IMPACT™ Technology
A Greener Polyether Process

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Polyurethanes
Presentation Overview

- Introduction to Polyether Polyol Market and Applications
- Polyether Polyols Chemistry
- IMPACT™ Technology – Catalyst and Process
- A Greener Polyether Process Technology
- Summary
Introduction to Polyether Polyols

- Main Application Area for IMPACT™ Technology is Polyether Polyols for Polyurethanes.

- Lower Molecular Weight (<10,000 Daltons) Polymers with Terminal Hydroxyl Groups.

- Starters for Polyols are Typically Propylene Glycol, Glycerin, Sorbitol, etc.

- Formed by the Catalytic Reaction of a Starting Polyol with an Epoxide Containing Monomer.

- Other Application Areas for Alkoxylation Technology include Surfactants and various Functional Fluids.
Polyether Polyol Use in Polyurethanes

**Isocyanates**

- MDI
- TDI

**Polyether Polyols**

Long Chain
- $n > 8$
- Functionality = 2 - 6

Short Chain
- $n < 8$
- Functionality = 2 - 8

**Polyurethanes**

- ~ 40% of Polyurethane
- ~ 350 Different Varieties
- Determine Unique Properties

**Polyether Polyols Use in Polyurethanes**

- Polyether Polyols:
  - Approximately 40% of Polyurethane
  - Approximately 350 Different Varieties
  - Determine Unique Properties

**Additives**

- Catalyst
- Blowing Agent

Bayer MaterialScience
Polyurethanes

World Consumption 1970 - 2010

Polyether Consumption ~ 4.6 mT or 10.2 billion lbs/yr

Steady growth at 4% (average) per year

2008: 11.6 mT
Polyurethanes

World Consumption by Application 2008

- Rigid Foam 25.5% (Construction, Insulation)
- Molded Foam 11.0% (Automotive, Furniture)
- Adhesives and Sealants 5.5%
- Elastomers 5.5%
- Others 18.5% (e.g. TPU, Shoes, RIM, Fibers)

Total: 11.6 Mio T

Source: Marketing-Dienste Dreger: div. professional articel, Plastics 10-2008
BMS expansion and estimate
Traditional Polyether Process Chemistry

- Polyether Polyols are made by ring opening polymerization of an epoxide group onto a starter alcohol.
- Main catalyst for the last 50 years is KOH.

\[
\text{OH} \quad \text{OH} \quad \text{OH} \quad + \quad \text{H}_2\text{C} = \text{CH} \quad \text{R} \\
\text{Starter} \quad \text{Glycerin as example} \\
\text{R} = \text{CH}_2 \text{ for Propylene Oxide (PO)} \\
\text{R} = \text{H} \text{ for Ethylene Oxide (EO)} \]

R = CH\text{\_2 for Propylene Oxide (PO)}
R = H for Ethylene Oxide (EO)
Traditional Polyether Process Chemistry

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Polymerizate or Crude Polyol
Traditional Polyether Process Chemistry

Polymerizate or Crude Polyol
Contains between 0.2 to 0.4% KOH
Traditional Polyether Process Chemistry

Crude Polyol with 0.2 to 0.4% KOH

Work-up for K+ Removal

Neutralization

\[ + \text{H}_2\text{SO}_4 \]
\[ + \text{H}_2\text{O} \]

Distillation

\[ -\text{K}_2\text{SO}_4 \]
\[ -\text{H}_2\text{O} \]

Solvent Recovery

Purification

Final Refined Polyether Polyol

Containing less than 10 ppm K+

Polyurethanes

Bayer MaterialScience
KOH Technology

- Advantages
  - Inexpensive catalyst.
  - Wide range of products / Industry standard.
  - Narrow molecular weight distribution.

- Disadvantages
  - Long reaction times.
  - Need to remove catalyst (multi-step, energy intensive).
  - Side reaction that reduces functionality at higher MW.

Polyurethanes
Double Metal Cyanide (DMC) Catalysts

- Zinc Hexacyanocobaltate, originally with glyme as ligand.
- Invented in 1964 by General Tire.

\[
\text{ZnCl}_2 + K_3[\text{Co(CN)}_6] \rightarrow \text{Zn}_3[\text{Co(CN)}_6]_{2.8} \cdot \text{H}_2\text{O.}
\]

Crystalline solid

\[
\text{Ligand} = \text{Glyme}
\]

Amorphous/Crystalline Catalysts

- Advantages of glyme DMC catalyst over KOH:
  - Lower by-product formation (50 – 70% reduction).
  - Faster (shorter cycle times).

- Disadvantages of glyme DMC catalyst over KOH:
  - Cost (Much more expensive than KOH).
  - Difficult DMC catalyst removal step.
IMPACT™ Catalyst

- Developed in mid-1990s by ARCO Chemical (now part of Bayer).
- Order of magnitude improvement in activity over glyme catalyst.
  - Low catalyst levels possible – no catalyst removal required.

Faster Reactivity, Increased Selectivity, Simpler Process:

The Key to a Greener Technology
Polyurethanes

IMPACT™ Catalyst

- Key invention was the novel combination of two ligands.
- Amorphous catalyst structure.

\[
\text{ZnCl}_2 + K_3[\text{Co(CN)}_6] \]

**XRD of IMPACT™**

![Graph showing X-ray diffraction data with peaks for Zinc Hexacyanocobaltate and IMPACT™.](image)

**Chemical Structure**

![Chemical structure diagram showing the combination of ZnCl₂ and K₃[Co(CN)₆] forming Zn₃[Co(CN)₆]₂•ZnCl₄(OH)₂•L₁•L₂•H₂O.](image)

**Polyurethanes**
IMPACT™ Characteristics

Zn₃[Co(CN)₆]₂ • ZnClₓ(OH)ᵧ:L₁:L₂•wH₂O

PO →H₂O Inactive

PO →H₂O

Low Molecular Weight Starter
PG, Glycerin
Catalyst Inhibited
Reversible

High Molecular Weight Starter
Very Active Catalyst
Heterogeneous
Particle Size Decreases

Catalyst undergoes activation in the presence of starter and oxide – MW dependent.

Industrial Challenge: Develop efficient process technology to use low molecular weight starters (Gly or PG) directly.

Polyurethanes
A more efficient process was required for commercial success.

Solution was provided in an inventive process named Continuous Addition of Starter or CAOS.

**Semi-batch process:**

- PO / EO
- Product: 3000 MW
- Starter: 700 MW made via KOH

**CAOS process:**

- PO / EO
- Product: 3000 MW
- Starter: 1000 MW made via IMPACT™

CAOS is a more efficient process technology that eliminates the need for KOH products as starters.
CAOS – Taking Advantage of Unique Kinetics

- IMPACT™ Catalyst can tolerate low levels of glycerin or propylene glycol.
- Conventional polymer kinetics predict broad polydispersity.
- Example with 500 MW and 2000 MW as starter mix.

KOH Catalysis as predicted by conventional polymer kinetics, Flory
CAOS – Taking Advantage of Unique Kinetics

- Example with 500 MW and 2000 MW as starter mix.

KOH Catalysis as predicted by conventional polymer kinetics, Flory

IMPACT™ Catalysis

“Catch-up Kinetics”
“Catch-up” Kinetics Demonstration

Lower Molecular Weight Species React Preferentially Providing a Narrow Polydispersity with Continuous Addition of Starter Technology.
Utilizing Unique Kinetics to Optimize the Process

- Highly active catalyst.
- Ability to add low molecular weight starter during monomer feed.

- Ideal conditions for a continuous reactor system
Utilizing Unique Kinetics to Optimize the Process

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- Ability to add low molecular weight starter during monomer feed.

➤ Ideal conditions for a continuous reactor system

IMPACT™ Continuous Technology

Polyurethanes
Polyether Process Technology Comparison

**KOH, Semi-Batch**
- Starter
- EO, PO Catalyst
- Reactor
- Neutralization or Solvent Addition
- Reactor
- Solvent / Water
- Tank Farm

**IMPACT™, Continuous**
- Starter
- EO, PO Catalyst
- Reactor - CSTR
- Cook out - PFR / CSTR
- Tank Farm

**Saving Areas:**
- Energy / Steam
- Waste
IMPACT™ Technology – Energy Savings

Energy Savings:

- Eliminate heat up and cool down for every batch.
- Reduces steam and cooling water.
IMPACT™ Technology – Energy Savings

KOH, Semi-Batch

Energy Savings:

- Eliminate distillation of water and/or solvent recovery.
**IMPACT™ Technology – Energy Savings**

**KOH, Semi-Batch**

**IMPACT™, Continuous**

Energy Savings:

- Steam and cooling water for batch process.
- Eliminate distillation of water and/or solvent recovery.
- Potential to generate steam with continuous process.

**Reductions** – Steam = 99%, Electricity = 75% and Cooling Water = 88%
IMPACT™ Technology – Waste Reduction

KOH, Semi-Batch

Solvent / Water

Salt

Waste Reduction:
• No aqueous waste generated from solvent removal and recovery.
• No solid waste generated from catalyst removal.

Reductions – Solid waste = 100%, Aqueous waste = 98%
IMPACT™ Technology – Green Highlights

- Case Study: Channelview, Texas facility – one KOH reactor and one continuous reactor making similar products.
- Easy conversion of existing KOH reactor to provide low cost capacity increase while reducing process complexity.
- Very consistent product quality – reliable on-line monitoring possible.
- Little to no by-product formation – lower volatile organic compounds (VOCs) in product.
- Lower un-reacted oxide inventory in the reactor during the reaction further reducing process safety risk.
- Wastewater reduction of 75 million pounds per year.
- Reduction of total energy consumption by 80 percent – this equates to a yearly reduction of 54 million pounds of CO₂.

Polyurethanes
Summary – IMPACT™ Technology: A Greener Process

- **New Polyether Technology Developed and Commercialized.**
  - First Significant Change in 50 Years of Production.
  - Technology Relies on Significant Catalyst Invention.
  - Commercialization Realized with Significant Process Invention.

- **IMPACT™ Technology is a Greener Technology.**
  - Dramatic Reduction in Energy Use and CO₂ Generation.
  - Complete Reduction in Solid Waste.
  - Significant Reduction in Aqueous Waste.

- **Development and Expansion of Technology Continuing.**
  - Licensed to all Major Polyether Producers.
  - Approximately 50% of Bayer’s Polyether Volume has Developed Technology.
  - Recent Extension to High and Low Molecular Weight Polyether Grades.
  - Recent Extension to Incorporate the Use of a Renewable Based Starter (NOP).

- **Over 3 Billion Pounds of Polyether Produced based on IMPACT™ Technology.**

- **Revolutionary Technology that Couples Positive Environmental Effects with Increased Capacity that Optimizes Existing Assets.**
The authors wish to acknowledge the many scientists and engineers that have contributed to the development and commercialization of the IMPACT™ Technology.