
1	0.0075	0.01	9.9	103	71
133	1	1.33	1316	13700	9500
100	0.75	1	987	10300	7100
0.101	0.00076	0.00101	1	10.4	7.2
0.0097	0.000073	0.000097	0.096	1	
0.014	0.000105	0.00014	0.138		1

For example:

- a) 9.9 ppm of MDI is equivalent to 103mg/m³ MDI
- b) 9.9 ppm of TDI is equivalent to 71 mg/m³ TDI
- c) 10 ppm of TDI is equivalent to 72 mg/m³ TDI

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