Methyl Ester Sulfonate
The Next Generation Surfactant

Presented to
CESIO - 2008
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CHEMITHON
Linear Alkylbenzene Sulfonate

- Historically the workhorse anionic surfactant
- Good surfactant properties, but...
  - Cost of raw material is increasing
  - Petroleum derived, non-renewable
  - Recent environmental concerns about biodegradation of production of aromatics
Search for Replacements

- Alternative surfactants require
  - Developed processing technology
  - Equivalent surfactant properties
  - Adequate volume to supply the industry
  - Developed formulation technology
  - Lower cost
Methyl Ester Sulfonates (MES)
One New Surfactant That Can Meet These Conditions

- Methyl Ester Sulfonates (MES)
  - Inexpensive raw material
  - Good surfactant properties
  - Process available that can be used in existing sulfonation plants
Methyl Ester Sulfonates

- Derived from renewable resources
  - Natural fats and oils
  - Supply of palm oil steadily increasing
  - Current price for ME is about US$1200/MT
- High detergency and calcium ion stability
  - Less MES for equivalent washing power
  - Good blending partner with soap, LAS
- Attractive biological properties
  - Low toxicity
  - Biodegrades similar to FAS and soap
  - Biodegrades quicker than LAS
Chemithon MES Process is Versatile

- Chemithon MES process uses either lower or higher MW ME feeds
- Chemithon MES process uses higher iodine value feeds thus saving hydrogenation costs
MES Product Specifications

- **Color of MES:**
  < 100 (5% Klett) usually is adequate, <10 is possible

- **Extractable oils in MES:**
  Includes some byproducts, <4±1% AMB

- **Volatile oils in MES:**
  Mostly methyl ester, <2±1% AMB

- **By-product di-salt:**
  Less than 6% AMB

- **Actives concentration:**
  25% to 85% (alcohol-free)

- **Undetectable residual peroxides**

- **Residual alcohol to required specification**
ME Carbon Chain Determines MES Quality

- Lower molecular weight (shorter carbon chain length) ME is easier to process
- Lower molecular weight ME gives lower disalt and color
- Laundry applications require higher molecular weight ME
- Only acid bleaching gives low disalt and low color long chain MES
Need MES in Dry Form

- Laundry powder formulations
  - Use MES in dry form
  - Agglomerate / blend to final product
- Detergent bar formulation
  - Co-mix molten or powder dry MES
  - Co-extrude / form final product
- Liquid formulations – dilute to desired concentration
BioDiesel Changes Everything

- BioDiesel is Methyl Ester
- Huge worldwide increase in BioDiesel production
- Huge potential increase in ME availability
Palm-Based BioDiesel

- Need to separate $C_{16}$
- $C_{16}$ has low IV number
  - Most double bonds on $C_{18}$ fraction
  - $C_{16}$ fraction IV before hydrogenation $\sim 5$
- Easy to hydrogenate to make sulfonation quality ME
C_{16} MES Product Quality

- Active/disalt ratio: 17/1
- MES total active: 88.7%
- Disalt (100% Al basis): 5.6%
- Color (5% Klett): 10 to 20
- PEE (100% Al basis): 2.00
- Water (%): 2.3%
- Methanol (%): <0.1%
MES in Commercial Detergents

- Analysis of commercial laundry powder
  - Safeway Select Ultra II
  - 23.5% MES
  - 40 wash loads/box US$0.125 per load

- Sun Liquid Detergent
  - 4% MES
  - 4% non-ionic
MES Used In Commercial Product
Continuous Air/\(\text{SO}_3\) Sulfonation

- Sulfur Supply
- \(\text{SO}_3\) Gas Generator
- Air Supply
- Optional \(\text{SO}_3\) Absorber
- Sulfonation Reactor
- Effluent Gas Treatment
- Acid Digestion
- Product Drying TTD
- Methanol Recovery
- Bleaching
- Neutralization
- Neutralizing Agent
- \(\text{H}_2\text{O}_2\)
- Methanol
Methyl Ester Acid Bleach System

METHYL ESTER ACID FROM SULFONATOR

METHANOL

HYDROGEN PEROXIDE

CORRECTIONS

RECYLE PUMP

RECYLE HEAT EXCHANGER

POST-DIGESTER/HEAT EXCHANGER

BLEACHED ACID TO NEUTRALIZER

POST-BLEACHING DIGESTER/HEAT EXCHANGER

Steam

CWS

CWR
### C16 Sodium Methylester Sulfonate (Feedstock MW 270.2)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Active</td>
<td>88.7</td>
</tr>
<tr>
<td>Disalt (100% Al)</td>
<td>5.57</td>
</tr>
<tr>
<td>wt % Soap</td>
<td>0.28</td>
</tr>
<tr>
<td>5% Active Klett</td>
<td>18</td>
</tr>
<tr>
<td>% Pet Ether Extractable (100% Al)</td>
<td>2.00</td>
</tr>
<tr>
<td>wt % H₂O</td>
<td>2.27</td>
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<tr>
<td>wt % Methanol</td>
<td>&lt;0.10</td>
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</table>

Condition 764; dried Feb. 5, 2003
Drying of MES with Spray Towers

- Form of product critical for MES
  - MES hydrolytically unstable
  - Will hydrolyze rapidly if formulation is aqueous and basic
- Example – spray drying

<table>
<thead>
<tr>
<th>Time</th>
<th>Initial</th>
<th>After Spray Dry</th>
<th>After 1 month</th>
<th>After 2 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-Salt</td>
<td>4.40%</td>
<td>33%</td>
<td>89%</td>
<td>98%</td>
</tr>
</tbody>
</table>

Takashi Imamura, et al., French Patent 2,571,368, “Method for the Preparation of Salts of Alpha-Sulfonated Fatty Acid Esters”
An Alternative to Spray Drying
Turbo Tube™ Dryer System

- Condensate
- Vapor
- Discharge
- Turbo Tube Dryer/Stripper
- Pre-Heater Flash Tank
- Steam
- From Paste Surge Tank
- Condensate
- Flash Tank
- Plodder
- Vacuum System
- Condensate
- Dry Product

Chemithon
Turbo Tube® Dryer System

- Advantages
  - Lower capital and operating costs
  - No product degradation during processing
  - Compact, self cleaning & energy efficient
  - No moving parts
  - No fire explosion hazards
  - No plume or particle emissions
  - Enhances spray tower and agglomerator capacities and efficiencies
  - And more…
Conclusion

- MES is a desirable alternative surfactant
  - Demonstrated processing technology
  - Lower cost production
  - Hundreds of thousands of metric tons have been produced and used in detergent formulations
  - Successful in detergent market for the last 5 years
  - Adequate availability
  - New Chemithon MES plants coming on stream