

TMXDI® (META)

ALIPHATIC ISOCYANATE



FACTS & FIGURES



About us

- Global company with nearly \$1.5 billion in sales
- Resin portfolio that comprises of more than 80% of low VOC and waterborne products
- Broad technology portfolio: liquid coating resins, energy curable resins, powder coating resins, crosslinkers and additives
- Approx. 2000 employees
- More than 2500 customers
- 16 manufacturing facilities
- 13 research and technology centers
- 2 joint ventures
- A myriad of solutions for key coating segments: automotive, industrial, packaging coating and inks, protective, consumer electronics & industrial plastics and specialty architectural



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TMXDI^{®1} (META) Aliphatic Isocyanate

Goal	Opportunities
<p>Provide information on the performance benefits, chemistry, and processing advantages of TMXDI monomer for water-based coating technology as it applies to polyurethane dispersions</p>	<ul style="list-style-type: none"> • Provide a coating technology that allows for the preparation of solvent-free waterborne polyurethane dispersions • Develop TMXDI monomer based polyurethane coatings with a broad range of hardness and performance properties

Application Areas for Technology

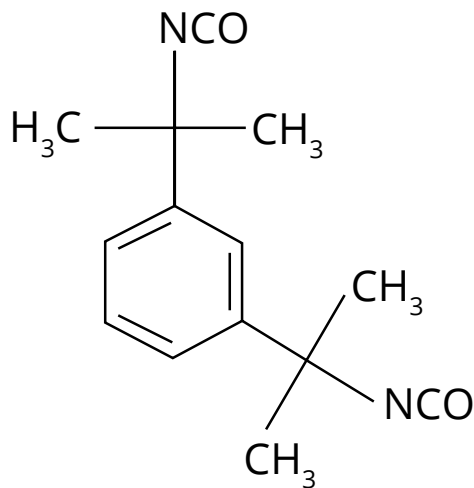
Aqueous Dispersions	Two-Component	UV Curable
<p>Adhesives Specialty Coatings Roof Coatings Floor Coatings Flexible Coatings Plastic Coatings</p>	<p>Adhesives Specialty Coatings Roof Coatings Floor Coatings Flexible Coatings Plastic Coatings Sealants RIM Potting/Encapsulation</p>	<p>Floor Coatings Flexible Coatings Plastic Coatings</p>
One Shot	Lacquers	Moisture Cure
<p>Castable Elastomers Adhesives Sealants</p>	<p>Flexible Coatings</p>	<p>Roof Coatings Floor Coatings Specialty Coatings Sealants</p>

¹ All TMXDI referred to herein are TMXDI (META) aliphatic isocyanate

TMXDI® (META) Aliphatic Isocyanate for Dispersions

Why use TMXDI monomer over other isocyanates?

- TMXDI is uniquely suited for waterborne application
- Manufacturing advantages
 - Processing ease due to low prepolymer viscosity
 - Solvent free, no acetone or NMP
 - Higher through-puts
- Performance advantages
 - Broad range of properties obtainable
 - Flexible coatings with superior adhesion
 - Exceptional toughness
 - Improved aluminum flake orientation
- FDA Sanction for use in food packaging adhesives under 21CFR 175.105, Non Food Contact



META-Tetramethylxylylene Diisocyanate

Physical Properties	
Molecular Formula	$C_{14}H_{16}N_2O_2$
Molecular Weight	244.3
NCO Content, % By Weight	34.4
Equivalent Weight	122.1
Boiling Point, °C mmHg	150 (3 mmHg)
Melting Point, °C	-10
Vapor Pressure, mmHg @ 25°C	0.003
Flash Point, °C (Setaflash Closed Cup)	153
Autoignition Point, °C	450
Solubility	Inert organic solvents

TMXDI® (META) Aliphatic Isocyanate

Chemistry Characteristics

- TMXDI is an aliphatic isocyanate because the NCO is not conjugated to the aromatic ring
 - Excellent light stability and exterior durability
- Steric hindrance by dimethyl groups provides lower reactivity and reduces hydrogen bonding
 - Lower reactivity with water
 - Controlled reactivity by use of catalysts
 - No self-condensation reactions leading to branching, e.g. allophanate, biuret, isocyanurate
 - Minimal reactivity with carboxyl groups
 - Significantly lower prepolymer viscosity
- Equal isocyanate reactivity
- Higher reaction temperatures possible for prepolymer formation
 - 100°C-120°C not a problem
 - Stable viscosity in absence of water

Polyurethanes Intermediates (Prepolymers)

- Almost all polyurethane-polyureas are prepared via NCO prepolymer intermediates
- The possibility to tailor-make any desirable intermediate by the polyaddition reaction is an important attribute

NCO-Terminated Prepolymers

- These are prepared by the reaction of di- or polyhydroxyl compounds with an excess of diisocyanates
 - Typical molecular weight 7,000 - 12,000
- Further reaction with difunctional chain extenders gives rise to the fully reacted high molecular weight polyurethane-polyurea network

Advantages in Prepolymer Formation

- Effects of reduced hydrogen bonding
 - Low prepolymer viscosity
 - Higher ionic containing prepolymer can be processed
 - Trifunctional polyols should be added to maintain film properties when replacing other isocyanates with TMXDI
- Processing advantages
 - Hot prepolymer can be pumped with ease (no viscosity build-up)
 - Higher prepolymer temperature (120°C) may be used to reduce viscosity
 - No solvent needed to reduce viscosity
 - Solvent removal step eliminated
 - Slower reaction rate allows heated prepolymer to be added into water below 40°C with minimal hydrolysis

Prepolymer Viscosities Formulated to Equal NCO Equivalents

Brookfield Viscosity (mPa•s @ 100°C)

Polyol	Prepolymer % Solids	TMXDI®	H ₁₂ MDI	IPDI
<i>Tone 230/305</i>	65 (Toluene)	220	970	340
<i>Tone 240</i>	100	1,255	1,965	1,540
<i>HD-AA</i>	100	2,300	100,000	100,000
<i>HD-AA</i>	85 (NMP)	400	1,300	780
<i>BD-11</i>	85 (NMP)	600	4,050	1,500
<i>HD-AA-IPA</i>	100	2,700	200,000	4,500

Physical Property Characteristics of Urethanes Made From Aliphatic Diisocyanate Monomers

Property	TMXDI	IPDI	H ₁₂ MDI
<i>Hardness</i>	Softer	Harder	Harder
<i>Tensile Strength</i>	Lower	Higher	Higher
<i>Elongation</i>	Higher	Lower	Lower
<i>Hydrolytic Stability</i>	Better	Good	Good
<i>Clarity</i>	Clear	Clear	Clear
<i>Prepolymer Viscosity</i>	Low	Middle	High

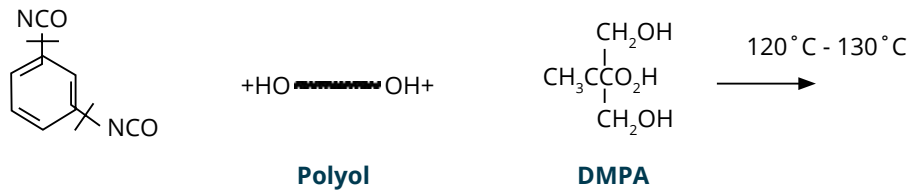
- TMXDI cannot be directly substituted due to:
 - NCO content
 - Reduced hydrogen bonding

Dispersion Structure / Property Relations

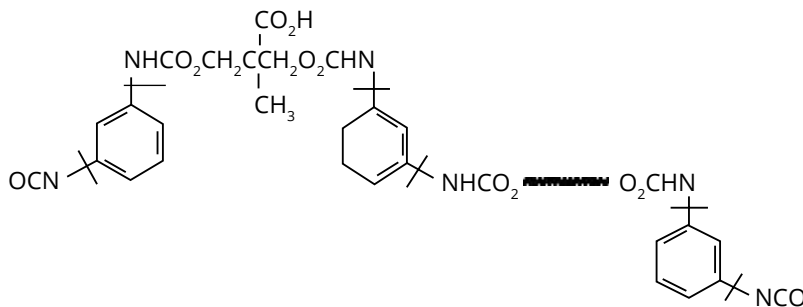
Formulation Variables	
<i>Polyols</i>	<i>Effect</i>
Trifunctional Caprolactones, TMP	Toughness Hardness Chemical/Solvent resistance Humidity resistance
Polyethers	Softness Flexibility Adhesion
<i>Chain Extenders</i>	<i>Effect</i>
2-Methyl Pentamethylene Diamine (Dytek A)	Toughness with elongation
Diethylene Triamine (DETA)	Hardness Chemical/Solvent resistance
Hydrazine Hydrate (HH)	Soft-Feel
Ethylene Diamine (EDA)	Toughness with elongation

Dispersion Process

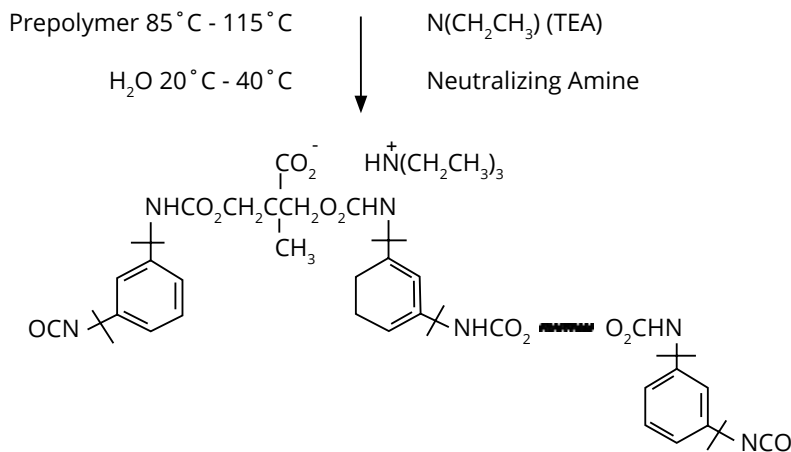
TMXDI® Monomer



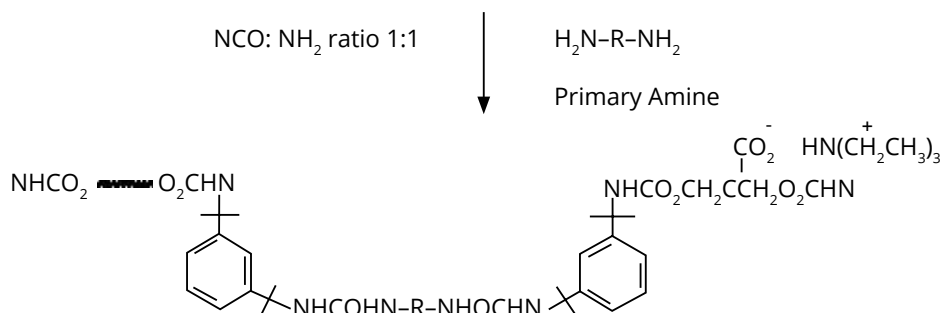
NCO-Terminated Prepolymers



Hydrophilic Modified NCO-Terminated Prepolymer



Aqueous Polyurethane-Polyurea Dispersion



Formulation Parameters

NCO:OH

- 1.4 to 1.7:1 to control molecular weight of isocyanate terminated prepolymer (7,000 - 12,000 MW typical)

Trimethylol Propane (TMP)

- Trifunctional polyol is added for controlled branching which improves strength and resistance properties

Dimethylol Propionic Acid (DMPA)

- The ionic content is a major factor for controlling the particle size of the dispersion
- Low ionic content (acid number 16) dispersion must be neutralized to 120% to achieve a stable dispersion during production
- Increasing acid number to 20 (4.78 wt% DMPA) widens the processing window, allows lower neutralizing amine level, and allows lower pH of the dispersion

Processing Parameters

Prepolymer (Intermediate)

- Dry nitrogen blanket must be maintained to keep out moisture
- Agitation must be sufficient to ensure proper bulk mixing with high viscosity prepolymers
- Higher processing temperature may be used (120°C) to speed-up reaction time and lower viscosity
- Prepolymer temperature must be lowered to 80°C - 85°C when using TEA for pre-neutralized systems
- Reaction is complete when NCO value is at or below theoretical (constant value)
- Prepolymer may be held at reaction temperatures until the dispersion step

Dispersion Equipment, High Speed

- Use pitched turbine or Cowles blades agitators
- Size blades so that the ratio of the dispersing vessel diameter to blade is 2
- Position blade at least one blade diameter off the bottom
- Adjust agitator speed to optimize dispersion step
- Use a closed system (not airtight) dispersing vessel to keep in amine
- Jacket vessel with sufficient cooling capacity to remove latent heat of prepolymer and reaction exotherm
- Do not exceed a water temperature of 40°C during dispersion and chain extension steps to avoid NCO reaction with water

Dispersing Parameters

Water Neutralization Process

- Tertiary amine is charged to the water. The hot prepolymer is added into the water with agitation while simultaneously neutralizing and dispersing the prepolymer
- Particle size of the dispersion is usually larger
- Amine volatility can be a problem
- Accurate prepolymer transfer can be a problem causing uncertainty in % neutralization and chain extension
 - for low ionic content dispersions at 120% neutralization, pH should be 9.3 - 9.5 during dispersion
 - for high ionic content dispersions at 80% neutralization, pH should be 7 - 8 during dispersion
 - Higher prepolymer temperature can be used to reduce viscosity

Pre-neutralization Process

- Tertiary amine is added to the prepolymer prior to dispersing it in water
- Particle size of the dispersion is smaller
- No uncertainty in determining the prepolymer's % neutralization
- Use lower prepolymer temperatures (80°C - 85°C) to allow the amine to be mixed into prepolymer without volatilizing the amine

Formulation Parameters

Neutralizing Amine

- Tertiary amines are required
- Triethylamine (TEA) is used for its base strength and low boiling point
- DMAMP-80 can be an alternate for TEA
- The level (%) of neutralization has an effect on pH, particle size and appearance for a given ionic content
- TEA can be used for water neutralized or pre-neutralized processes. DMAMP-80 used only for water neutralized process (OH group will react)
- The % neutralization has an effect on the final viscosity of the dispersion for a given ionic content

Chain Extension Parameters

- The amount of chain extending amine should be calculated to give a stoichiometric addition based on the amount of NCO titrated, and the amount of prepolymer added
- IPDI & H12MDI systems are typically under chain extended (~85%)
- Under chain extension of TMXDI® prepolymers can lead to grit formation
- Expect an exotherm. Dilution of the chain extending amine will reduce the exotherm and also prevent shocking the system
- The final pH of the dispersion is normally close to the initial pH of the neutralized dispersed prepolymer. This will happen as the chain extending amine reacts with the isocyanate forming high MW polymer in water

Aqueous Polyurethane Dispersions

Dispersion Characteristics

- Prepared without solvents
- No added surfactants
- Low VOC
- Low viscosity
- Shelf stability > 1 Year
- Can be formulated for freeze-thaw stability

Urethane Characteristics

- Superior toughness
 - Combination of high tensile strength / elongation
- High elongation
 - Attained for soft and hard systems
- Excellent abrasion resistance

Polyols Used In Starting Point Formulations

<i>Polyol</i>	<i>Type</i>	<i>Eq. Wt.</i>
A	Hexanediol adipate polyester	500
B1	Neopentyl glycol adipate polyester	500
B2	Neopentyl glycol adipate polyester	250
C	Polytetramethylene ether glycol diol	500
D1	Poly (propylene glycol) diol	500
D2	Poly (propylene glycol) diol	1000
D3	Poly (propylene glycol) diol	240

Abbreviations Used In Formulations

<i>DMPA</i>	Dimethylol propionic acid
<i>TEA</i>	Triethylamine
<i>DMAMP-80</i>	Dimethylamino methyl propanol
<i>Dytek A*</i>	Methylpentamethylene diamine
<i>DBTDL</i>	Dibutyl tin dilaurate (catalyst)
<i>NPG</i>	Neopentyl glycol
<i>TMP</i>	Trimethylol propane

* Product of DuPont

Starting Point Polyester Formulations

Dispersions	I	II	III
Component	Wt%	Wt%	Wt%
<i>Polyol A</i>	57.50	-	-
<i>Polyol B1</i>	-	27.25	31.82
<i>Polyol B2</i>	-	22.49	7.08
<i>TMXDI monomer</i>	38.10	45.00	52.11
<i>DMPA</i>	3.82	4.50	4.49
<i>TMP</i>	0.57	0.75	0.50
<i>NPG</i>	-	-	3.99
<i>DBTDL</i>	0.01	0.01	0.01
Total	100	100	100
% NCO	5.38	5.86	7.49
NCO:OH	1.70	1.91	1.72
Acid Number	16.0	18.8	18.8

Dispersion	Wt	Wt	Wt
<i>TEA</i>	3.46	4.07	-
<i>DMAMP-80</i>	-	-	4.59
<i>Dytek A</i>	7.43	8.09	10.38
<i>Water</i>	196.1	196.7	200.4
Total Dispersion	307.0	308.9	315.37
% Neutralization	120	120	100
Free Film Properties			
<i>Tensile strength,</i>	<i>MPa</i>	46.6	37.7
	<i>psi</i>	6800	5500
<i>% Elongation @ Break</i>		400	260
<i>100% modulus,</i>	<i>MPa</i>	6.5	23.3
	<i>psi</i>	950	3400
Coating Properties*			
<i>Sward Hardness</i>		18	55
<i>Knoop Hardness</i>		1	5.7
<i>Pencil Hardness</i>		2H	2H
<i>Gloss 20° / 60°</i>		89/109	87/106
<i>Glass Transition Tg (°C)</i>		-31.25	-15.34

* Baked 30 min @ 120°C

Key Benefits Offered by Dispersions Based on TMXDI®

- Very low VOC
 - 36 g/L (0.3 lb/gal) from neutralizing amine
 - Either zero or limited amount of organic solvent required in formulating
 - Formulator has choice of solvent
- Coating toughness
 - Combination of high tensile strength with high elongation and tear strength
 - Excellent abrasion resistance
- Coating flexibility
 - Particularly suited for coating flexible substrates
 - Harder coatings maintain a good degree of flexibility
- Coating appearance
 - High gloss; 20° gloss >88
 - Excellent gloss retention
- Excellent coating adhesion
 - Adheres well to most metallic and non-metallic surfaces

Appendix - Example Lab Scale Preparation & Calculations

Prepolymer Formula & Preparation*				
Components	Wt%	Wt.	Eq. Wt.	Eq.
1,6 Hexane-Diol Adipate Polyester (OH #114)	57.57	252.29	492.1	0.513
TMXDI® monomer Mw 244/2	37.96	166.36	122.0	1.364
Trimethylol Propane (TMP) Mw 135/3	0.54	2.36	45.0	0.052
Dimethylol Propionic Acid (DMPA) Mw 134/2	3.83	16.77	67.0	0.250
Dibutyl Tin Dilaurate (T-12) (10% Soln. in NMP)	0.10	0.44	-	-
	100.00	438.22		

* 2 - 4 Hrs @ 120°C

Theoretical % NCO = 5.26

Actual % NCO Titrated = 4.87

Viscosity @ 80°C = 5500 mPa·s, Brookfield Cone-plate Sp.52, 10 RPM

Dispersion Preparation

Water	779.02
Triethylamine (TEA)	13.81
Prepolymer from above	400
Chain extender: Dytek A Diamine (1-Methyl Pentamethylene Diamine)	26.92

Calculations

Theoretical % NCO

$$\frac{(\text{NCO EQ.} - \text{Total OH EQ.}) \times 42 \times 100}{\text{Formulation Wt.}} = \underline{\hspace{2cm}}$$

Neutralizing Amine

Amount added is determined by calculating the carboxyl eq. of the prepolymer.

Example:

Prepolymer	DMPA Wt. (3.83%)	MW DMPA	EQ.	
400 Grams	15.32 Grams	÷ 134	=	0.114
Carboxyl Eq.	MW TEA	TEA Added	+ 20% Excess	Total
0.114 x	01 =	11.51 Grams	+ 2.30 Grams	= 13.81 gms

Chain Extension Amine

Calculating the NCO equivalent of the prepolymer and adding stoichiometric amount of amine. Exact % NCO is determined from titration methods.

Example:

% NCO	NCO MW	DYTEK A MW = 116/2	
4.87	÷ 42	=	0.116 x 58 Eq. Wt. = 6.73 gms/100 gms Prepolymer

400 Grams Prepolymer
26.92 Grams Dytek A diamine

Isocyanate Determination

Reagents

n-Dibutylamine/Toluene solution: 1080 ml dry n-dibutylamine
diluted to 4000 ml with dry toluene

1N HCl

0.04% Aqueous Bromophenol Indicator

Procedure

1. Accurately weigh sample* into a clean, dry 500 ml Erlenmeyer flask.
2. Add 100 ml (graduate) dry toluene.
3. Pipette 25 ml n-dibutylamine/toluene solution into flask containing sample.
4. Heat solution while stirring to dissolve.
5. Cool solution to ambient temperature.
6. Prepare a blank using 100 ml toluene and 25 cc n-dibutylamine/toluene solution.
7. Add 200 cc dry isopropanol and approximately 0.5 ml n-bromophenol indicator to blank.
8. Titrate blank with 1N HCl to a yellow color which persists for a least 1 minute. Call this Solution A.
9. Add 200 cc of isopropanol and approximately 0.5 ml of n-bromophenol indicator to flask containing sample. Titrate to a yellow color as in Step #8. Call this Solution B.

Calculation:

$$\% \text{ NCO} = \frac{(\text{Solution A} - \text{Solution B}) 4.2}{\text{g. sample}}$$

* For samples of TMXD® (META) aliphatic isocyanate prepolymers, use 6-10 g. sample.

Allnex Global Operational Headquarter
Square Marie Curie 11
1070 Brussels
Belgium

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ASIA
AUSTRALIA
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