-Development in the Palm Oleo Chemical Industry-

Application of Palm-based Surfactants to Liquid Detergent for Sustainable Growth in the Asian Market

LION Corporation
Masanori Nikaido
World Consumption of Fats and Oils

- **Food**: 74%
- **Chemical**: 10%
- **Feed**: 5%
- **Fuel**: 11%
- **Surfactant**: 92%
- **Others**: 8%

M.R. Chandran, JOPA (2012)
Global Market of Surfactants and Detergents
Global-Market Surfactants Production

- Anionic: 56%
- Nonionic: 34%
- Cationic: 4%
- Amphoteric: 1%
- Others: 5%

Market Volume: 13.1 million metric tons

Source: Colin A. Houston & Associates, Inc. CESIO 2011
Demand for Global Surfactants

- 50% of surfactants are used in the household fields.

Source: Surface Active Agents, October, 2008
Average growth rate of total market is about 6% per year.

Liquid market is remarkably increasing with powder one.
Asia has become the largest region in detergent market.
The Potential of Palm-based Surfactants
Palm-based Surfactants and Applications in the Household Field

- PO/PKO
- Fatty Acid Methyl Ester (FAME)
- Glycerol
- Extracts Carotene
- Anionic Surfactants (MES)
  - Powder Detergent
- Cationic Surfactants (TES)
  - Fabric Softener
- Nonionic Surfactants (MEE)
  - Liquid Detergent
- Fatty Acid Salt
  - Soap
Features of MES-Na for Powder Detergents

**Green Ingredient**
- Plant-based source, Good biodegradability

**High Detergency**
- Excellent detergency even in low concentrations
- High calcium tolerance, Anti-Soil deposition effect
- Good compatibility with enzymes

> These features help replace the petroleum-based surfactants in powder detergents.

\[ \text{MES} \quad \text{CH}_3(\text{CH}_2)_{n_1}\text{CHCOOCH}_3 \quad \text{SO}_3\text{Na} \]

The alkyl chain is consisted of C16 & C18.
Production capacity will reach 550kt in 2014, which corresponds to 4% of the global anionic surfactant market.

I. Adami, The 1st ICIS Asian Surfactants Conference(2011)
Company Profile
- Established: 2007
- Shareholder: Lion Corporation (100%)
- Product: MIZULAN (Methyl Ester Sulphonate (MES))
- Commencement of Commercial Production: 2010
- Capacity: 25,000 t/y ⇒ 50,000 t/y (September, 2013)
Recent Trend of Detergent Market in Asia
Liquid detergent is gradually growing in Asia together with development of powder detergent.
The total share of Liquid detergents has already exceeded that of powder detergents since 2010.
Key Driver for the Drastic Growth of the Asian Detergent Market

- Summary of the Asian Market Trend
  1. Surfactant and detergent markets are growing.
  2. Liquid market is increasing gradually together with powder one.
  3. Liquid share has already exceeded powder one in Japanese market.

Liquid detergents represent a crucial force that drives the drastic growth of Asian detergent market.
Provision of New features for MES in Liquid Detergents
1. **New Features of liquid detergents that can be obtained using MES**

The Detergency Properties of MES were studied under the washing conditions of liquid detergents, neutral pH and without chelating builders.

2. **The Development of a clear liquid detergent formulation**

Because C16-18 MES shows significantly higher dissolution temperature than other anionic surfactants, the low-temperature solubility of MES has to be improved.
1. Features of liquid detergents with MES
Soil Detergency

We focused on high sebum detergency, which prevents fabrics from malodor and yellowing.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Detergency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sebum</td>
<td>MES ≒ AES &gt; LAS</td>
</tr>
<tr>
<td>Stain</td>
<td>MES ≒ AES ≒ LAS</td>
</tr>
<tr>
<td>Protein</td>
<td>MES ≒ AES &gt; LAS</td>
</tr>
<tr>
<td>Clay</td>
<td>MES ≒ AES ≒ LAS</td>
</tr>
</tbody>
</table>

Condition: Neutral pH and without chelating builders
Detergency for Main Sebum Components

Conditions: pH7, Water hardness 36ppm, Surfactant 320ppm (anionic surfactant 13wt%, AE(C124EO15) 3wt%)

Oleic acid: Detergency is correlated with interfacial tension.
Triolein: Detergency is not correlated with interfacial tension.
Observation of Triolein Soil Released from Cotton

Microscope Observation

- Detergent Solution
- Soil
- Stirrer

25°C, Ca 2°DH, pH7
Surfactant 1% (Anionic / AE = 13/3)
Soil: Triolein soil + Oil Red
Observation at 60 min after contact

MES
60 min
Remove smoothly

AES
Remove very slowly

LAS
Stop during removal process
# High Detergency Mechanism for Triolein by MES

<table>
<thead>
<tr>
<th></th>
<th>AES</th>
<th>LAS</th>
<th>MES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image</td>
<td><img src="Image.png" alt="Image" /></td>
<td><img src="Image.png" alt="Image" /></td>
<td><img src="Image.png" alt="Image" /></td>
</tr>
<tr>
<td>O/W Interface</td>
<td>Adsorption</td>
<td>Slow</td>
<td>Very fast</td>
</tr>
<tr>
<td>Viscoelasticity</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Mechanism</td>
<td>Slow adsorption on o/w interface, rolling-up; slow.</td>
<td>High viscoelasticity, rolling-up; stop.</td>
<td>Well-balanced o/w properties, rolling-up; smooth.</td>
</tr>
</tbody>
</table>
2. Development of Clear Liquid Detergent Formulation
**MES Solubility at Low Temperatures**

**<Evaluation of Solubilization temp.>**
Check Solubilization temp. visually after the temperature rises 1 °C each and holding at each temp. for 1 hour.

**Conditions:** Anionic surfactants (MES-Na*, AES(2)-Na, LAS-Na) 15%

*MES is the mixture C16MES and C18MES

**Approach**
1. co-surfactant
2. Hydrotropes
3. Counter-ion exchange

![Graph showing solubility temperatures for MES-Na, AES(2)-Na, and LAS-Na at low temperatures.](image_url)
Improvement of Solubility at Low Temperatures by Alkanolamine

R-SO₃⁻Na⁺ + H₂SO₄ + H₂N~OH ↔ R-SO₃⁻H₃⁺N~OH + Na⁺₂SO₄²⁻

MES-Na  Alkanolamine  MES-Alkanolamine

Conditions: MES-Na 15%, Alkanolamines 5%. pH was controlled to 7.5 by sulfuric acid.

<table>
<thead>
<tr>
<th>Solubilation temp./°C</th>
<th>None</th>
<th>MEA</th>
<th>DEA</th>
<th>TEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Structure of Alkanolamines

<table>
<thead>
<tr>
<th></th>
<th>MES-Na</th>
<th>MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>HO-</td>
<td>NH₂</td>
</tr>
<tr>
<td>DEA</td>
<td>HO-</td>
<td>NH</td>
</tr>
<tr>
<td>TEA</td>
<td>HO-</td>
<td>NH</td>
</tr>
</tbody>
</table>

OH
The additives combination of MEA and Aromatic Sulfonic Acid improved the low temperature stability of MES equally to LAS-Na.
Summary

1. Market Trend
Liquid detergents are gradually growing in Asia, and they will serve as a driving force for a further growth of the Asian detergent market.

2. Two Strategies for the application of MES in Liquid Detergents
> MES shows excellent detergency properties suitable for liquid detergents. One of the most important features of MES is the ability of smoothly removing sebum.
> The low-temperature solubility of MES was improved by using MEA and aromatic sulfonic acid as additives.
Thank you for your attention!
Asian surfactant market will dramatically expand by 2030
Application for Concentrated MES Solution

No additives

+MEA 5%, Sulfonic acid 15%

- fluidity area, L1: Micellar phase, H1: Hexagonal phase, I1: Cubic phase, S: Solid phase
Detergency for Sebum / Concentration of Surfactant

Detergency for Sebum / Water Hardness

Conditions: pH7, Washing 10min., Rinsing 3min.(2 times), 25°C, Bath ratio 30, White cotton swatches (5 × 5cm) 10pcs, Model sebum: 1% on weight of fabric, Surfactant 320ppm (anionic surfactant 13wt%, AE(C124EO15) 3wt%), Extracted soil: Oleic acid, Triolein, Squalene, Cholesterol
Detergency for Sebum / Temperature

Conditions: pH7, Washing 10min., Rinsing 3min.(2 times), Bath ratio 30, White cotton swatches (5 × 5cm) 10pcs, Model sebum: 1% on weight of fabric, Water hardness 36ppm, Surfactant 320ppm (anionic surfactant 13wt%, alcohol ethoxylate (AE: C124EO15) 3wt%), Extracted soil: Oleic acid, Triolein, Squalene, Cholesterol
Dynamic Interfacial Tension

Conditions: pH7, 25ºC, Water hardness 36ppm, Surfactants concentration 300ppm (anionic surfactants /AE=13/3)

Decrease rate of interfacial tension: LAS > MES > AES
But why does rolling-up stop in the case of LAS?
Interfacial Viscoelasticity

**Conditions:**
- pH 7, 25°C, Water hardness 36ppm,
- Surfactants concentration 300ppm (anionic surfactants /AE=13/ 3)
- Oil: Triolein, Time: 30s later from forming a Oil drop
- Oscillation method: Amplitude dA/A (deformation submitted to the interface of the oscillation) was about 10%

Easy to lift to the cotton surface

Interfacial Modulus: MES < AES < LAS
Launched Liquid Detergent with MES

Top liquid (Malaysia)

SOUTHERN LION launches Liquid Detergent with MES in Malaysian Market

*Clear
*Free flow liquid
Oleo Chemical Materials and Surfactants

- CPO
- PKO
- Fatty Acid
- Methyl Ester
- Glycerol
- Ester, Soap Amide, Amine
  - N-derivatives
    - MEE
    - MES
  - SO₃
    - AS
    - AE
    - AES
  - EO
    - SO₃
    - EO

Features of MES: Green Ingredient

MES Granule (MIZULAN)

Plants (Palm Oil)

Domestic sewage water

Plant-based Detergent (Surfactant)

Carbon offsetting

Biodegradation ( Decomposes into CO2 and H2O)

O2

CO2

H2O

MES is carbon neutral.
**MES (Methyl Ester Sulfonate)**

**Palm Oil**

\[ \text{CH}_3(\text{CH}_2)_n\text{COOCH}_2 \]
\[ \text{CH}_3(\text{CH}_2)_n\text{COOCH} \]
\[ \text{CH}_3(\text{CH}_2)_n\text{COOCH}_2 \]

**Fatty Acid Methyl Ester**

Trans esterification

\[ 3\text{CH}_3\text{OH} \rightarrow 3\text{CH}_3(\text{CH}_2)_n\text{COOCH}_3 \]

Sulfonation

\[ 3\text{SO}_3\text{Na} \]

**MES**

\[ 3\text{CH}_3(\text{CH}_2)_{n1}\text{CHCOOCH}_3 \]

| SO\(_3\)Na

*The alkyl chain is consisted of C16 & C18.*
Expansion of Methyl Ester Derivatives to other Field

This application study will be presented in Oils and Fats International Congress at Kuala Lumpur next month.
Global Trend of Electrical Insulating oil

〜1972 PCB
Low toxicity

1975〜 Mineral Oil
Eco-friendly

1990〜 Vegetable Oil Derivatives
Biodegradability
Low Cost

LION Chiba Plant
Many kinds of vegetable based oils are coming to the market.

Synthetic esters: IEC61099
Natural esters: IEC62770(FDIS)
Higher flash point (350°C)

Lower flash point (100°C)

Higher kinetic viscosity 40 mm²/s (40°C)

Lower kinetic viscosity 5 mm²/s (40°C)

Vegetable oil

Polyol ester

Mineral oil

PFAE

Silicone

Classification of Insulating Oils
**Characteristics of Palm Fatty Acid Ester (PFAE)**

1) Safety (High Flash Point)
2) High Fluidity (High cooling quality)
3) High Insulation Quality

\[ R-C-O-R' \]  
( \( R, R' \) : C6 ~ 18 )

<table>
<thead>
<tr>
<th>Items</th>
<th>Condition</th>
<th>Unit</th>
<th>PFAE</th>
<th>Vegetable oil</th>
<th>Mineral oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point</td>
<td>COC</td>
<td>DegC</td>
<td>186</td>
<td>330</td>
<td>152</td>
</tr>
<tr>
<td>Kinetic viscosity</td>
<td>40DegC</td>
<td>mm(^2)/s</td>
<td>5.1</td>
<td>32.9</td>
<td>8.1</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>(80DegC)</td>
<td></td>
<td>2.95</td>
<td>2.91</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Global Trend of Electrical Insulating oil
Cooling Efficiency of PFAE

Cooling efficiency can be improved by 10% compared to mineral oil based on lower viscosity.
Installation records of transformers PFAE filled

KEIO Railway
Kamikitazawa transformer substation
For outdoor, diaphragm conservator
Lower noise type
4,380/2 x 2,265kVA
Operation started from Mar/2011

TOBU Railway
Fujimino transformer substation
For indoor, nitrogen sealed
Lower noise type
3,000kVA
Operation started from Mar/2011

This application study will be presented in Oils and Fats International Congress at Kuala Lumpur next month.
## Properties comparison between PFAE and other oils

<table>
<thead>
<tr>
<th>Items</th>
<th>Condition Unit</th>
<th>PFAE</th>
<th>Mineral oil</th>
<th>Vegetable oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>(15DegC) g/cm³</td>
<td>0.86</td>
<td>0.88</td>
<td>0.93</td>
</tr>
<tr>
<td>Kinetic viscosity</td>
<td>40DegC mm²/s</td>
<td>5.1</td>
<td>8.1</td>
<td>32.9</td>
</tr>
<tr>
<td>Flash point</td>
<td>COC DegC</td>
<td>186</td>
<td>152</td>
<td>330</td>
</tr>
<tr>
<td>Pour point</td>
<td>DegC</td>
<td>-32.5</td>
<td>-45</td>
<td>-20</td>
</tr>
<tr>
<td>Total acid value</td>
<td>mgKOH/g</td>
<td>0.005</td>
<td>&lt; 0.01</td>
<td>0.035</td>
</tr>
<tr>
<td>Moisture</td>
<td>mg/kg</td>
<td>15</td>
<td>&lt; 10</td>
<td>43</td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>(80DegC)</td>
<td>2.95</td>
<td>2.2</td>
<td>2.91</td>
</tr>
<tr>
<td>tanδ</td>
<td>(80DegC) %</td>
<td>0.31</td>
<td>0.001</td>
<td>0.67</td>
</tr>
<tr>
<td>Volume resistivity</td>
<td>(80DegC) Ω·cm</td>
<td>$1.9 \times 10^{13}$</td>
<td>$7.6 \times 10^{15}$</td>
<td>$3.7 \times 10^{12}$</td>
</tr>
<tr>
<td>Breakdown Voltage</td>
<td>(2.5mm) kV</td>
<td>81</td>
<td>70 - 75</td>
<td>77</td>
</tr>
</tbody>
</table>

- Lower viscosity than mineral oil
- Higher flammable point than mineral oil
- PFAE-immersed transformer has better cooling and insulating performance in paper-and-oil composite insulation systems
Oxidation stability of PFAE (Appearance)

JIS C2101 at 120°C for 75 hours with continuous oxygen supply

Before

After

The appearance of PFAE was clear, whereas mineral oil turned into a reddish-brown with sludge.
Vision

Various Lipids Sources

Lipid
- $R_1\text{COOCH}_2$
- $R_2\text{COOCH}$
- $R_3\text{COOCH}_2$

FAME
- $R_1\text{COOCH}_3$
- $R_2\text{COOCH}_3$
- $R_3\text{COOCH}_3$

Lipid Residue

Saccharide

Crude Glycerol
- $\text{H}_2\text{C}\text{OH}$
- $\text{HC}\text{OH}$
- $\text{H}_2\text{C}\text{OH}$

Industrial Applications

Oleaginous yeast
Lipid Production from Crude Palm Glycerol

【Conditions】Strain: Lipomyces starkeyi CB1807, YD Medium, 30°C, Crude Glycerol: 60g/L

Residual Glycerol (g/L) vs. Lipid Production (g/L) over Culture Time (d)
### Lipid Production from Crude Palm Glycerol

<table>
<thead>
<tr>
<th>Properties of oil</th>
<th>Yeast Oil from Crude Glycerol</th>
<th>Refined Palm Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid Value (mg-KOH/g)</strong></td>
<td>0.7</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td><strong>Iodine Value (g-I₂/100g)</strong></td>
<td>59.0</td>
<td>45～56</td>
</tr>
<tr>
<td><strong>Fatty Acid Distribution (wt%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C16F0</td>
<td>33.7</td>
<td>45～48</td>
</tr>
<tr>
<td>C16F1</td>
<td>5.2</td>
<td>trace</td>
</tr>
<tr>
<td>C18F0</td>
<td>5.3</td>
<td>4～5</td>
</tr>
<tr>
<td>C18F1</td>
<td>52.9</td>
<td>38～41</td>
</tr>
<tr>
<td>C18F2</td>
<td>2.6</td>
<td>8～10</td>
</tr>
<tr>
<td>others</td>
<td>0.4</td>
<td>1～2</td>
</tr>
</tbody>
</table>

*Few impurities such as gum substance and free acid
*Approximately the same fatty acid distribution as palm oil