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## Polyurea Spray Coatings: General Overview with Practical Applications in Brazil

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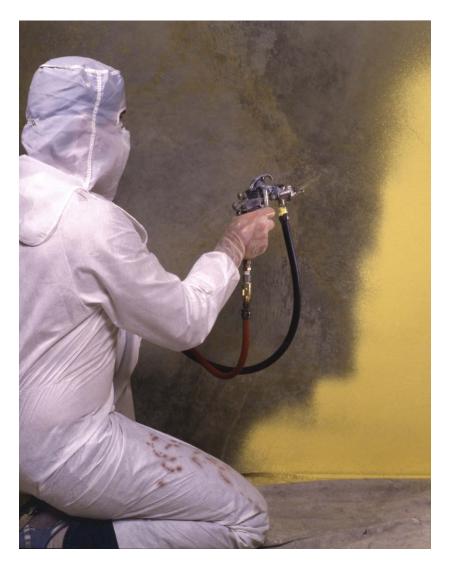
Feiplar Composites & Feipur November 6-8, 2012

#### Polyurethanes

#### Polyurea Spray Coatings: General Overview

Polyurea is a remarkable coatings, linings and joint sealant technology.

A polyurea system has a very fast application rate and when fully Cured, it becomes a very tough and flexible material with excellent wear and chemical resistance properties.



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# Spray Polyurea Coatings: An Introduction



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- Polyurea Applications
- Why Polyurea?
- Brief History
- Polyurea and Polyurethanes
- Raw Materials
- Formulation
- Physical Properties
- Chemical Resistance
- Processing Variables



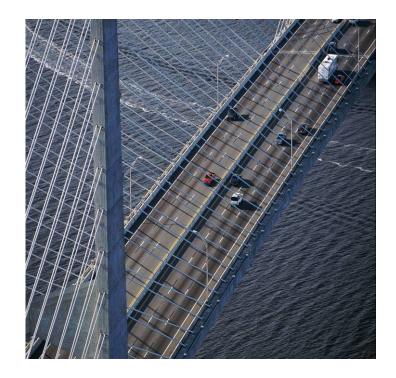
## **Bridge Coatings**

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A polyurea outlasts paint and fights out corrosion, a major reason these systems are specified for bridge deck and structure coatings. The most common applications are over steel and concrete.

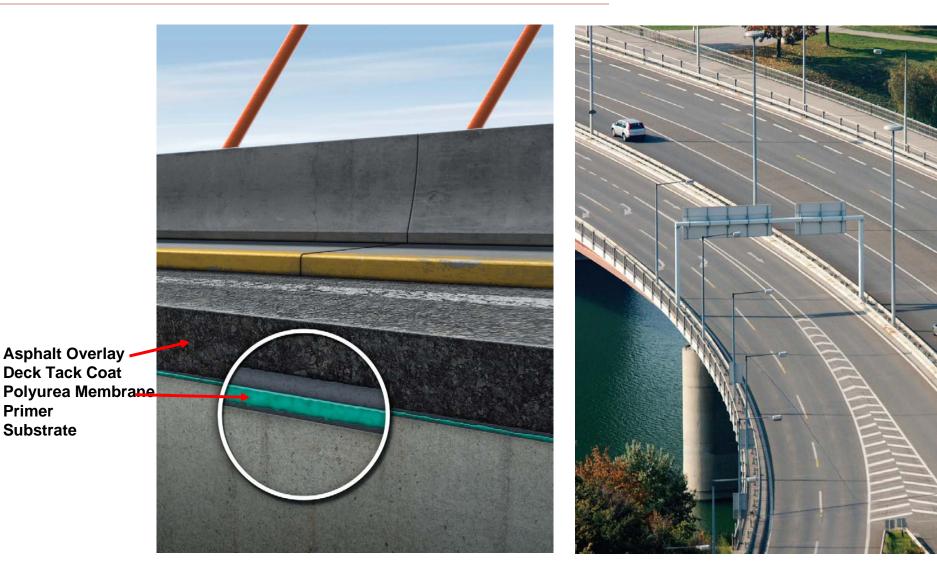




#### **Bridge Deck Coating**



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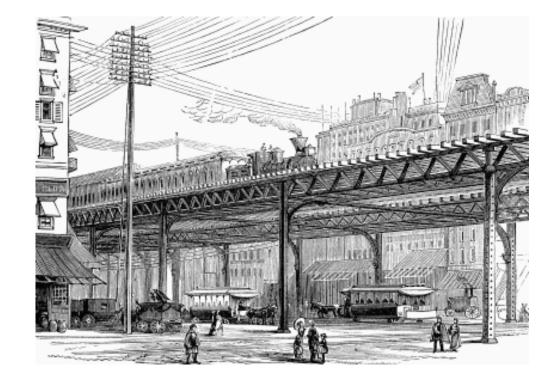
Primer



# Railways



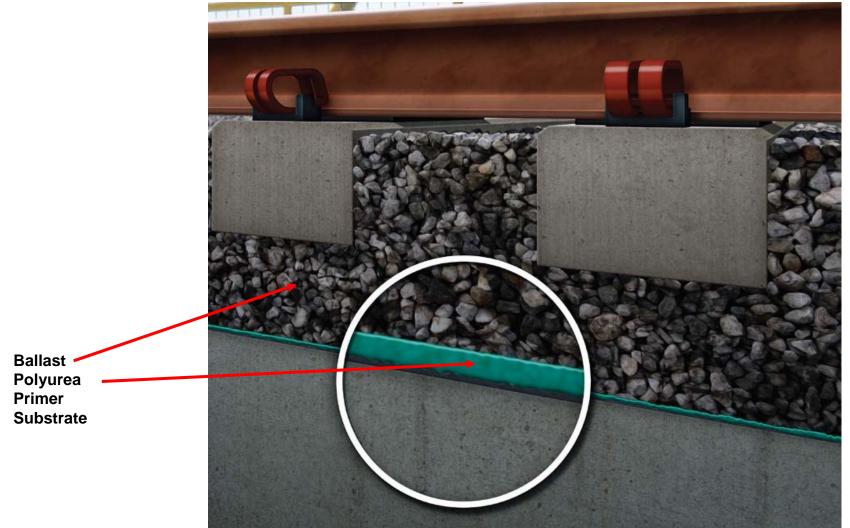
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#### **Railway Bridge Deck Coating**



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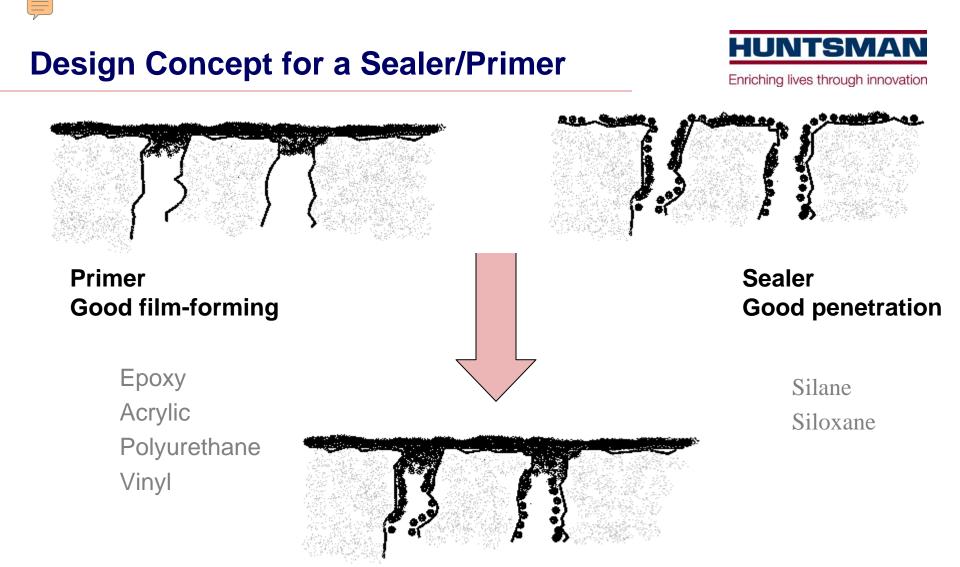


### **High Speed Railway**



China plans to expand it's high speed railway network to 10,000 miles in 2020.

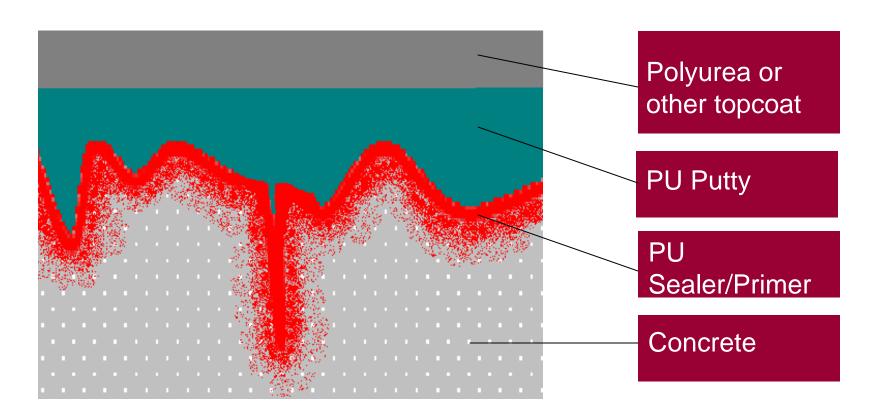




Sealer/Primer: Both good film-forming and penetration

# Combination of PU Sealer/Primer with Polyurea





#### Case Study of PU Sealer/Primer for Spray Polyurea



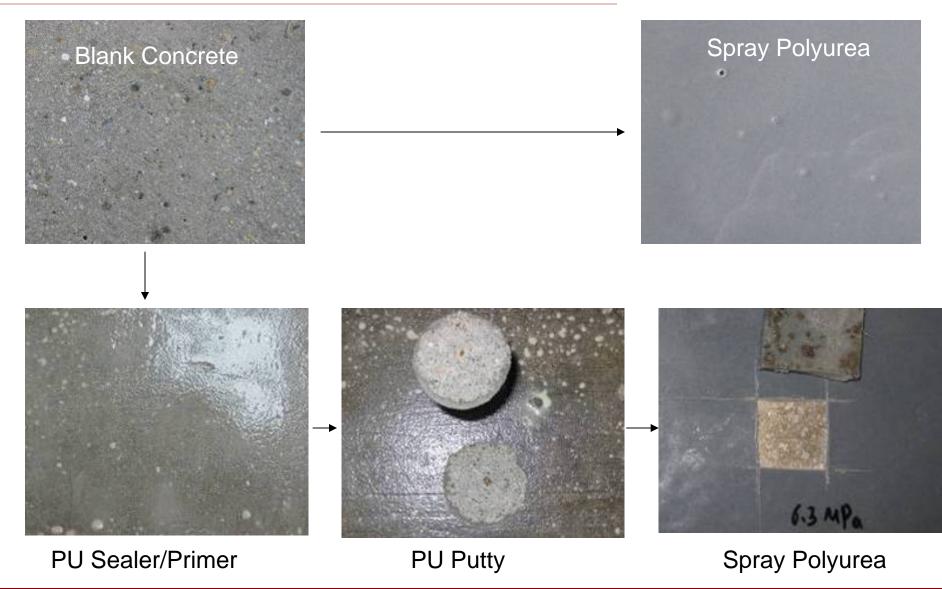
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# **PU Sealer/Primer for Spray Polyurea**

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- Induced hydraulic fracturing or fracking, is a technique used to release petroleum or natural gas for extraction. It creates fractures from a wellbore drilled into reservoir rock formations.
- The energy from the injection of a highly pressurized fracking fluid creates channels in the rock, which can increase the extraction rates and recovery amount of the hydrocarbons.
- Fracking is probably the singly, most important event in the last 50 years for the U.S. chemical industry. Natural gas became a cheap and abundant raw material and a source of 'clean' energy.
- The potential for environmental impact could be very important and needs to be understood.

# Fracking



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# **Chemical Resistance ASTM D 3912**

D

С

А

Е

В

С

А

А

А

А

А

- Methanol
- Gasoline
- Diesel Fuel
- Toluene
- MTBE
- Motor Oil
- Hydraulic Fluid
- 2-Methylbutane
- Water, 82° C/14 days
- 10% NaCl, room temp
- 10% NaCl, 50C/14 days
- Sulphuric acid, 10%
- Hydrochloric acid, 10%
- Ammonium Hydroxide, 20% A
- Sodium Hydroxide, 20%
- Potassium Hydroxide, 20%
- Sodium Hydroxide, 50%
- Acetic Acid, 10%
  A
- Sodium Hydroxide, 1%, 50C, 14 days

Exposure by immersion for one year at 25C unless otherwise noted.

A no visible damage

В

С

D

Е

- slight color change
  - slight surface discoloration
    - swelling < 48 hours
    - swelling < 24hours

#### **Manhole & Sewer Linings**



Polyurea is able to solve many issues with groundwater infiltration and installation speed. With proper surface preparation and substrate conditions, primers and polyurea can be applied very fast to return the cavity to service. Polyurea forms a monolithic, durable liner that protects the cavity from sediment and groundwater infiltration into municipal wastewater systems.



# **Pipe and Pipeline Coatings and Linings**

Polyurea coatings protect steel pipes from corrosion.

It is a protective coating system for polyurethane foam insulated pipes and used to line the inside of water and sewer pipes for rehabilitation work.





#### **Secondary Containment**

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Polyurea is resistant to many fuels and chemicals and is commonly used in fuel pits and secondary containment. Polyurea is not resistant to all chemicals and compatibility tests and surface preparation are always required.

# **Chemical Resistance (ASTM D 1308)**

- Acetone Α **Brake Fluid** В NR Bleach, 10% Gasoline Α Hexane Α Hot tub water Β Hydraulic oil Α Methanol Α Motor oil Β Sodium Hydroxide 5% А 10% А 25% А 50% В Sulfuric Acid 5% А 10% В
  - 50% NR

Spot test or watch glass method, simulates coating exposure through possible spillage (7 days).

- A no visible damage B little visible damage
- B little visible damage NR not recommended

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#### **Roof Coatings**

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Polyurea makes an excellent protective covering for polyurethane foam roofs. It can be formulated to meet specific performance requirements as well as make them reflective to further reduce the energy consumption of the building.

# **Line Striping**

Polyurea is ideal for use in line striping and pavement marking. It can be returned to service for traffic and pedestrian use in only a few minutes after application. Polyurea is much more durable than paint and will last longer between maintenance cycles.







#### Marine

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Above and below the water line, polyurea can be very effective in protecting steel, aluminum and fiberglass in a variety of water sport and commercial marine applications.









Molded slides, protective coatings of seats for wet/dry amusement rides, tank linings, water containment, aquariums, and concrete stadium seats are a few polyurea applications in the amusement and theme park industry. Polyureas replace paint and fiberglass because of it's fast cure and ability to reduce maintenance cycles.





#### **Theme Park and Decorative Design**

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Theme Parks often use polyurea to protect foam, EPS and other structures to create ornamental building, themed characters, artificial rocks, pools and environments.

#### **Architectural Coating**



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#### Waterproofing

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Polyurea is being used as a multi-purpose joint fill, caulking and sealant material. It can provide a flexible, durable, weather tight and traffic resistant seal for expansion joints. It has excellent crack-bridging properties with high elongation and tensile strength.

Polyurea caulk may be formulated to be applied in cold chambers at freezing temperatures.



### **Truck Bed Liners**

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Polyureas (typically hybrid PU-polyurea formulations) are used to make a durable, water and air-tight permanent liner for the exterior of pick up trucks, dump trucks and steel containers, to protect them from their harsh duty environments. The liners are easy to clean and protect against rust and corrosion. They can be wrapped over the top edge of the truck bed to provide added protection from impact and abrasion.

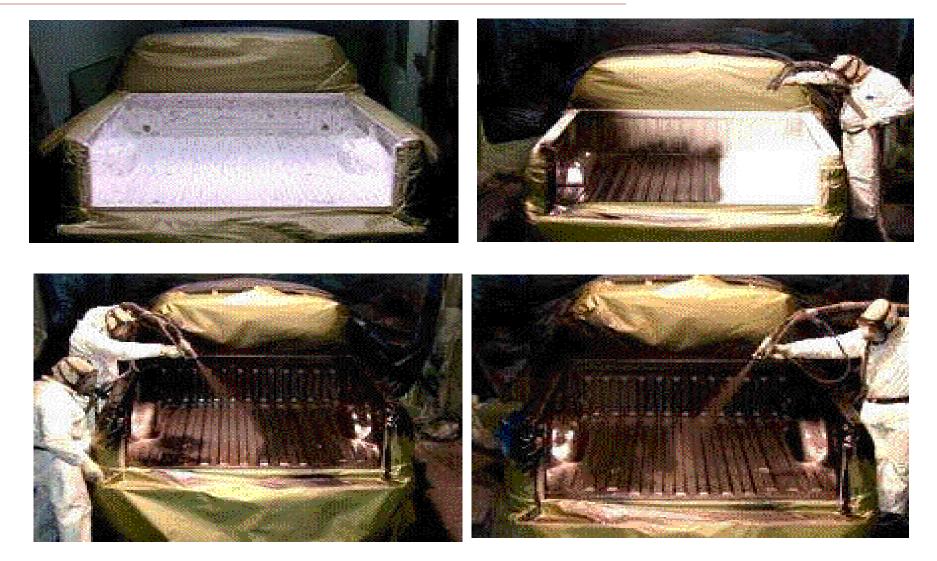




#### **Truck Bed Liners**

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#### **Truck Bed Liners**



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## Why Polyurea?

# Why Polyurea?

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Fast cure. No drip or run formation.

Relative humidity, residual moisture or temperature have little effect on adhesion or coating performance.

Two component, one coat system, 100% solids.

Excellent physical properties.

Stable up to 175° C.

Formulation flexibility.

Pigments and colorants may be added. Reinforcement fibers and fillers can be incorporated during application.



#### 1980s

Polyurea elastomers were first introduced by the Texaco Chemical Company, focusing on RIM applications for automotive parts: fascia and body panels.

ICI Polyurethanes started development of special polyurea prepolymers.

Texaco introduced the concept of polyurea spray coatings.

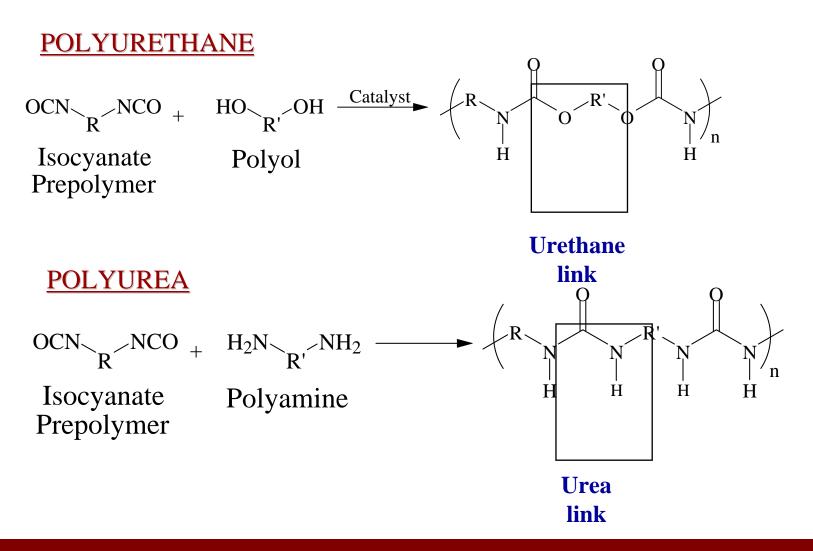
#### 1990s

Huntsman acquires Texaco Chemical Co. (1994) and later ICI Polyurethanes (1999)

The creation of PDA, Polyurea Development Association further promotes the growth of polyurea based spray coatings

### **Isocyanate Most Common Reactions**





#### **Interfacial Area Detail**

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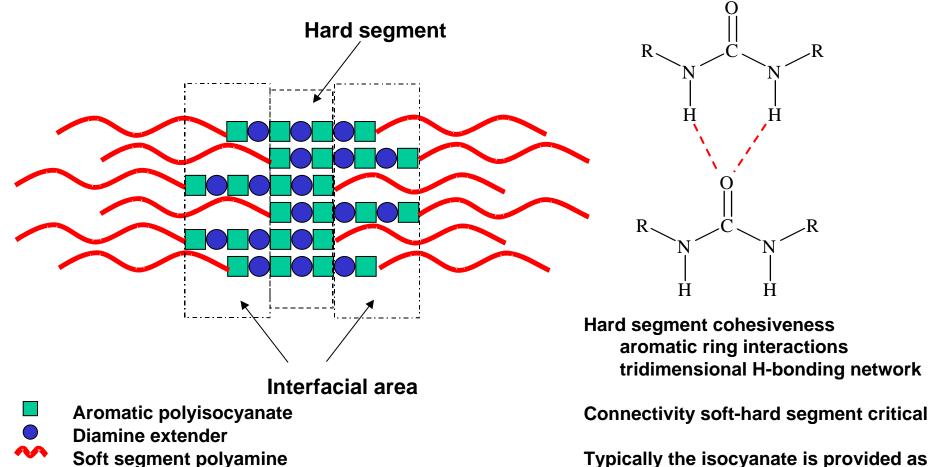
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R

Η

a prepolymer containing part of the

flexible segments



Soft segment polyamine

Resin components	POLYUREA	HYBRID	HYBRID	POLYURETHANE
Primary	Polyether amine	Polyether amine	Polyether polyol	Polyether polyol
Extender	Aromatic or aliphatic diamine	Glycol	Aromatic or aliphatic diamine	Glycol
Catalysts	None	yes	yes	yes

Other additives: UV stabilizers, pigments, adhesion promoters, compatibilizers, viscosity reducers, fillers, moisture scavengers

#### POLYUREAS

- Fast cure no catalyst
- Lower reaction activation energy
- Broader temperature application range – mainly lower temperatures
- Independent from ambient humidity.
- Good physical properties
- Generally good chemical resistance
- Better temperature stability
- Typically 100% solids
- Higher cost

#### POLYURETHANES

- Slower cure. Requires catalysts.
- Higher activation energies: more dependence on component temperature
- Broader formulation range:
  - Harder and softer coatings
- Lower stability at high temperatures
- Physical properties have a wide range
- Typically will require moisture scavengers.
- Lower cost

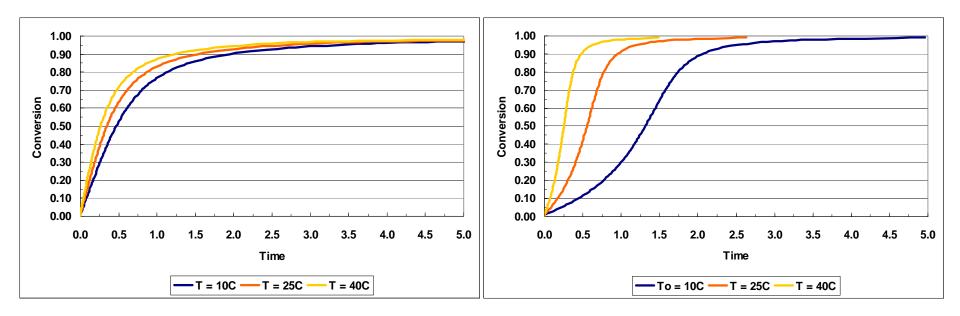
# **Reaction Conversion**

#### POLYUREAS

- Fast cure without catalyst
- Lower reaction activation energy
- Broader temperature application range, mainly lower temperatures

#### POLYURETHANES

- Catalysts used to adjust cure kinetics
- Higher activation energies: more dependence on component temperature
- Maximum rate of reaction not at start





## **Raw Materials for Polyureas and Polyurethanes**





### **MDI-base prepolymers**

# **Comparison Between Main Isocyanates**



#### AROMATIC

Very fast cure More cost competitive Wide variety Not UV stable: will yellow

#### ALIPHATIC

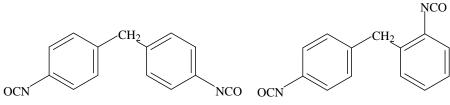
Slower cure Higher cost UV stable: suitable for finishing coatings



# **Common MDI Prepolymers**



**MDI** polyisocyanates



4,4'-MDI



Polyether polyols

Main variables in prepolymer design: Isomer ratio Polyether type: Functionality EO content Functionality via Isocyanate Polyol Viscosity modifiers What is the influence on performance?



# MDI-based Polyurea Prepolymers From Huntsman

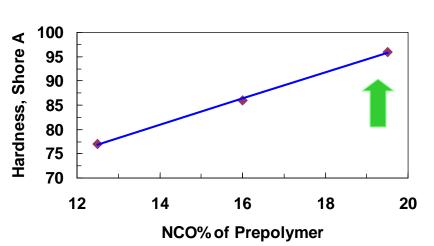


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Prepolymers	NCO%	Functionality	Viscosity @ 25°C	Comments
RUBINATE <sup>®</sup> 9009	16.0	2.13	1,250	Fast gel times. Hard polyurea. High physical properties.
SUPRASEC <sup>®</sup> 9603	16.0	2.0	250	Low viscosity. Good water resistance.
RUBINATE <sup>®</sup> 9480	15.2	2.0	370	Longer gel time, low viscosity, good mix quality. Good low temperature stability.
RUBINATE <sup>®</sup> 9495	15.1	2.06	400	Low viscosity, fast cure
RUBINATE <sup>®</sup> 9447	12.1	2.03	1150	Higher viscosity, soft elastomers
RUBINATE <sup>®</sup> 9272	8.4	2.0	2400	High viscosity, very soft elastomers

Contain Jeffsol PC as viscosity modifier

## **Hard Polyurea Issues**



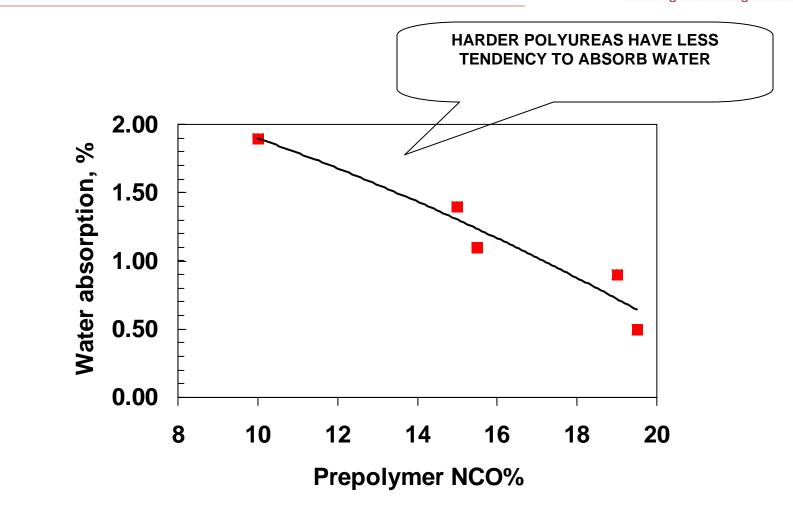
#### DEPENDENCE OF HARDNESS ON NCO%

Implications of hard polyureas:

- Higher NCO prepolymers
- Simple formulations contain too much extender
- Reaction is very fast and product may be extremely brittle
- Mixed chain extenders and secondary amines are commonly used

### Water Absorption vs. Prepolymer NCO







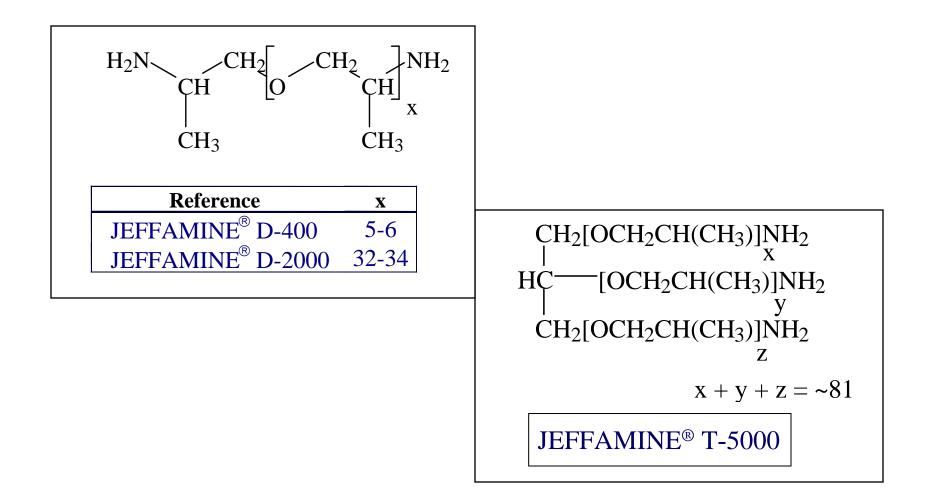
# **Amine Terminated Polyols**



### **Polyether Amines From Huntsman**

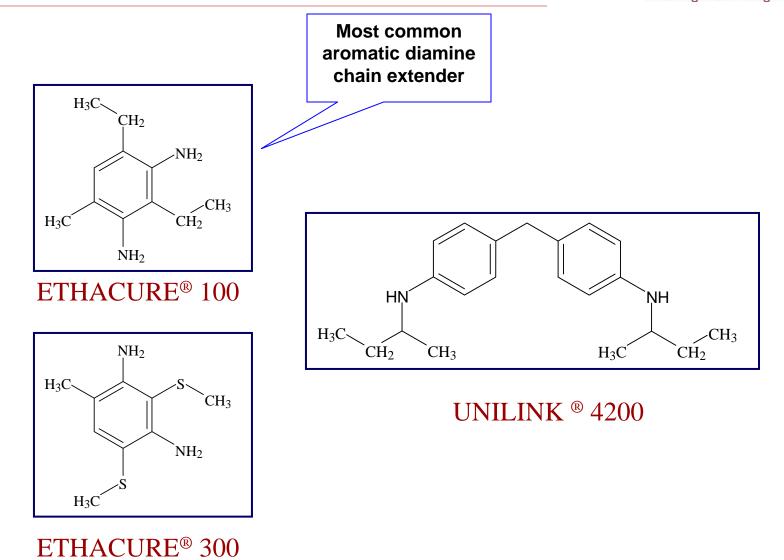


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## **Common Aromatic Chain Extenders**





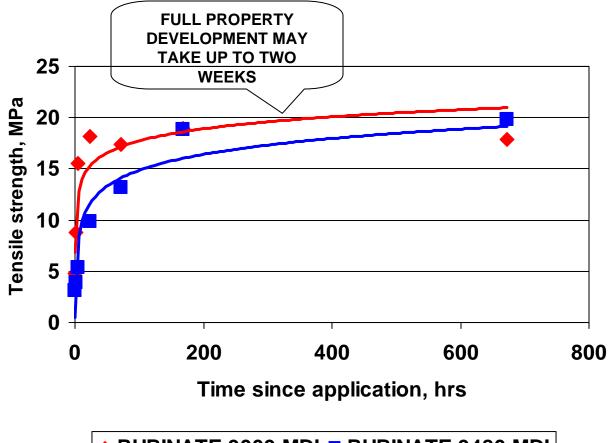


# **Physical Properties**

#### **Tensile Strength Development**



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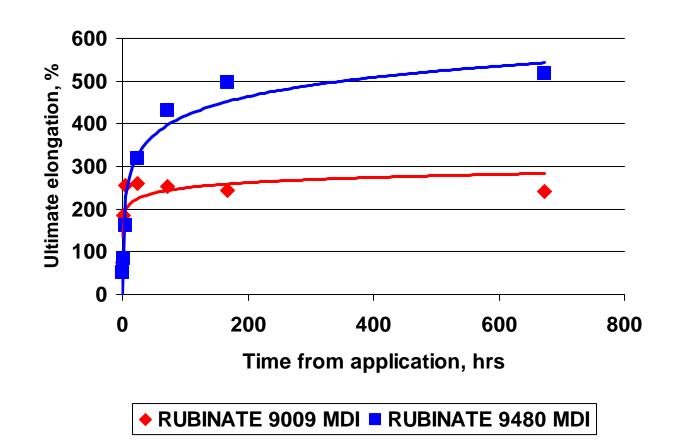


◆ RUBINATE 9009 MDI ■ RUBINATE 9480 MDI

### **Elongation Development**

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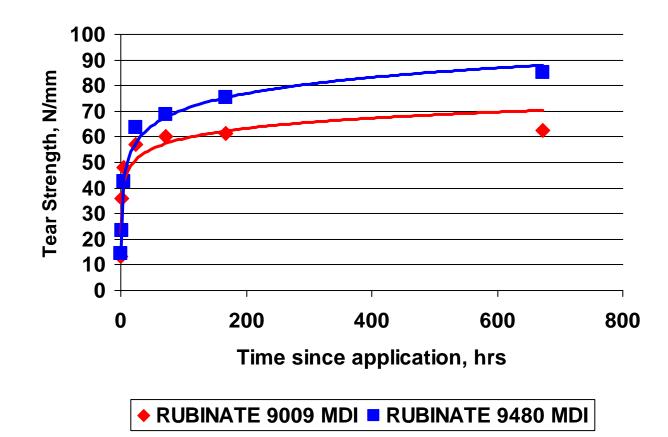




#### **Tear Strength Development**



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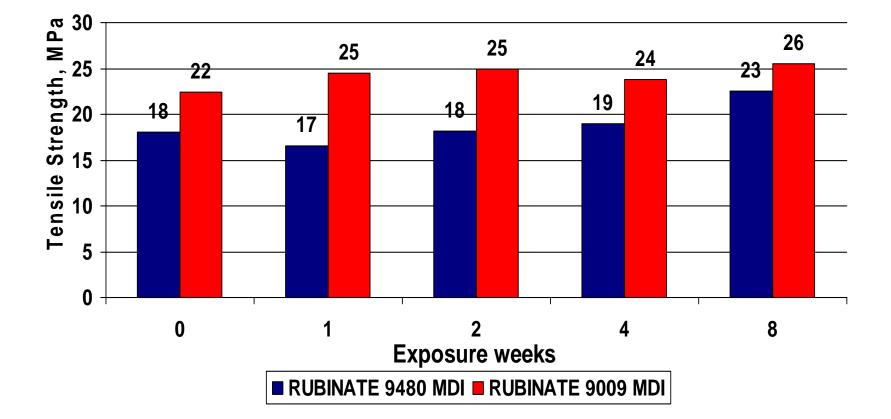




## Water Immersion at 50° C



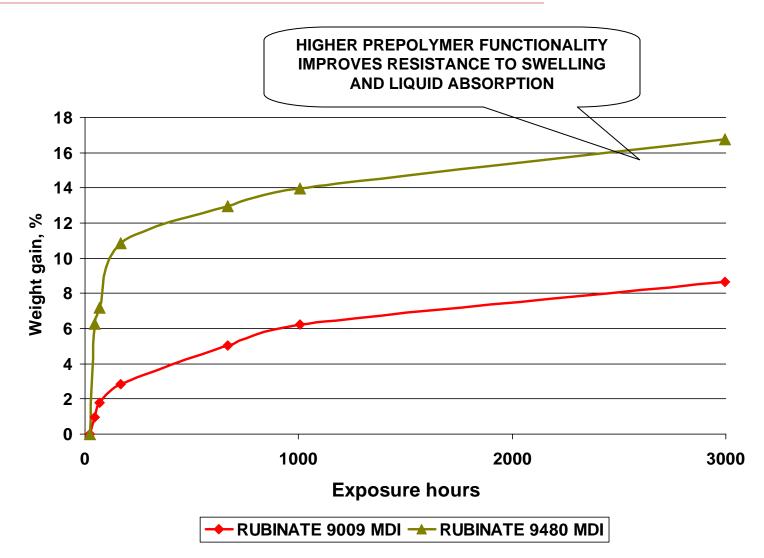
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## **ASTM Oil Exposure**

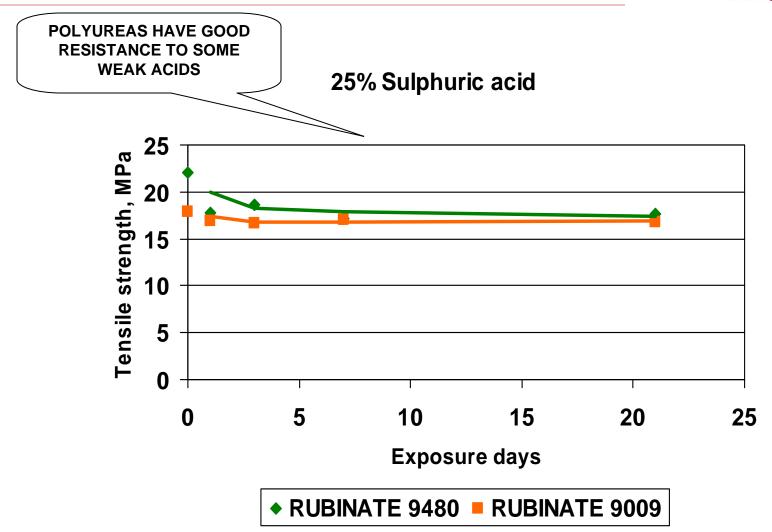
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# **Sulphuric Acid Exposure**

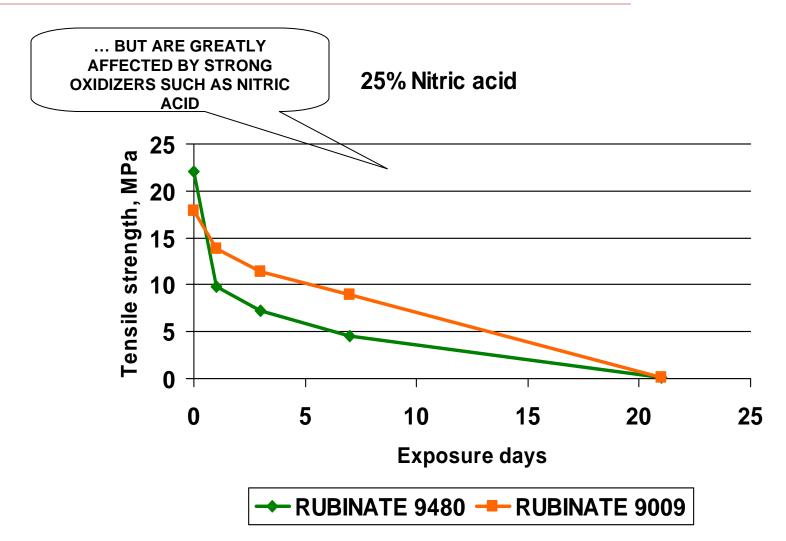




## **Nitric Acid Exposure**



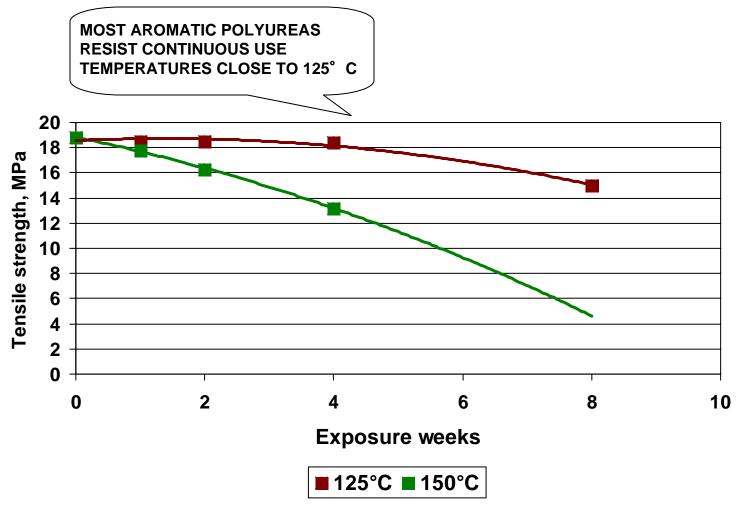
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## **High Temperature Exposure**

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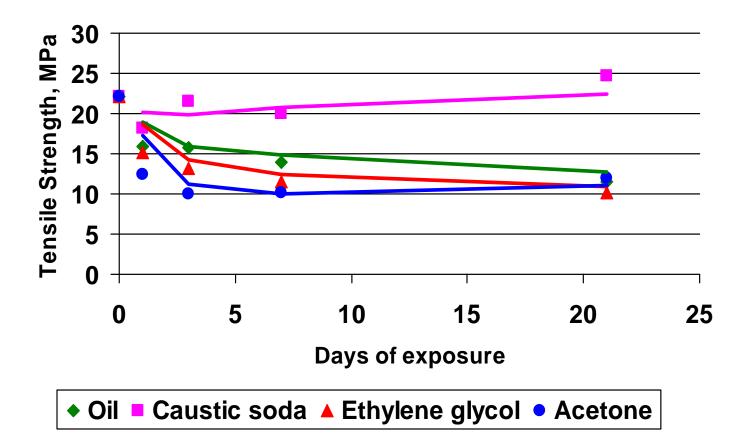
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#### RUBINATE® 9009

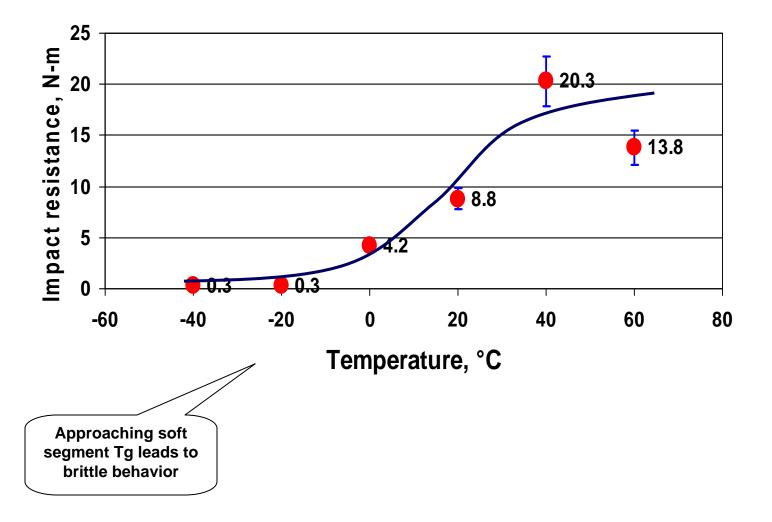


#### **Base: RUBINATE 9480**



### **Temperature Effect on Impact Resistance**





**RUBINATE® 9480-based** 

#### Method: ASTM D 3763-93

✓Polyurea properties can be adjusted with suitable formulation approaches.

Prepolymer choice influences key properties and processing characteristics:

Key variables for properties are functionality and NCO%
 Key variables for processing are viscosity, isomer content, functionality and NCO%

 ✓ Polyurea coatings can withstand high temperature exposures (ca. 125° C or 250° F) for extended periods.

✓Polyurea coatings are resistant to chemicals but each situation should be tested appropriately.

Processing variables may have significant impact



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