Polyurea Spray Coatings: General Overview with Practical Applications in Brazil

Daniel Rosenvasser, Huntsman Polyurethanes
Marcelo Alarcon Lui, Radial Revestimentos Tecnicos

Feiplar Composites & Feipur
November 6-8, 2012
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.
Spray Polyurea Coatings: An Introduction

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

Asphalt Overlay
Deck Tack Coat
Polyurea Membrane
Primer
Substrate

With permission by owner.
Railways
High Speed Railway

China plans to expand its high speed railway network to 10,000 miles in 2020.
Design Concept for a Sealer/Primer

Primer
Good film-forming

Sealer
Good penetration

Epoxy
Acrylic
Polyurethane
Vinyl

Silane
Siloxane

Sealer/Primer: Both good film-forming and penetration
Combination of PU Sealer/Primer with Polyurea
Case Study of PU Sealer/Primer for Spray Polyurea
PU Sealer/Primer for Spray Polyurea

Blank Concrete → PU Sealer/Primer → PU Putty → Spray Polyurea
Fracking

- **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
Chemical Resistance ASTM D 3912

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

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

- A: no visible damage
- B: slight color change
- C: slight surface discoloration
- D: swelling < 48 hours
- E: swelling < 24 hours
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.
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)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Grade</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>A</td>
<td>Spot test or watch glass method, simulates coating exposure through possible spillage (7 days).</td>
</tr>
<tr>
<td>Brake Fluid</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Bleach, 10%</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>Gasoline</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>A</td>
<td>A no visible damage</td>
</tr>
<tr>
<td>Hot tub water</td>
<td>B</td>
<td>B little visible damage</td>
</tr>
<tr>
<td>Hydraulic oil</td>
<td>A</td>
<td>NR not recommended</td>
</tr>
<tr>
<td>Methanol</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Motor oil</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– 5%</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>– 10%</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>– 25%</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>– 50%</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>– 5%</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>– 10%</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>– 50%</td>
<td>NR</td>
<td></td>
</tr>
</tbody>
</table>
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.
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.
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 Parks often use polyurea to protect foam, EPS and other structures to create ornamental building, themed characters, artificial rocks, pools and environments.
Architectural Coating
Waterproofing

Polyurethanes
Joint Fill/Caulk

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

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
Truck Bed Liners
Why Polyurea?
Why Polyurea?

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 prepolymer.

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

**POLYURETHANE**

\[
\text{OCN}_R \text{NCO} + \text{HO}_R \text{ROH} \xrightarrow{\text{Catalyst}} \text{(R-N=O-R')}_n
\]

Isocyanate  
Prepolymer  
Polyol

**POLYUREA**

\[
\text{OCN}_R \text{NCO} + \text{H}_2\text{N}_R \text{NH}_2 \rightarrow \text{(R-N=O-R')}_n
\]

Isocyanate  
Prepolymer  
Polyamine

**Urethane link**  
**Urea link**
Interfacial Area Detail

Typically the isocyanate is provided as a prepolymer containing part of the flexible segments.

Connectivity soft-hard segment critical

Hard segment cohesiveness

aromatic ring interactions

tridimensional H-bonding network

Aromatic polyisocyanate

Diamine extender

Soft segment polyamine
## Elastomer Families

<table>
<thead>
<tr>
<th>Resin components</th>
<th>POLYUREA</th>
<th>HYBRID</th>
<th>HYBRID</th>
<th>POLYURETHANE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>Polyether amine</td>
<td>Polyether amine</td>
<td>Polyether polyol</td>
<td>Polyether polyol</td>
</tr>
<tr>
<td>Extender</td>
<td>Aromatic or aliphatic diamine</td>
<td>Glycol</td>
<td>Aromatic or aliphatic diamine</td>
<td>Glycol</td>
</tr>
<tr>
<td>Catalysts</td>
<td>None</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

Other additives: UV stabilizers, pigments, adhesion promoters, compatibilizers, viscosity reducers, fillers, moisture scavengers
# Polyureas vs. Polyurethanes

## 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 prepolymer
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

Huntsman Polyurethanes supplies only these products.
Common MDI Prepolymers

MDI polyisocyanates

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

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

*Contain Jeffsol PC as viscosity modifier*
Hard Polyurea Issues

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

HARDER POLYUREAS HAVE LESS TENDENCY TO ABSORB WATER
Amine Terminated Polyols
Polyether Amines From Huntsman

Reference

<table>
<thead>
<tr>
<th>Reference</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEFFAMINE® D-400</td>
<td>5-6</td>
</tr>
<tr>
<td>JEFFAMINE® D-2000</td>
<td>32-34</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
&\text{CH}_2[\text{OCH}_2\text{CH(CH}_3\text{)}]_x\text{NH}_2 \\
&\text{HC}[\text{OCH}_2\text{CH(CH}_3\text{)}]_y\text{NH}_2 \\
&\text{CH}_2[\text{OCH}_2\text{CH(CH}_3\text{)}]_z\text{NH}_2
\end{align*}
\]

\[x + y + z = \sim 81\]

JEFFAMINE® T-5000
Common Aromatic Chain Extenders

ETHACURE® 100

ETHACURE® 300

Most common aromatic diamine chain extender

UNILINK® 4200
Physical Properties
**Tensile Strength Development**

- **Tensile strength, MPa**
- **Time since application, hrs**

- **RUBINATE 9009 MDI**
- **RUBINATE 9480 MDI**

FULL PROPERTY DEVELOPMENT MAY TAKE UP TO TWO WEEKS
Elongation Development

Time from application, hrs

Ultimate elongation, %

RUBINATE 9009 MDI  RUBINATE 9480 MDI
Tear Strength Development

- **RUBINATE 9009 MDI**
- **RUBINATE 9480 MDI**

Graph showing the tear strength development over time for two different MDIs, RUBINATE 9009 and RUBINATE 9480.
Water Immersion at 50° C

Exposure weeks

<table>
<thead>
<tr>
<th>Exposure weeks</th>
<th>Tensile Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
</tr>
</tbody>
</table>

- **RUBINATE 9480 MDI**
- **RUBINATE 9009 MDI**
Polyurethanes

ASTM Oil Exposure

HIGHER PREPOLYMER FUNCTIONALITY IMPROVES RESISTANCE TO SWELLING AND LIQUID ABSORPTION

Exposure hours

Weight gain, %

RUBINATE 9009 MDI
RUBINATE 9480 MDI
Sulphuric Acid Exposure

POLYUREAS HAVE GOOD RESISTANCE TO SOME WEAK ACIDS

25% Sulphuric acid

Tensile strength, MPa

Exposure days

RUBINATE 9480
RUBINATE 9009
Nitric Acid Exposure

... BUT ARE GREATLY AFFECTED BY STRONG OXIDIZERS SUCH AS NITRIC ACID

![Graph showing tensile strength loss over exposure days for 25% Nitric acid](image)
High Temperature Exposure

MOST AROMATIC POLYUREAS RESIST CONTINUOUS USE TEMPERATURES CLOSE TO 125°C

Exposure weeks

Tensile strength, MPa

125°C  150°C

RUBINATE® 9009

Polyurethanes
Immersion in Different Substances

Base: RUBINATE 9480

Days of exposure

Tensile Strength, MPa

0 5 10 15 20 25

0 5 10 15 20 25

Oil  Caustic soda  Ethylene glycol  Acetone

Polyurethanes
Temperature Effect on Impact Resistance

Approaching soft segment Tg leads to brittle behavior

Method: ASTM D 3763-93

RUBINATE® 9480-based
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.
Thank you

Daniel Rosenvasser
Huntsman Polyurethanes
2190 Executive Hills Boulevard,
Auburn Hills, MI 48326
Tel +1 248 322 7340 / +1 248 563 6700
Disclaimer

- While the information and recommendations in this publication are, to the best of our knowledge, information and belief, accurate at the date of publication, Nothing herein is to be construed as a warranty, express or otherwise.

- In all cases, it is the responsibility of the user to determine the applicability of such information and recommendations and the suitability of any product for its own particular purpose.

- Nothing in this publication is to be construed as recommending the infringement of any patent or other intellectual property right, and no liability arising from any such infringement is assumed. Nothing in this publication is to be viewed as a licence under any intellectual property right.

- Except where explicitly agreed otherwise, the sale of products referred to in this publication is subject to the general terms and conditions of Huntsman International LLC or of its affiliated companies.

- Huntsman Polyurethanes is an international business unit of Huntsman International LLC. Huntsman Polyurethanes trades through Huntsman affiliated companies in different countries such as Huntsman International LLC in the USA and Huntsman Holland BV in Western Europe.

- SUPRASEC®, and DALTOREZ®, are registered trademarks of Huntsman Corporation or any affiliate thereof, in one or more countries, but not all countries.

- Copyright © 2012 Huntsman LLC or an affiliate thereof. All rights reserved.