TMXDI® (META)

Aliphatic Isocyanate

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The Coating Resins Company

About allnex

Facts & Figures

- Global company with over €2.1 billion in sales
- Broad Technology portfolio: liquid coating resins, energy curable resins, powder coating resins, crosslinkers and additives, composites and construction materials
- Approximately 4000 employees
- Customers in more than 100 countries
- 33 manufacturing facilities
- 23 research and technology centers
- 5 ventures
- Extensive range of solutions for key coating segments: automotive, industrial, packaging coating and inks, protective, industrial plastics and specialty architectural

With manufacturing, R&D and technical facilities located throughout Europe, North America, Asia Pacific and Latin America, allnex offers global and reliable supply of resins and additives combined with local, responsive customer support.

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TMXDI®[1] (META) Aliphatic Isocyanate

Goal
Provide information on the performance benefits, chemistry, and processing advantages of TMXDI monomer for water-based coating technology as it applies to polyurethane dispersions

Opportunities
- 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 propertie

Application Areas for Technology

Aqueous Dispersions
Adhesives
Specialty Coatings
Roof Coatings
Floor Coatings
Flexible Coatings
Plastic Coatings

Two-Component
Adhesives
Specialty Coatings
Roof Coatings
Floor Coatings
Flexible Coatings
Plastic Coatings
Sealants
RIM
Potting/Encapsulation

UV Curable
Floor Coatings
Flexible Coatings
Plastic Coatings

One Shot
Castable Elastomers
Adhesives
Sealants

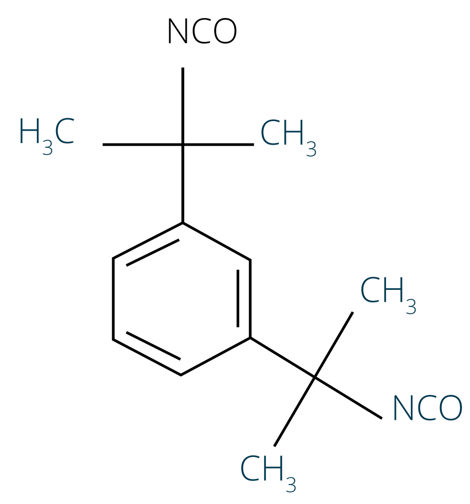
Lacquers
Flexible Coatings

Moisture Cure
Roof Coatings
Floor Coatings
Specialty Coatings
Sealants

[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

[1] Data obtained from sponsored research program at the Emulsion Polymers Institute, Lehigh University

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 wate
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
Tone 230/305	65 (Toluene)	220	970	340
Tone 240	100	1,255	1,965	1,540
HD-AA	100	2,300	100,000	100,000
HD-AA	85 (NMP)	400	1,300	780
BD-11	85 (NMP)	600	4,050	1,500
HD-AA-IPA	100	2,700	200,000	4,500

Physical Property Characteristics of Urethanes Made From Aliphatic Diisocyanate Monomers

Property	TMXDI	IPDI	H_{12}MDI
Hardness	Softer	Harder	Harder
Tensile Strength	Lower	Higher	Higher
Elongation	Higher	Lower	Lower
Hydrolytic Stability	Better	Good	Good
Clarity	Clear	Clear	Clear
Prepolymer Viscosity	Low	Middl	High

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

Dispersion Structure / Property Relations

Formulation Variables

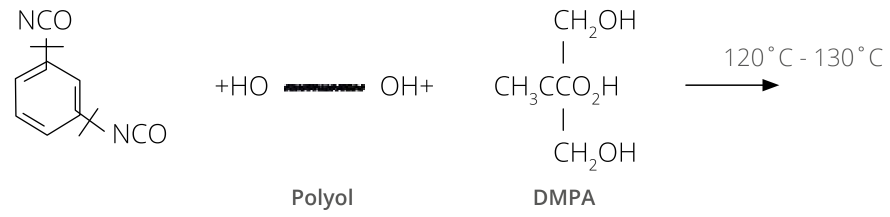
Polyols	Effect
Trifunctional Caprolactones, TMP	Toughness Hardness Chemical/Solvent resistance Humidity resistance
Polyethers	Softness Flexibility Adhesion

Chain Extenders	Effect
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

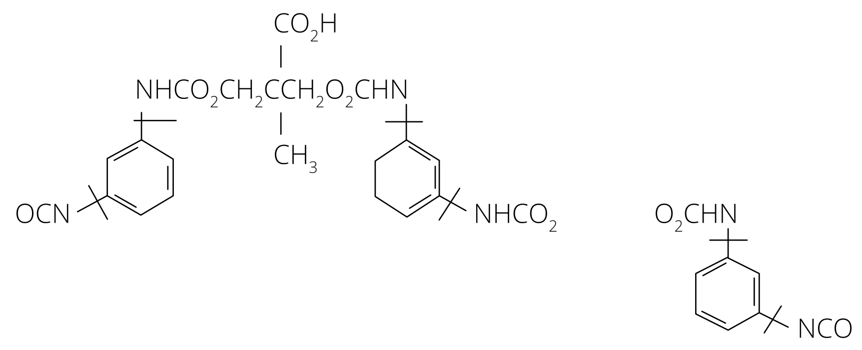
[1] Temperature to achieve 200 MEK double rubs without marring coating with 20 minutes bake cycle.

Dispersion Process

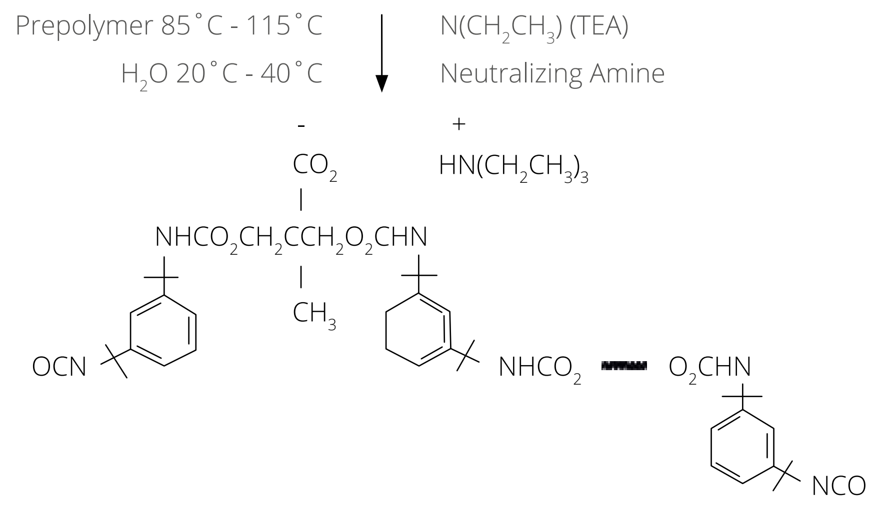
TMXDI® Monomer



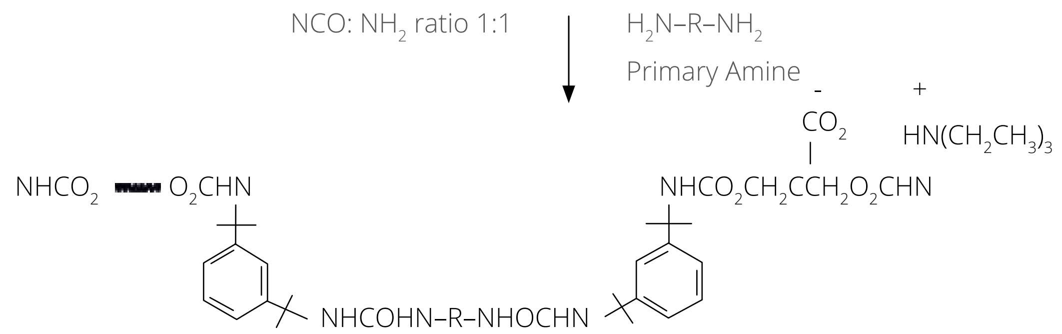
NCO-Terminated Prepolymers



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 wreaction 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

Polyols	Type	Eq. Wt.
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

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

Starting Point Polyester Formulations

Dispersions	I	II	III
Component	Wt%	Wt%	Wt%
Polyol A	57.50	–	–
Polyol B1	–	27.25	31.82
Polyol B2	–	22.49	7.08
TMXDI monomer	38.10	45.00	52.11
DMPA	3.82	4.50	4.49
TMP	0.57	0.75	0.50
NPG	–	–	3.99
DBTDL	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
TEA	3.46	4.07	–
DMAMP-80	–	–	4.59
Dytek A	7.43	8.09	10.38
Water	196.1	196.7	200.4
Total Dispersion	307.0	308.9	315.37
% Neutralization	120	120	100
Free Film Properties			
Tensile strength, MPa	46.6	37.7	41.8
psi	6800	5500	6100
% Elongation @ Break	400	260	30
100% modulus, MPa	6.5	23.3	–
psi	950	3400	–
Coating Properties			
Sward Hardness	18	55	58
Knoop Hardness	1	5.7	13.8
Pencil Hardness	2H	2H	3H
Gloss 20° / 60°	89/109	87/106	91/109
Glass Transition Tg (°C)	-31.25	-15.34	-26.42

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	*(NCO EQ. - Total OH EQ.) x 42 x 100* / *Formulation Wt.* = ________
Neutralizing Amine Amount added is determined by calculating the carboxyl eq. of the prepolymer.	***Example:*** *Prepolymer 400 Grams* · *DMPA Wt. (3.83%) 15.32 Grams* ÷ *MW DMPA 134* = *EQ. 0.114* *Carboxyl Eq. 0.114 x* · *MW TEA 01 =* ÷ *TEA Added 11.51 Grams* + *20% Excess 2.30 Grams* = *Total 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 4.87* ÷ *NCO MW 42* = *DYTEK A MW = 116/2 0.116 x 58 Eq. Wt.* = *6.73 gms/100 gms Prepolymer* *400 Grams Prepolymer* *26.92 Grams Dytek A diamine*

Key Benefits Offered by Dispersions Based on TMXDI®

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:

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

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

Notes