Update and Overview of Polyurea Spray Technology and New Amine Chain Extenders Useful in Polyurethane Systems

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Huntsman LLC : Austin Research Labs

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HUNTSMAN

The History and Background of Polyurea Spray Elastomers

Key Developments Along the Polyurea Spray Elastomer Timeline

1980's: Texaco Chemical's Austin Research Laboratories develop polyurea reaction-injection-molding (RIM) for automotive exterior body panel applications.

1989: Texaco Chemical's Austin Research Laboratories develop and introduce 100% solids polyurea spray elastomer coatings.

1990's: Numerous equipment advances by industry leaders.

1990's: Huntsman Corporation and ICI Polyurethanes co-develop and commercialize isocyanate prepolymers for polyurea spray.

1995: UOP introduces key aliphatic secondary amine chain extender for use in polyurea elastomer coatings.

1990's: Bayer introduces slower aspartic ester secondary amine products in late 1990s. Allows first "roll-on" polyureas.

Key Developments Along the Polyurea Spray Elastomer Timeline-cont.

2000: Formation of the Polyurea Development Association

2002: Huntsman commercializes JEFFLINK® 754 chain extender for polyurea and other polymer markets.

2002: UOP suddenly exits chain extender market in December.

2003: UOP sells rights to UNILINK® 4200 and CLEARLINK® 1000 chain extenders to Dorf Ketal in India.

2004: Nissan is first company to offer OEM truck-bed liner.

2005: Huntsman commercializes Secondary Polyetheramines.

THE POLYUREA SPRAY ELASTOMER MARKET AT A GLANCE*

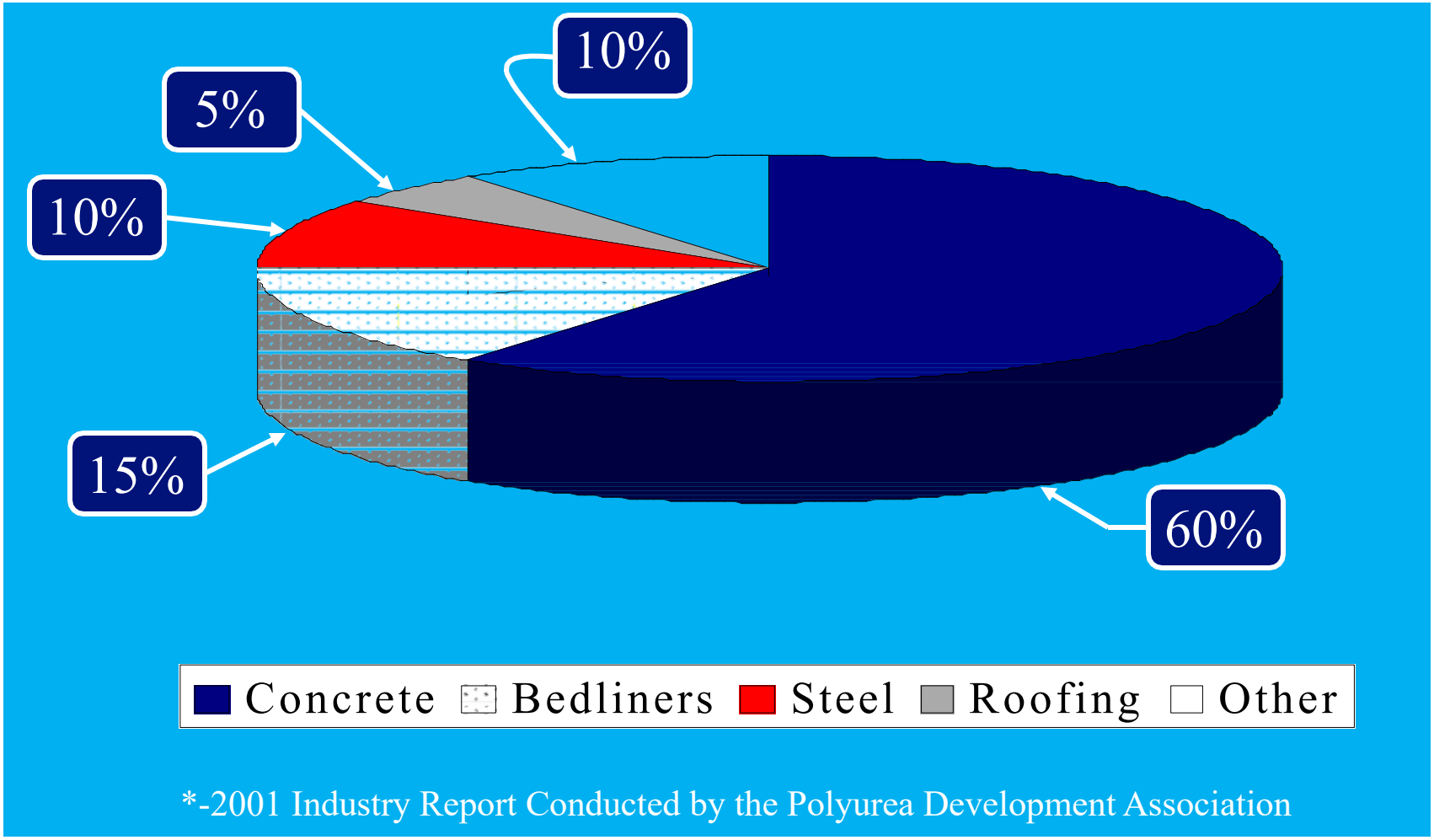
ESTIMATED 2001 SYSTEM SOLD:	20-25MM LBS
ESTIMATED MARKET VALUE:	$60-75MM

GEOGRAPHIC BREAKDOWN:

NORTH AMERICA	85%
APAC	10%
EUROPE	4%
SOUTH AMERICA	1%

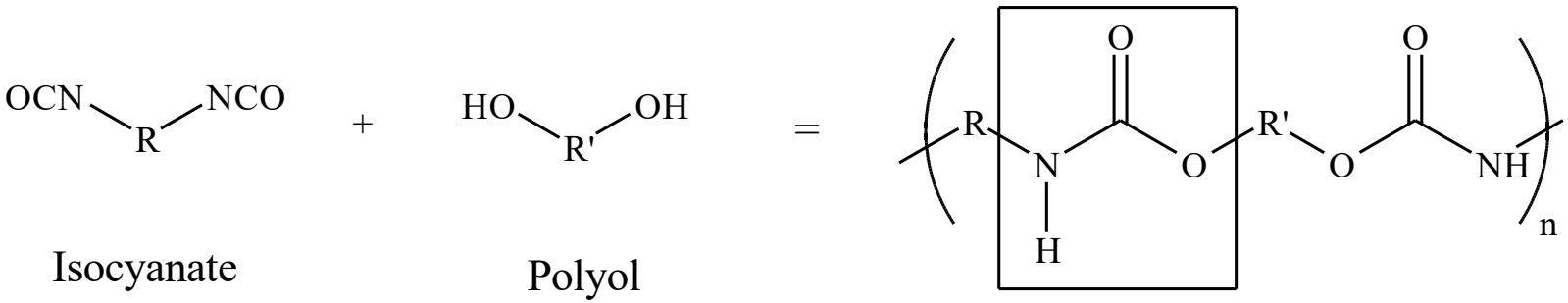
*-2001 Industry Report Conducted by the Polyurea Development Association

POLYUREA SPRAY ELASTOMER APPLICATION AREAS*

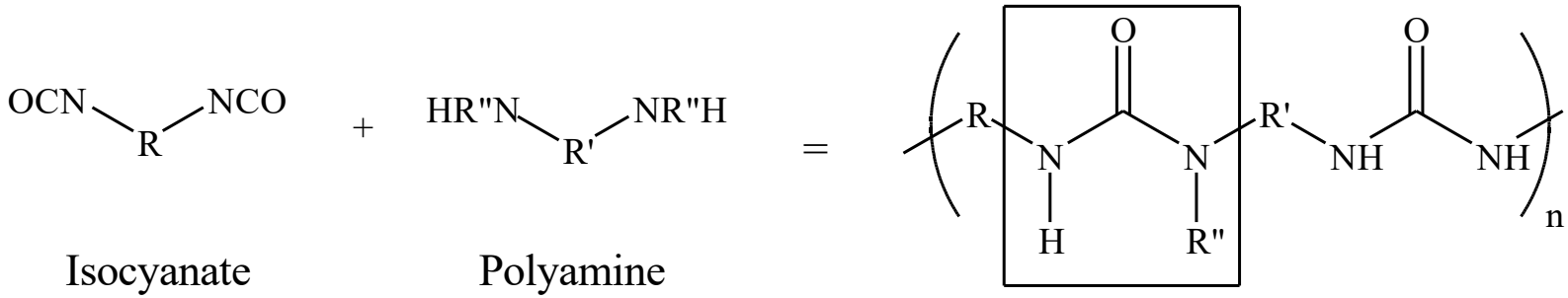


*-2001 Industry Report Conducted by the Polyurea Development Association

CHEMICAL REACTIONS: POLYURETHANE AND POLYUREA



Isocyanate Polyol Urethane



Isocyanate Polyamine Urea

THE POLYUREA/POLYURETHANE ELASTOMER SPECTRUM

Resin Component	POLYUREA	Class 1 Hybrid	Class 2 Hybrid	Class 3 Hybrid	PU
Main	Polyetheramine	Polyetheramine	Polyetheramine	Polyol	Polyol
Chain Extender	Polyamine	Polyamine (Hydroxyl Containing)	Polyol	Polyamine	Polyol
Catalyst Package	**NONE**	**NONE**	YES	YES	YES

NOTE:

A myriad of other additives can be incorporated into any of these systems. Examples include pigments, adhesion promoters, UV-absorbers, anti-oxidants, and texturing agents.

BENEFITS OF POLYUREA SPRAY ELASTOMERS

- Sprayable coating application.
- Two component, 100% solids systems, Zero VOC.
- 1:1 volume mix ratio, wide formulation latitude.
- Fast reactivity and cure without a catalyst, lack of catalyst leads to better long term stability.
- Relatively moisture and temperature insensitive during application.
- Excellent physical properties.
- High thermal stability (up to 175° C).
- Excellent abrasion resistance.

TYPICAL PHYSICAL PROPERTIES FOR POLYUREA ELASTOMERS

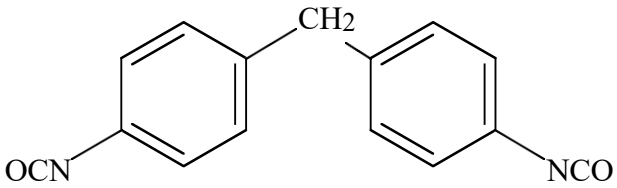
- **Tensile Strength** **up to 28 MPa (4000 psi)**
- **Shore Hardness** **A30 to D75**
- **Elongation** **up to 1200 %**
- **Tear Strength** **up to 127000 N/m (725 pli)**
- **100% Modulus (Stress@100%)** **up to 14 MPa (2000 psi)**
- **300% Modulus (Stress@300%)** **up to 17 MPa (2500 psi)**

Common Raw Materials for Polyurea Spray Elastomers

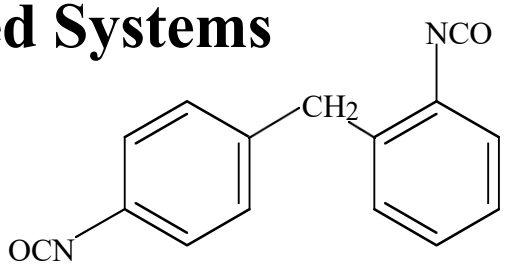
"New" Amines for Possible Use in Polyurethanes

ISOCYANATE SYSTEMS FOR POLYUREA ELASTOMER COATINGS

Aromatic-Based Systems

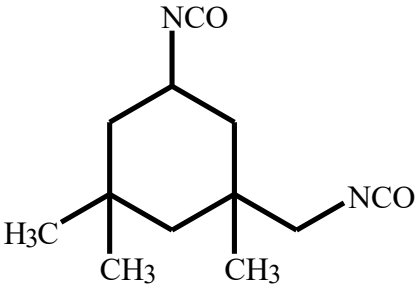


4,4'-MDI

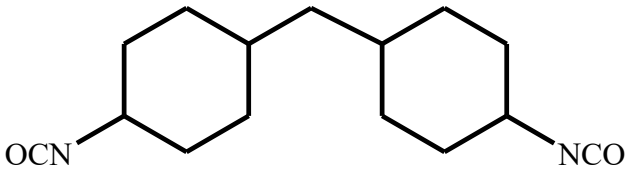


2,4'-MDI

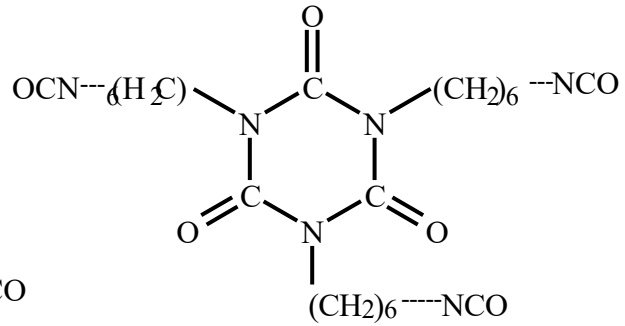
Aliphatic-Based Systems



IPDI



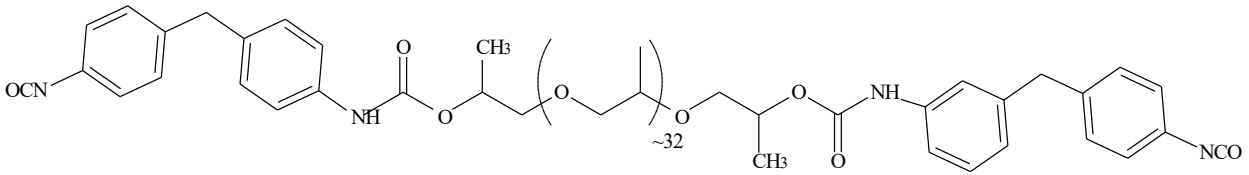
H12MDI



HDI Trimer

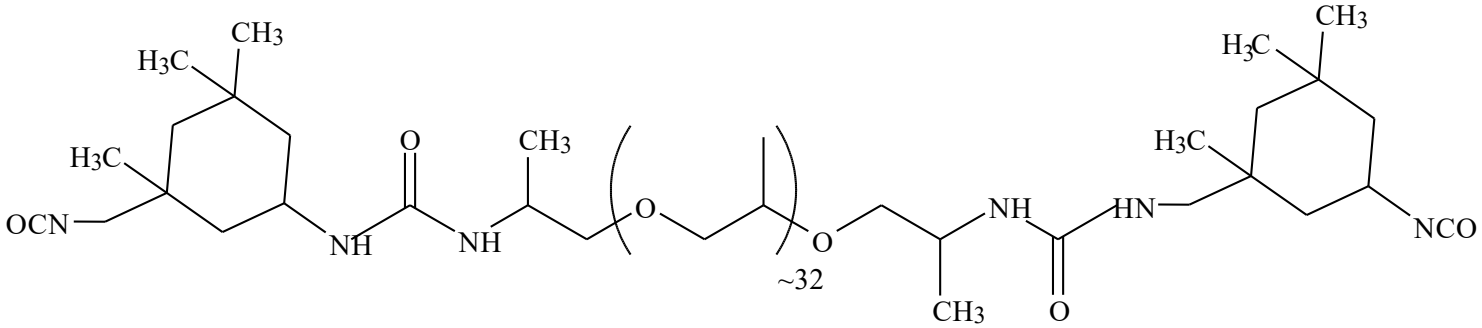
ISOCYANATE PREPOLYMERS FOR ELASTOMER COATINGS

Aromatic-Based Systems



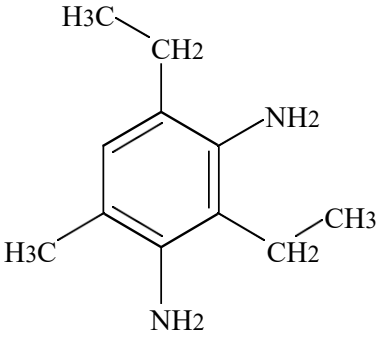
MDI-PPG-2000 Prepolymer

Aliphatic-Based Systems

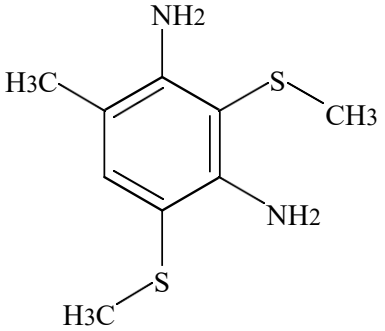


IPDI - D-2000 Prepolymer

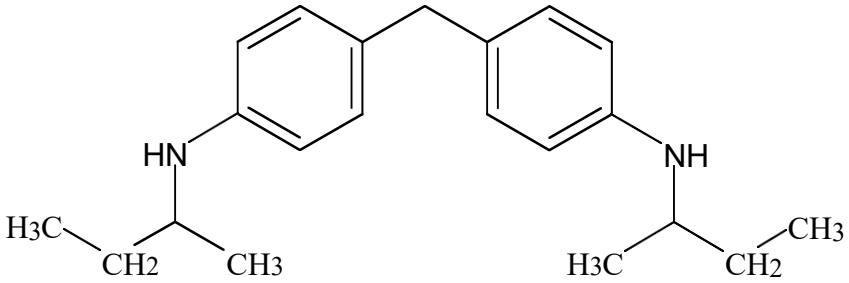
AROMATIC CHAIN EXTENDERS FOR POLYUREA ELASTOMER COATINGS



ETHACURE® 100 curing agent



ETHACURE® 300 curing agent

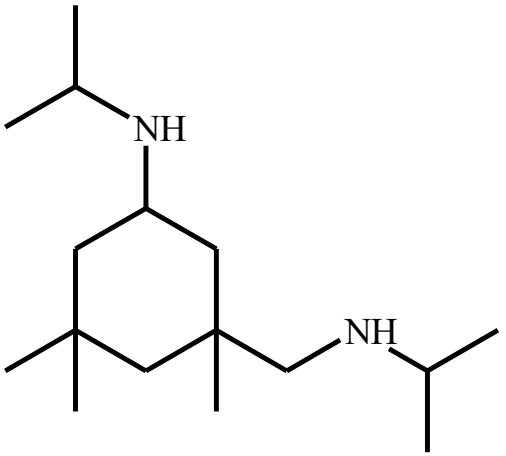


UNILINK® 4200 chain extender

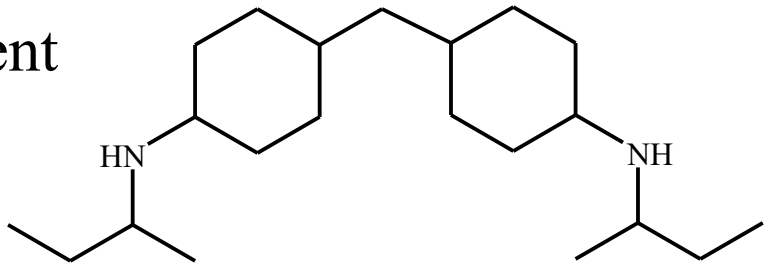
ETHACURE is a trademark of Albemarle. UNILINK is a trademark of Dorf Ketal.

CYCLOALIPHATIC CHAIN EXTENDERS

JEFFLINK® 754 curing agent

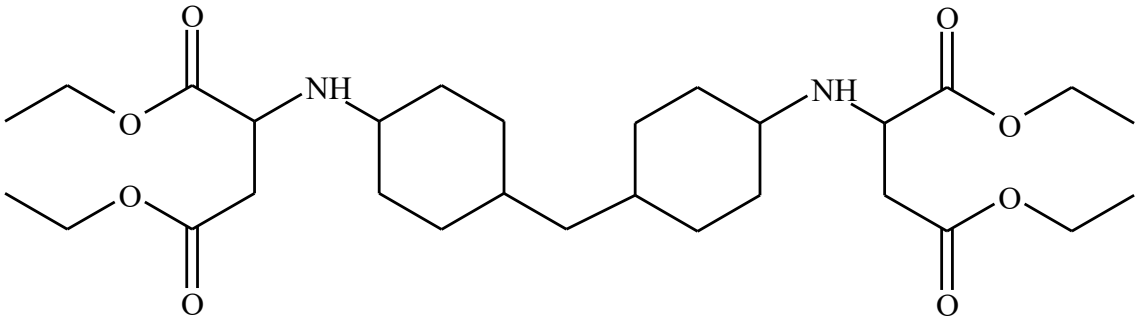


CLEARLINK® 1000 curing agent



CLEARLINK is a trademark of Dorf Ketal.
JEFFLINK is a trademark of Huntsman LLC or an affiliate thereof in one or more, but not all countries.

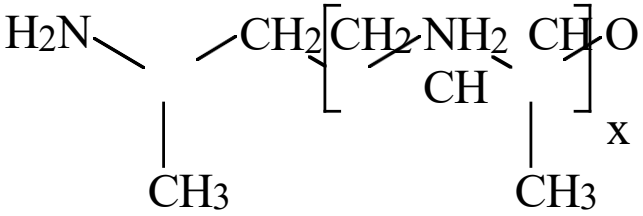
Secondary Aspartic Ester Amines



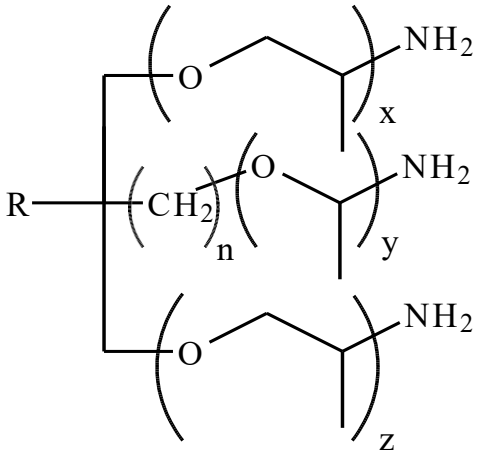
DESMOPHEN® NH1420 curing agent

DESMOPHEN is a trademark of Bayer.

JEFFAMINE® POLYETHERAMINES FOR POLYUREA ELASTOMER COATINGS



Product	x
JEFFAMINE→ D-400 amine	5-6
JEFFAMINE→ D-2000 amine	32-34



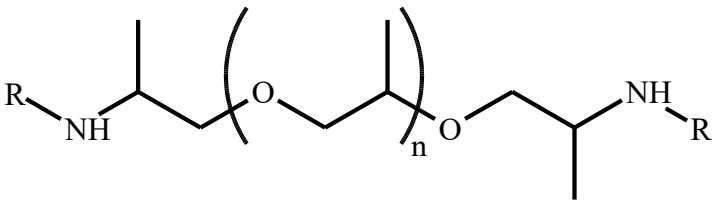
JEFFAMINE(R) T-403 amine x + y + z = ~ 5.3
R = C_2H_5 n = 1

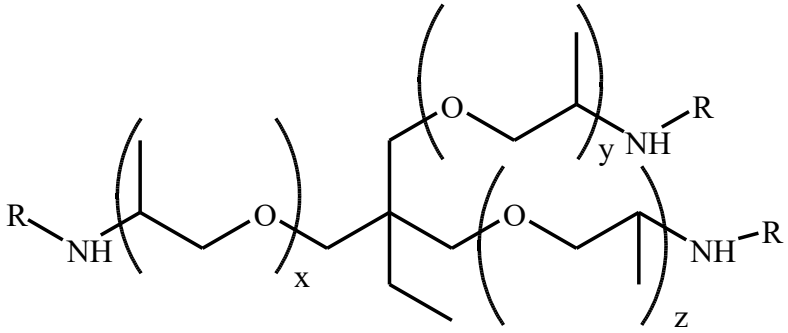
JEFFAMINE(R) T-3000 amine x + y + z = ~ 50
R = H n = 0

JEFFAMINE(R) T-5000 amine x + y + z = ~ 85
R = H n = 0

New Secondary Polyetheramines

- Proprietary Huntsman catalyst technology allows high secondary amine formation with little primary or tertiary.





- Intrinsic reactivity drops roughly a factor of 20 for secondary compared to primary amines.
  - Steric hindrance plays an additional role
- Cure speed (gel time) of a formulation is dependent on concentrations and intrinsic reactivity.
- Products are stable, so there is no off-gassing of reversible blocking agents.

Huntsman's New Secondary Polyetheramines

Product Name	XTJ-584	XTJ-585	XTJ-576	XTJ-586
Secondary Version of	D-230	D-400	D-2000	T-403
Approximate Functionality	2	2	2	3
Density, 25°C, g/cm3	0.885	0.921	0.978	0.923
Kinematic Viscosity, 25°C, cSt	7	18	209	46
Total Amine, meq/gram	5.3-6.3	3.5-4.0	0.9-1.0	4.5-5.5
Target Equivalent weight, grams/eq	172	270	1042	204

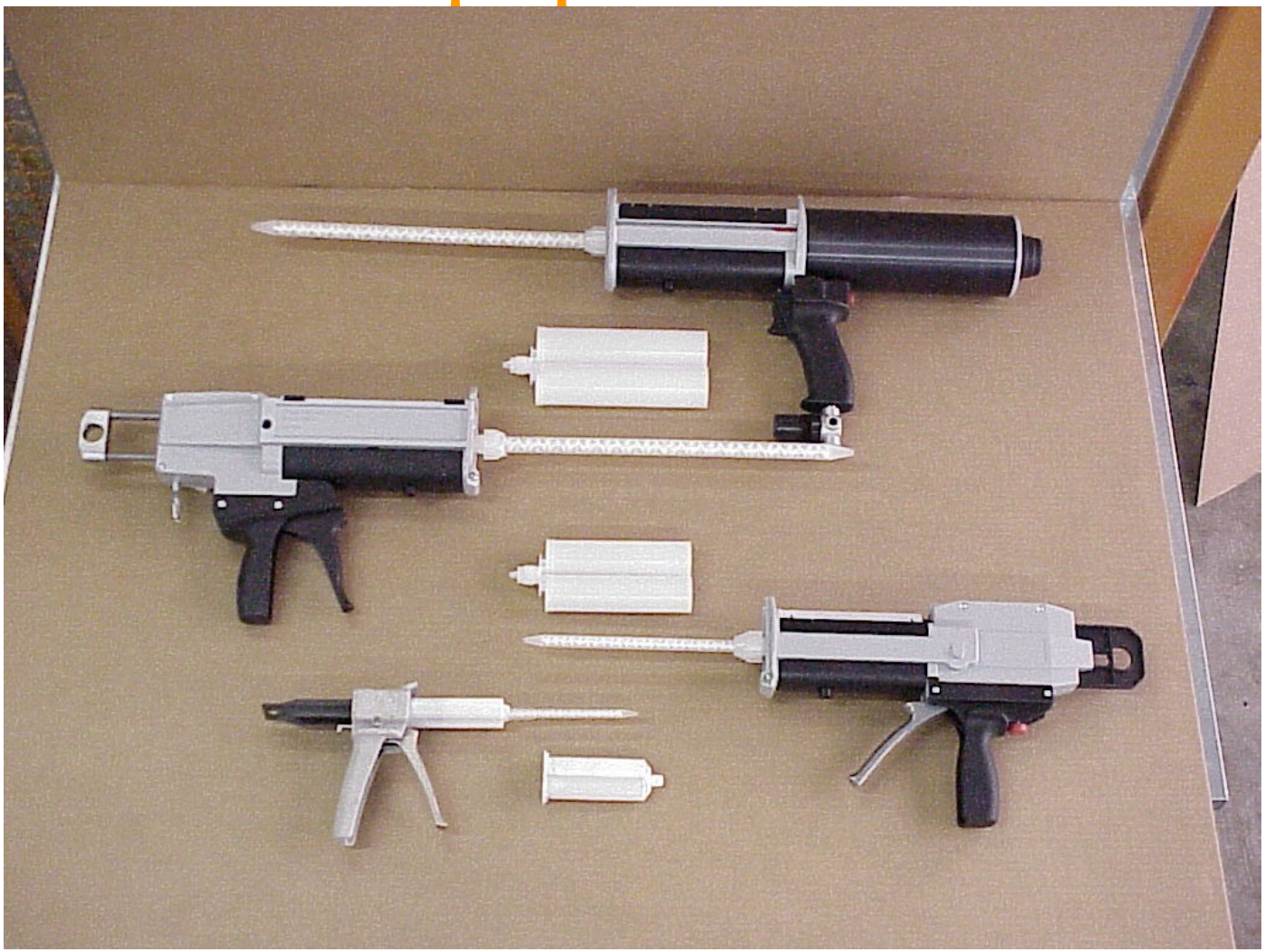
OTHER FORMULATION ADDITIVES

COMMON ADDITIVES:

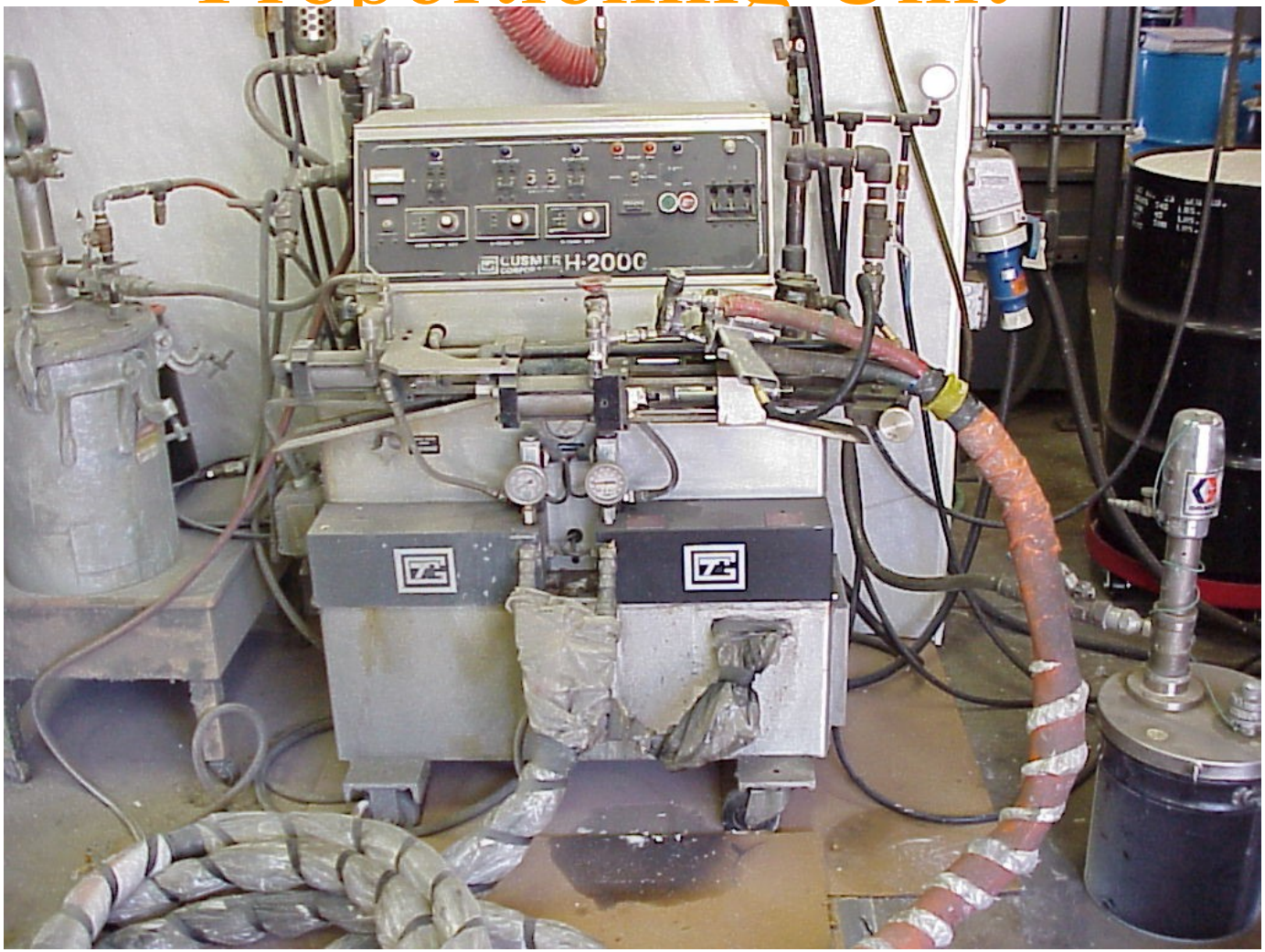
- Pigment, such as TiO_2
- Adhesion Promoter
- UV-Stabilizers/Antioxidants
- Thixotrope
- “Defoamer”/”Dispersant”
- Solvent
- Plasticizer
- “Filler”

Processing Polyurea Spray Elastomers

Static-Mix Dispensing Equipment



Gusmer H-2000 Proportioning Unit



HIGH TEMPERATURE/ HIGH PRESSURE IMPINGEMENT-MIX SPRAY APPLICATION

STANDARD SPRAY PROCESSING PARAMETERS

- Component Viscosity: <2000 cPs (at RT)
  - If too high: pump cavitation may occur
  - If mismatched: large pressure differential may exist
  - along with poor mixing
- Operating Pressure: >138 bar (2000 psi)
  - If too low: poor mixing and loss of spray
  - pattern may occur.
- System Temperature: 60-80C (150-170F)
  - If too low: poor mixing and loss of spray
  - pattern may occur.

Formulating Polyurea Spray Elastomers

KEY FORMULATION PARAMETERS AFFECTING ELASTOMER PROPERTIES

SYSTEM TYPE: **aromatic or aliphatic (cost *vs.* UV-color stability)**

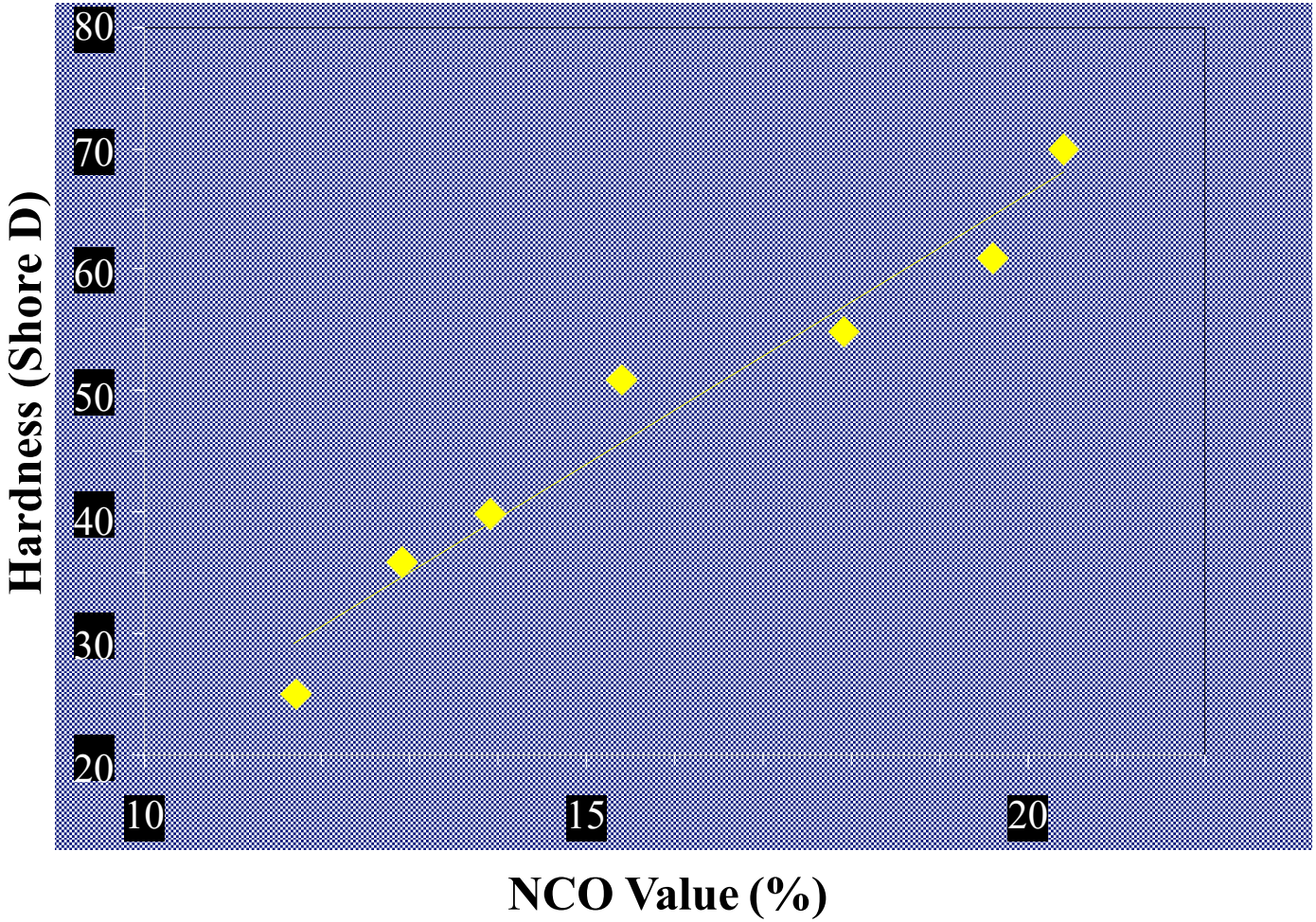
PREPOLYMER TYPE: **isocyanate type, isomer distribution, and polyol (polyetheramine) composition can greatly affect elastomer properties**

INDEX: **can be used to help overcome brittleness and extend working time (INDEX = Free Eq's Isocyanate/ Free Eq's Amine)**

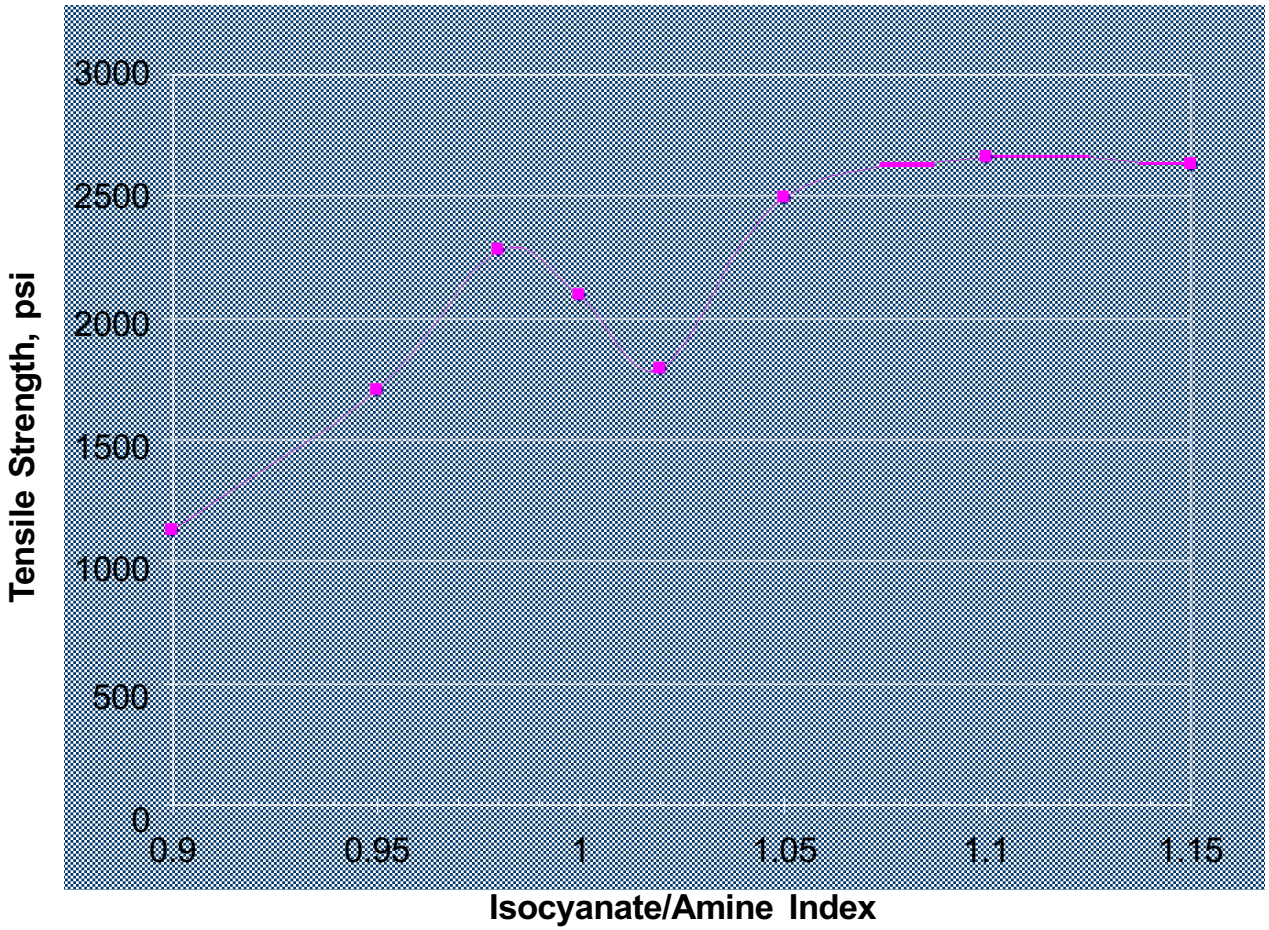
CROSSLINK DENSITY: **can affect brittleness/flexibility, permeability, and chemical resistance**

SECONDARY AMINE CONTENT: **modulates system speed**

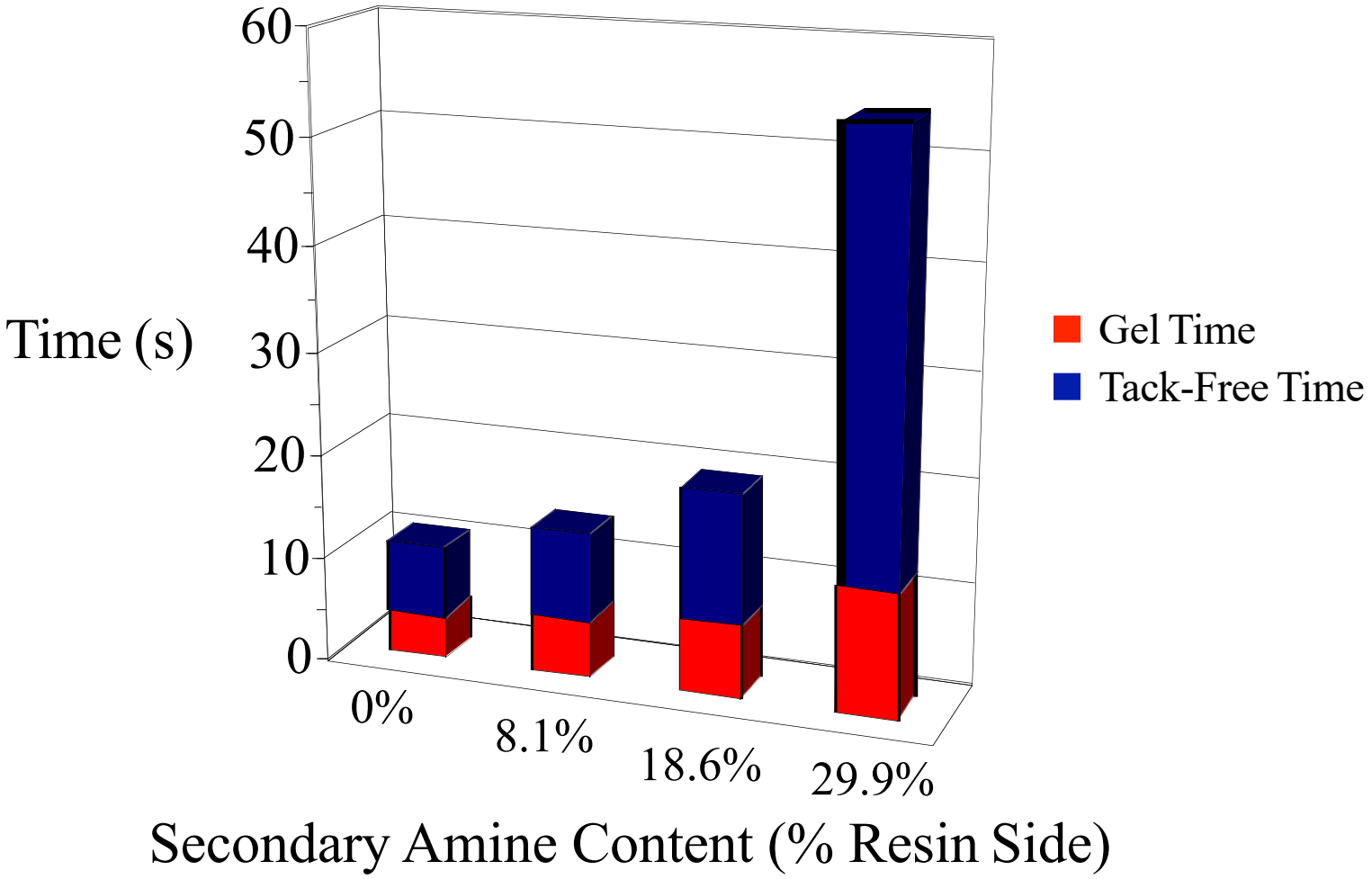
THE EFFECT OF %NCO VALUE ON ELASTOMER HARDNESS



FINDING THE OPTIMAL SYSTEM INDEX



THE DECELERATING EFFECTS OF SECONDARY AMINES



THE TYPICAL POLYUREA SPRAY ELASTOMER FORMULATION PROFILE

VOLUME RATIO: 1:1

ISOCYANATE COMPONENT	
Adduct, Prepolymer, or	
Quasi-Prepolymer	100%
RESIN COMPONENT	
Polyetheramine	40-70%
Chain Extender	10-50%
Additives	0-10%

STARTING-POINT FORMULATION FOR AN AROMATIC POLYUREA COATING

ISOCYANATE COMPONENT

15.4% NCO MDI-Based Quasi-Prepolymer	100%

RESIN COMPONENT

JEFFAMINE® D-2000 amine	57.7%
JEFFAMINE® T-5000 amine	5.3%
ETHACURE® 100 curing agent	18.6%
UNILINK® 4200 curing agent	18.6%

Index: 1.05 Volume Ratio: 1:1

Gel Time:	7.0 s
Tack-Free Time:	12.5 s
Hardness:	D51
Tensile Strength:	2128 psi
Elongation:	529 %
Modulus, 100%:	1027 psi
Modulus, 300%:	1471 psi
Tear Strength:	456 pli

STARTING-POINT FORMULATION FOR AN ALIPHATIC POLYUREA COATING

ISOCYANATE COMPONENT

IPDI / D-2000 or PPG-2000

Pre-polymer: 16.8% NCO 100%

RESIN COMPONENT

JEFFAMINE® D-2000 amine	39.0%
JEFFAMINE® T-5000 amine	10.0%
JEFFLINK® 754 curing agent	44.0%
TiO_2	7.0%

Index: 1.06 Volume Ratio: 1:1

Lot Number:	8276-59
Gel Time:	5.0 s
Tack-Free Time:	22.0 s
Hardness:	D55
Tensile Strength:	2670 psi
Elongation:	875 %
Modulus, 100%:	1003 psi
Modulus, 300%:	1120 psi
Tear Strength:	526 pli

Application Examples of Polyurea Spray Elastomers

Polyurea Applications

- Steel coating - automotive, bridges, tanks, etc.
- Concrete coating - roads, parking structures, water-proofing, explosion mitigation, etc.
- Naval vessels - corrosion protection, non-skid, anti-fouling, explosion mitigation.
- Water/waste-water tanks and piping
- Other substrates - polystyrene, plastic, ….

SLOW-SET POLYUREA ELASTOMER TANK LININGS

POLYUREA ELASTOMERS AS PROTECTIVE COATINGS

Truck Bed Liner

Forms of Polyurea and Hybrids

- Caulk for concrete joints (low strength, high elongation)
- Adhesive for a variety of substrates.
- Polyurea Spray Foam.
- Polyetheramines and amine chain extenders can be added to PU foam formulations to make hybrid PU foams.
- Reaction-Injection Molding (RIM) and other molded polyurea parts.
- Roll-on polyurea with hours of work time
- Sprayed-on elastomers with seconds to hours dry time.

Polyurethane Uses of Amines

- Isocyanate Prepolymers
- Chain extenders for quicker viscosity build
- Cast Polyurea parts
- Polyurethane Dispersions
- 1K coatings (especially secondary amines)
- Polyurethane/Polyurea Hybrids

Conclusions

- The lines between polyurethane and polyurea are becoming blurred.
- There are many new amines available, especially secondaries, that can be used in PU formulations.
- The ability to use both polyols and amines greatly increases formulating flexibility.
- Formulators and applicators with knowledge of both chemistries will increase their breadth of projects and profits.

More Information

- http://www.huntsman.com/performance_products/index.cfm?PageID=2136
- JEFFAMINE.com
- Huntsmanchainextenders.com
- Polyurea Development Association (PDA)

  www.pda-online.org
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