Higher Performance Raw Materials for Improved Polyurea Properties

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The Hanson Group, LLC
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Houston, Texas

Primeaux Associates LLC
Polyurea Technology & Application Consulting

Higher Performance Raw Materials for Improved Polyurea Properties

- High Chemical Resistance
- High Temperature Resistance
- High Tensile Strength
- Better Flow
- Better Adhesion
- AntiGraffiti Coatings

Basic Pure Polyurea Technology

PART A ISO

Isocyanate Prepolymer

PART B Resin

Amines
Polyetheramines

Amine Chain Extenders
1° & 2° Aromatic Amines

Pigment Dispersions
Dispersions in Polyetheramines

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Advantages of Polyureas

- Insensitive to moisture and humidity
- Weather tolerant: Cures at -25^0 to >300^{0}F
- Fast Set, Return to service in minutes
- No VOC's and little to no odor
- Excellent resistance to thermal shock
- Flexible, waterproof, seamless and resilient
- Relative unlimited application thickness
- Spray, hand mix and joint sealant grade materials

Improvements & Needs that Don't Compromise Basic Advantages

- You want to improve Polyurea performances without losing certain properties
- Sometimes improved tensile will compromise elongation or adhesion or other properties
- More crosslinking to improve chemical resistance can reduce abrasion and other properties

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What are some of the New Performance Needs for Polyureas?

- **Asked the Customers**
  - **Acid Resistance**
  - **Higher Tensile, Tear & Toughness**
  - **Higher Impingement Abrasion**
  - **Better Adhesion**
  - **Better Surface Appearance**
  - **Anti-Graffiti, Low-Slip Polyureas**
  - **Single Component**

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Acid Resistance

- Where & Why
  - Secondary Containment, Chemical Plants
  - Mining



Acid Resistance

How Have They Been Improved

- Can modify Part A (Isocyanate portion)
  - Higher performance Iso Pre-polymers
  - Modifications made to the polymer that enhances the chemical resistance
  - HXP ISO 12 developed for this need:
    - 16% NCO
    - 750 cps



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Acid Resistance

HXP ISO 12 Properties Cured with Standard Part B “Resin” Polyurea

- Developed by The Hanson Group LLC

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CHEMICAL IMMERSION TEST ON POLYUREAS BASED ON VARIOUS ISO PRE-POLYMERS

Test Methods:

ASTM D1308-02 (Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes)

ASTM D543-95 (Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents)

Basic Formulation & Conditions

PART A

Isocyanate Pre-polymer
15.5-16% NCO

PART B

Resin Blend

BASF Polyether Amines

Aceto Polylink DETDA

Aceto Polylink 4200

Rebus White Pigment Dispersion

Processing

Index:	110-115
ISO/Resin Volume Ratio:	1:1
Spray Pressure:	2,000 psi minimum
Primary Heat:	150-160 ^{0}F
Hose Heat:	150-160 0F
Spray Gun:	Impingement Mix, Mechanical Purge

CHEMICAL REAGENTS

FULL LIST OF CHEMICALS USED ON POLYUREAS BASED ON VARIOUS ISO PRE-POLYMERS

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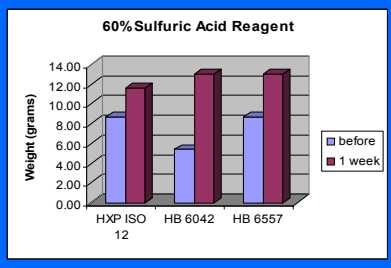
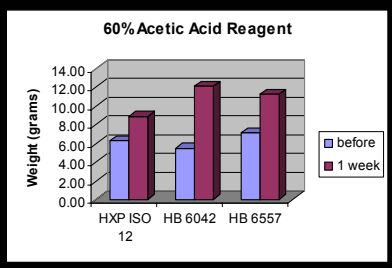
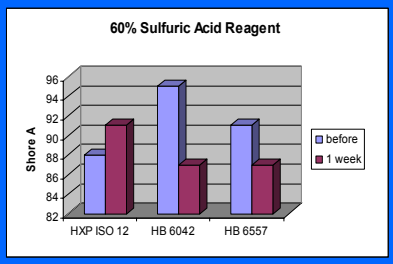
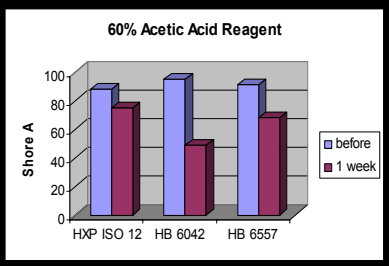
Reagent				
Xylene				
60% acetic acid				
20% HCl				
60% Phosphoric acid				
20% Nitric acid				
Methanol				
30% Phosphoric acid				
acetic acid, 100%				
Acetone				
Water				
60% formic acid				
40% HCl				
denatured alcohol				
Toluene				
25% acetic acid				
40% nitric acid				
30% sulfuric acid				
MEK				
50% citric acid				
Bleach				
99% isopropyl alcohol				
60% sulfuric acid				

CHEMICAL IMMERSION TEST ON POLYUREAS BASED ON VARIOUS ISO PRE-POLYMERS









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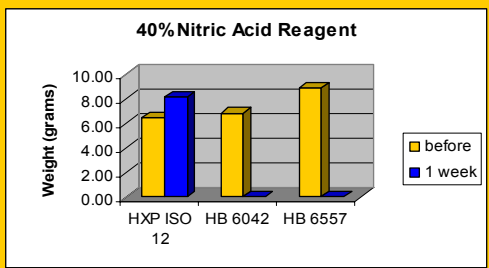

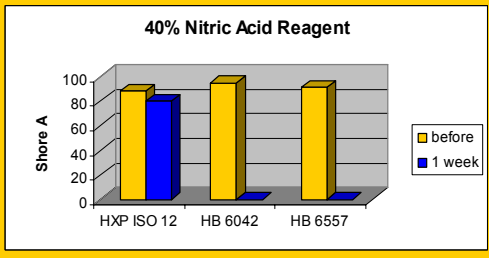

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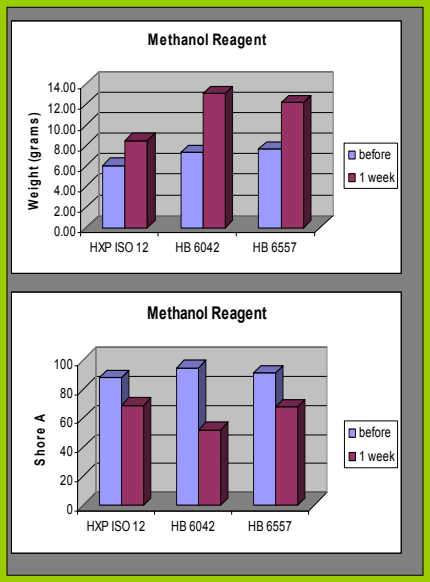

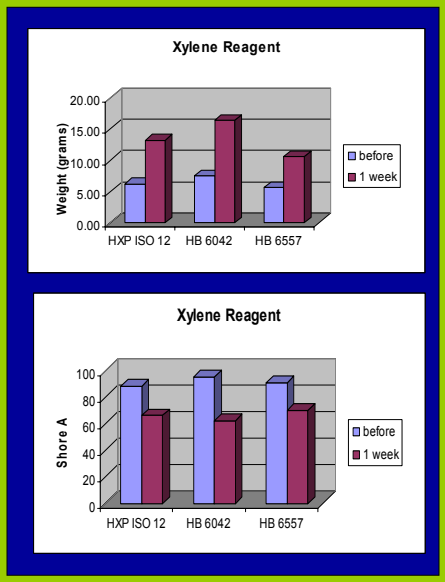

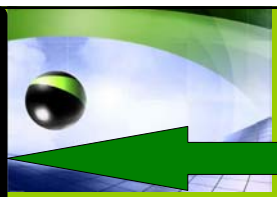

Acid Resistance Results

Based on Surface Hardness and Weight Gain

- Bottom line Showed that the HXP ISO 12 ISO-Pre-polymer showed much better Acid Resistance than the PPG Based Prepolymers

Additional Acid Resistance Improved by Modifying Part B

- Can modify Part B Resin
  - Silane Modified Amines
  - High Functional Polyetheramines
    - T-series or higher
    - "others"

Higher Tensile, Tear & Film Properties

- Where and Why???
  - High wear and tear areas
    - Impingement abrasion resistance
  - High Abrasion Environments
    - Sand storms
    - Flooring
  - Blast Mitigation

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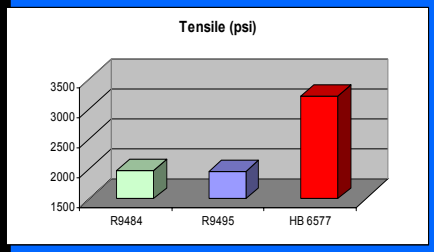
Improved Materials for Higher Tensile & Tear

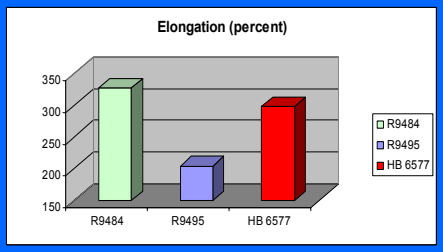
- Modify Part A (ISO)
  - Higher performance Iso-prepolymers modified with specialty polymers
  - Key is to pick the right polymer that you can also make into a usable product (viscosity, etc…)
  - HB 6577
    - 16% NCO
    - 850 cps

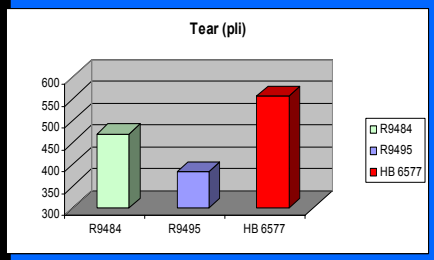
Improved Tensile & Tear with New Dow ISO Pre-polymer Chemistry

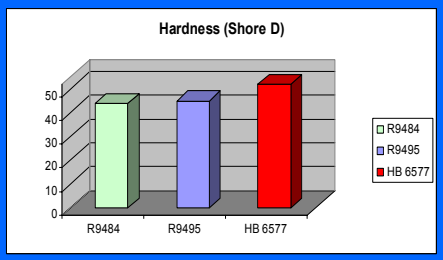
System	1 2,4' MDI	2 4,4' MDI	3 HB 6577
Tensile strength psi	1974	1961	3218
Elongation, %	328	204	298
Tear strength, pli	470	382	556
Modulus, psi			
100%	1202	1417	1827
200%	1521	1985	2487
300%	1881		2656
Hardness (Shore D) **	44	45	52
Viscosity at 25°C (cPs)	225	450	1325
Gel time, secs	11	5	9
Tack free secs	20	9	18
Spec. Grav., 20°C, g/cc	1.13	1.16	1.15

Improved Tensile & Tear with New ISO Pre-polymer Chemistry





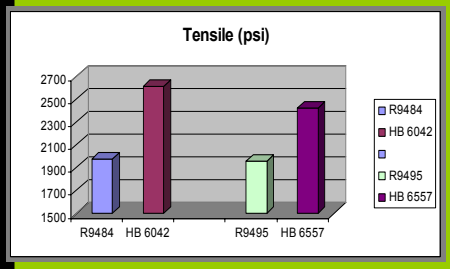


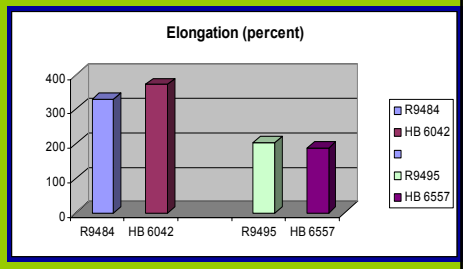


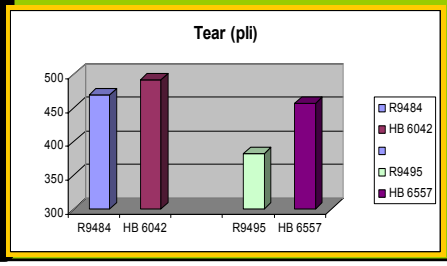
Tech Info about Higher Strength ISO's

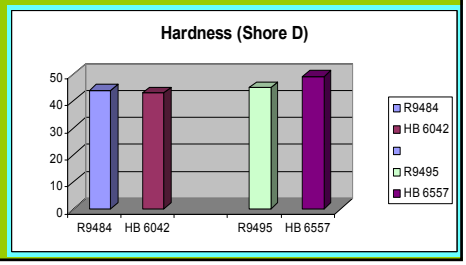
System	Test Method	1 2,4' MDI w/o PC	2 2,4' MDI w/ PC	3 4,4' MDI w/o PC	4 4,4' MDI w/PC
Tensile strength, psi	ASTM D638	2613	1974	2423	1961
Elongation, %	ASTM D638	371	328	188	204
Tear strength, pli	ASTM D624	492	470	457	382
Modulus, psi					
100%		1237	1202	1767	1417
200%		1659	1521	2602	1985
300%		2191	1881		
Hardness Shore D		43	44	49	45
Viscosity at 25°C (cPs)		700	225	1075	450
%NCO		15.8	15.92	16.0	14.66
Gel time, sec		9	11	5	5
Tack free, sec		15	20	10	9
Spec. Grav., 20°C, g/cc		1.11	1.13	1.14	1.16

Tech Info about Higher Strength ISO's









Improved Cold Temperature Stability for ISO's
HB 6042 ISO that was in -40 ^{0}C for 30 days

Equivalent Properties of Std HB 6042

System	Test Method	1 HB 6042	2 HB 6042/Freeze
Tensile strength, psi	ASTM D638	2613	2835
Elongation, %	ASTM D638	371	311
Tear strength, pli	ASTM D624	492	485
Modulus, psi			
100%		1237	1279
200%		1659	1704
300%		2191	2229
Hardness (Shore D) **		43	48
Viscosity at 25°C (cPs)		700	770
Gel time, sec		9	9
Tack free, sec		15	18
Spec. Grav., 20°C, g/cc		1.11	1.12

Improved Cold Temperature Stability for ISO's

HB 6042 ISO that was in -40 ^{0}C for 30 days

770 cps Viscosity, no haze, no gels

Good Spray Pattern of Frozen HB 6042

Improved Materials for Higher Tensile & Temperature

- Modify Part B (Amines)
  - Higher crosslinking amines will improve the tensile strength and temperature resistance
  - BASF T-403 and T-5000

Better Adhesion, Surface Appearance and Less Gun Gelling

- Chain Extender Modifications have been proven to give Polyureas better overall properties but mostly *"It Just Sprays Better"*

- PolyLink 4200
- PolyLink DETDA
- PolyClear 136



A Well Balanced Blend of Amine Chain Extenders will Make your Polyureas "Just Spray Better"

- PolyLink 4200 (aromatic diamine)
  - Better Adhesion, Better Flow and Less Gun Gelling
- PolyLink DETDA (aromatic diamine)
  - Faster Green Strength Development and Higher Physical Properties
- PolyClear 136 (aliphatic diamine)
  - Longer Gel Time, Better Adhesion, and Surface Appearance



Benefits of PolyClear 136

- PolyClear 136 (aliphatic chain extender)
  - Only aliphatic chain extender TSCA & EINECS approved (can sell in US, Europe & Asia)
  - Slows down the gel time allowing better adhesion, flow & leveling
  - Faster cure – develops properties similar to aromatic polyureas
  - Higher thermal properties
  - Much lower overall formulating costs (can save up to 20%/gal)
  - US Patent pending, September 2005

Benefits of PolyClear 136

System	PolyClear 136	Amine C	Amine J
Amine Eq weight	~ 136	~ 161	~ 127
Viscosity, cps 25°C	~ 100	110	13
Flash point, PMCC, °C	210	141	104
Specific Gravity, 20°C	0.98	0.90	0.858
Percent of Resin Blend	29	36	28
Gel time, secs	5 - 6	5 - 6	2 - 4
Tack free, secs	9 - 11	9 - 11	5 – 7
Hard Set, Minutes	2 - 3	4 - 5	4 – 5
Tensile strength, psi	1620	1940	~ 1700
Elongation, %	160	150	~ 150
Shore D Hardness	40 - 45	40 - 45	40 - 45
T_g, °C (High Temp)	~ 70 - 80	~ 60 - 70	~ 50 - 60

1:1 by volume, ISO:Resin, aliphatic system, 15% NCO IPDI based quasi-prepolymer

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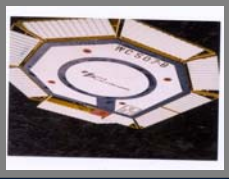
Applications For PolyClear 136

- PolyClear 136
  - Light stable OEM Polyurea Elastomeric Coatings
  - Light stable top coats
  - Light stable Polyurethane Elastomers


Anti-Graffiti: Low Slip Coatings

- Where & Why???
  - Utility and Public Access Areas
- How can you obtain these properties:
  - Modify Part A (ISO)
    - Fluorinated IPDI and MDI Pre-polymers

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ALIPHATIC AND AROMATIC PREPOLYMERS

DESIGNATION	PREPOLYMER TYPE
AI03154-2	MDI PREPOLYMER
AI03155-1	FLUORINATED MDI PREPOLYMER
AI03156-1	PPG-IPDI PREPOLYMER
AI03157-1	FLUORINATED PPG-IPDI PREPOLYMER

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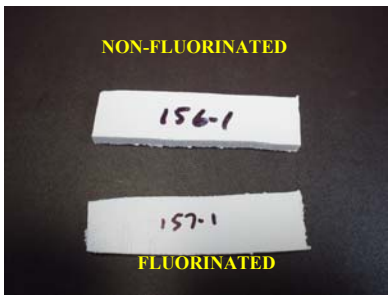
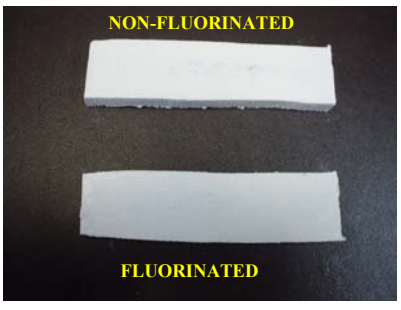
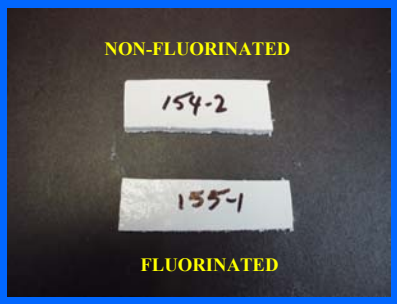
SURFACE PROPERTIES OF PPG IPDI FLUORINATED VS. NON-FLUORINATED

BEFORE CLEANING	AFTER CLEANING

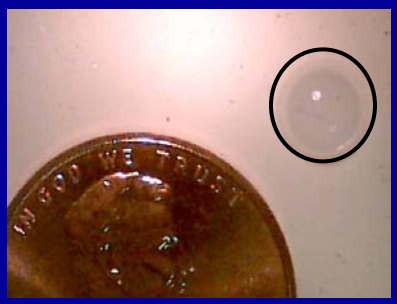




SURFACE PROPERTIES OF MDI FLUORINATED VS. NON-FLUORINATED

BEFORE CLEANING	AFTER CLEANING
	

SURFACE TENSION MEASUREMENT: AROMATIC POLYUREA (60X MAG.)

AI03154-2 (Non-fluorinated)	AI03155-1 (Fluorinated)
	

Higher Performance Raw Materials

Improved Polyurea Properties

- **Wrap-up**
  - Polyurea technology is not new, but the market is now accepting it faster than ever.
  - Our team has been involved with Polyureas since 1986. We are continually developing newer and better raw materials to meet the ever demanding market needs.
  - What do you need your Polyureas to do?

Just Make That Call!

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