

**수용성 폴리우레탄 접착제의
제조와 응용**

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Fundamentals of Waterborne Polyurethane Adhesives

DONGSUNG NSC CO., LTD.

**Dongsung
NSC Ltd.**
A member of the ICI Group

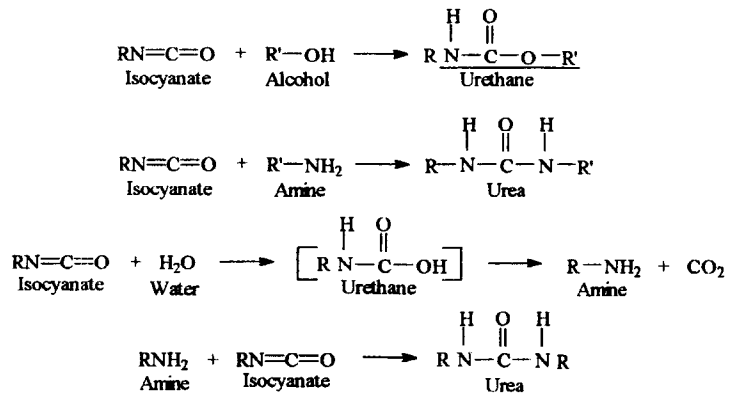
Why Water based Adhesives?

- Nike's VOC elimination program leads the movement from solvent based adhesives to water based adhesives.
- Nike is trying to reduce 90% of VOC emission by 2001.
- All of big shoe buyers are following Nike's environmental friendly policy in their shoe production.

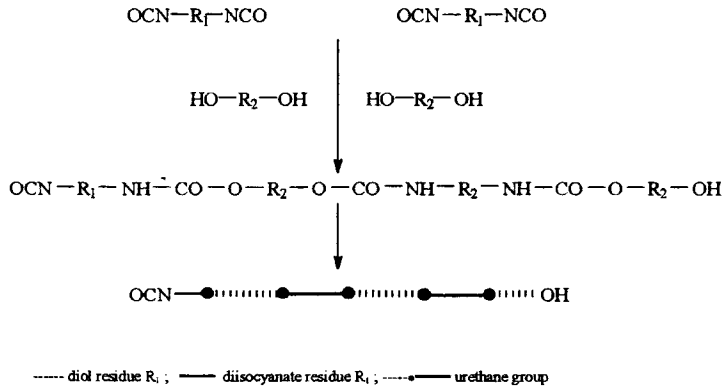
Requirements for the Replacement

- High initial strength
- Possibility of crosslinking
- Easy application
- Safety

Basic Reactions in Polyurethane



Formation of a linear polyurethane



Isocyanate Types and Properties

■ Types

- MDI

- IPDI

- TDI

■ Properties

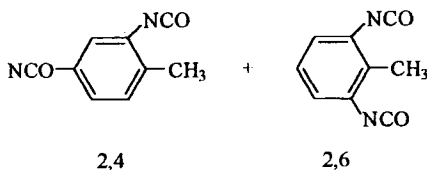
- Low melt solid
- Rigid
- Aromatic UV degrades
- Low cost

- Low viscosity liquid
- Semi-rigid
- Aliphatic UV stable
- High cost

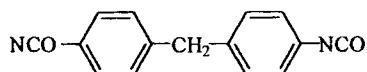
- Health & safety issue
- Minimal use

Aromatic Isocyanates

Toluene Diisocyanate (TDI)

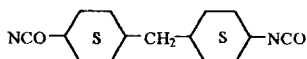


Diphenylmethane Diisocyanate (MDI)

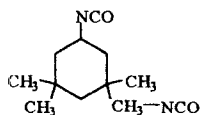


Aliphatic Isocyanates

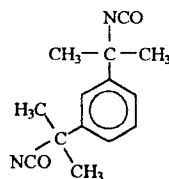
Methylene - Bis - 4 - Cyclohexylisocyanate (H₁₂MDI)



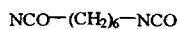
Isophorone Diisocyanate (IPDI)



Tetramethylxylylene Diisocyanate (TMXDI)



Hexamethylene Diisocyanate (HDI)



Polyols and Properties

■ Types

– Polyether

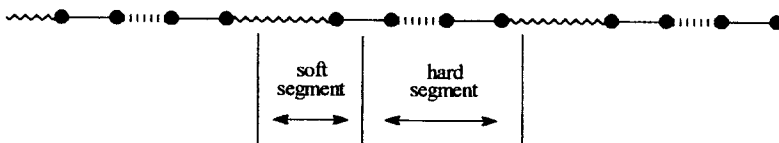
– Polyester





■ Properties

- Low viscosity
- Flexible cure
- Low cost

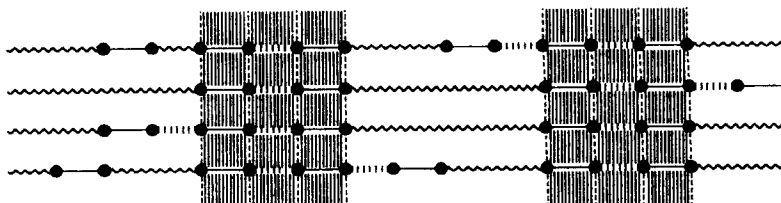
- Solid or high viscous liquid
- Rigid cure
- More polar
- Improved adhesion
- Higher cost

Representation of the Ideal Primary Structure of a polyurethane



- (soft)  = long chain diol (high molecular weight)
- (hard)  = extender amine (low molecular weight)
- (hard)  = diisocyanate
- (hard)  = urethane group

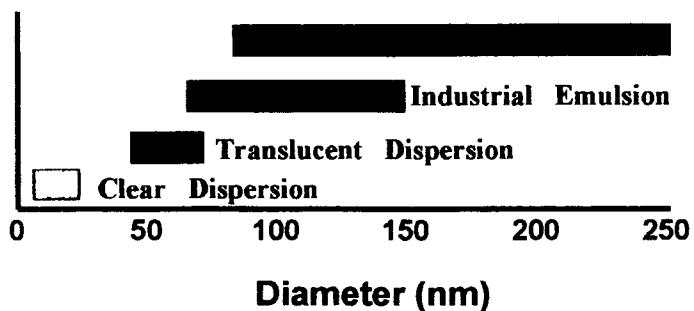
Interchain Interaction Between the Hard Segments



Domains of interchain interaction (hydrogen bonding)
between hard segments

Source : G. Gertel, *Polyurethane Hand Book* Hanser Publishers, New York (1983) p. 34

Waterborne Polymer Particle Size Ranges



Water Borne Polyurethanes

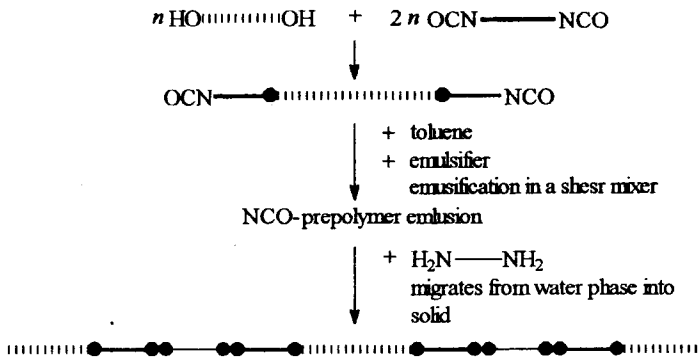
■ *Two Main Classifications*

- *Those stabilized with dispersants : not widely used in industries*
- *Those ionically stabilized by hydrophilic structures on the polymer*

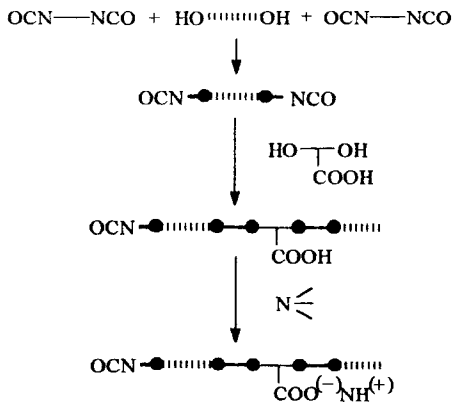
Types of Water Borne Polyurethanes

<i>Type</i>	<i>Hydrophilic center</i>
■ <i>Conventional</i>	<i>Emulsifiers</i>
■ <i>Cationic</i>	<i>t-amine +alkylating agent</i>
■ <i>Anionic</i>	<i>Carboxylic acid + neutralizing agent</i>
■ <i>Non-ionic</i>	<i>Polyethylene oxide chains</i>

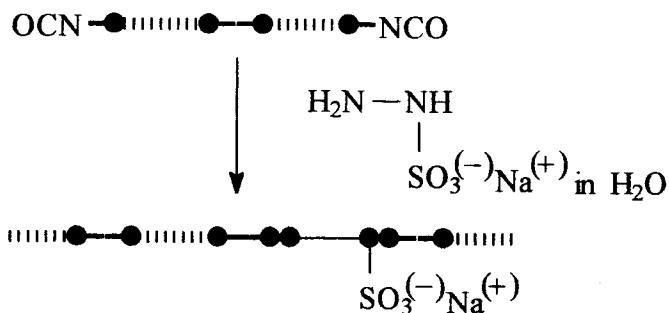
PUR dispersion from NCO prepolymer by use of emulsifier



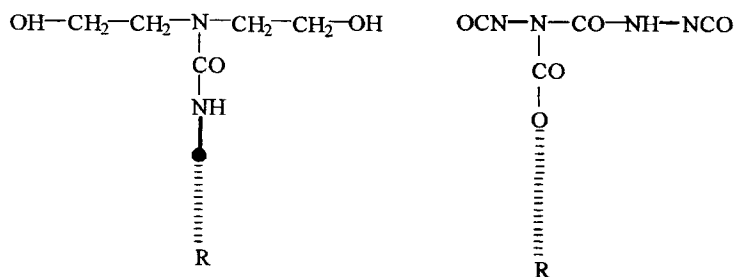
Anionic polyurethanes with carboxylate groups



Anionic polyurethane-polyurea with sulphonate groups



Nonionic, hydrophilic components for the preparation of nonionic PUR dispersion.



Patent Applications in the Area of Waterborne Polyurethane Dispersion

Time Period	No. of Applications	Applications Per Year
1943 - 1961	30	1.6
1962 - 1966	131	26
1967 - 1971	215	43
1972 - 1976	198	40
1977 - 1981	156	39
1981 - 1985	129	38
1986 - 1991	591	118

Waterborne Urethanes

■ Advantages

- **Fully reacted, isocyanate free**
- **Film formers with good hardness / toughness**
- **Low VOC's**
- **High molecular weight / low viscosity**
- **Choice of aliphatics or aromatics (to reduce cost)**
- **Good weathering characteristics**
- **Functional groups available for crosslinking**
- **Broad compatibility with other waterborne polymers**
- **Coatings have good sanding characteristics**
- **Application by conventional application techniques / equipment**

Waterborne Urethanes

■ *Issues*

- *Unique formulating characteristics*
- *Cost (as compared to other polymers such as acrylics or polyesters)*
- *Contains "High Boiling" co-solvents such as N-Methylpyrrolidione*

Waterborne Urethanes

Current End Uses

■ *Coatings*

- *Floors (Wood, Concrete, Plastics)*
- *Plastic Parts (Automotives, Business machines)*
- *Top coats in heavy duty systems*
- *Flexible substrate (Textiles, Leather, paper, rubber)*
- *Coil coat primer*
- *Furniture and sports equipment*

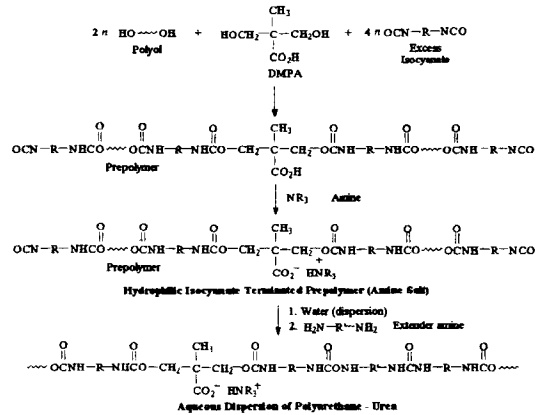
■ *Printing Inks*

- *Screen printing*
- *PVC gravure inks*
- *Plastic film*

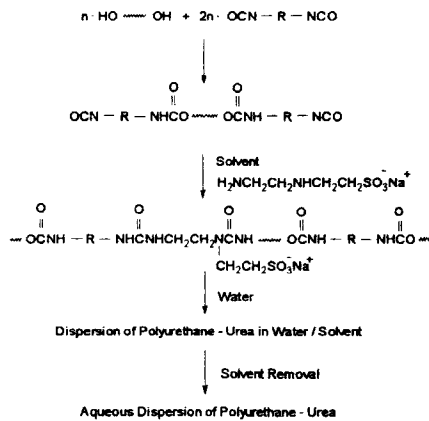
■ *Adhesives*

- *Industrial laminating*
- *Structural adhesives*
- *Sealants*

PUR Dispersion by Prepolymer Mixing Process

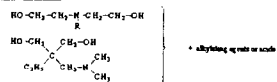


PU Dispersion by Acetone Process

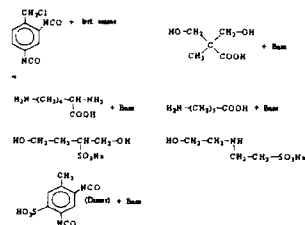


Hydrophilic monomers in PUR dispersion

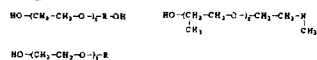
1. Cateolic



2. Aminoic



3. Nantoic



Waterborne Urethanes Crosslinking Mechanisms

- | | <i>Temp. Required</i> |
|--|-----------------------|
| ■ Polyfunctional aziridines | <i>ambient</i> |
| ■ Polycarbodiimides | <i>> 180 °F</i> |
| ■ Melamine formaldehyde | <i>> 250 °F</i> |
| ■ Water dispersable polyisocyanate | <i>ambient</i> |
| ■ <i>Use of external crosslinking limits shelf life</i> | |
| ■ <i>Polyfunctional aziridines not recommended for trade sales or industrial spray applications due to potential toxicity concerns</i> | |
| ■ <i>Melamines emit formaldehyde during curing cycle</i> | |