High Performance Low VOC Coatings for 2006

Final Report Seminar
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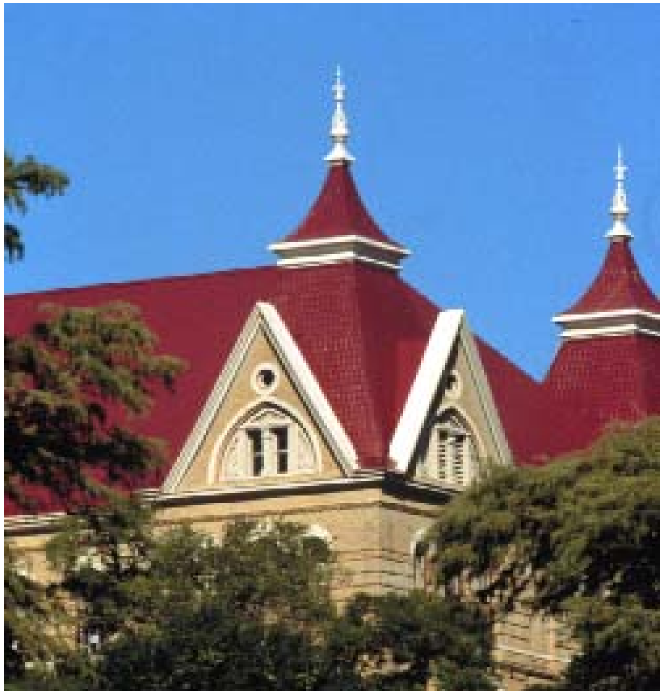

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Sherwin-Williams

Valspar

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- Chirag Shaw
- Bin Zhong

Objectives

- High Performance Alkyd Coatings
  - Container
  - General Metal
  - Wood
- VOC Compliant- target ~100 g/L
- Economical
- Easy to Produce

Approach

HYPERBRANCHED POLYOL

Low Mw polymer

- Low VOC
- Good flow

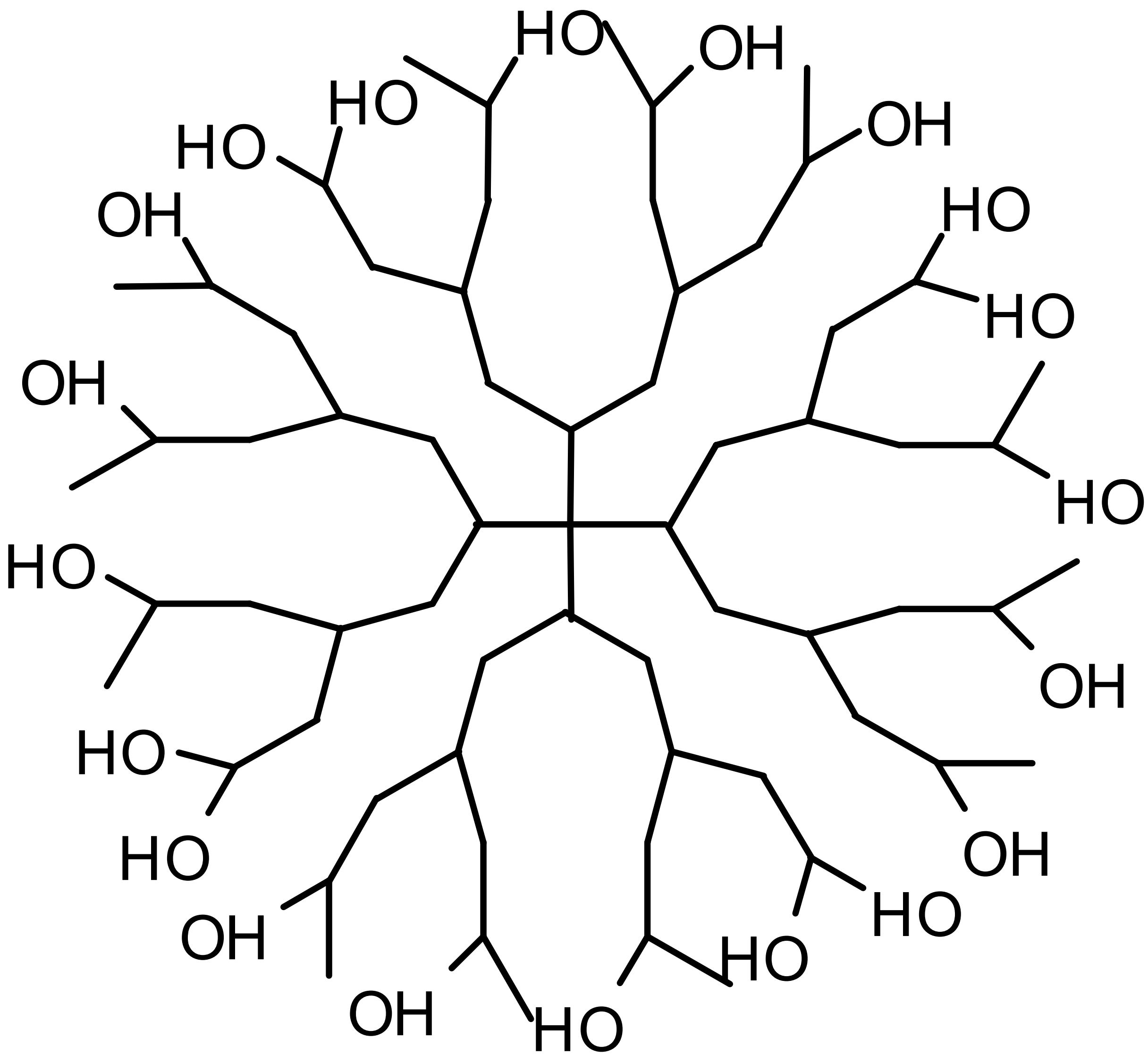
High crosslink density

- Hardness
- Solvent resistance

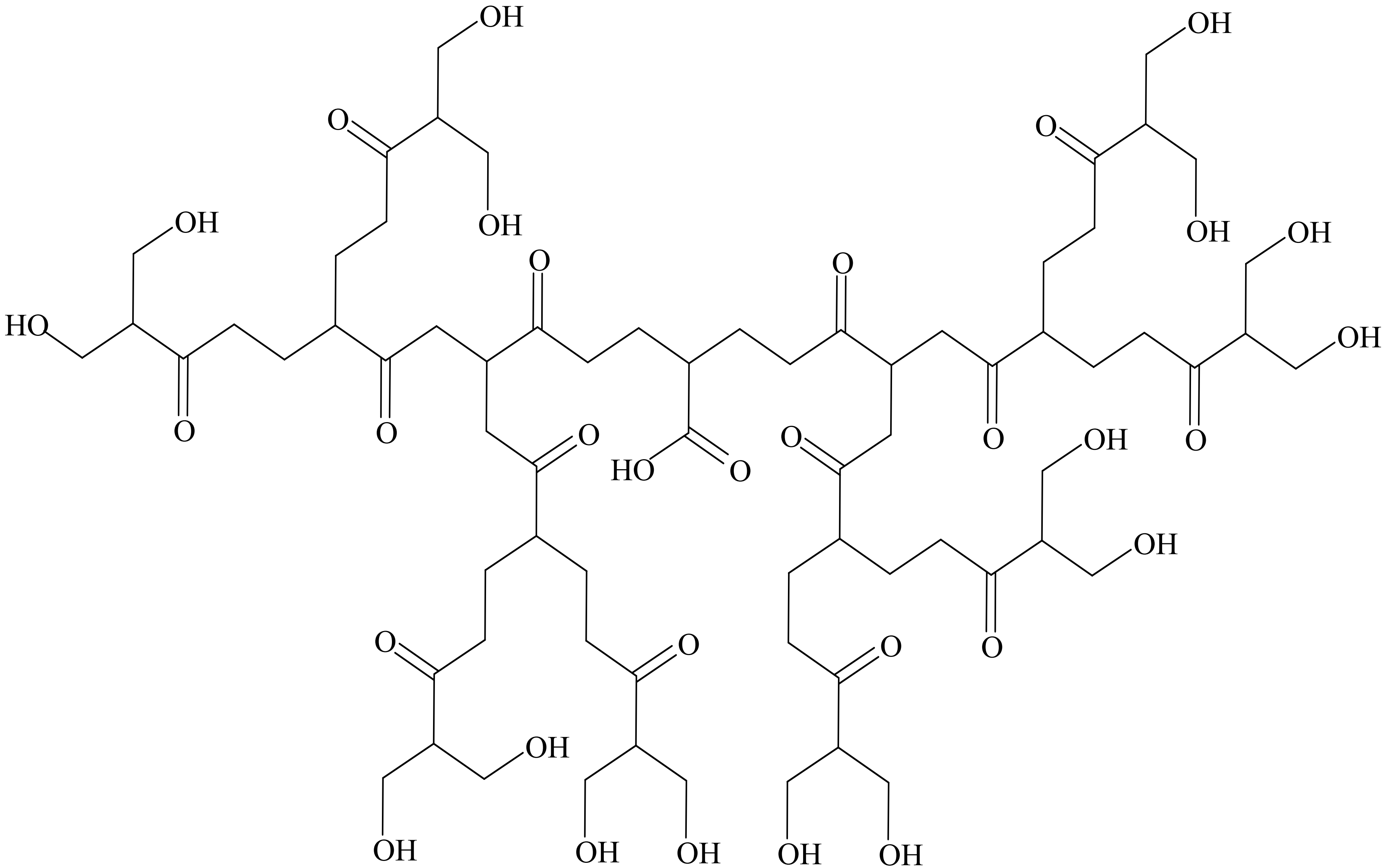
Hyperbranched Polyols

- High functionality, low viscosity
- Lin, et al compared 2 hyperbranched polyols A2 and P2 in alkyd coatings with traditional alkyd resins
  - equivalent or better properties at lower VOC

P2 Polyol



A2 Polyol



TxState Approach

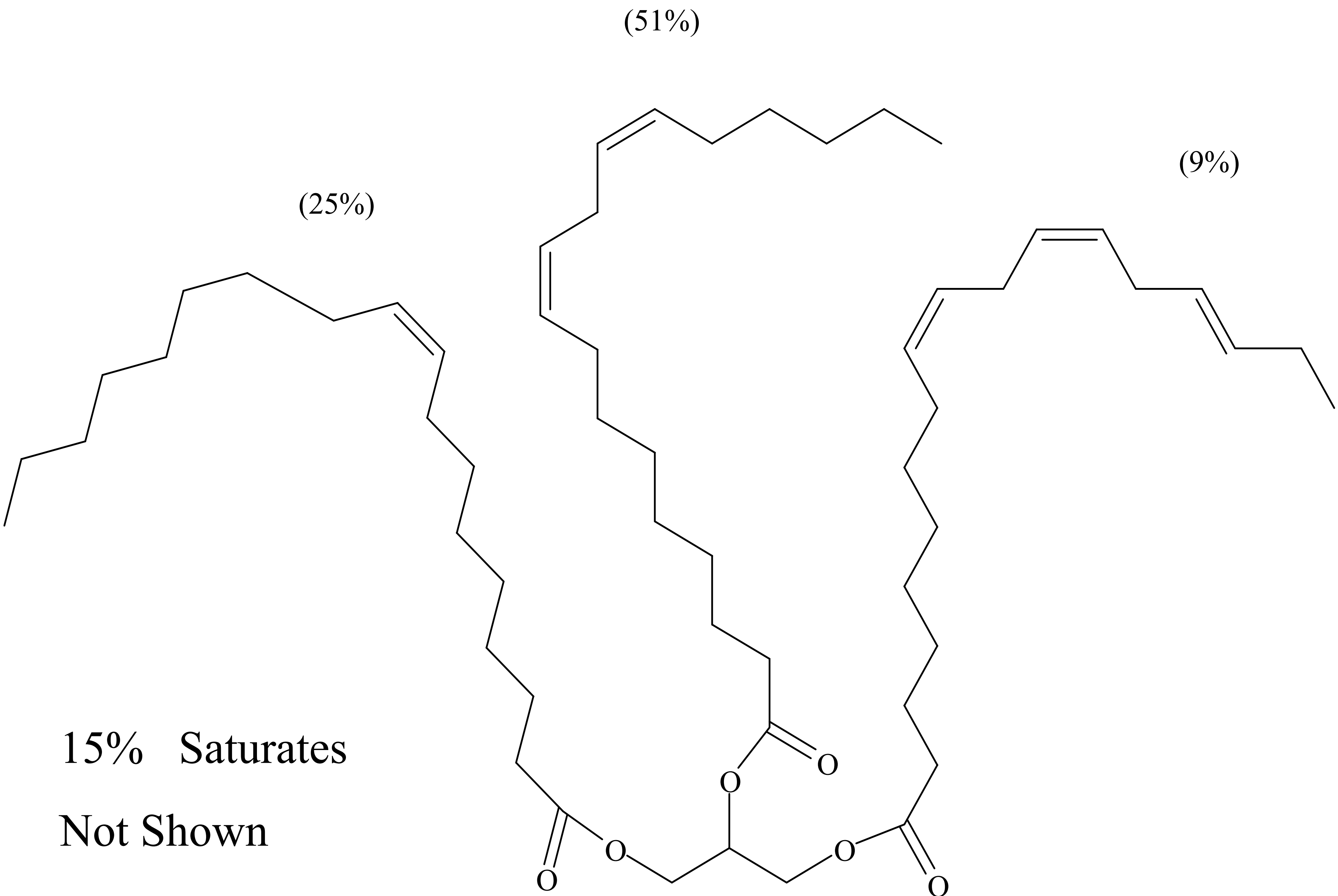
- Phosphate Acid Ester
  - Water dispersible for low VOC
  - Reacts with metal
    - No residual surfactant
    - Adhesion to metal
    - Protects metal

TxState Approach

Soybean Oil Backbone

- Renewable resource
- Inexpensive
- Versatile

Soybean Oil



15% Saturates

Not Shown

Epoxidized Soybean Oil

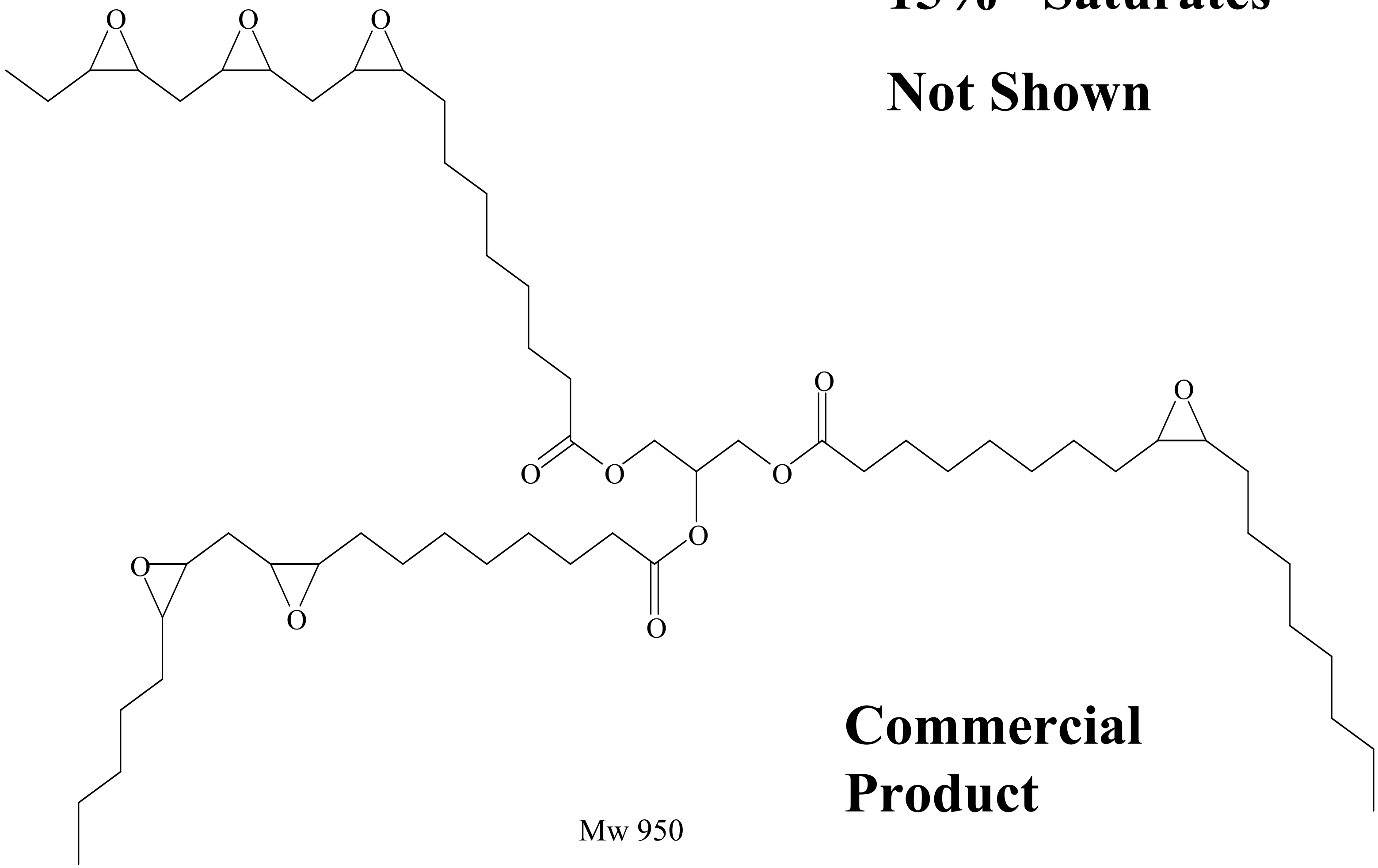
Versatile industrial raw material

- Co-resin with cycloaliphatic epoxies in cationic cured epoxy formulations
- Acrylate esters used commercially in UV cured free radical formulations
- **Converted to the corresponding glycol by hydrolysis to make a variety of polyols**

Epoxidized Soybean Oil

15%   Saturates

Not Shown

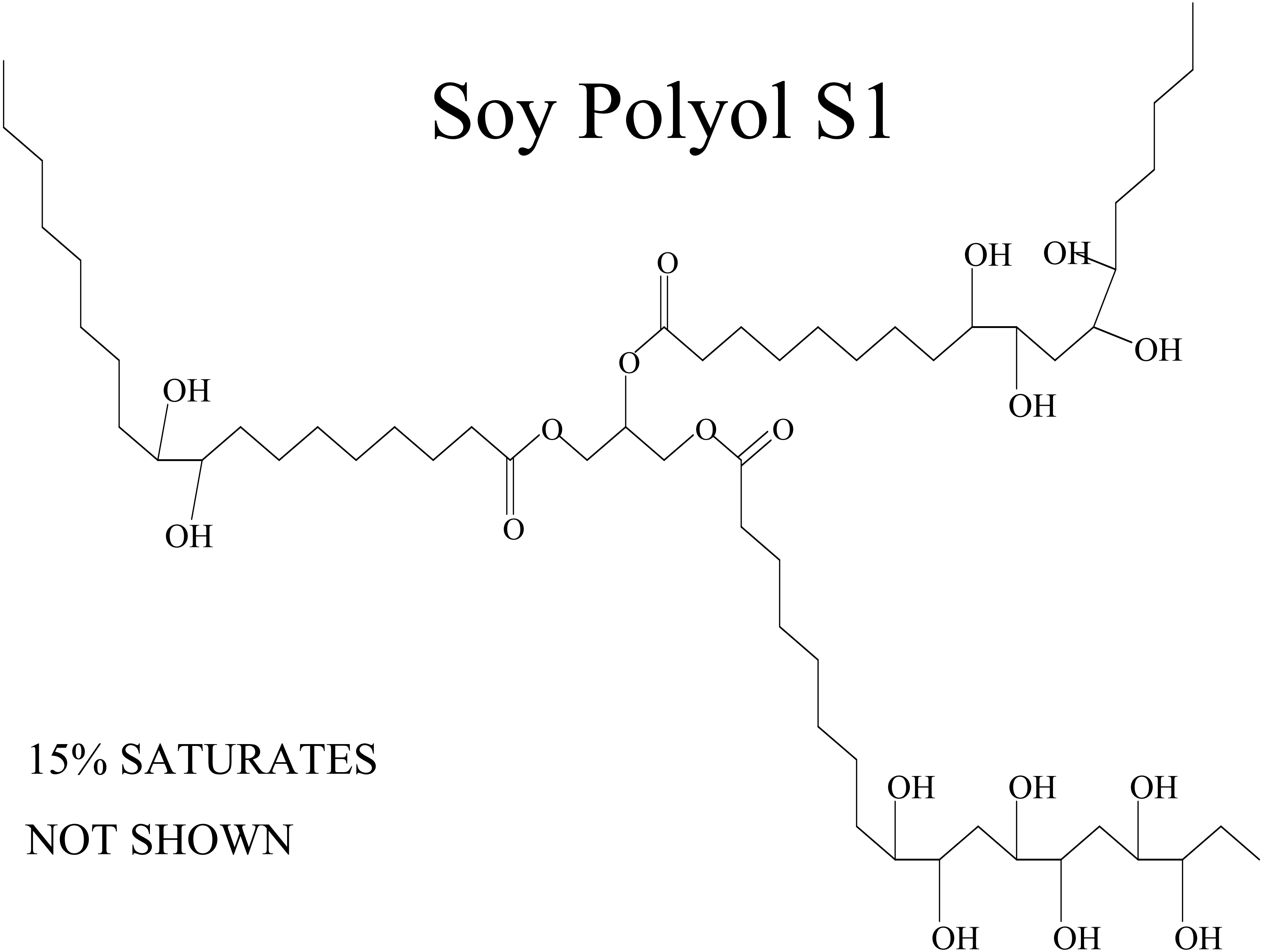


Commercial Product

Mw 950

average about 4.5 functional

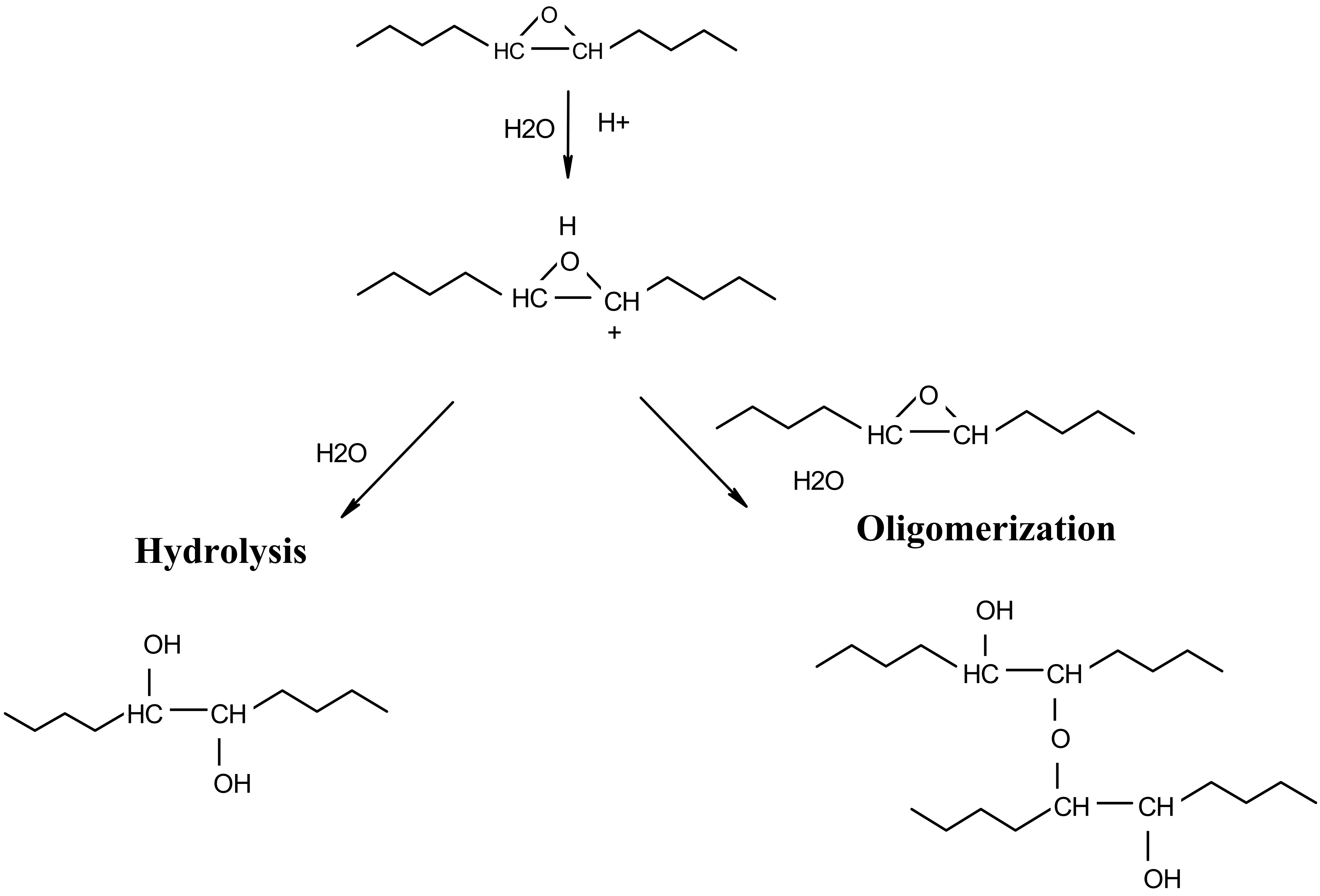
Soy Polyol S1

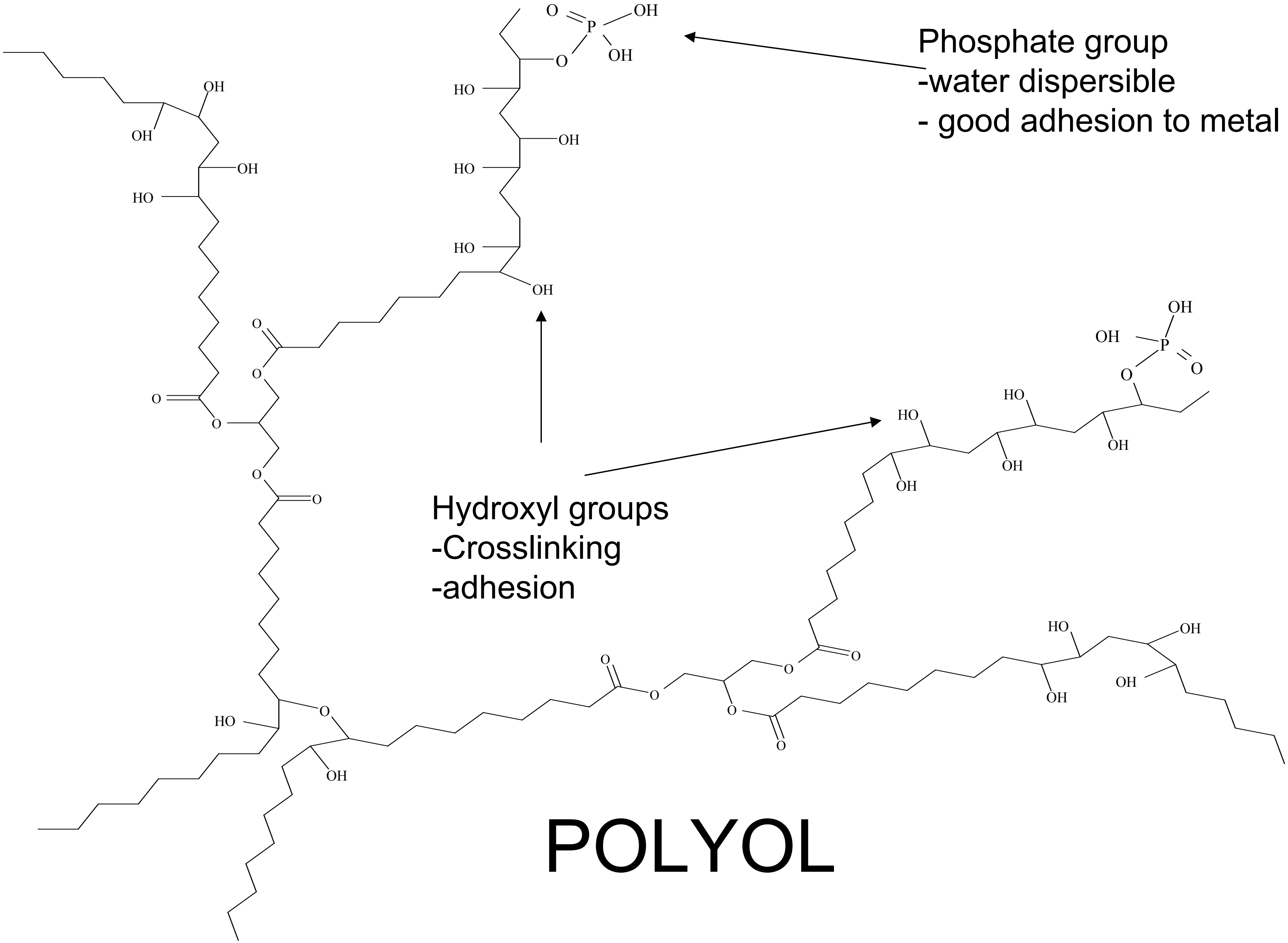


15% SATURATES

NOT SHOWN

COMPETING REACTIONS




Phosphate group
-water dispersible
- good adhesion to metal
Hydroxyl groups
-Crosslinking
-adhesion

POLYOL

KEY FEATURES & BENEFITS

PHOSPHATE GROUPS :

- IMPROVED ADHESION
- CORROSION RESISTANCE
- WATER DISPERSIBILITY

KEY FEATURES & BENEFITS

HYDROXYL GROUPS

- CROSS-LINKING SITES
- ADHESION TO METAL SUBSTRATE
- ENHANCED COMPATIBILITY WITH WIDE RANGE OF RESINS / SOLVENTS

KEY FEATURES & BENEFITS

ABSENCE OF UNSATURATION

- **NON-YELLOWING**
- **UV RESISTANCE**

LOW VISCOSITY

- **LOW VOC COMPOSITIONS**

- **GOOD FLOW AND LEVELLING**

Objective

Investigate Effect of %PO4 on:

- Dispersibility of Soy Polyol
- Salt Fog Resistance of Soy Polyol Coatings

Goals

POLYOL Hyperbranched Resins with 1%-10% Phosphoric Acid Ester

INVESTIGATE:

- Dispersibility vs. [% PO4 Acid Ester]
- Corrosion Resistance of Coatings

Experimental

- Polyols with 0-32% phosphate substitution were made.
- Alkyd Resin. The conventional linear alkyds, Beckosol™ 12-054 (50% solids), 12-021 (60% solids), and 11-045 50% solids, air dry, medium oil) were supplied by Reichhold, Inc. The waterborne alkyd Chempol 810-0432 71% solids, AV=47) was obtained from Atofina.
- Crosslinker. Aminoplast crosslinker Cymel™ 303 (Cytec) and Resimene 747 (Solutia).
- Substrate. Test panels were B-1000 from Q-Panel,
- Cure Conditions. 130-170°C for 15-30 minutes in an electric forced air oven.

Experimental

Coating characteristics and dry film properties were determined with the following tests:

- Dry times determined according to ASTM D1640-83 using a B-K Drying Recorder
- Weight per gallon (ASTM D1475), Non Volatile by Weight (ASTM D2369), VOC (ASTM D3960-87), Pencil Hardness (ASTM D3363-74), Crosshatch Adhesion (ASTM D3359-90), Impact Resistant (ASTM D2794), and Viscosity (Brookfield viscometer) were also determined.

Soy Phosphate Stoichiometry

- H_3PO_4 Mw 98
- ESBO Mw ~ 900

~7% Oxirane ~ 4.2 Epoxies per molecule

%PO4	1	3	8
% Sub	3	9	25
PO4/Soy	0.15	0.5	1.1

Effect of Phosphate Ester Content on Resin Dispersibility

<u>% PO4</u>

3.5% stable dispersion with amine

>8% dissolved in water with amine
(clear solutions)

Table 1. POLYOL Dispersibility vs. %PO4

%Acid	Acid Value	Dispersion Characteristics
1.0	13	unstable
2.5	21	unstable
3.0		
3.5	32	Stable
4.0		
5.0	46	Stable
8.0	69	Clear solution
10.0		Clear solution

Formulation

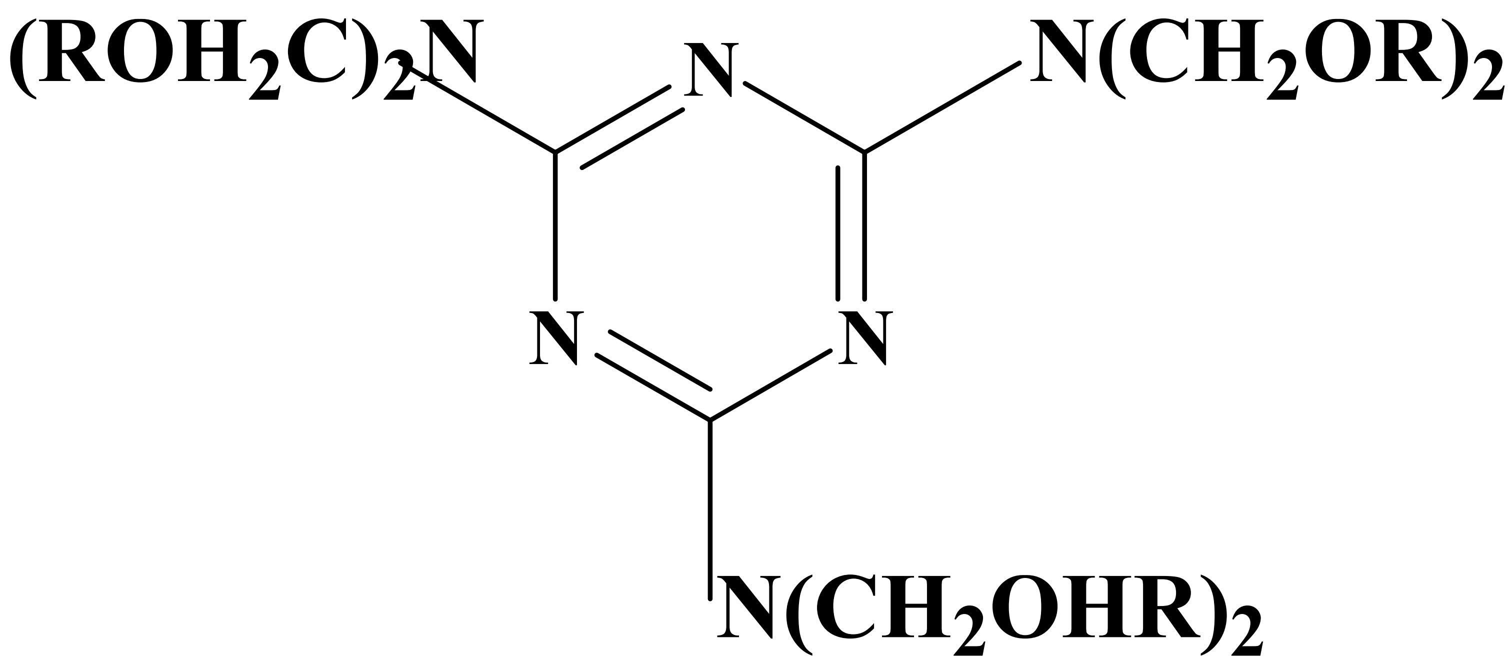
- POLYOL Replaced Short-oil Alkyd
  - 0 to 100%

- Varied RESIN/MF ratios
  - 20-50% MF for POLYOL
  - 15-20% MF for short-oil alkyds

Crosslinking

HMMM crosslinker-

low tendency to self-condense, high-solid systems, and long shelf-life



Film Properties Of POLYOL / HMMM Solvent Compositions

	POLYOL				ALKYD
% HMMM →	50	40	30	20	18
DFT (mils)	1.1	0.9	1.1	1	0.6
Pencil Hardness	3H	3H	H	F	3H
Impact (D/R)	80/10	85/10	160/85	140/140	160/130
Adhesion %	35	75	95	85	90
MEK DR	>200	>200	>200	50	>200
VOC, g/L	200				445

Commercial Waterborne Alkyd Film Properties

% HMMM	20	15
Dry Film Thickness	0.90	0.80
Pencil Hardness	2H	2H
Impact Resistance	110/30	130/40
MEK Double rubs	>200	>200
Adhesion, %	> 95	> 95

140ºC/30 min

POLYOL Coating

	POLYOL-3.5	Container Enamel*
Film Appearance	-Both Smooth and Glossy- -Free from any film defects-	
Pencil Hardness	H	H
Impact Resistance	160/100	160/140
MEK DR (pass)	50	75
Adhesion	4B	4B
VOC, lbs/Gal	1.45	2.7

* Commercial product being used

Effect of Phosphate Ester Content on Corrosion Resistance

- Crosslinker Higher for POLYOL
  - POLYOL (3-8% PO4) 30% HMMM

    (**<u>All Waterborne Formulations</u>**)
  - Commercial resins 15% HMMM

    (One Solvent/ One Water Formulation

- Cured at 170 ºC

Effect of Phosphate Ester Content on Corrosion Resistance

Theoretically

- More PO4 = better adhesion and corrosion resistance

  <u>until surface saturated with PO4/POLYOL</u>

- More PO4 would lead to water sensitivity of the coatings

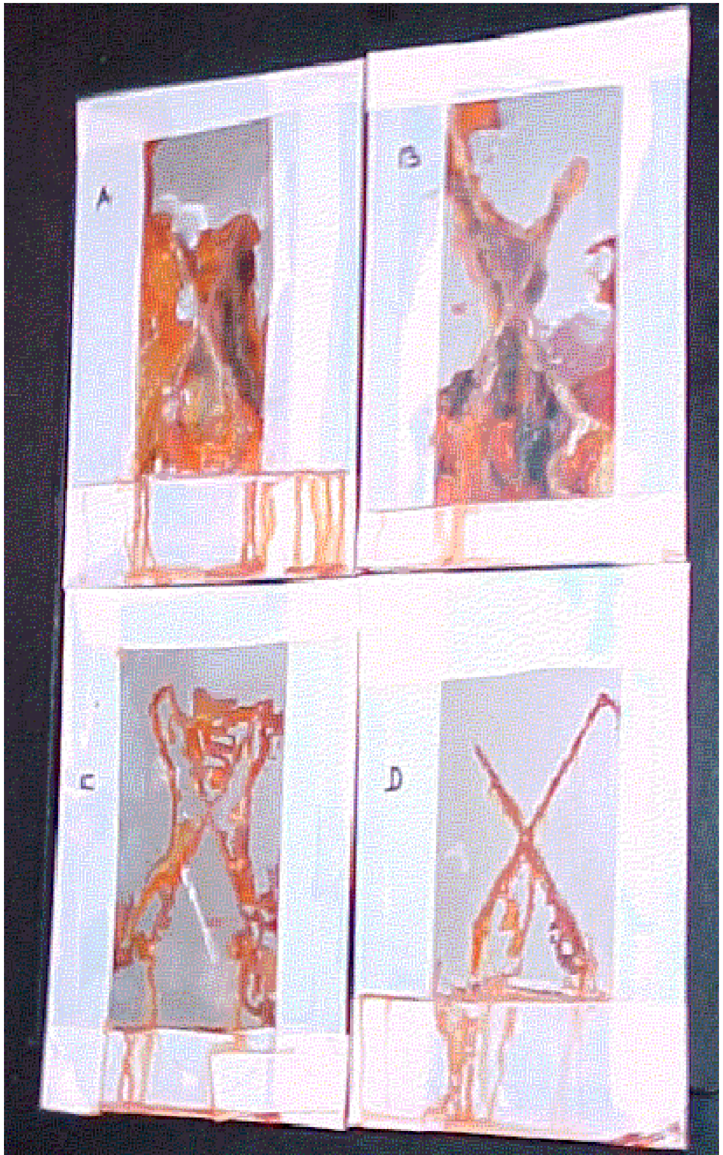
Effect of Phosphate Ester Content on Corrosion Resistance

- No corrosion inhibitors were used in this comparison

SALT FOG CORROSION TEST (ASTM B-117, 96 hrs exposure)

A

B



C

D

A– Solvent Control
B- Water Control

C- SOPEP-3 D-SOPEP-3.5

E- SOPEP-5 F-SOPEP-8

E F

Conclusions

Soy Phosphate Ester POLYOL

- Film-forming component of waterborne and solvent bake coatings
- Hyperbranched = performance, low VOC
- Soy = reduced cost
- Percent acid PO4 in POLYOL can be optimized for good salt fog resistance

QUV Results

- POLYOL3.5 coatings
  - much better resistance to yellowing and chalking than commercial short oil alkyd

- Absence of aromatic acid improves weathering resistance of POLYOL coatings

Task Results

<u>Task 3-</u> <u>Commercial POLYOL Evaluations</u>

- Paint company representatives contacted re: POLYOL sampling and test program

- Cooperating companies performed an initial evaluation of the performance of POLYOL

- Arkema/Cook Composites and Polymers, Precision Coatings, Rohm & Haas, Dunn Edwards, Valspar, Niemann & Associates, Sherwin-Williams, National Ink

Task Results

Task 4-POLYOL Modifications

Modifications made to POLYOL to improve:

- Adhesion
- Compatibility with resins
- Low temperature cure

Task Results

Task 4-POLYOL Modifications

Modifications included

- Optimization of phosphoric acid content for adhesion
- Addition of aromatic acids and diacids to the oxirane group to make new resins
- Improvements to the process used to make POLYOL
  - solventless process for POLYOL validated
  - solvent process developed for high phosphate, low viscosity polyol.

Task Results

Task 6-Verification of POLYOL Performance

- Quality and performance of POLYOL verified at every scale-up operation
- Process conditions affect POLYOL viscosity
- Formulation properties, VOC levels, curing properties, and physical properties of paints made from POLYOL were evaluated

Task Results

Task 7-Production of Prototype Resin

- A prototype alkyd resin made from POLYOL was produced
- POLYOL is a suitable coating binder resin for many applications.
- Reaction of the oxirane group with aromatic acids prior to hydrolysis to POLYOL was evaluated to make resin
- Process for making low viscosity, highly-branched alkyd resins from POLYOL by addition of aromatic acid

Task Results

Task 8-Prototype Paint Development

- Prototype paints for metal and wood were developed
- Prototype paints formulated to meet specifications for specific applications (i.e., drum coatings, wood coatings, direct to metal (DTM) were formulated at the request of the demonstration partners

Task Results

Task 15-Precision Coatings Demonstration

- Precision Coatings conducted a test program on commercial containers to demonstrate the feasibility of using coatings made with POLYOL
- A DEMONSTRATION was made on a container production line in the Southern California
- 1.45 lb/Gal VOC (174 g/L)

Task Results

<u>Task 16-Other Demonstrations</u>

- Valspar
- Sherwin-Williams
- Dunn-Edwards
- Rohm-Haas
- Cook, Composites, and Paints

<u>Task 17-Data Reduction</u>

Properties of SOPEP 3.5 Pilot Resins

VISCOSITY

(40^{O}C) CPs BROOKFIELD VISCOMETER

RPM	116-119	116-128	116-129
100	18450	11925	8550

Properties of SOPEP 3.5 Pilot Resins

Acid value and % Oxirane

Sample Code	Acid Value, mg KOH/gm	% Oxirane
116-119	55.62	0.01
116-128	82.83	0.01
116-129	104.53	0.04

Properties of SOPEP 3.5 Pilot Resins

The scale-up procedure was supplied by Texas State University

- Oxirane was consistent
- Viscosity and Acid number varied with solvent removal procedure

- Baking <u>116-119</u> formulation 10º higher/10 min longer ~ matched properties of lab sample

- 5 gallon sample was released to Precision Coatings.

COMPARISION RESULTS OF THE ARKEMA SAMPLES

Properties	SOPEP 3.5 LAB result	Control Lab result	116-119	116-128	116-129	Control
Film appearance	Smooth glossy	Smooth glossy	Smooth glossy	Smooth glossy	Smooth glossy	Smooth semi gloss
Pencil Hardness	H	2H	H	H	H	2H
Impact resistance D/R	160/100	110/30	160/112	160/136	156/128	104/28
MEK double rub	50	>200	150	50	150	>200
Adhesion (cross hatch)	4B	3B	1B	2B	4B	4B
DFT (mil)	1.0	1.0	0.3	0.3	0.3	0.3
Salt-fog resistance (B-117/96 hrs.)	6	3	5	3	4	6

COMPARISION RESULTS OF THE PILOT SAMPLES

Conclusions

Pilot sample has inferior adhesion in 1 mil coatings, comparable for 0.3 mil coatings.

The other physical properties are comparable

Curing the 1.0 mil coatings at higher temperature and longer time gave good adhesion results.

Demonstration

Precision Coatings- Bake Coatings

- Low bake coatings
  - lab data looked good
  - <100 g/L VOC
- Precision Coatings
  - Confirmed Performance in Lab
    - SOPEP1.0 confirmed
    - SOPEP 3.5 confirmed

Demonstration #1

Precision Coatings- Bake Coatings

- **Arkema Scale-up POLYOL**
  - **10 gallon reactor**
  - **SOPEP1.0**
    - **Good in lab tests**
  - **SOPEP3.5**
    - **OK in lab tests with adjustments**

Demonstration Project

Precision Coatings- Bake Coatings

Precision Scale-up formulation

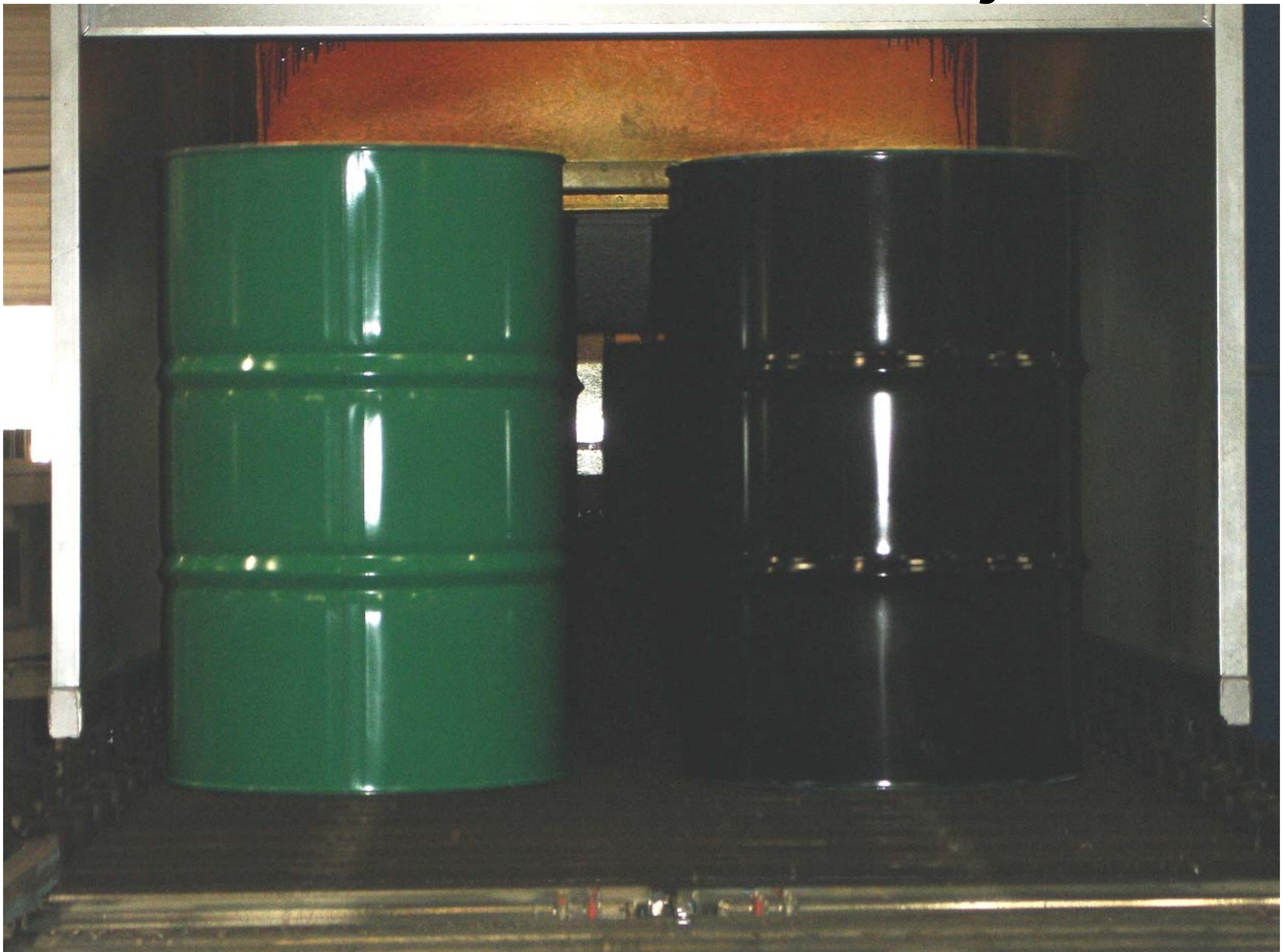
- **SOPEP1.0** **Good for low VOC**
- **SOPEP3.5** **Low VOC**
  High Gloss
  MEK resistance
  Adhesion

Demonstration Project

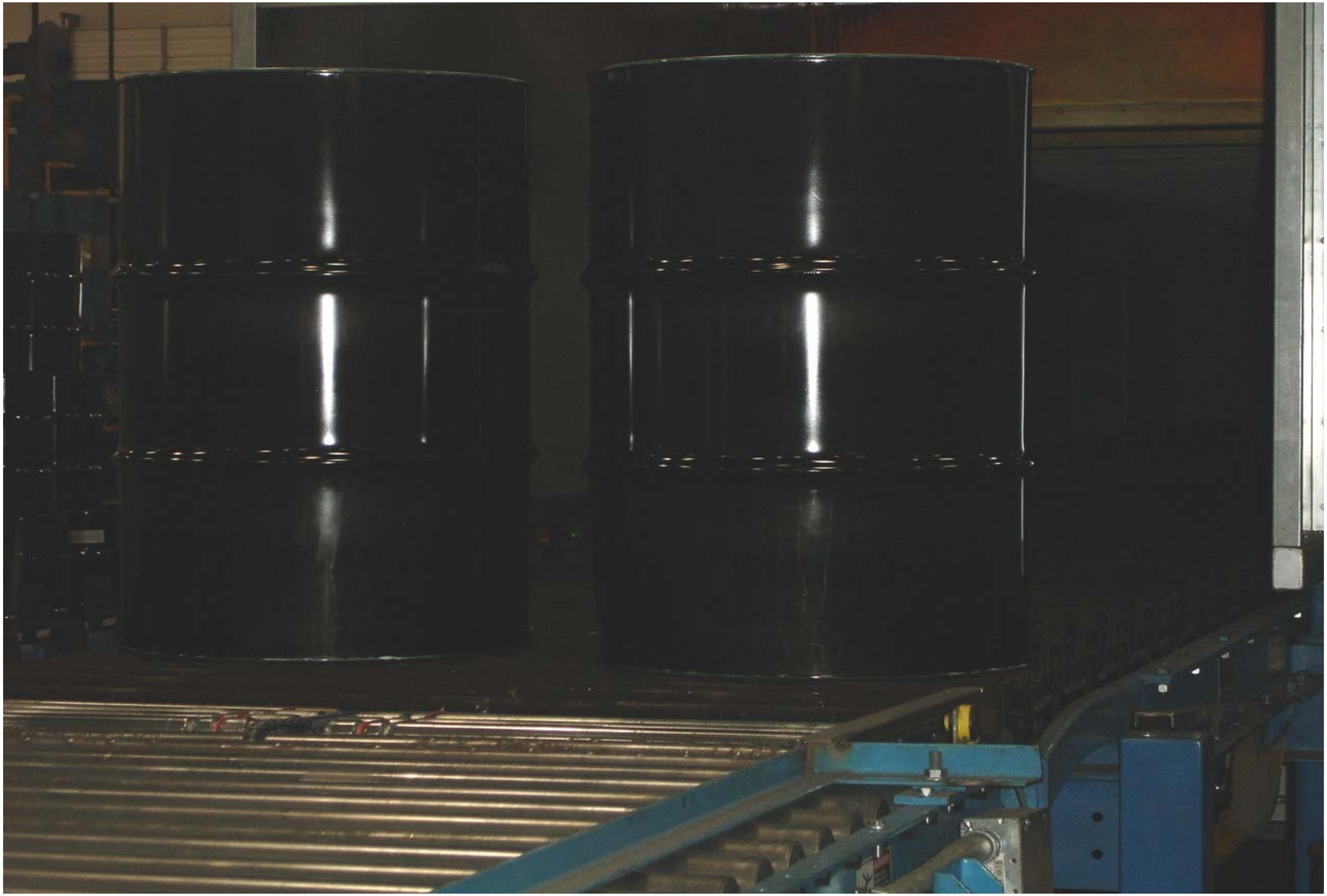
- **Commercial Plant Line**

Demonstration Project

Demonstration Project



Demonstration Project



Demonstration Project

Demonstration Project

Evaluation of Containers Off-Line

Demonstration Project

- Coating looked good
  - Good gloss
  - Good flow
  - Good adhesion
  - Good MEK resistance
  - 1.45 Lb/Gal VOLC

Demonstration Project

- Coating had some streaks
  - Due to poor wetting
  - Will be corrected by re-formulation
- Precision Coatings Plans to Commercialize
  POLYOL Based Low VOC Coatings

Project #2

- Niemann & Associates
- Coatings and Adhesives for “Green”Products
- Sampled 1.0 and 3.5
- Requested Drum Quantities
  - Not available for months
- Gave NA POLYOL synthesis procedure
- Customer Demonstration- canceled

Project #3

Cook, Composites, and Polymers (CCP)

Evaluated POLYOL lab sample

- POLYOL evaluated as reactive diluent in high solids polyester baking enamel
- POLYOL drop-in:
  - reduced yellowing in QUV testing
  - reduced gloss retention
  - <u>slower polyester cure</u>
    - needed +25ºC higher cure for physicals and salt spray resistance

Project #4

Rohm and Haas- Bake coatings

Evaluated performance of SOPEP1.0

- **Tested as low VOC coalescent**
  - **did not lower the MFFT of latex**
- **Tested as as pigment dispersant**
  - **not much success**

Project #5

Dunn-Edwards

- Air dry Direct-to Metal coatings
- No interest in Bake coatings
- No interest in 2-K
- A 1-K PU formulation was prepared:

- Low MEK resistance (25)

Project Milestones Status

Commercial Demonstration- done

Precision Coatings

Technology Transfer-

Presentations

AOCS

Waterborne Conference

ACS

FSCT

Publications- 1 Published (JCT, April 2006)

2 in progress

Project Milestones Status

Commercial Demonstration- done

Precision Coatings

Commercial Plant Line