

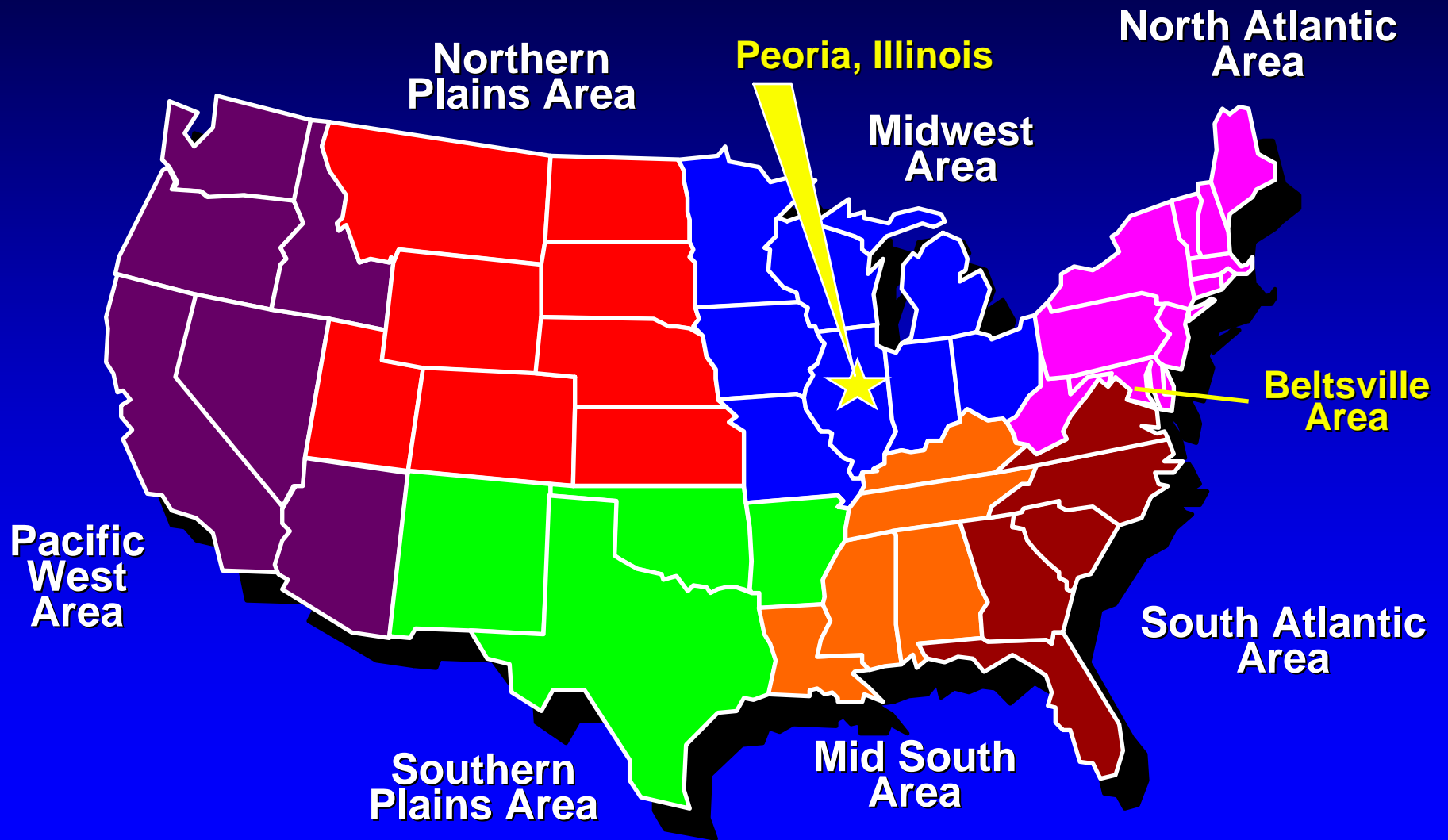
The Use of Vegetable Oils in Biobased Products



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Agricultural Utilization
Research
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Agricultural Research Service Area Organization





The NCAUR Mission

- ***Invent new uses*** of agricultural commodities for industrial and food products
- ***Develop new technology*** to improve environmental quality
- ***Provide technical support*** to Federal regulatory and action agencies

NCAUR Research Units

- **Bioproducts and Biocatalysis**
- **Cereal Products and Food Science Research**
- **Crop Bioprotection Research**
- **Fermentation Biotechnology Research**
- **Food and Industrial Oils Research**
- **Microbial Genomics and Bioprocessing Research**
- **Mycotoxin Research**
- **New Crops and Processing Technology Research**
- **Plant Polymer Research**



Food and Industrial Research Unit USDA, ARS, NCAUR, Peoria, IL

- **Chemical Systems for the conversion of vegetable oils to industrial products.**
- **Vegetable oil-based alternative to diesel fuels, extenders and additives**
- **Optimizing flavor quality and oxidative stability of commodity vegetable oils**
- **Functionality, structure, and quality interactions in food oil systems**

Chemical Systems for the Conversion of Vegetable Oils to Industrial Products

Objective:

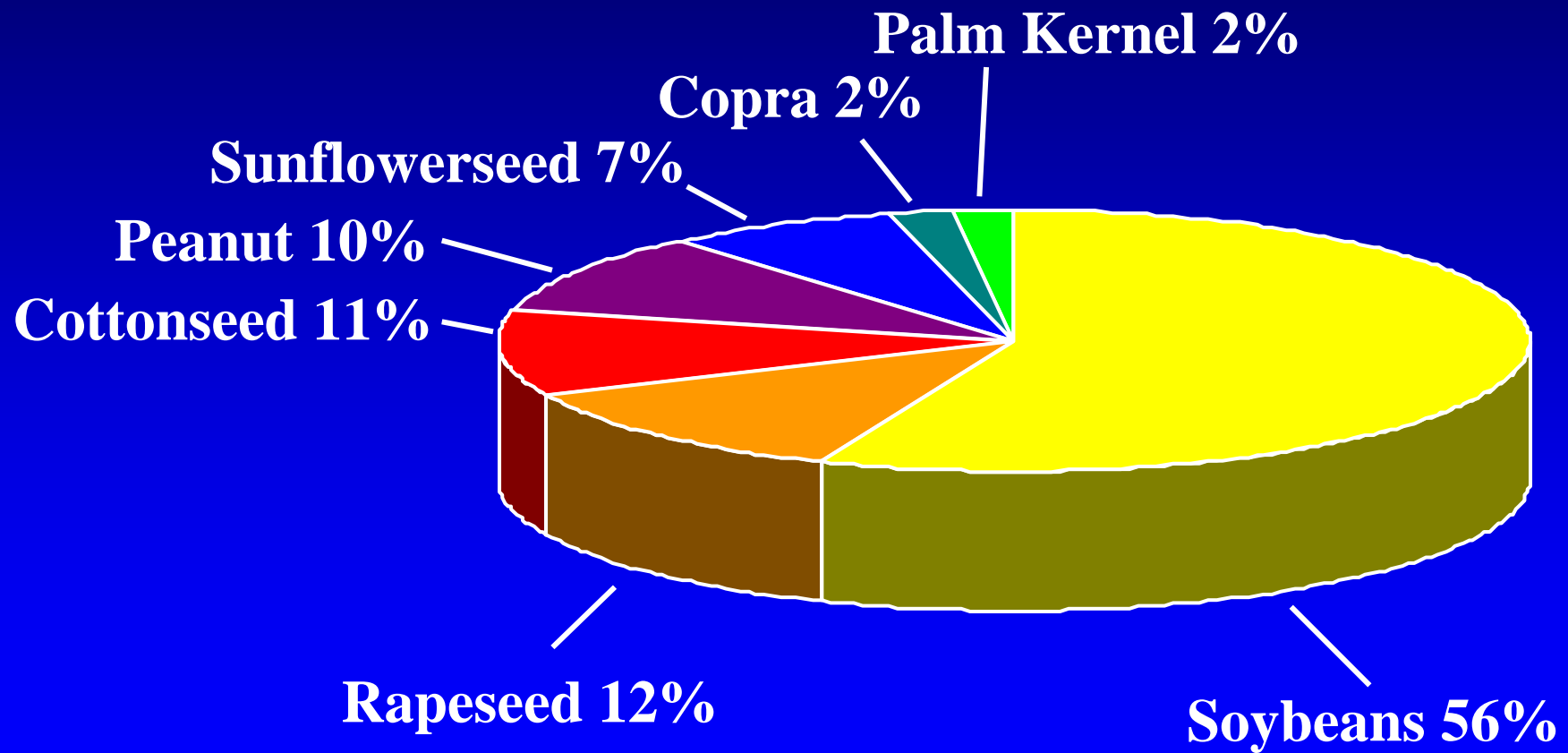
Investigate and develop economically feasible new industrial products from vegetable oils (with emphasis on soybean oil) and thus, expand their domestic and export markets.

Focus:

Modifying chemical and physical properties of vegetable oils to enhance their use as additives, or major components of: Lubricants, Inks, Surface Coatings, Fuels, Polymers, Composites, Surfactants and other Industrial Chemicals

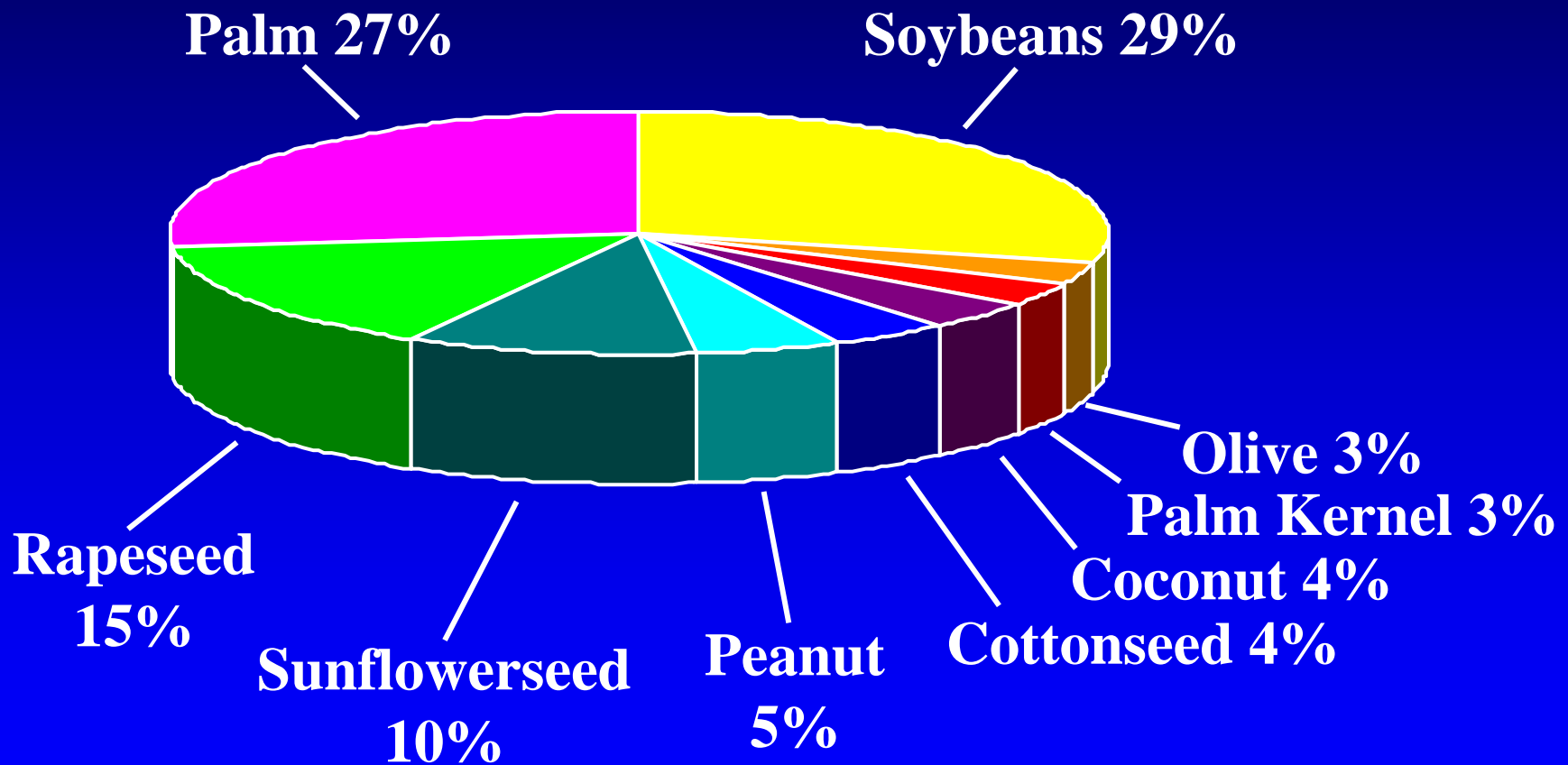


World Oilseed Production



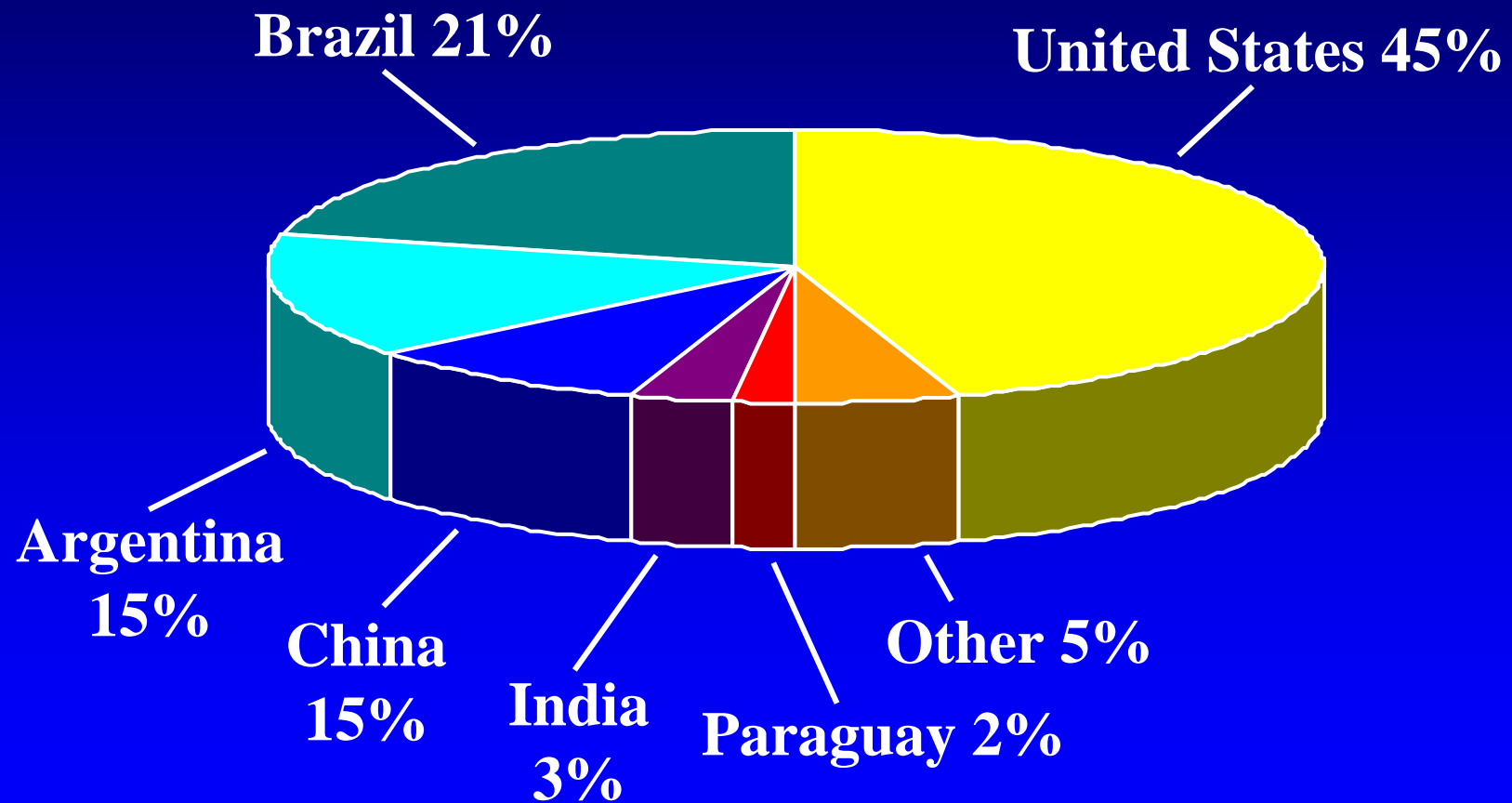


World Vegetable Oil Consumption



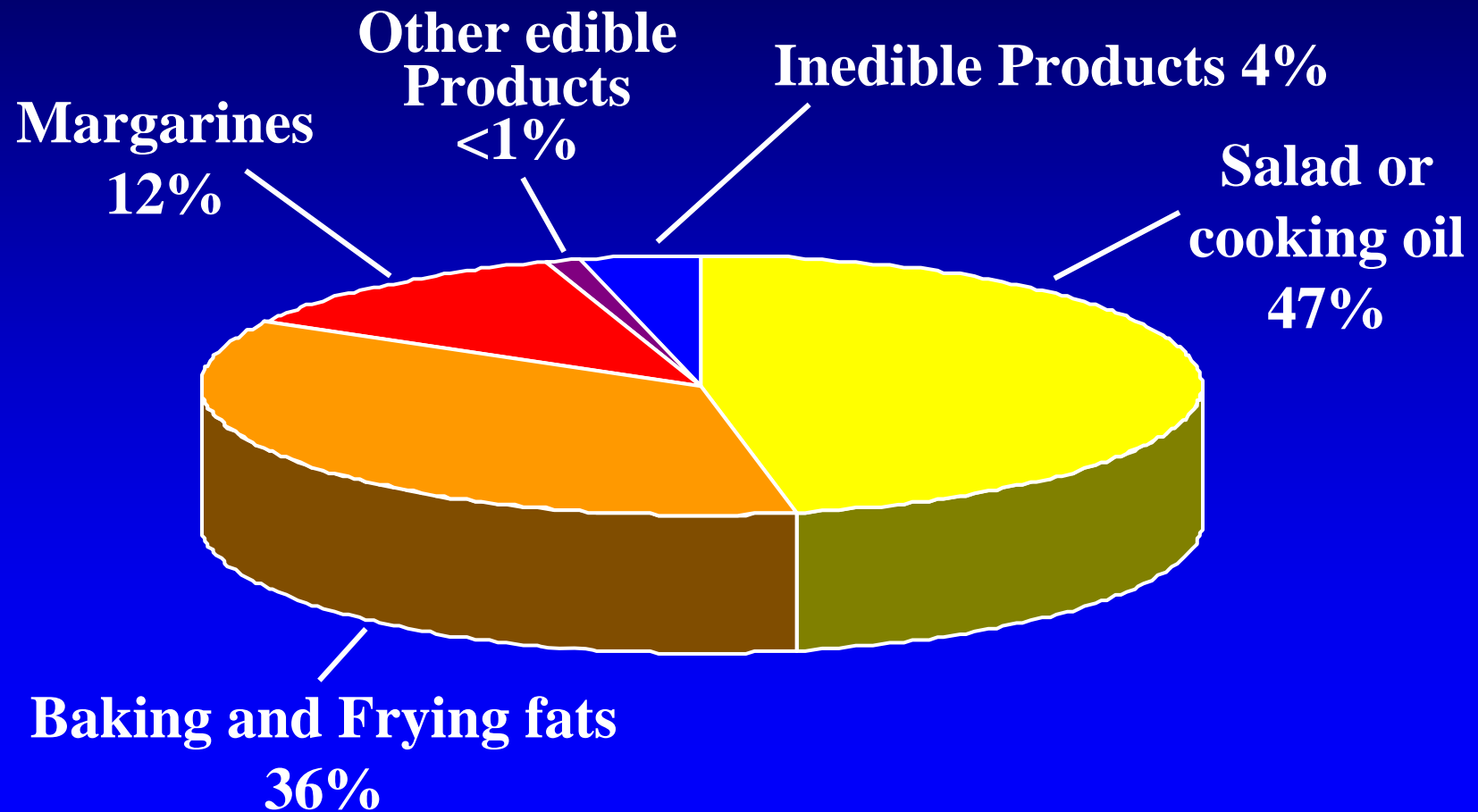


World Soybean Production





U.S. Soybean Oil Consumption



Biobased Products

Biobased products are industrial products (including fuels but not food or feed) made from renewable agriculture and forestry resources.

Potential Benefits of Biobased Products

- 💧 **New markets for agriculture commodities**
- 💧 **Add value to commodities/wastes**
- 💧 **Economic development**
- 💧 **Reduced dependence on imports**
- 💧 **Environmental advantages**

Issues with Biobased Products

- 💧 **Cost**
- 💧 **Performance**
- 💧 **Availability**
- 💧 **Energy efficiency**

**E.O. 13101 Greening the
Government Through Waste
Prevention, Recycling, and
Federal Acquisition (Sept. 1998)**

E.O. 13134 Developing and Promoting Biobased Products And Bioenergy (August 1999)

- 💧 Stimulate the creation and early adoption of technologies needed to make biobased products and bioenergy cost-competitive in large national and international markets**
- 💧 Goal of tripling U.S. use of biobased products and bio-energy by 2010**

Biomass Research & Development Act of 2000

- 💧 Improve interagency coordination and focus the federal R&D efforts on conversion of biomass into biobased products**
- 💧 Establishes Technical Advisory Committee and Biomass R&D Board**
- 💧 Authorizes additional funding at USDA for biomass R&D Initiative**

Biomass Industrial Products: Priorities for Research and Commercialization (NRC, 2000)

- 💧 Proposed intermediate- and long-term targets for adoption and use**
- 💧 Recommended increased Federal R&D support**
- 💧 Recommended research priorities for biology and engineering**
- 💧 Envisioned government-industry partnership**

USDA Biobased Products & Bioenergy Coordination Council (BBCC)

- 💧 1995, Secretary of Agriculture created New Uses Coordinating Council**
- 💧 1997, Renamed Biobased Products Coordination Council**
- 💧 2002, Biobased Products and Bioenergy Coordination Council established by Departmental Regulation**

USDA Biobased Products & Bioenergy Coordination Council (BBCC)

- 💧 USDA working group on biobased products & bioenergy**
- 💧 13 USDA Agencies/Offices**
- 💧 Coordinate USDA activities**
- 💧 Work with other Federal agencies, public and private sector**
- 💧 Research priorities and policy recommendations to Secretary**

Pertinent Websites

- 🔥 USDA Biobased Products & Bioenergy Coordination Council (BBCC)

<http://www.ars.usda.gov/bbcc>

- 🔥 Biobased Products & Bioenergy Initiative

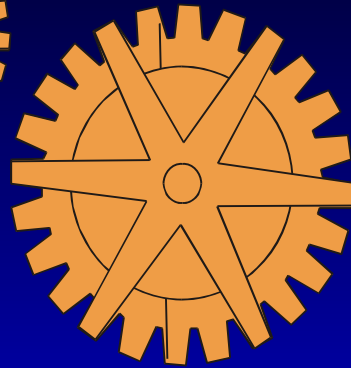
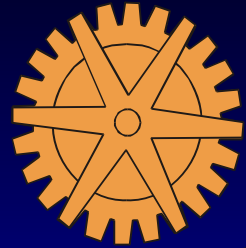
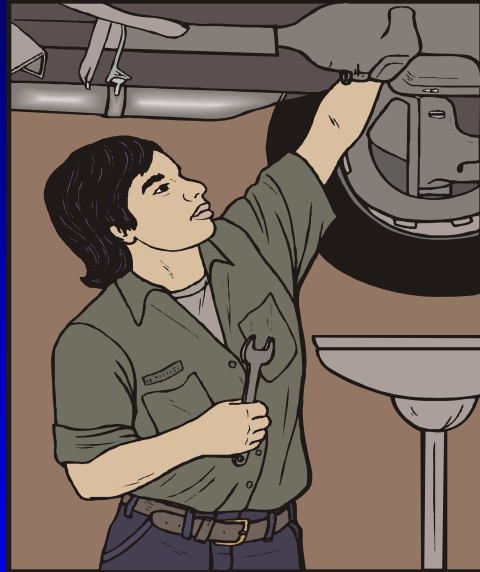
<http://www.bioproducts-bioenergy.gov/>

- 🔥 USDA Biobased Industrial Products Site

<http://www.usda-biobasedproducts.net>

- 🔥 ARS National Programs 306 & 307

<http://www.nps.ars.usda.gov/>



Lubricants

World Lubricant Consumption

- 🔥 **Industrial Uses – 2.25 billion gallons**
- 🔥 **Automotive Uses: - 5.63 billion gallons**

Industrial Lubricants

- 🔥 Lubricant market in the U.S. is about \$8 billion
- 🔥 More than 90% of all lubricants are based on petroleum
- 🔥 The demand for biodegradable lubricants is expected to grow at about 10% annual rate

Concerns

💧 Environmental

- 💧 Pollution – Air, Water and Soil
- 💧 Ecological Balance

💧 Handling and Toxicity

- 💧 Health
- 💧 Contamination

💧 Disposal

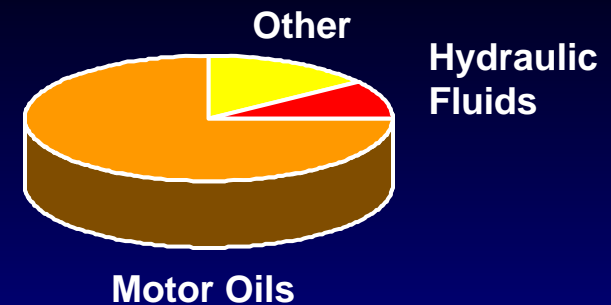
- 💧 Biodegradability
- 💧 Cost

Primary Functions of Lubricants

- 💧 Reduce friction and minimize wear
- 💧 Dissipate heat
- 💧 Disperse deposits
- 💧 Inhibit rust/corrosion
- 💧 Seal critical contact joints

Consumption of Lubricants

~ 20 M tons / year in US



Commercial Uses of Biodegradable Lubricants

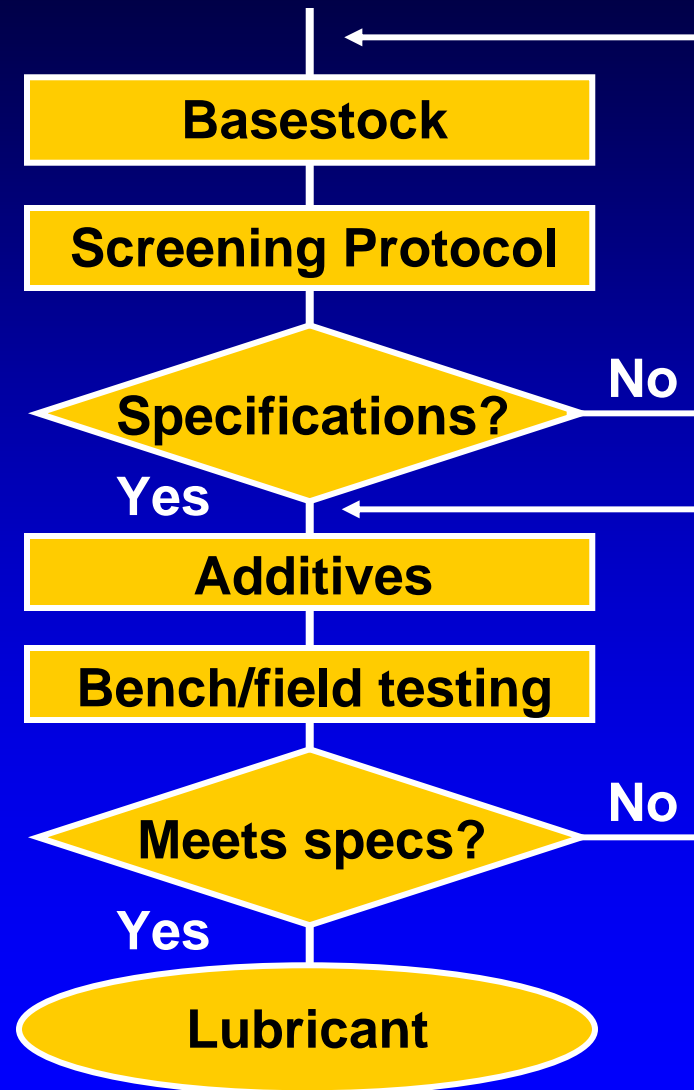
- Chain saw lubricants
- Drilling oils
- Food industry fluids
- Gear oils
- Greases
- Hydraulic fluids
- Marine lubricants
- Pump oils
- Railroad lubricants
- Shock absorber fluids
- Mould release oils
- Two stroke engine oils

Biodegradability is delivered by **basestock**, not additives

Basestock: 80-100% of Lubricant

Flowchart of Lubricant Development

Screening protocols depend on application



Properties to be Included in Basestock Screening

Biodegradability

Viscosity

Low temperature solidification

Deposit forming

Volatility

Oxidative stability

Hydrolytic stability

Solvency, miscibility

Seal compatibility

Special requirements

**(e.g. electrical
conductivity,
transparency, density,
heat conductivity etc.)**

Properties to be Controlled by Additives

Wear protection

Corrosion

Foaming, air release

Shear stability

Demulsibility, water rejection

Friction, traction

Adhesion

Surface tension

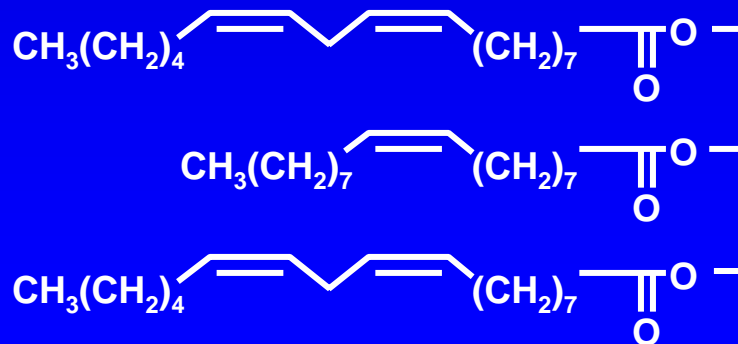
Special requirements

**(e.g. color, purity,
Magnetic properties, etc.)**

Vegetable Oils as Lubricants

Advantages:

- **Low volatility**
 - Due to high molecular weight of the triglyceride molecule
- **Good boundary lubrication properties**
 - Polar ester groups are able to adhere to metal surfaces
- **Excellent viscosity – temperature characteristics**
 - Narrow range of viscosity changes with temperature
- **Biodegradability**
- **Compatibility with mineral oil and additive molecules**

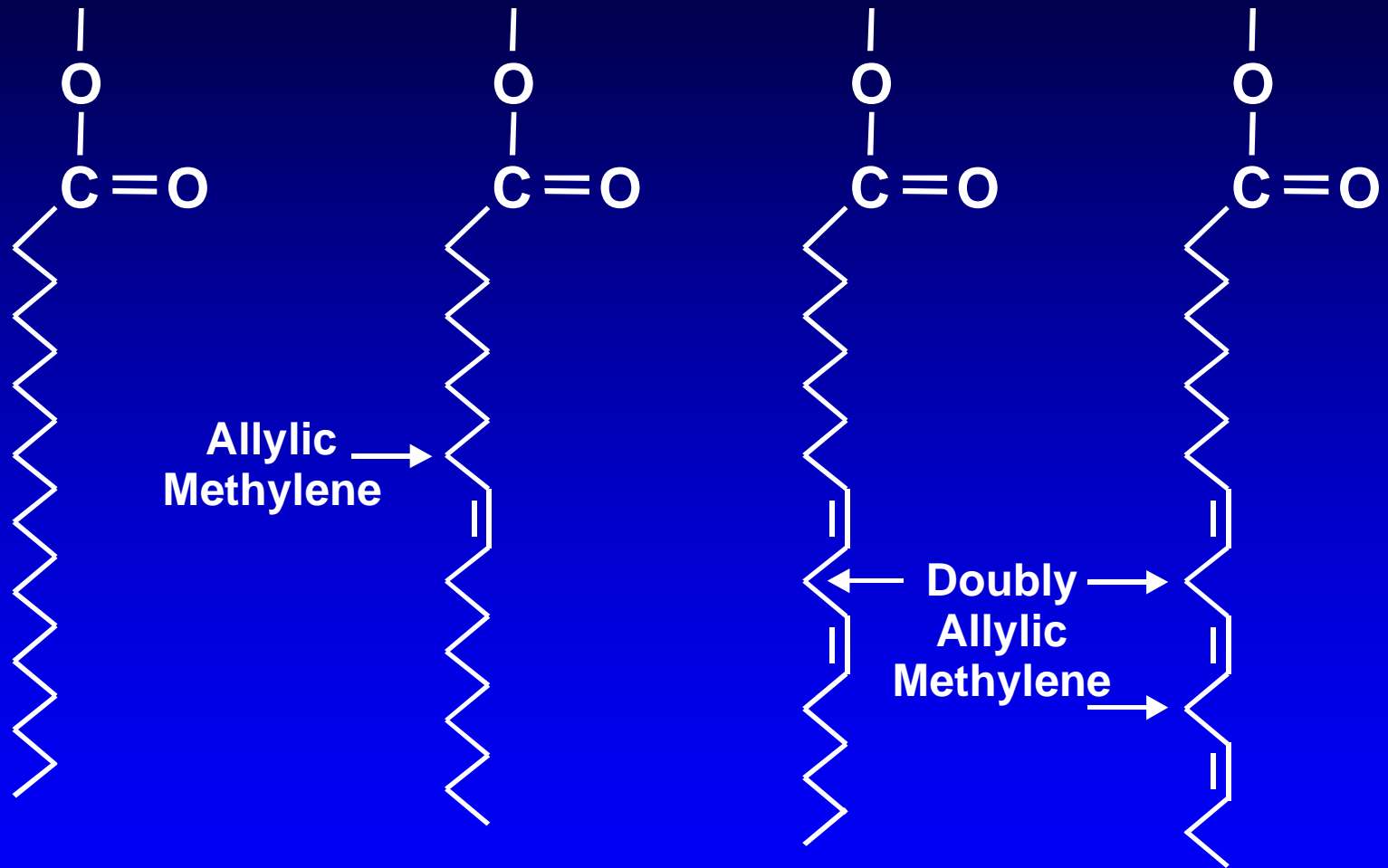


Vegetable Oils as Lubricants

Disadvantages:

- **Poor oxidative stability**
 - Due to the presence of bis-allylic protons
- **Poor low temperature fluidity**
 - Due to high molecular weight
- **Hydrolytic instability**
 - Due to the presence of ester functionality

Rate of Oxidation



	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Rate	1	10	100	200

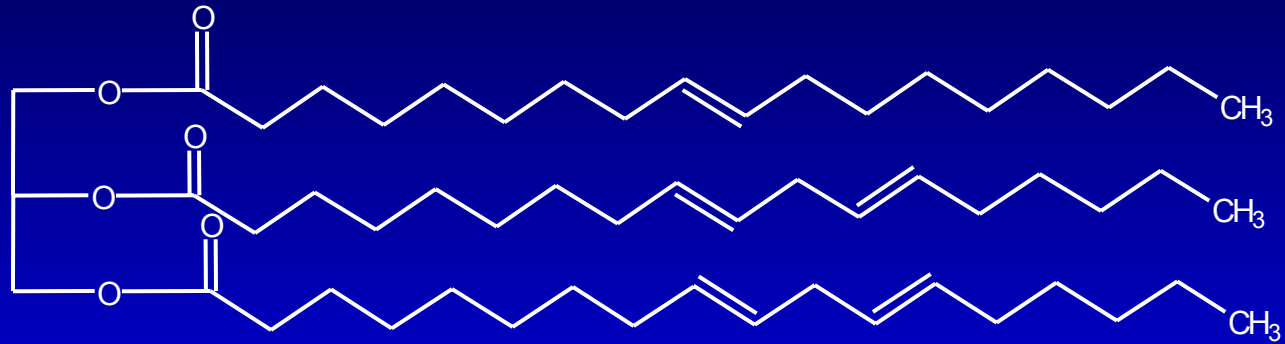
General Solutions to the Problems

- **Modification of vegetable oils**
 - Chemical modifications
 - Genetic modifications
- **Additives**
 - Antioxidants, pour point depressants
- **Blending**
 - With diluents or functional fluids to achieve enhanced performance

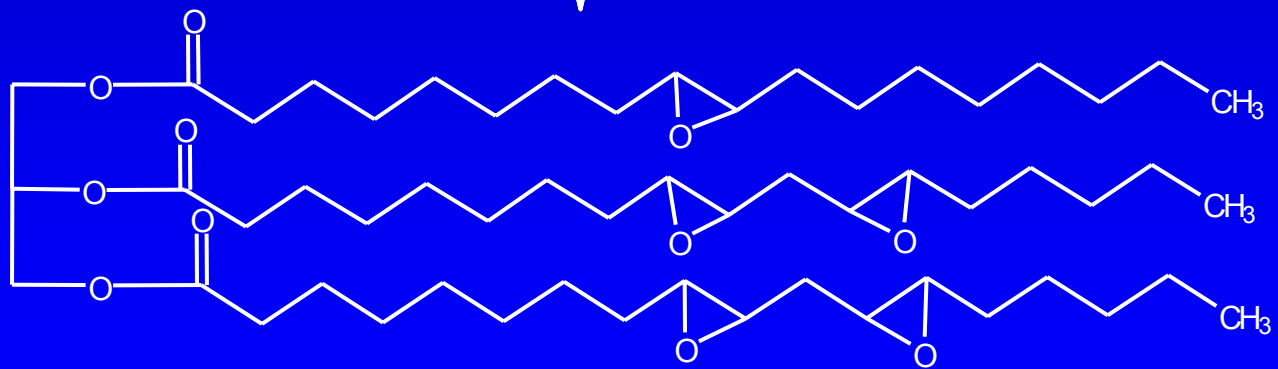
Chemical Modification

- **Converting the C=C bond into epoxy group**
- **Attaching branched structures at epoxy sites of triglyceride chains**

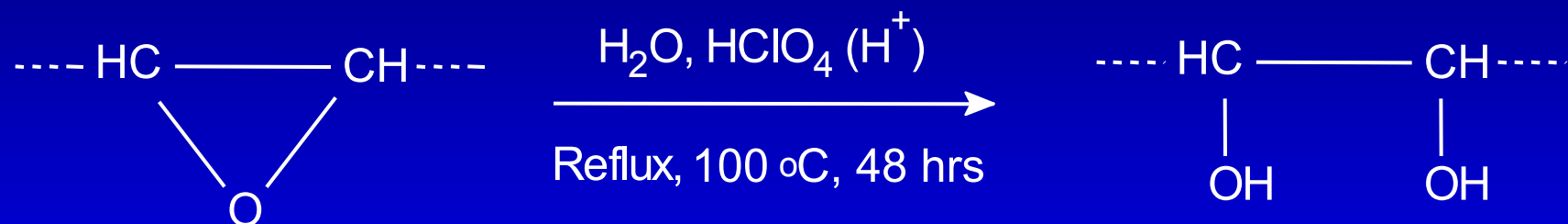
Triacylglycerol Structure of Vegetable Oil (Soybean Oil)



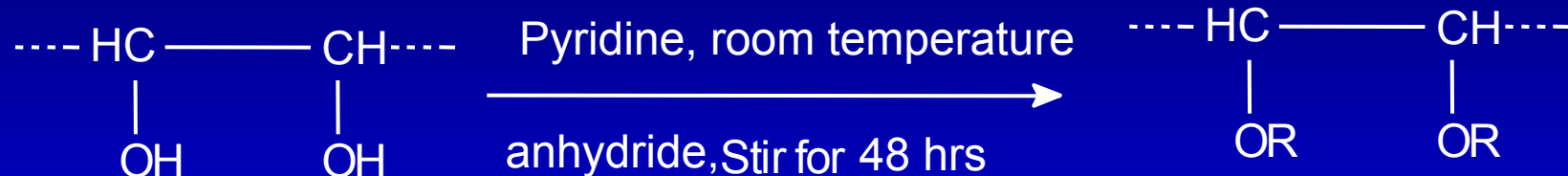
↓
epoxidation



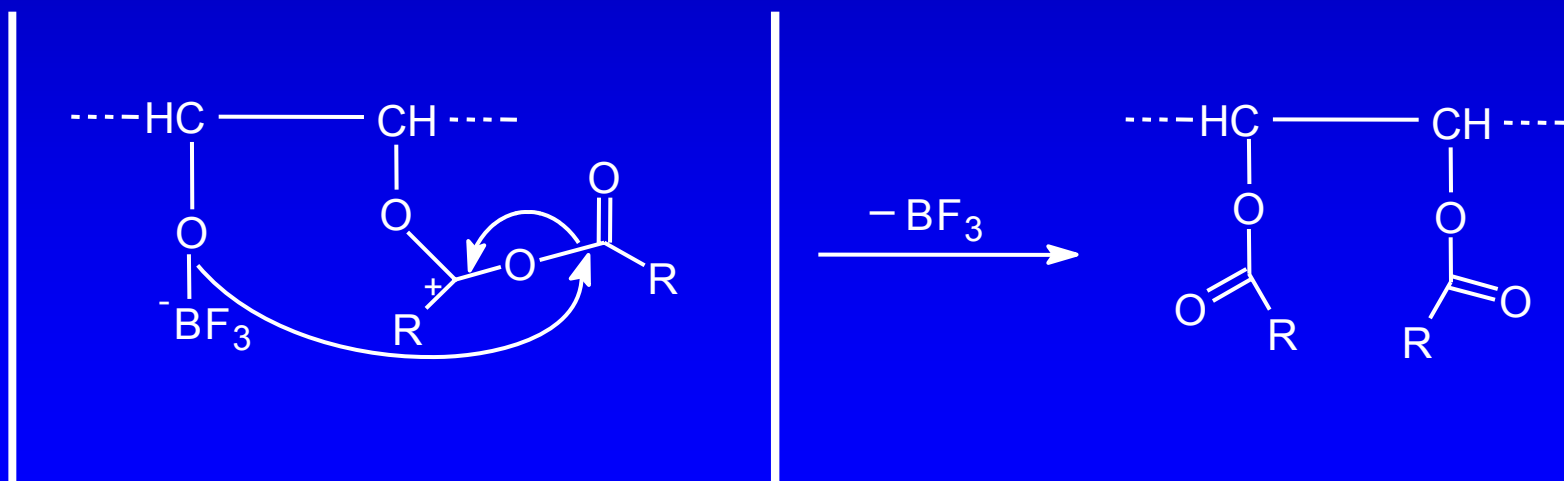
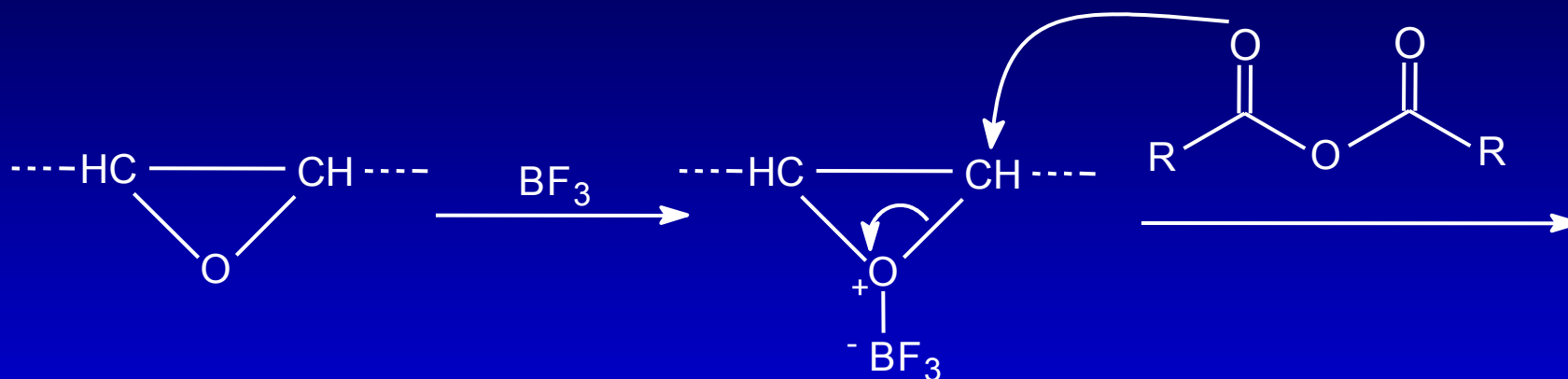
Epoxy Ring Opening and Di-hydroxylation



Reaction with Anhydride to Form Diester Derivative



Catalytic Ring Opening and Reaction with Anhydride



Pressurized Differential Scanning Calorimetry of the Oils @ 10°C/min.; Air at 200 Psi; Constant Pressure

<u>Test oils</u>	<u>Start Temperature (Ts)°C</u>	<u>Onset Temperature (To)°C</u>
SBO	161.3	178.2
ESBO	177.4	203.9
OAc-SBO	135.7	165.1
OBu-SBO	140.1	170.2
OHx-SBO	171.9	196.6

Pour Point of the Oils - ASTM D 97

<u>Test oils</u>	<u>Pour point (°C)</u>
SBO	-6
ESBO	0
OAc-SBO	-3
OBu-SBO	-3
OHx-SBO	-18

Pour Point Improvement with Additive and Diluent

<u>Test oil</u>	<u>PPD (%)</u>	<u>Diluent : oil (ratio)</u>	<u>Pour point (°C)</u>
OHx-SBO	0	0 : 100	-18
OHx-SBO	1	0 : 100	-30
OHx-SBO	1	20 : 80	-39

Conclusions

- **Chemical modification of vegetable oil is achieved with significant improvement in thermo-oxidative and low temperature stability**
- **Basic vegetable oil structure is retained with high biodegradability**
- **The methodology can be applied to any vegetable oil with triacylglycerol structure**
- **The modified oil can be used as an industrial base fluid; the chemical technology being cost effective has a good potential for commercial production**
- **This technology has been patented, U.S. patent 6,583,302 (2003)**

Base Fluids

- Soybean oil – alkali refined (SO)
- High Linoleic Soybean Oil (HLSO)
- Mid Oleic Soybean Oil (MOSO)
- High Oleic Soybean Oil (HOSO)
- Polyalphaolefin (PAO)

Additives

- **Antioxidant additive**
 - Alkylated diphenyl amine (AO1)
 - Butylated hydroxy toluene (AO2)
 - Mixture of alkylated phenol/dithiophosphoric acid ester/diphenyl amine (AO3)
 - Zinc diamyl dithiocarbamate (AO)
- **Antiwear additives**
 - Antimony diakyl dithiocarbomate (AW1)
 - Amine-phosphate compound (AW2)
 - Molybdenum diakyl phosphorodithioate (AW3)
- **Pour Point Depressant**
 - P-methyl methacrylate

Test Methods

- **Pressurized Differential Scanning Colorimeter (PDSC)**
 - Temperature ramping method
(measures onset temperature OT)
- **Rotary Bomb Oxidation Test (RBOT)**
 - ASTM D 2272
- **Low Temperature Flow Property**
 - ASTM D 97 Pour Point Test

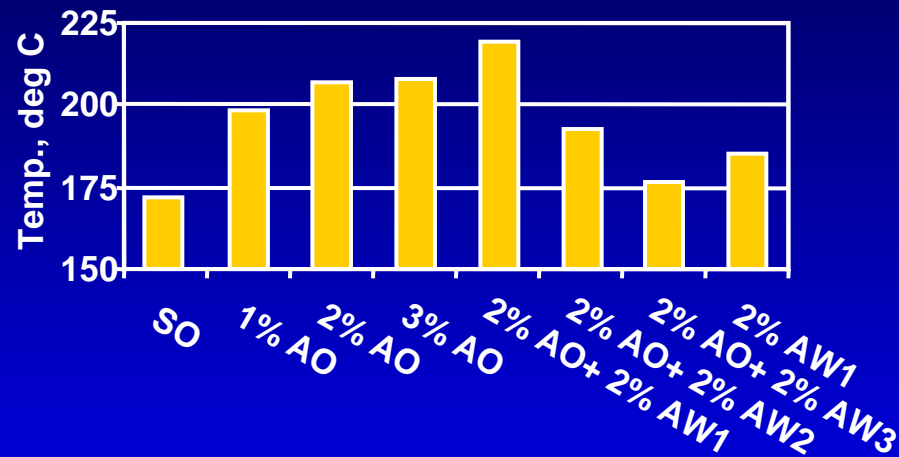
Oxidation Stability of Soybean Oil

Vegetable oils	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	UN	OT (°C)
SO	11.14	4.77	24.20	53.60	6.29	1.50	173
HLSO	10.61	5.63	27.49	56.27	-	1.40	179
MOSO	9.13	4.33	60.71	24.18	1.65	1.14	190
HOSO	7.08	3.30	86.78	1.08	1.76	0.94	198

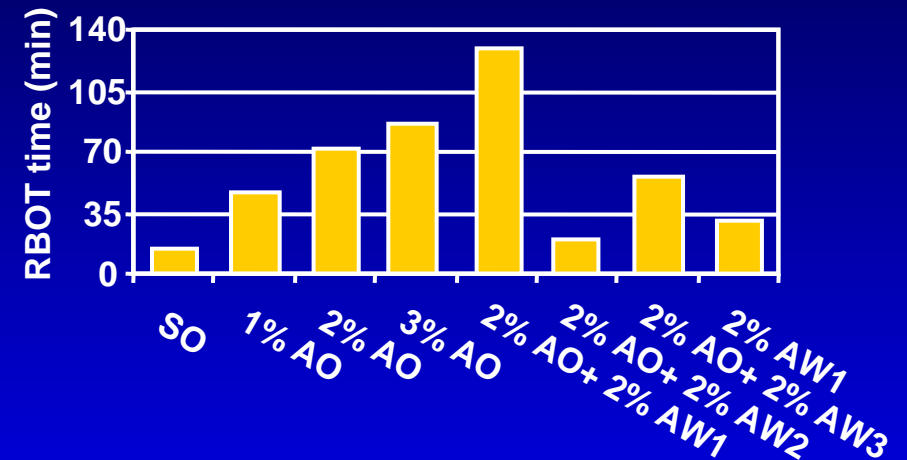
- **Good correlation between UN and OT R-sq 0.99**
- **Oxidation stability of vegetable oils is predictable using its fatty acid composition rather than individual fatty acid percentage.**

Synergistic Effect of Additive Combinations in Soybean Oil

PDSC Results



RBOT Results



- AO reached a limit in effectiveness at 2%
- AW2 and AW3 acts as pro-oxidant
- Only AW1 showed synergistic effect on antioxidant capability of AO
- AO-AW1 will be used.

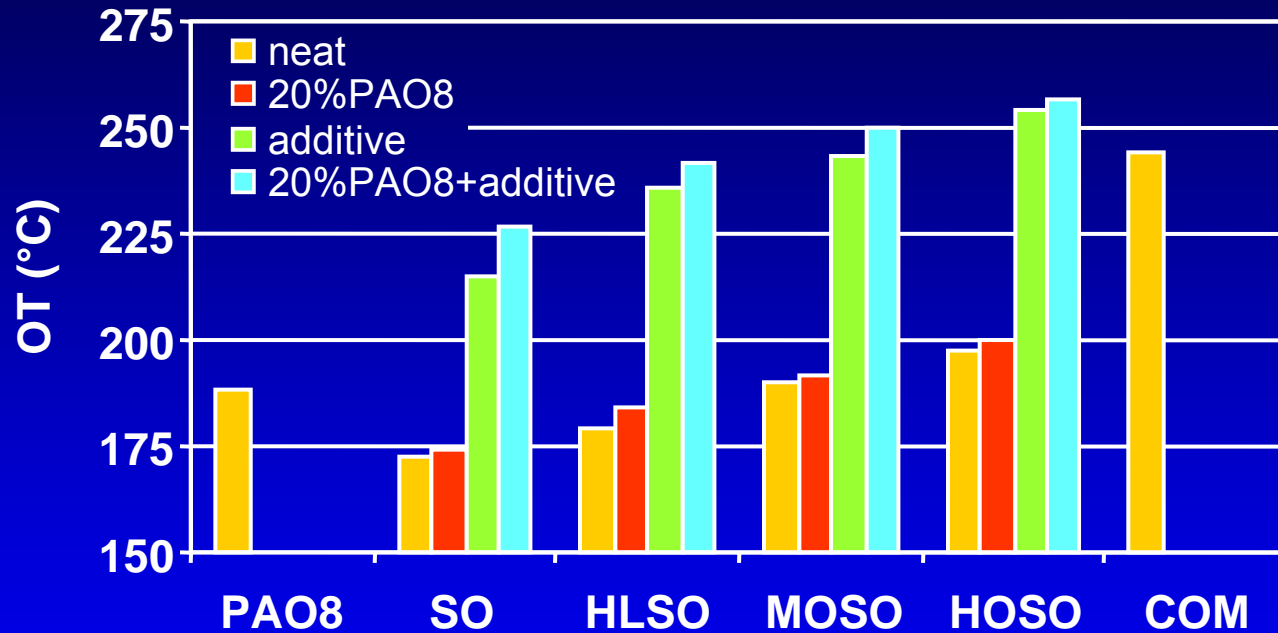
AO – Zinc diamyl dithiocarbamate

AW₁ – Antimony dialkyl dithiocarbamate

AW₂ – Amine-phosphate compound

AW₃ – Molybdenum dialkyl phosphorodithioate

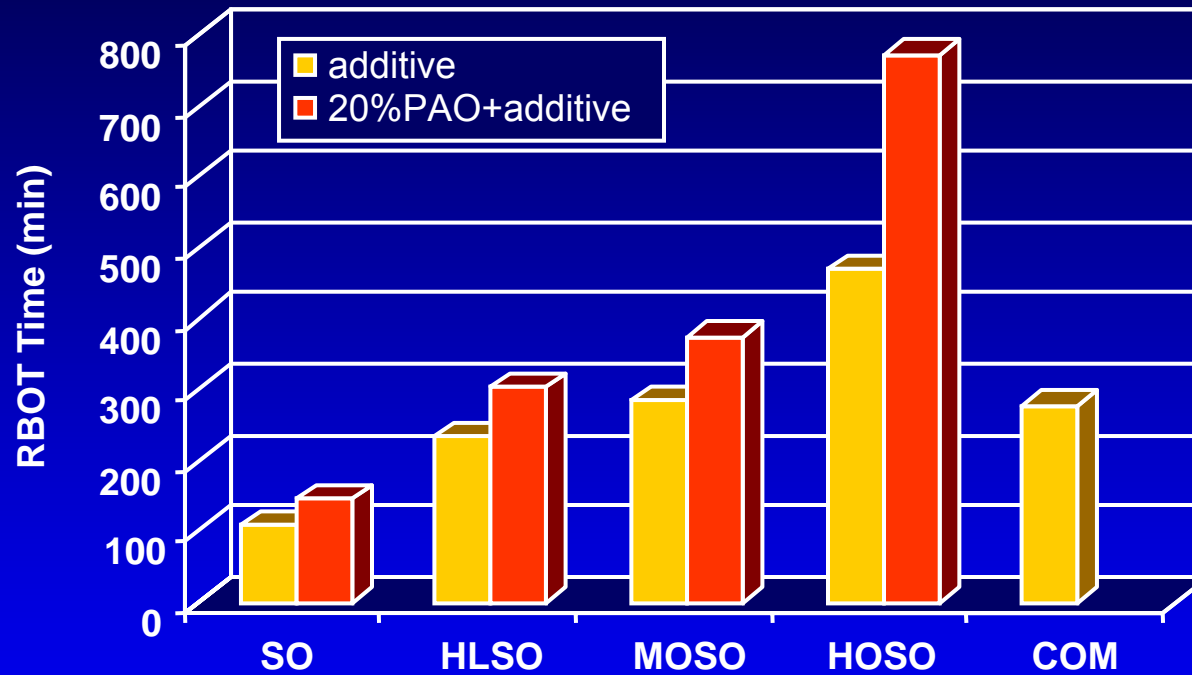
Effect of Antioxidant-Antiwear (AO-AW₁) Additive Mixture on Vegetable Base Oils and Formulated Lubes



PDSC Onset Temp.

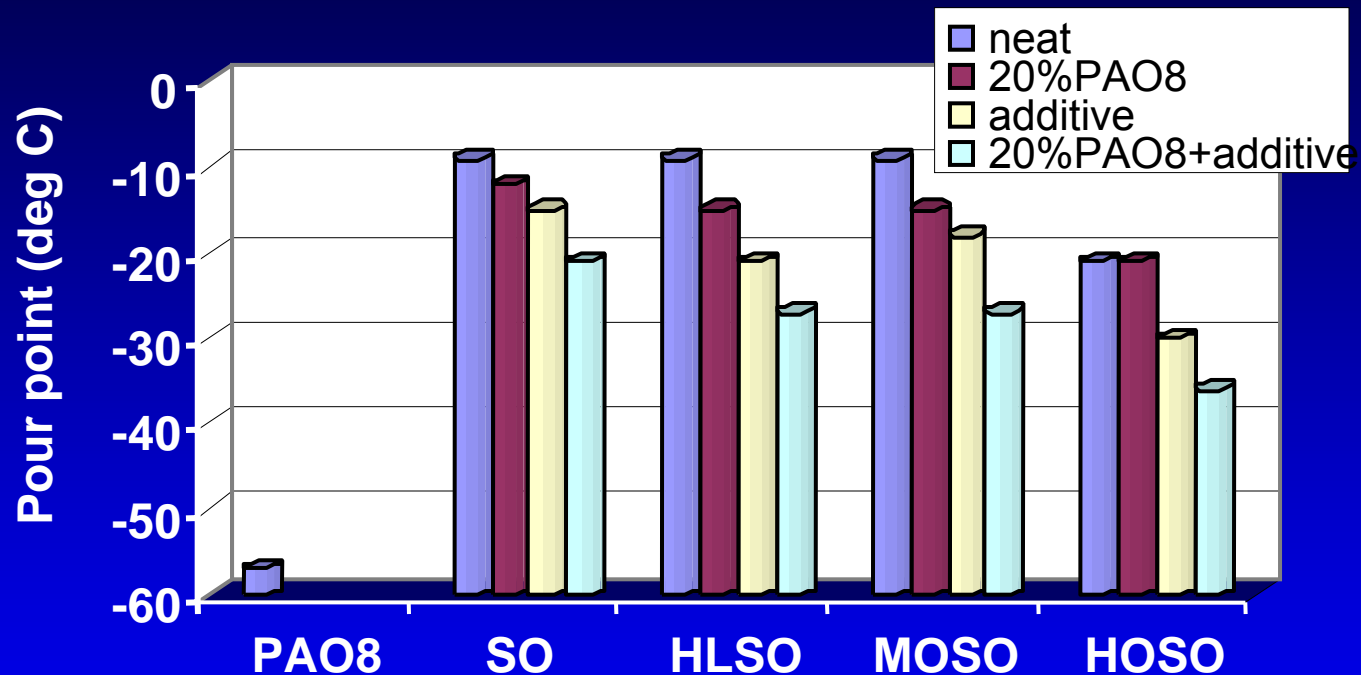
- PAO oxidatively more stable base fluid with OT of 188°C.
- additive combination increased the oxidation stability by 50°C.

RBOT Results of Formulated Vegetable Oil Based Lubes



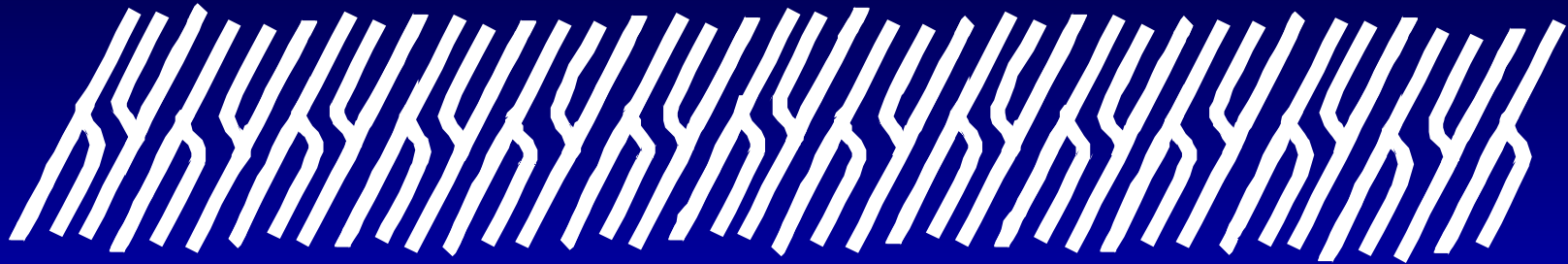
- RBOT time of 100 min and above considered good for industrial lubricants.
- Excellent oxidation stability of VO formulations compared with COM

Pour Point improvement using PAO and PPD

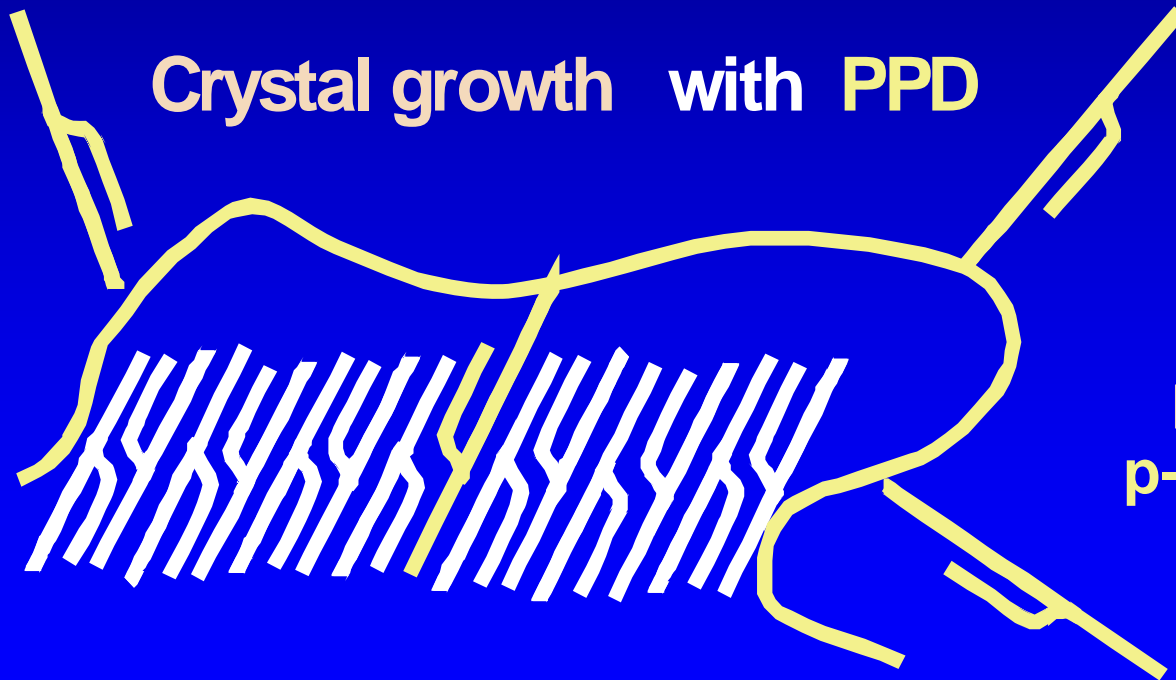


- PAO added as diluent (PP -57 °C) to improve LTP
- 20% PAO improved the PP by -3 to -6 °C
- Addition of up to 40% PAO made no significant improvement
- Further improvement using 1% PPD

Crystal growth without Pour Point Depressant (PPD)



Crystal growth with PPD



Crystal size limited by hindrance of **p-methacrylate** backbone

Conclusions

- Additive combinations need to be evaluated in various base fluids to assess effectiveness
- Antioxidant ZDDC (zinc diamyl dithiocarbamate) performed better than diphenylamine, hindered phenol, or their mixture
- All antioxidants showed more synergism with antiwear additive ADDC (antimony diacyl dithiocarbamate) compared to molybdenum phosphorodithioate, while amine-phosphate did not show any synergism
- ZDDC and ADDC combination showed the best results in vegetable oils

Conclusions Continued

- **This additive combination improves the performance of MOSO to make it acceptable for most industrial applications**
- **The overall approach provides VO based lubricants that exhibit superior performance than commercially available bio-based industrial lubricants and are comparable with petroleum-based lubricants.**



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