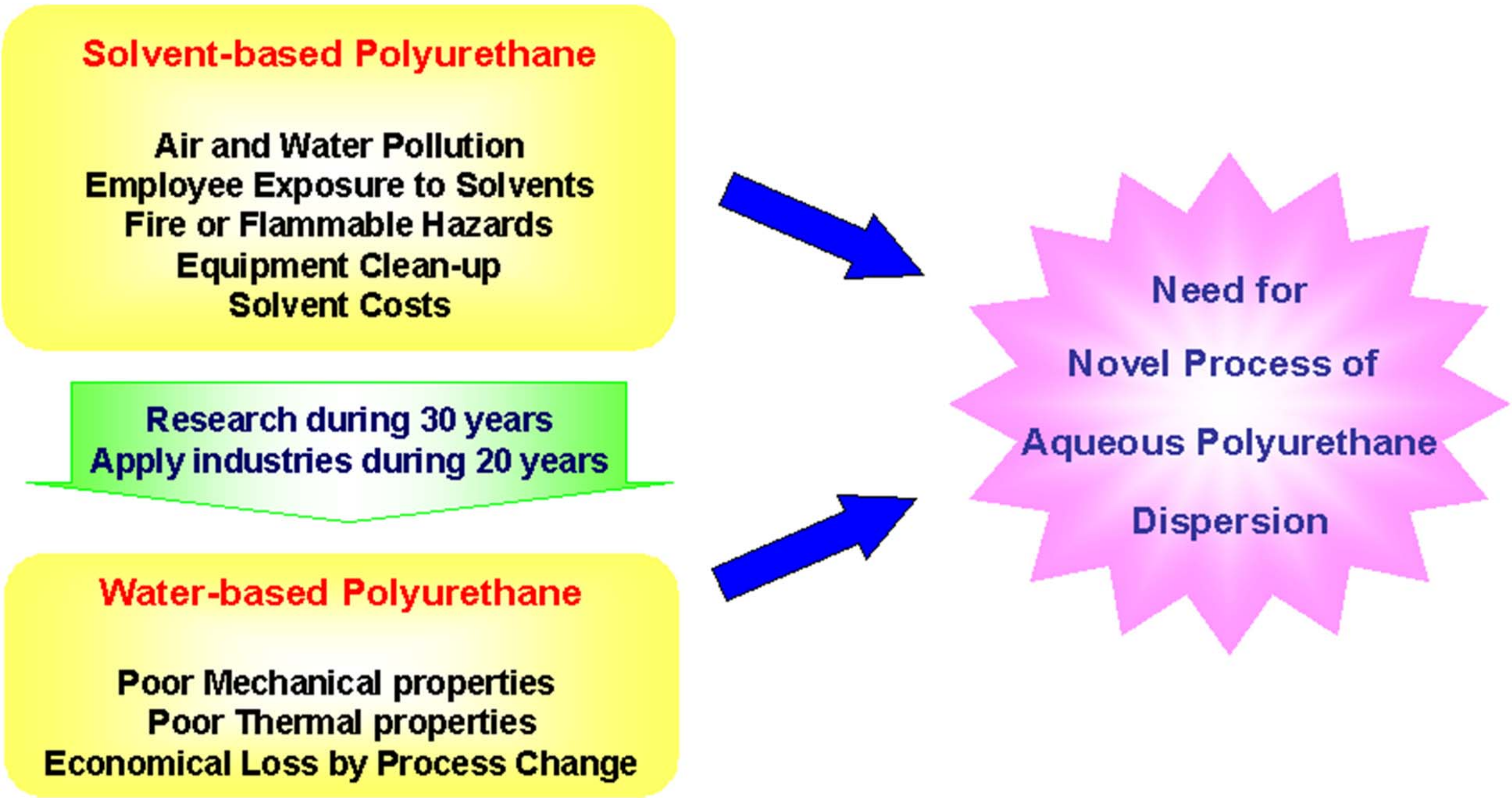
Aqueous Polyurethane Dispersion Technology

Kim, Jung-Hyun, Ph.D.

Nanosphere Process & Technology Laboratory
Department of Chemical Engineering, Yonsei University

Introduction

Background of Aqueous Polyurethane Dispersion



Introduction

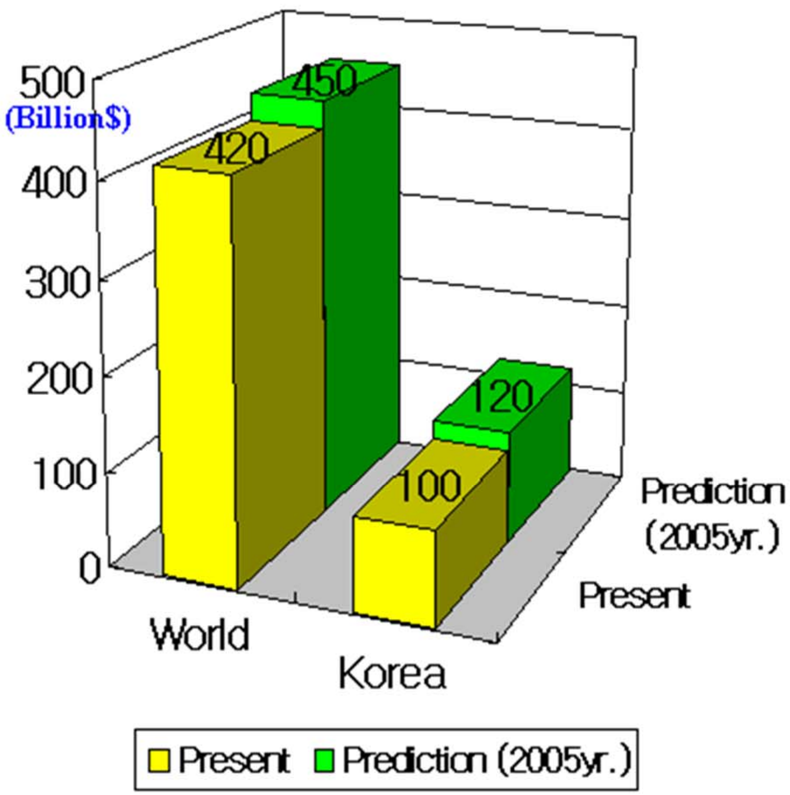
Difference Solvent-based and Water-based

	Solvent-based	Water-based
Type	Homogeneous	Heterogeneous
Storage Stability	Not requested	Requested
Molecular weights	~ 250,000	~ 200,000
Ionic pendant groups	Not requested	Requested
100% Modulus (kg/ ㎠)	~ 200	~ 150
Tensile Strength (kg/ ㎠)	~ 950	~ 350
Elongation (%)	~ 1200	~ 550
Curing time	Fast	Slow

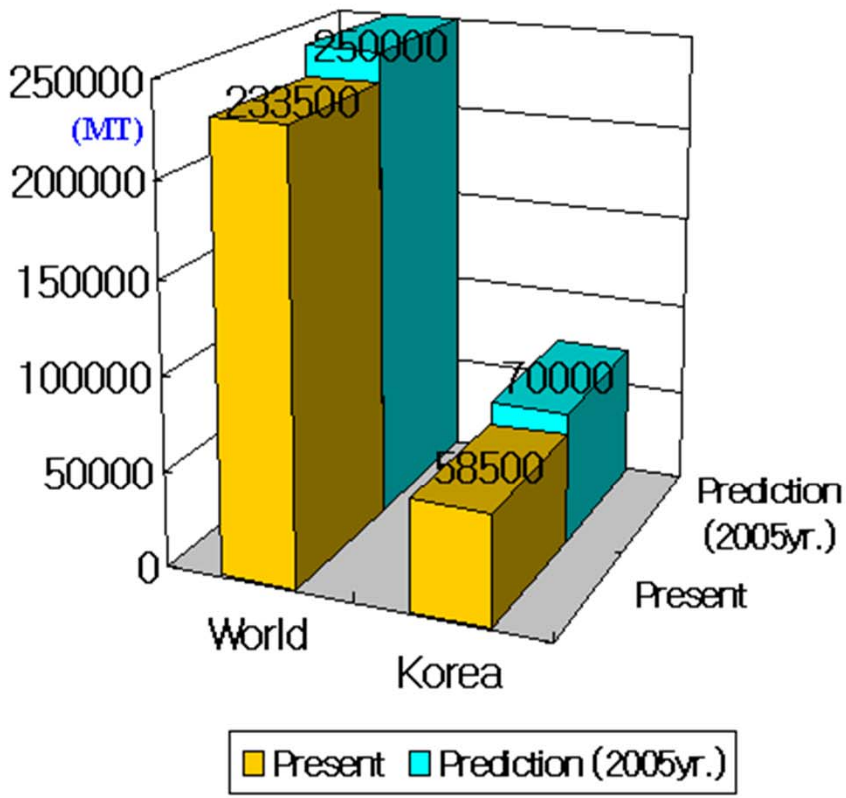
Introduction

Markets for Synthetic Leather Applications

Markets of Solvent-based Polyurethane



Productions of Solvent-based Polyurethane



Introduction

Markets for Applications

Markets of Polyurethane Adhesives

PVC/PU foam PVC/PU film PVC/ABS PVC/PVC PVC/metalized Mylar	Paper/OPP Paper/LDPE Paper/ Alum. foil Paper/ PE film Mylar/paper Mylar/paint	PU film/fabric Fabric/fabric PVC plastisol/glass PVC plastisol/metal	PE/PP LDPP/LDPP MDPP/MDPP

Markets of Polyurethane Textiles

Coating	Finishing	Coagulation
Breathable Waterproof Gasoline resistant Helium impermeable Suede	Abrasion resistant Upgrade fabric Improve fabric drape Improve breathability	Acid Thermal

Markets for Applications

Markets of Polyurethane Medical Films

Function	to produce a high strength, non-cytotoxic, breathable film for medical applications; the advantage is to reduce cell death (maceration) and increase healing by 40%
Examples	Surgical drapes Protective wound coverings
MVTR Figures	Natural evaporation: 1600-1800 (gms/day/m^2) Polyurethane film: 800-1000 (gms/day/m^2)

Introduction

Terminology

Two-component urethane	Polyols reacted with an isocyanate or isocyanate terminated adduct Markets: PU foams, clear coatings for metals (automotive industry), roof coatings, heavy-duty finishes such as aircraft paints
Oil-modified urethane /urethane alkyds	Hydroxyl terminated ester intermediate reacted with a diisocyanate Markets: wood & floor finishes
Blocked isocyanate urethane	Reaction of a polyol with an excess of diisocyanate followed by the introduction of an mono functional hydrogen compound to block the excess isocyanate groups Markets: automotive primers and finishes, and wire coatings
Moisture-cure polyurethane	Reaction of a polyol with an excess diisocyanate. Moisture reacts with diisocyanate to form a hard coating Markets: wood & concrete floors

Introduction

Terminology

One-package polyurethane lacquer/solvent base	Reaction of a polyol with a diisocyanate to form a polyurethane or urethane. The urethane is reduced with solvents. Markets: abrasion-resistant top coatings, adhesives, medical films, paints, ink, fabric coatings, etc.
One-package polyurethane latex	Reaction of a polyol and diisocyanate followed by surfactant stabilization Markets: top coating, adhesives, medical, foams, etc.
One-package polyurethane dispersion (ionic dispersions)	Reaction of a polyol and diisocyanate with the incorporation of ionic groups on the polymer backbone and dispersion in water Markets: top coating, adhesives, paint, medical, textile, etc.

Introduction

Techniques of Polyurethane Dispersion

I. External Stabilizers: Urethane + Surfactant & Water

***Disadvantage:**
- **High shear required**
- **Relatively unstable dispersion of large particle size**
- **Poor physical properties and chemical resistance**

II. Internal Stabilizers:

A) Cationic Dispersion: Urethane^{+} + Water

B) Anionic Dispersion: Urethane^{-} + Water

Development of Dispersion Process	→	**Neutralization emulsification** (Particle Size, Viscosity, Mechanical Property, etc.)
Control of Molecular Weight	→	**Enhancement of Mechanical Property** (Adhesion, Flexibility, Strength, Elongation, etc.)
Control of Particle Morphology	→	**Core-Shell Type** (Control of Residual NCO Group, Film Property, etc.)
Reduction of Organic Solvent	→	**Environmentally-Friendly Process**

Introduction

Formulation

- Wet-out
- Thickening/Thinning
- Extending with Acrylics
- Fire Retardation
- Pigmentation
- Slip Aids
- Crosslinking

Introduction

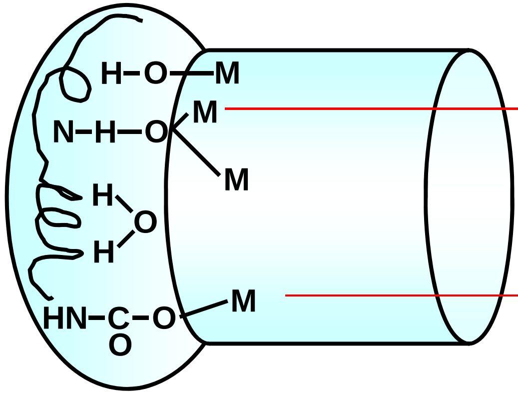
Seven Segmented Water-based Polyurethane Adhesives

Design Requirements

- Viscosity
- Tensile Strength to Substrate
- Service Life
- Working Time
- Curing Time
- Compatibility with Mixed Components
- Low Modulus and Some Elasticity

Adhesion Mechanism in Polymer/Substrate Interface

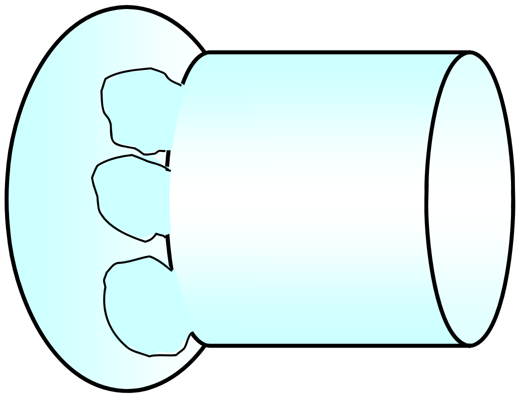
☆ Chemical Adhesion



Hydrogen Bonding to the Substrate Changed Surface Layer (Van der Waals Interaction)

Actual Chemical Reaction of the Excess Isocyanate with Functional Component

☆ Mechanical Adhesion



Flow of the Adhesive into Rough Surface

Material Selection

Polyol Selection

Polyether types: Polyethyleneglycol, Polypropyleneglycol

☆**Advantages**

- Excellent softness and flexibility
- Excellent MVTR figures
- Good hydrolytic stability
- Cheaper in most cases than polyesters
- Low to high molecular weights available
- Better solvent resistant

☆**Disadvantages**

- Reduced adhesion to low energy surfaces
- UV and weather not as good as polyester
- Not as tough as polyester or polycarbonate
- Lower physical properties than polyesters

Material Selection

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Polyol Selection

Polyester types: Polyester Adipate and other copolymers, Polycaprolactone

☆**Advantages**

- Low to high molecular weights available
- Excellent toughness and abrasion resistance
- Highly polar-excellent adhesion to low energy surfaces
- Excellent flexibility and softness
- Better exterior stability
- Better physical properties than polyethers

☆**Disadvantages**

- Less solvent resistant
- Hydrophilic stability not as good as other diols
- Reduced MVTR figures
- Higher raw material cost than polyethers

Material Selection

Polyol Selection

Polycarbonates

☆Advantages

Good hydrolytic stability

Good flexibility

Good abrasion resistance

☆Disadvantages

High cost

Availability

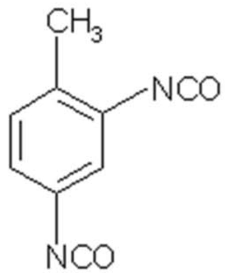
Material Selection

Isocyanate Selection

Aromatic Isocyanate

Benefits
- Inexpensive
- Harder

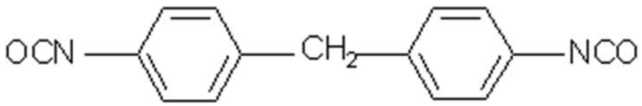
TDI (toluene diisocyanate)



The poor resistance to yellow on exposure to UV light

Applications:
- primers
- wood finishes
- interior finishes (no exposure UV light)

MDI (diphenylmethane diisocyanate)



Using the manufacture of foams and elastomers

Applications:
- interior coatings (floor paints)

Material Selection

Isocyanate Selection

Aliphatic Isocyanate

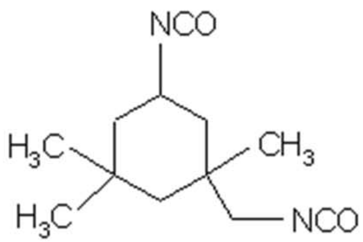
Benefits
- Light stable
- Better flexibility

HDI (hexamethylene diisocyanate)

Form the rigid network with polyols
→ Not used to produce elastomers

Applications:
- high performance coatings (excellent weatherability, chemical resistance and mechanical properties)

IPDI (isophorone diisocyanate)



Two isocyanate groups of different reactivity
- Selective reaction depending on conditions and catalysts

Applications:
- non-yellow coatings (excellent durability)

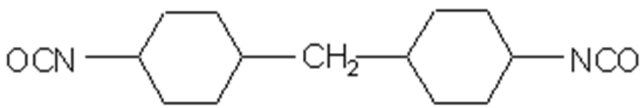
Material Selection

Isocyanate Selection

Aliphatic Isocyanate

Benefits
- Light stable
- Better flexibility

H12MDI
(4,4-dicyclohexylmethane diisocyanate)

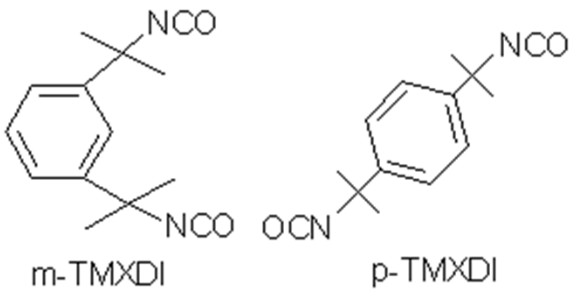


The manufacture of polyurethane elastomers

Light sensitive applications:
- cast elastomers
- optical equipment
- glazing

Biomedical applications

TMXDI
(tetramethylxylylene diisocyanate)

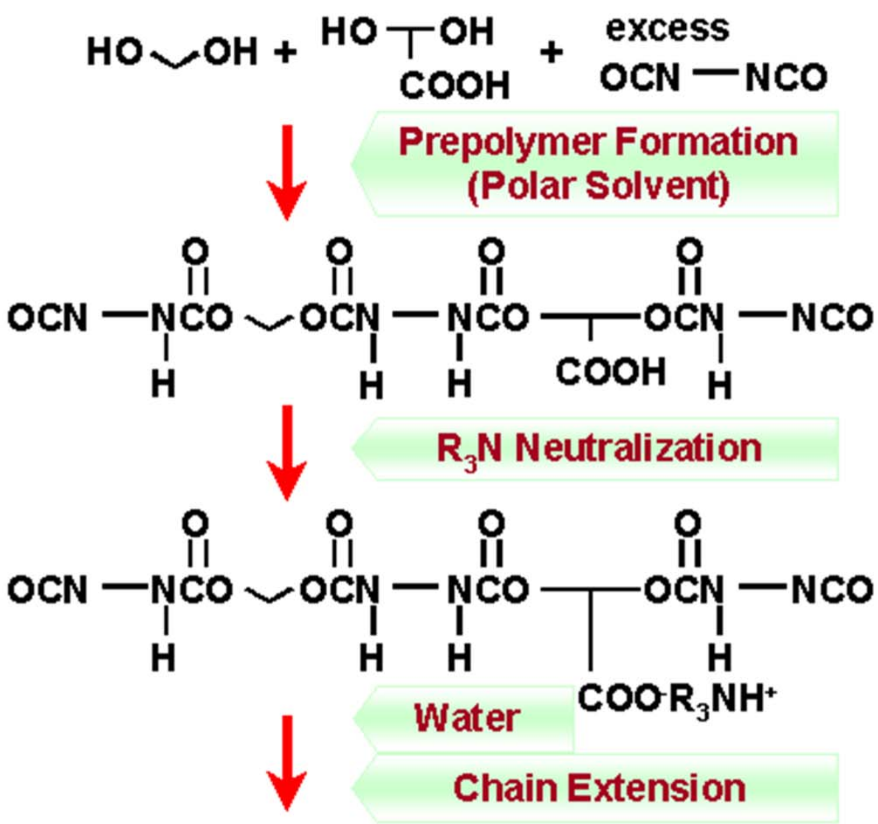


The class of aliphatic isocyanates
- relatively low reactivity
- preparation of low viscosity polyurethane dispersions

Theory

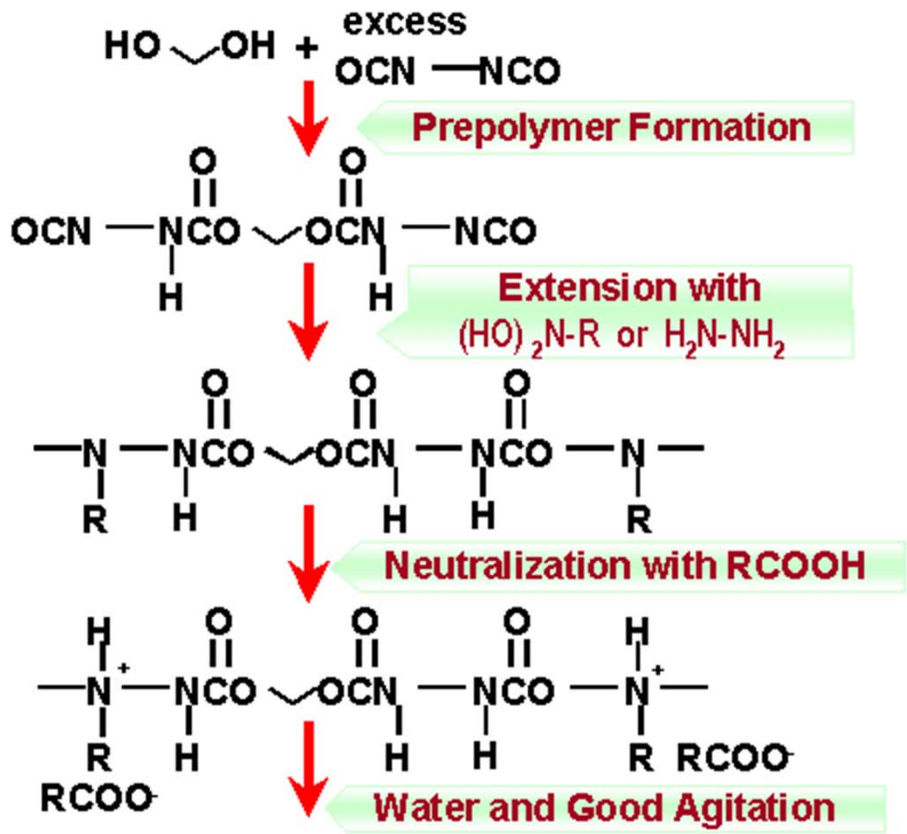
Preparation of Aqueous Polyurethane Dispersion

✲ Anionic Dispersions



ANIONIC URETHANE DISPERSION

✲ Cationic Dispersions

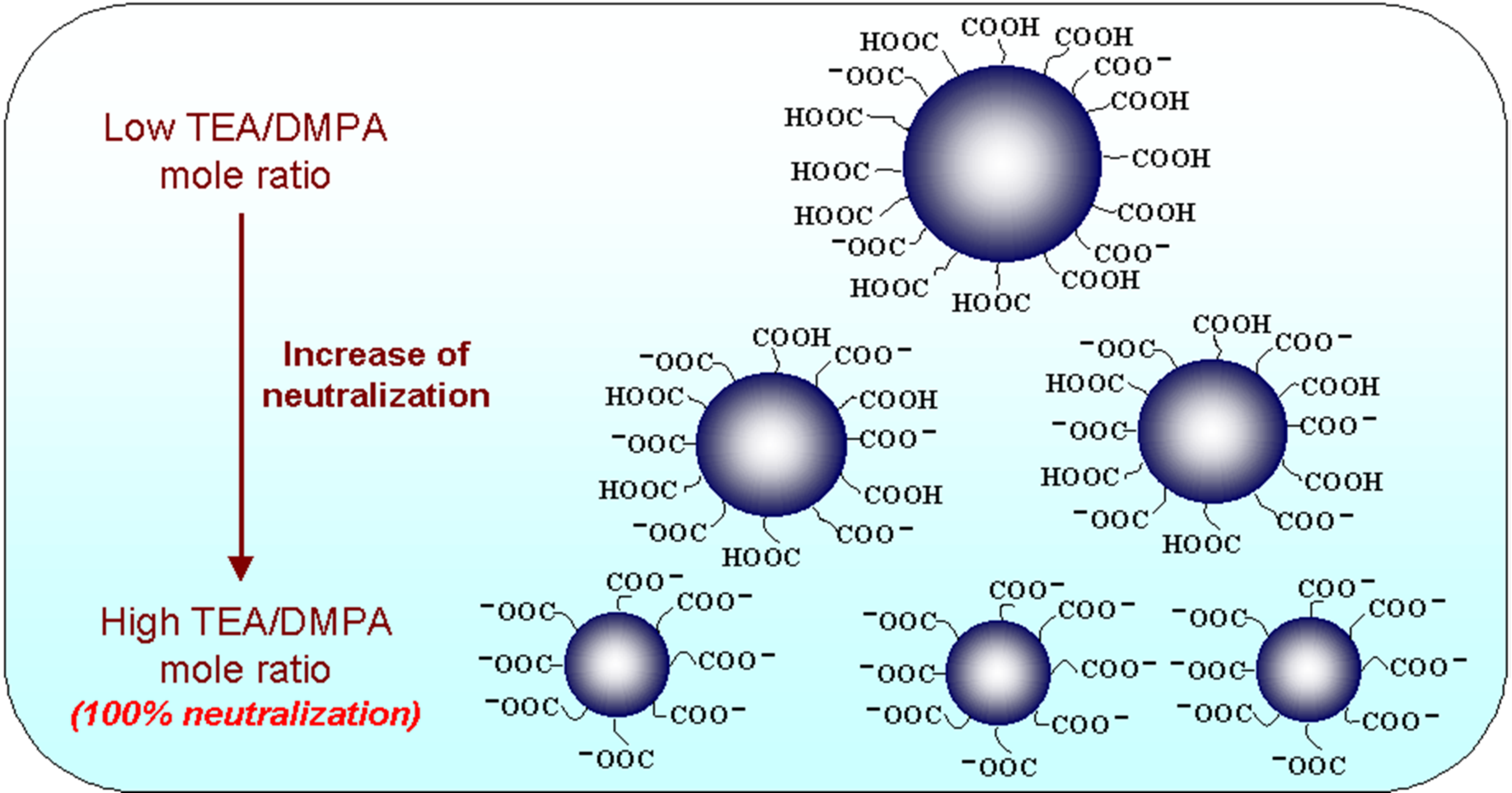


CATIONIC URETHANE DISPERSION

Particle Size Control

Particle Size Control by TEA/DMPA Mole Ratio

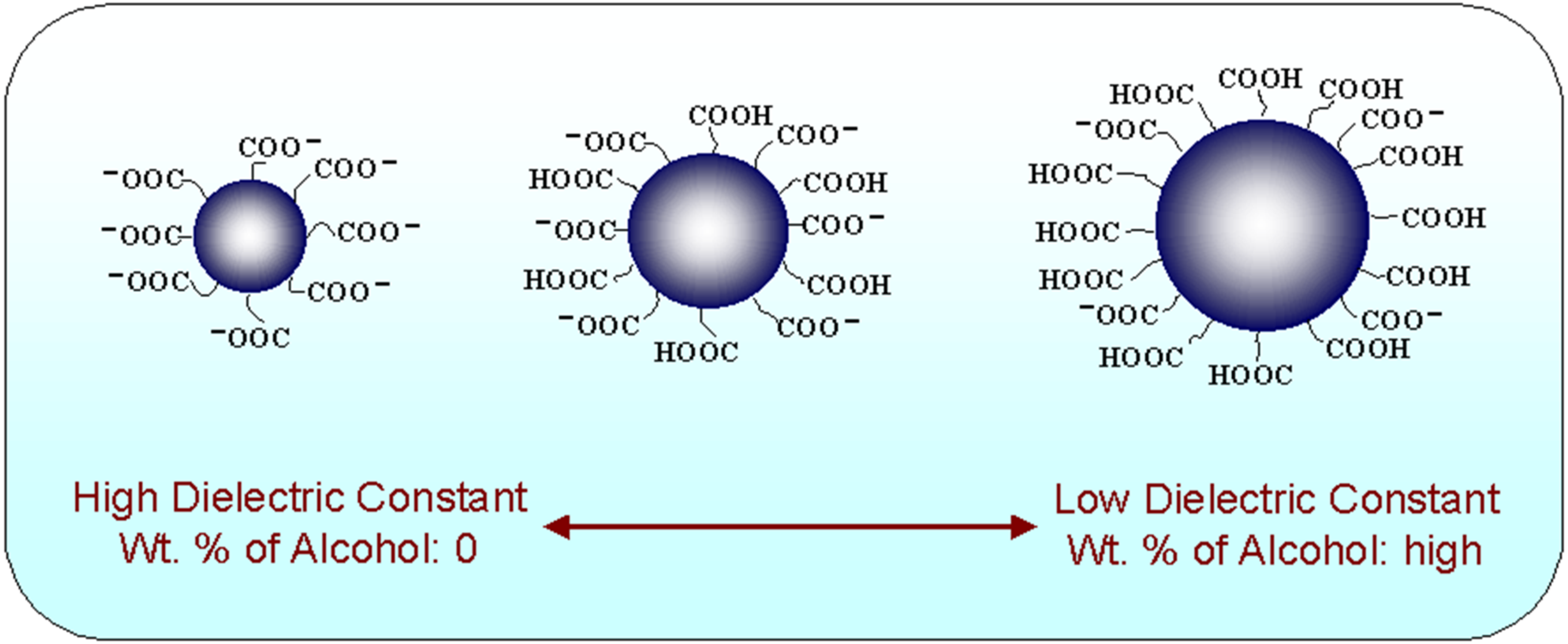
☆Model: Effect of TEA/DMPA mole ratio



Particle Size Control

Particle Size Control by Manipulating Dielectric Constant

☆ Model: Effect of Dielectric Constant



Neutralization of carboxylic group can be affected by the dielectric constant, consequently, particle size of polyurethane dispersion can be controlled by manipulating the dielectric constant of dispersion medium

Members

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피혁 분야

코드번호	지원분야	과제명	RFP
TE-00-03-01-①	원•부재료기술	피혁 가공용 **Polymer** 형태의 가지제 제조 기술 개발	저공해성 원부자재 개발
TE-00-03-01-②	생산공정기술, 원•부재료기술	저오염 피혁용 **Immersion** 염료의 합성 및 적용 공정 개발	
TE-00-04-02-①	재자원화기술	탈모 회수된 **Hair**로부터 **Keratin** 단백질의 재이용 기술 개발	가공부산물 재자원화 기술 개발
TE-00-04-02-②	재자원화기술	제혁가공 부산물로부터 동물성 유지 및 단백질 성분의 회수 및 재활용 기술 개발	
TE-00-04-02-③	생산공정기술	용매 추출과 증류에 의한 유기용제 **DMF**의 회수공정	
TE-00-04-02-④	생산공정기술	폐 **DMF**를 회수하는 용매 추출공정의 개발	
TE-00-02-03-①	원•부재료기술	**Non-PVC**계 인조피혁의 제조 기술 개발	환경친화성 인조피혁 제조 기술 개발
TE-00-02-03-②	생산공정기술	유독성 유기용제를 사용하지 않는 신발창의 접착력 향상을 위한 자동화, 단일화된 저온 플라즈마 장치 및 공정개발	
TE-00-07-04-①	진도지도	피혁가공 공정의 진단지도 사업	피혁가공 공정의 진단지도 사업

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정밀화학 분야

코드번호	지원분야	과제명	RFP
FC-00-3-1	생산공정기술	수분산형 방오가공 불소계 우레탄 개발	환경친화형 수용성 코팅제 개발
FC-00-3-5	생산공정기술	열활성 접착 특성을 갖는 2액 가교형 수성 우레탄 접착제 제조 기술	
FC-00-3-5	원•부재료기술	요소, 멜라민계 대용 합판용 수성접착제	환경친화성 수용성 접착제 개발
FC-00-3-5	생산공정기술	유독성 VOCs가 발생하지 않는 수분산형 신발용 접착제의 개발 및 응용	