Applications of Basic Oleochemicals

PIPOC - November 2009
Kuala Lumpur Convention Centre

- Eva Suyenty -
Petrochemicals vs Oleochemicals

- Synthetic oil → Petrochemicals
- Animal fat → Oleochemicals
- Vegetable oil → Oleochemicals
Oleochemicals

- Fatty Alcohol: $R-(CH_2)_n-OH$
- Fatty Acid: $R-(CH_2)_n-COOH$
- Methyl Ester: $R-(CH_2)_n-COOCH_3$
- Fatty Amine: $R_3-N$
- Glycerin: $C_3H_5(OH)_3$
Oleochemicals in Daily Life

INGREDIENTS: WATER, GLYCERIN, CETEARYL ALCOHOL, *ALOE BARBADENSIS LEAF JUICE, CETEARETH-20, CETYL ESTERS, **CHOLESTERYL ISOSTEARATE, DIMETHICON, C12-15 ALKYL BENZOATE, GLYCERYL DILAURATE, MINERAL OIL, STEARIC ACID, CETYL ALCOHOL, ISOPROPYL MYRISTATE, SODIUM CARBOMER, METHYLPARABEN, PROPYLPARABEN, DMDM HYDANTOIN, FRAGRANCE.
Fatty Acid

**Application**

- **Direct**
  - Rubber
  - Textile
  - Lubricants
  - Metal working
  - Crayon & pencils
  - Candles
  - Ore flotation
  - Personal care

- **Derivative**
  - Cosmetic & toiletry
  - Slipping agents
  - Softener
  - Biocides
  - Food processing
  - Synlubes
  - Paints & coating
  - Elastomer
Fatty Acid – Direct Use

**Rubber**
- Vulcanizing additives in dry rubber compounding process
- Dispersing agent for carbon black & conferring plasticity to the rubber
- Vulcanization is promoted with fatty soaps of zinc formed in-situ
- Hydrogenated tallow fatty acids & stearic acid (1-5 parts/100 parts rubber)

**Lubricants**
- Metallic soaps (preformed/in-situ) → thickening agents in grease
- Hydrogenated castor oil fatty acids, stearic acid, 12-hydroxy stearic acid, etc
Fatty Acid – Direct Use

Metal working
- Rolling oils → 2-4% fatty acid
- Cutting oils → 2-15% fatty acid
- Common acids: oleic, stearic, TOFA

Ore flotation
- Anionic collectors
- Common acids: TOFA and oleic acid

Personal care
- Stearic acid → give firmness in shaving bars, ingredient in creams and lotions
- Tallow, stearic, and myristic acid → ingredients in shaving cream
Fatty Acid – Direct Use

**Crayon & pencils**
- Crayons → fatty acids (stearic and tallow fatty acids) incorporated into petroleum wax
- Fatty acids → firm the crayon tip, disperse the pigment in the wax
- Soft crayons → up to 40% of fatty acids
- Colored pencils → 10-15% of fatty acids → fill up the porosity of the core

**Candles**
- Fatty acids → opacifier, melting rate controller, and give hardness of the taper
- Stearic, palmitic-rich stearic acid, hydrogenated tallow fatty acids
- Stearic acid → gives fine luster and non-greasy feel
- Usage: from a few percent to 100%
Fatty Acid – Derivative

**Cosmetic & toiletry**
- Amine soaps, calcium and magnesium salts of fatty acids, alkanolamides, betaine, imidazolinium, etc
- Hair care, oral hygiene products, deodorants, bath products, etc
- Level of usage: 0.5 – 50% or more

**Softener**
- Amido amine, imidazolinium, quaternary ammonium, amido amine quats
- Hydrogenated tallow (long chain acid)
- Environmental issues → ester quats (biodegradable surfactants)
Fatty Acid – Derivative

**Biocides**
- Quaternary ammonium compounds (replacing chloro & phenol compounds)
- Swimming pool sanitizers, fungicides, preservatives in cosmetic & pharmaceuticals, etc

**Food processing**
- Esters-mono and diglycerides, propylene glycol stearates, sorbitan esters, etc
- Emulsifiers, dispensing agents, thickeners, stabilizers

**Paints & coatings**
- Glycerides, purified fatty acids, or derivatives (imidazolines)
- Film-forming surfaces, thickeners, pigment dispersion agents, biocides
Fatty Acid – Derivative

**Slip agent**
- Fatty acid soaps $\rightarrow$ LDPE and PP production
- C18-C22 primary amides $\rightarrow$ approved by US FDA for food wrappings

**Elastomers**
- 5 – 7%w fatty acid soaps $\rightarrow$ emulsifiers in the production of Styrene-Butadiene Rubber (SBR)
- Nitrile rubber production $\rightarrow$ hydrogenated tallow, stearic acid, oleic acid, low linoleic TOFA

**Synthetic lubricants**
- Diesters & polyesters of short chain acids $\rightarrow$ synlube base fluids
Fatty Acid – Derivative (4)

**Firefighting**
- Glycerol Mono Oleate (GMO) → fire retardant hydraulic fluid

**Paper**
- Calcium Stearate → lubricant coated paper

**Specialty surfactant**
- Coco-range fatty acid → anionic surfactant synthesis (acyl isethionates, acyl sarcosinates, acyl taurates)

**Plastics**
- N,N Ethylene Bis Stearamide (EBS) → Acrylonitrile-Butadiene-Styrene (ABS) and Polyvynil Chloride (PVC) resins as internal lubricant → improves polymer flow during injection molding
New Trend in Fatty Acid Application

- Convert to fatty alcohol
  - Fatty Acid → Methyl Ester → Fatty Alcohol
  - Fatty Acid + Fatty Alcohol → Wax Ester → Fatty Alcohol

- Convert to biodiesel
  - Fatty Acid + Methanol → Biodiesel
Fatty Acids Applications

- **Soap & detergent**: 30%
- **Intermediate**: 18%
- **Plastic**: 14%
- **Coating & resin**: 6%
- **Lubricant & grease**: 6%
- **Paper**: 6%
- **Rubber**: 6%
- **Personal care**: 5%
- **Food & feed**: 2%
- **Candle**: 2%
- **Various**: 5%

Source: *The Changing World of Oleochemicals*, Wolfgang Rupilius and Salmiah Ahmad
Methyl Ester

Current applications of methyl esters:

- Manufacture of fatty alcohols
- Biodiesel
- Lubricants
- Cosmetic
- Production of ‘superamides’
- Production of imidazolines and betaines
- Preparing antibiotics formulations
Potential Future Application

- **Production of Methyl Ester Sulfonate**
  - Raw material: palm stearin, C16 ME from Europe’s biodiesel
  - Alternative ester sulphonates to substitute Linear Alkyl Sulphonate (LAS)
  - Flotation agent in mining, defatting agent in leather industries

- **Production of Methyl Ester Ethoxylates**
  - Have different foaming and solubility from alcohol ethoxylates
  - Total production cost should be lower than alcohol ethoxylates
  - Large price difference between unsaturated alcohol and unsaturated methyl ester → attractive technology
  - Limitation: less hydrolytic stability of the ester bond
Potential Future Application

- **Production of Sucrose Polyester (SPE)**
  - No calorie and no cholesterol fat substitutes
  - Have potential application in food industry

- **Production of monoglycerides for food industry**
  - Salad oil is already being produced in Israel by methyl ester interchange process

- **Production of fatty acid cyanamide soaps**
  - Excellent detergency for all-purpose liquid cleaners (particularly C12-C14, C12-C18, and C16-C18 ranges)

- **Production of monoglycerides for industrial products**
  - Glycerolysis of methyl esters (40, 60, and 90% monoglycerides)
  - Lubricants and emulsifiers for cutting oils, grinding or polishing pastes
Fatty Alcohol

- Most important market → household detergent (C12 and higher)
  (Generally for detergent-surfactant)

- Alcohol Ether Sulfate (AES)
  Alcohol Ethoxylates (AE)
  Alcohol Sulfate (AS)
  Linear Alkyl Benzene Sulfonate (LABS)
  Alkyl Phenol Ethoxylates (APE)

Composition as alcohol surfactant:

- AES, AE, AS 75%
- Others 25%
Fatty Alcohol – Detergent Applications

Applications of alcohol-based surfactants:

- Heavy duty washing powders
- Heavy and light duty washing liquids
- Fabric softener
- Personal care
- Auxiliaries for the processing of textiles and leather
- Petroleum drilling and processing
## Fatty Alcohol – Non-detergent Applications

<table>
<thead>
<tr>
<th>Compound</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free alcohol</td>
<td>Foam depressants, rolling oil, solvent, lubricants, evaporation control agent, pharmaceutical preparation</td>
</tr>
<tr>
<td>Fatty ester</td>
<td>Emollients, plasticizers</td>
</tr>
<tr>
<td>Thiodipropionate esters</td>
<td>Antioxidants</td>
</tr>
<tr>
<td>Alkyl polyglucosides</td>
<td>Personal care, food products</td>
</tr>
<tr>
<td>Sulfosuccinates esters</td>
<td>Household cleaners, wetting agent</td>
</tr>
<tr>
<td>Polymethacrylate esters</td>
<td>Lubricating oils, plasticizers</td>
</tr>
<tr>
<td>Alkyl phosphates</td>
<td>Cosmetic emulsifiers, textile auxiliaries</td>
</tr>
</tbody>
</table>
Fatty Alcohol Derivatives

- AES: 35.7%
- AE: 22.0%
- AS: 14.8%
- Quaternary ammonium: 3.1%
- Methacrylate esters: 2.5%
- Amine oxide: 1.3%
- APG: 1.1%
- Others: 19.5%

Source: Internal
Fatty Alcohol Applications

<table>
<thead>
<tr>
<th>Category</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergent &amp; Cleaner</td>
<td>48%</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>11%</td>
</tr>
<tr>
<td>Flavor &amp; Fragrance</td>
<td>7%</td>
</tr>
<tr>
<td>Personal Care</td>
<td>7%</td>
</tr>
<tr>
<td>Petroleum</td>
<td>4%</td>
</tr>
<tr>
<td>Food</td>
<td>4%</td>
</tr>
<tr>
<td>Agriculture</td>
<td>3%</td>
</tr>
<tr>
<td>Fabric Softener</td>
<td>3%</td>
</tr>
<tr>
<td>Polymer Emulsion</td>
<td>2%</td>
</tr>
<tr>
<td>Textile</td>
<td>2%</td>
</tr>
<tr>
<td>Others</td>
<td>9%</td>
</tr>
</tbody>
</table>

Source: Internal
Fatty Amine

- Organic compound with nitrogen as the key atom

![Structures of Primary, Secondary, and Tertiary Amines]

- Applications:
  - > 75% → fabric softener actives (e.g. DHTDMAC)
  - < 25% → directly consumed in certain applications
Primary Amines

- Production of quaternary ammonium compounds and amphoterics via tertiary amine

- **Long chain primary amines & their salts:**
  - Rubber mold release agents
  - Prevent nicking in granular and blended fertilizers

- **Short chain amines:**
  - Larvicides
  - Fly repellents

- **Blends of various lengths amines & their salts:**
  - Cationic collectors in ore flotation

- **Amine ethoxylates (2-50 EO):**
  - Corrosion inhibitors
  - Emulsifiers for textile spinning oils
  - Emulsifier for agricultural herbicide
Secondary Amines

- Chemical intermediaries → difatty dimethyl ammonium salts (fabric softener actives)
- Do not have any direct market
Tertiary Amines

**Symmetrical**
- Trialkylamine

**Asymmetrical**
- Dialkylmonomethylamine
- Alkylidimethylamine

The largest market share
Tertiary Amine Applications

- Production of quaternary ammonium compounds and amine oxides

- **Use of dimethylalkylamine:**
  - manufacture of quaternary ammonium compounds for biocides, textile chemicals and oilfield chemicals, amine oxides, betaines, catalyst in polyurethane foam synthesis

- **Use of methyldialkylamine:**
  - softener, conditioner for shampoo, cosmetics, agricultural wetting agents

- **Use of trialkylamine:**
  - cationic collector in ore flotation
Glycerin

- Polyol with more than 2000 applications:
  - water-soluble
  - odorless
  - colorless
  - has certain sweetness
  - absorbs and retains water
  - has a capacity to dissolve flavors and dyes
  - has plasticizer and antioxidant properties
  - nontoxic and easily biodegradable
Application of Glycerin

Foods
- Solvent for preparation of concentrated flavor extracts from natural products
- Texture improver and emulsifier in ice-cream
- Conditioner for wine gums, fondants, soft creams
- Emulsifiers in bread production (glycerol esters of acetic and tartaric acids)

Cosmetics
- Emulsifier, moisturizer, and conditioning agent
- Creams, lotions, tooth pastes and dental mouthwashes, and skin & hair care products
Application of Glycerin

**Pharmaceuticals**
- Cough syrup, expectorant, ointments
- Mild laxative in suppositories
- Softener in gelatin capsules
- Glycerol trinitrate → treatment for heart disease

**Plastics, resins, and cellophane**
- Production of phthalic and maleic alkyd resins
- Moisturizer and plasticizer in cellulose films
- Polyether polyols of glycerol are polymerized with diisocyanates to form flexible or rigid polyurethane foams
Application of Glycerin

**Tobacco**
- Solvent, humidifier, and plasticizer in tobacco
- Glycerol triacetate (triacetin) → softener for cigarette filters

**Others**
- Hydraulic fluid formulations
- Inks and printing colors → to prolong the self-life
- Humidifier, plasticizer, and lubricant in paper industry
Glycerin’s Future Application

**Propylene glycol**
- Traditionally produced by propylene oxide hydration
- Has similar properties with EG, but less toxic
- Colorless, odorless, tasteless
- Has humectant properties → moisturizer in medicines, cosmetics, toothpastes, foods, and tobacco products
- Has antibacterial properties → hand sanitizers, antibacterial lotions, etc

**Epichlorohydrin**
- Traditionally synthesized from epoxidation of allyl chloride
- As building block in the manufacture of epoxy resins, elastomers, and synthetic glycerol
Glycerin’s Future Application

**Acrolein**
- Lab scale → reaction of potassium bisulfate with glycerin, dehydration of glycerin at 280 °C
- Preparation of acrylic acid, polyester resin, polyurethane, propylene glycol, acrylonitrile

**Renewable fuel & H₂ production**
- Renewable fuel → by cracking process to hydrocarbon
- Hydrogen → by reforming process

**Eicosapentaenoic acid (EPA); omega-3 fatty acid**
- Common source: fish oil, microalgae, human breast milk
- Can be synthesized from crude glycerin by enzymatic process using *Pythium irregulare* (new research at Virginia Polytechnic Institute)
Glycerine Applications

- Soap, cosmetic, pharm.: 37%
- Alkyd resin: 13%
- Food: 12%
- Polyurethanes: 11%
- Tobacco: 9%
- Explosive: 3%
- Others: 15%

Source: *The Changing World of Oleochemicals*, Wolfgang Rupilius and Salmiah Ahmad
Question?

www.ecogreenoleo.com
Terima Kasih
Thank You
谢谢
どうもありがとうございます