U.S. Department
of Transportation

**Pipeline and Hazardous
Materials Safety
Administration**

1200 New Jersey Avenue, SE
Washington, DC 20590

June 24, 2020

Ernest Marcel, CDGP, DGSA
LANXESS Solutions, US, Inc.
PTSE/PSRA Group
2 Armstrong Road
Shelton, CT, 06484

Reference No. 19-0077

Dear Mr. Marcel:

This letter is in response to your June 10, 2019, email requesting clarification of the Hazardous Materials Regulations (HMR; 49 CFR Parts 171-180) applicable to mixtures containing a hazardous material that is listed in the Hazardous Materials Table (HMT) with a "+" in Column (1) and assigned Special Provision (SP) 279 in the UN Model Regulations and the International Maritime Dangerous Goods (IMDG) Code. Specifically, you ask about the classification of a product containing less than 5% toluene diisocyanate.

We have paraphrased and answered your questions as follows:

Q1. You seek confirmation that SP 279 in the IMDG Code and the "+" sign in Column (1) of the HMT assigns the UN Number, Proper Shipping Name, Hazard Class, and Packing Group (PG) to shipments of UN2078, but not to products containing toluene diisocyanate.

A1. Your understanding is correct. Special Provision 279 and the "+" in Column (1) apply to the listed material, and do not extend to all mixtures or solutions that contain the material. It is the responsibility of the shipper to classify mixtures and solutions of toluene diisocyanate taking into account the classification criteria within the IMDG Code and the HMR.

Q2. You ask whether the UN Model Regulations and the IMDG Code classify "UN2078, Toluene Diisocyanate, Class 6.1, PG II" as a toxic-by-inhalation hazard (TIH) material.

A2. The answer is no. Neither the UN Model Regulations or the IMDG Code specifically identify UN2078 as a TIH material.

Q3. You ask whether a hazard classification under the UN Globally Harmonized System of Classification and Labelling of Chemicals (GHS) takes precedence over the hazardous classification criteria of the various hazardous material transportation regulations (e.g., the HMR, IMDG Code, etc.).

A3. The answer is no. For purposes of transportation within the United States, the classification criteria in the HMR take precedence over other standards, unless expressly authorized for use. For example, § 171.22 provides authorization and conditions for the use of international standards and regulations.

Sincerely,

Shane C. Kelley

Shane Kelley
Director,
Standards and Rulemaking Division
Office of Hazardous Material Standards

Casey
19-0077

January, Ikeya CTR (PHMSA)

From:	INFOCNTR (PHMSA)
Sent:	Thursday, June 13, 2019 4:45 PM
To:	Hazmat Interps
Subject:	FW: UN2078, Toluene Diisocyanate, 6.1, II in Mixture(s)
Attachments:	Toluene Diisocyanate letter.docx; TDI DG fin -model and measured data v .xlsx; TDI DG Presentation LXS Solutions May 2018.pptx

Hello Alice and Ikeya,

Please see the attached documents for a letter of interpretation request.

Sincerely,

Lynsie, HMIC

From: Marcel, Ernest [mailto:Ernest.Marcel@lanxess.com]
Sent: Tuesday, June 11, 2019 2:18 PM
To: INFOCNTR (PHMSA) <INFOCNTR.INFOCNTR@dot.gov>
Subject: UN2078, Toluene Diisocyanate, 6.1, II in Mixture(s)

To whom it may concern:

I would like to submit the attached letter and documents as for a formal letter of interpretation. If further information is needed, please don't hesitate to contact the undersigned.

Best Regards,

Ernest J. Marcel, CDGP, DGSA
Head, Dangerous Goods
Transportation Compliance
LANXESS Solutions, US, Inc.
PTSE/PSRA Group

2 Armstrong Road, Shelton, CT 06484, USA
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Energizing Chemistry

LANXESS Solution, Inc.
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10 June 2019

Pipeline & Hazardous Materials Safety Administration (PHMSA) -U.S. DOT
Office of Hazardous Materials Safety, International Standard Program
1200 New Jersey Avenue S.E., E24-422, Washington D.C. 20590
E24-422

Re: UN2078, Toluene Diisocyanate, 6.1, II in Mixture(s)

To Whom it my concern:

Lanxess Solutions is requesting an interpretation letter on international classification of UN2078, Toluene Diisocyanate, Class 6.1, II in mixture(s).

UN2078 is listed in the 172.101 with a "+" sign in Column 1 and has SP279 in the UN Recommendations and the IMDG Code.

2.0.2.9 for Classification of mixtures or solutions which states:

"A mixture or solution, containing one or more substances identified by name in this Code or classified under an N.O.S. or generic entry and one or more substances not subject to the provisions of this Code, is not subject to the provisions of this Code if the hazard characteristics of the mixture or solution are such that they do not meet the criteria (including human experience criteria) for any class"

Lanxess used a mathematical calculations methodology for the classification of the product. A team consisting of two toxicologists and a chemist were assigned to develop and run the calculations. The team determined that with less than 5% of UN2078 in the mixture that the product did not meet the hazardous materials classification requirements of 49CFR, the UN Recommendations or the IMDG Code. As a result of this testing Lanxess has been moving this product as non-hazardous for over ten years.

Recently there have been challenges to this classification from an international source. We are being told the following:

[redacted]

1. That the SP279 means that any product with UN2078 in it must always move using the hazardous classification even if it does not meet the criteria for any hazard class.

It is our understanding that SP279 only assigns the UN Number, Proper Shipping Name, the Hazard Class, and the Packing Group to UN2078. There are no further restrictions mentioned in SP279.

If it is determined that the product is not hazardous per the Classification criteria in the UN Recommendations 2.0.2.7 or the IMDG Code 2.0.2.9 then the product would not be listed as UN2078. (However, it does require UN2078 to be properly listed as one of the chemicals in the mixture on the SDS form). Is our understanding of SP279 correct?

2. That UN2078 is a Toxic Inhalation Hazard (TIH) per the UN Recommendations and the IMDG Code.

Checking the latest versions of both documents; neither shows UN2078 as a (TIH). Has UN2078 been updated to say that it is a TIH?

3. GHS is mentioned multiple times in regards to UN2078 being a TIH and stating that GHS over rules the various hazardous material transportation regulations.

Would GHS classification criteria inhalation hazard take precedence over criteria found in Chapter 2.6 of the IMDG Code when classifying a material for transport? Issues in the work place are very different from those found in the transportation of hazardous materials.

We have attached the following documents for your reference:

- Latest version of the calculation method to determine the packing group for TDI in Urethane Prepolymer
- TDI DG Presentation

If further information is needed, please don't hesitate to contact the undersigned. I can be reach by office phone: 203.573.2057, mobile: 203.558.3408 or email at: ernest.marcel@lanxess.com

Thank you very much for your attention in this important subject matter

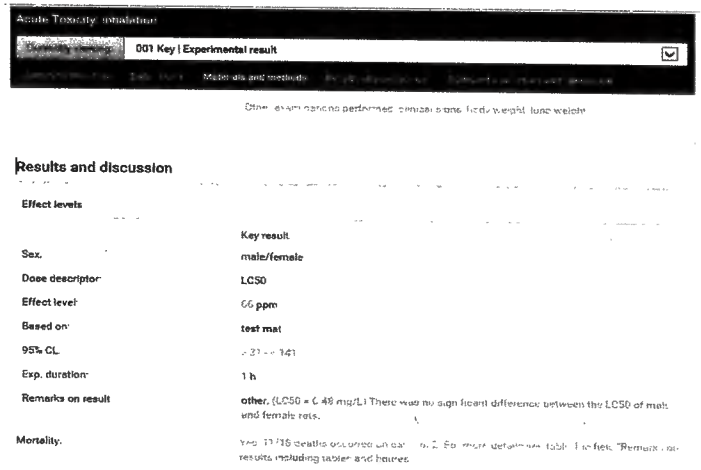
Sincerely,

Ernest J. Marcel, CDGP, DGSA
Head, Dangerous Goods Transportation Compliance
LANXESS Solutions, Inc.

[redacted]

SUMMARY and CONCLUSIONS

1. The LC50 for Rat is 66 ppm (ml/m3)



2. For Polymer Solutions the vapor pressure of the Solute is calculated using Flory Huggins Theory (The Ideal Solution Calculation Method is not valid)
    1. Using the vapor method with F-H Polymer Solutions Theory and the LC50 above --> PG III is reached at % TDI ~ 40 wt% .
    2. Using measured vapor data and extrapolating from there using the LC50 above --> PG III is also reached at % TDI ~ 40 wt% .
    3. Using the vapor method with measured data and applying a 95% confidence interval and the LC50 above --> PG III is reached at % TDI ~ 6.1 wt% .
    4. For the Mist /Dust method and the LC50 above --> PG III is achieved at %TDI < 32 wt% TDI in a Polymer Solution

3. To be EXTRA conservative the cut-off is set to 5.0 wt%

CONCLUSION:

Polymer Solutions containing TDI monomer are not DG if % TDI monomer is < 5wt.%

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Our Company Commitment

RC and GPS are both global initiatives to improve the chemical industry's environmental, health, safety, and security performance.

Principles

- Process Safety
- Product Safety
- Security
- Human Health and Safety
- Environmental Protection
- New Product and Process Devel
- Product Stewardship
- Community Outreach
- **Transportation and Distribution**
- **Emergency Response**
- Stakeholder Communication

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Outline

- Assessing DG Classification of TDI in Simple Solvents
- Is Solvent Methodology Applicable for TDI in Polymer Solutions?
- Calculating Vapor Pressure and Mist Concentration of TDI in Polymer Solutions.
- Concentration at which TDI in Polymer Solutions is Packing Group III

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Dangerous Goods – Criteria for Determining Packing Group

2.6.2.2.4.2 The criteria for inhalation toxicity of dusts and mists in 2.6.2.2.4.1 are based on LC_{50} data relating to 1 hour exposures and where such information is available it shall be used. However, where only LC_{50} data relating to 4 hours exposures to dusts and mists are available, such figures can be multiplied by four and the product substituted in the above criteria, i.e. LC_{50} (4 hours) × 4 is considered the equivalent of LC_{50} (1 hour).

2.6.2.2.4.3 Liquids having toxic vapours shall be assigned to the following packing groups, where "V" is the saturated vapour concentration in millilitres per cubic metre of air (volatility) at 20 °C and standard atmospheric pressure:

(a) Packing group I: If $V \geq 10\ LC_{50}$ and $LC_{50} \leq 1\ 000$ ml/m^3;

(b) Packing group II: If $V \geq LC_{50}$ and $LC_{50} \leq 3\ 000$ ml/m^3, and not meeting the criteria for packing group I;

(c) Packing group III[1]: If $V \geq 1/5\ LC_{50}$ and $LC_{50} \leq 5\ 000$ ml/m^3, and not meeting the criteria for packing groups I or II.

2.6.2.2.4.4 In Figure 2.6.1, the criteria according to 2.6.2.2.4.3 are expressed in graphical form, as an aid to easy classification. However, because of approximations inherent in the use of graphs, substances on or near packing group borderlines shall be checked using numerical criteria.

Establish LC50 in mg/L for TDI

Reference	REACH Dossier
LC50 (ppm)	66
Species	Rat
Duration (hours)	1
Convert to 1 hr duration:	
Corr Factor to 1 hour	1
Corrected LC50 vapor	66

TDI LC50 (1 hr) = 66 ppm

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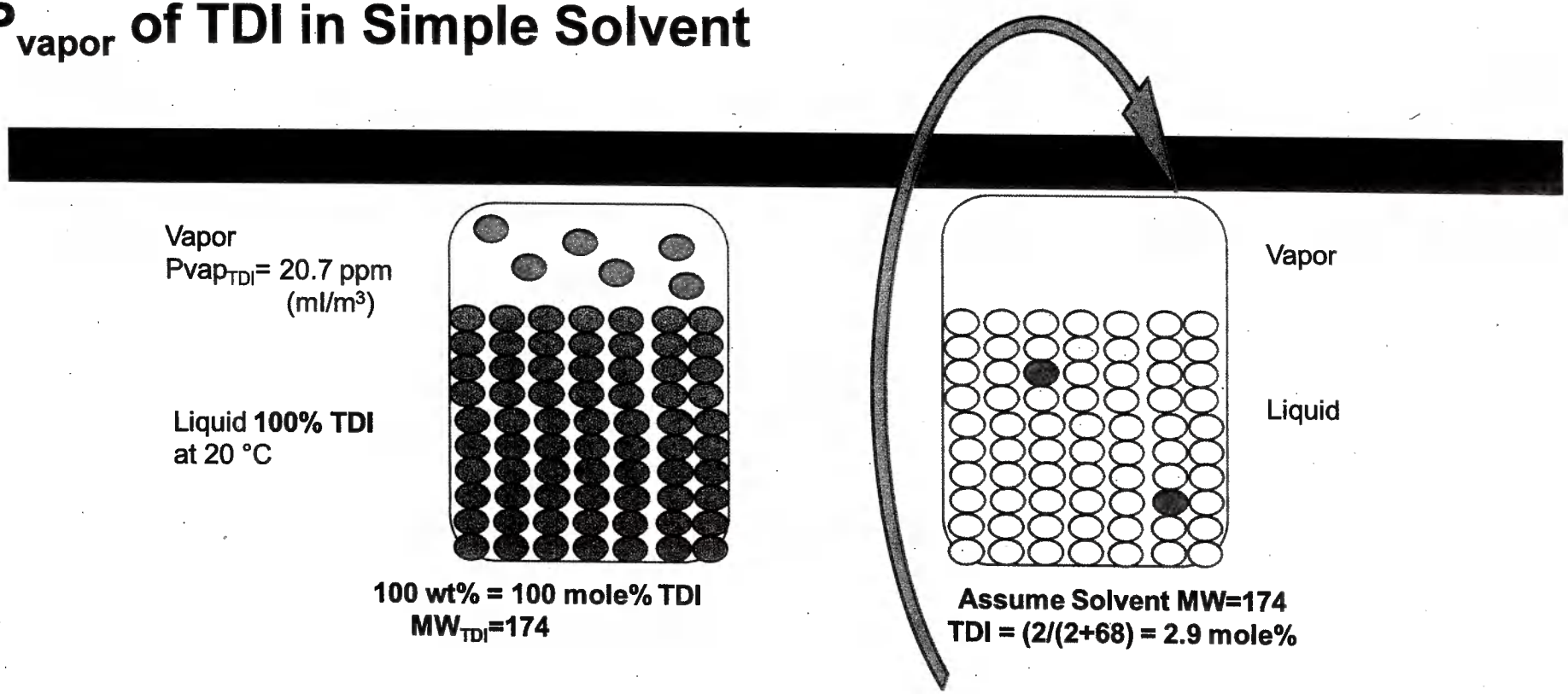
P_{vapor} of TDI in Simple Solvent



$$Pvap_{TDI\ in\ Solvent} = Mole\%\ TDI \times Pvap_{100\%\ TDI\ at\ 20C}$$

If no data available–> Use Calculation Method for Determining Packing Group

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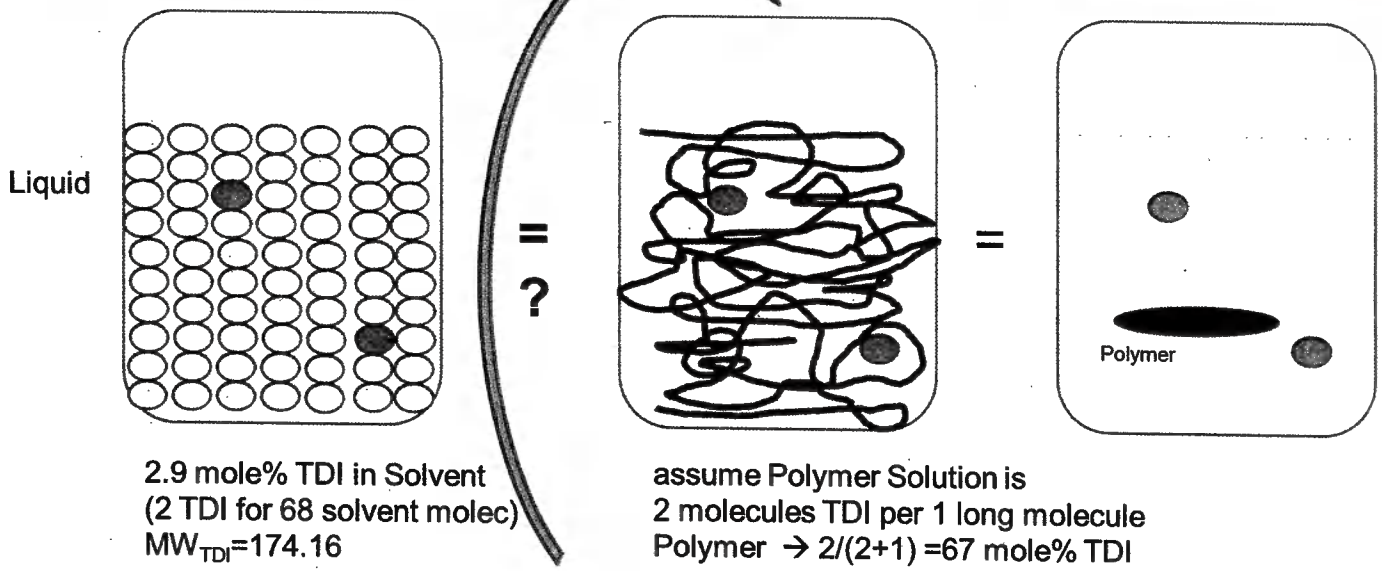
TDI in Simple Solvent vs. TDI in Polymer Solution



2.9 mole% TDI in Solvent
(2 TDI for 68 solvent molec)
MW_{TDI}=174.16

assume Polymer Solution is
2 molecules TDI per 1 long molecule
Polymer → 2/(2+1) =67 mole% TDI

$$Pvap_{TDI\ in\ Solvent} = Mole\%\ TDI \times Pvap_{100\%\ TDI\ at\ 20C}$$

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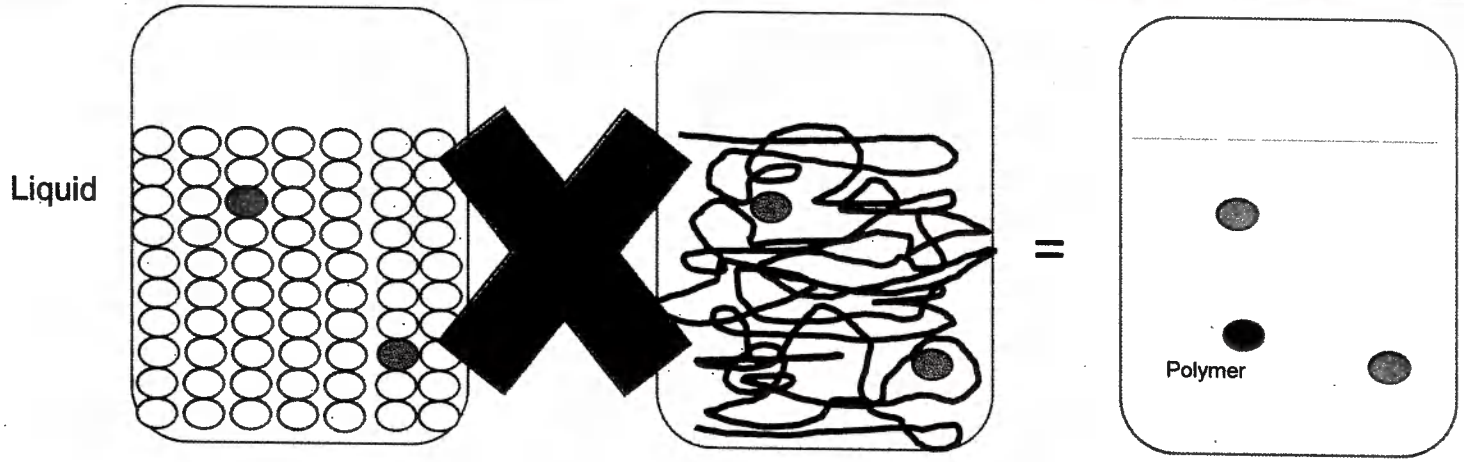
TDI in Simple Solvent vs. TDI in Polymer Solution



2.9 mole% TDI in Solvent
(2 TDI for 68 solvent molec)
MW_{TDI}=174.16

5.6 wt% TDI but assume Polymer Solution is 2 molecules TDI per 1 moleculePolymer → 67 mole% TDI

$$Pvap_{TDI\ in\ Solvent} = Mole\%\ TDI \times Pvap_{100\%\ TDI\ at\ 20C}$$

SIMPLE SOLUTE/SOLVENT THEORY IS NOT CORRECT FOR SOLUTE/POLYMER SYSTEMS

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Rather … Use Flory – Huggins Polymer Solution Theory

Basically …
The proper variable for calculating Pvap of solute (=TDI) in Polymer Solution is a function of **VOLUME %** …. *not* MOLE %

For a two component system such as we have here per Flory-Huggins, the activity of the Solute (= a1) in the Polymer =

$$\ln a_1 = \left[\ln(1-\phi_2) + \left(1-\frac{1}{x}\right)\phi_2 + \chi_1\phi_2^2\right]$$

$$Pvap_{TDI} = a_1\ Pvap_{100\%\ TDI}$$

where	ϕ_2	=	volume fraction of polymer
	χ_1	=	Solute - Polymer Interaction Parameter and is always positive. M Maximum value (before incompatbility = phase separation) = 0.5
	x	=	Molar Volume Ratio of Polymer/Solute
Density of TDI		1.21	gr/cm3 at 25C
Density Adiprene		1.07	gr/cm3 for range 25C to 40C

See Spreadsheet for Calculation Details and Parameter Values

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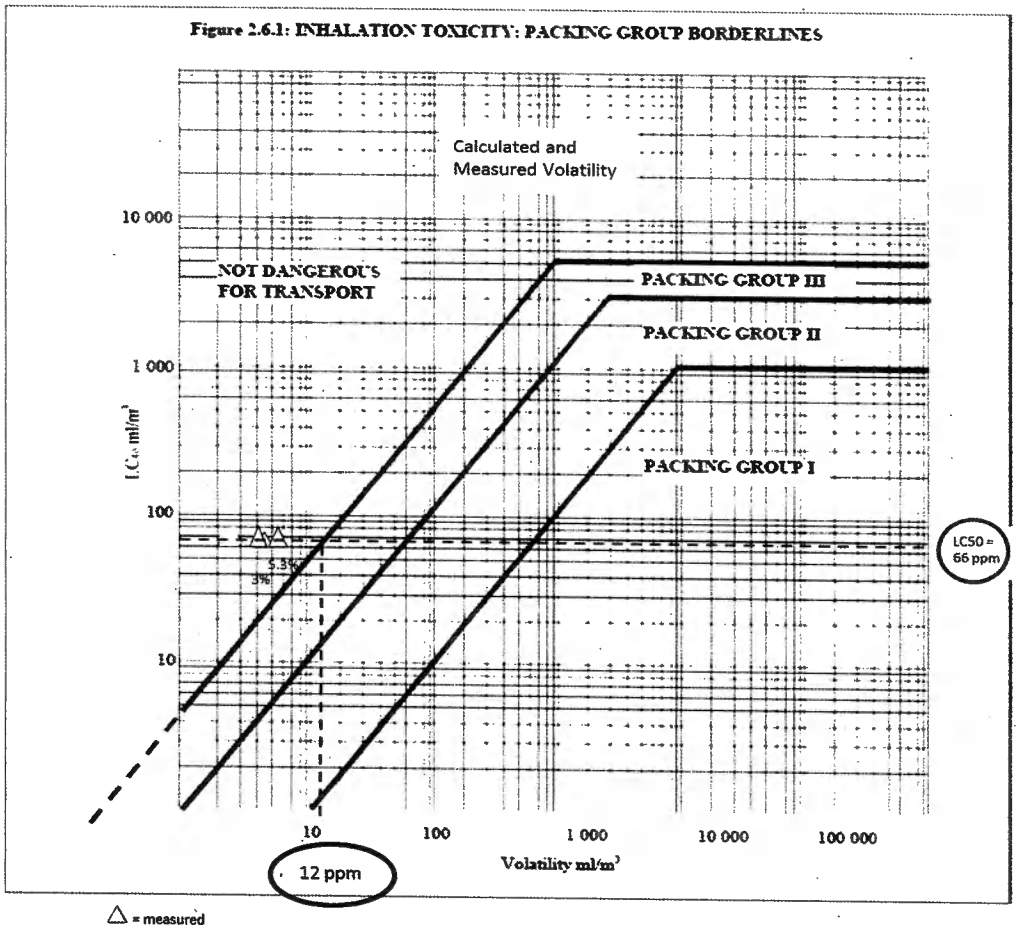
Dangerous Goods Cut-Off Calculation and Actual Measured TDI Partial Pressure Results



Volatility = (Pvap x 10^6) / 101.3

Volatility [=ml/m^3] [= ppm]

Pvap [=kPa]

[redacted]

Not DG if **Volatility TDI** from TDI in **Polymer Solution** is **< 12 ppm**

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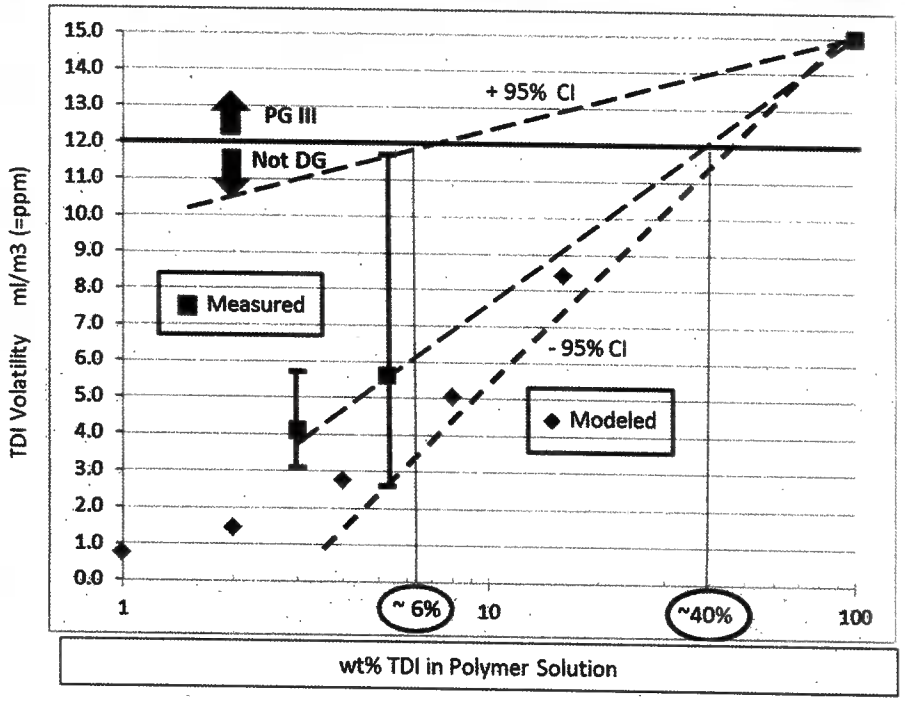
Establishing the Cut-Off for TDI in Polymer Solutions

Measured and F-H Calculated Volatility Values				
If wt% TDI in PrePolym =	Calculated F-H Theory	Measured	+/_ 95% Confidence Intervals of measured values	
1	0.7			
2	1.4			
3		4.1	3.1	5.7
4	2.8			
5.3		5.6	2.6	11.7
8	5.0			
16	8.4			
100		15		



Conclusion: Based on Measured Data for Free TDI in Polymer Solutions the DG Cut-Off is set extra conservatively at **5 wt.%**

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Notes – for additional details see the embedded Spreadsheet

1. For mists the cut-off is higher, therefore the vapor pressure method is used to set the cut-off (see spreadsheet for details).

2. TDI becomes PG II when it is almost pure (=100% TDI).

Microsoft Excel Worksheet

Detailed calculations

Microsoft Word 97 - 2003 Document

Reference Book Chapter on Flory Huggins Polymer Solution Theory

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