MES Technical Presentation for Liquid Detergent

April, 2014
LION ECO CHEMICALS SDN BHD
R&D
Agenda

1. Characteristics of MES
2. Model Formula with MES for Powder Detergent
3. Application of MES for Liquid Detergent
4. Model Formula with MES for Liquid Detergent
Characteristic of MES
Clean CH O Na+ - O3S

Sulphonic group

Methyl ester group

Alkyl chain group
Characteristic of MIZULAN

1. Higher detergency in low concentration
2. Higher detergency in hard water.
3. Compatibility with enzyme
4. Anti-soil deposition effect
5. Lower foaming, but can be controlled
6. Higher biodegradability
7. Carbon neutral concept
8. Possible to reduce the STPP/Zeolite
Detergency of MES based on Each Carbon Chain

Conditions: artificial soil (cotton), Terg-O-Tometer, 25°C,
Water hardness 54ppm(CaCO3)

16MES > C18MES > LAS > C14MES = AS

米山雄二、油化学、44、2 （1995）
梅原謙二、皐月輝久、油脂、44、54 （1991）
High Detergency in Low Concentration

High Detergency at Low Dosage in Hard Water Condition

Conditions: Terg-O-Tometer 120 rpm 15 min., 35°C, 180mg/L as CaCO$_3$, Krefeld 10D (cotton), Na-Ash 250ppm, Zeolite 300ppm

MIZULAN shows superior detergency
High Detergency in High Water Hardness

Precipitation behavior of MIZULAN and Anionic Surfactants

<Conditions>
Surfactant 400ppm, Water Hardness 90ppm as CaCO3, Temp 25°C, Scale 10ml

Hold Time

1min

10min

MIZULAN/LAS = 1/1

MIZULAN | LAS | Soap | FAS-Na
MIZULAN: higher water hardness tolerance.

Conditions: Terg-O-Tometer 120rpm 15min, Krefeld10D (cotton), Surfactant 270ppm, Na-Ash 270ppm 25°C
Compatibility with Enzyme

MIZULAN keeps enzyme activity in water solution.

Conditions:
Surfactant 800ppm, Protease 50ppm, Zeolite 1000ppm, Sodium carbonate 1000ppm, 40°C
Enzyme Stability in Liquid Detergent

Enzyme: Protease
Storage condition: 35°C

MES formula keeps good enzyme stability
MIZULAN has good anti-soil deposition effect

Conditions: Terg-o-Tometer, Washing 10min., Rinsing 3min.(2 times), 25º, Total 3 times wash, Actual Tap water in Malaysia (Fe 0.3-0.4ppm, CaCO3 28ppm)
Bath ratio: 30, White cotton swatches (5 × 5cm) 10pcs, Artificial Soil 1% on weight of fabric: Surfactant 300ppm (pH=7)
Anti-soil Deposition effect

After 3 washes (repeat)

MIZULAN has good anti-soil deposition effect

MIZULAN  AES  LAS  AE

Conditions: Terg-o-Tometer, Washing 10min., Rinsing 3min. (2 times), 25º, Total 3 times wash,
           Actual Tap water in Malaysia (Fe 0.3-0.4ppm, CaCO3 28ppm)
           Bath ratio: 30, White cotton swatches (5 × 5cm) 10pcs, Artificial Soil 1% on weight of fabric
           : Surfactant 300ppm (pH=7)
Conditions: Twin-tub 25°C, Water hardness 5DH (CaCO₃ 89.5ppm), after Washing 10min
Dosage: 2g/L (2,000ppm), Oil soil 0.2%owf+Test cloths
Formula (%): Surfactant 20, Na-ASH 12.5, Zeolite 15, Na₂SO₄ 30
Foam level of MES Formula

We can keep same foam level with 5000ppm detergent dosage compare to control products
How to control foam volume with Low dosage

Control of foam level is very important for detergent, MES is lower foam ability than LAS. But we can control foam level with additional agent (C12-14 Alcohol)

Twin tub: 25°C water 30L (CaCO3 90ppm), Cotton Shirts 1Kg, Detergent 50g (1667ppm) Surfactant 18% , Oil soil 0.2% owf, Washing 10 min

Control of foam level is very important for detergent, MES is lower foam ability than LAS. But we can control foam level with additional agent (C12-14 Alcohol)
MES for Non(Low) Phosphate

LAS Detergent

- Decrease STPP content

LAS Detergent + MES Post Addition

- Maintain
  - *Powder Property*
  - *Drying Capacity*

*Powder Property: lower*
*Drying Capacity: down*

MES enabled to obtain the low(No) phosphate powder without detergency decrease with high process productivity.
By Post Addition of MES, compact detergent can be developed easily and simply (EU manufacturer have developed compact by this idea)
Biodegradability of MES

Test method: OECD 301C
Source: METI (Ministry of International Trade and Industry) in Japan
Lion Japan referred to METI data base, made this figure
Global Environment Friendliness

Carbon Neutral

MIZULAN™ (MES Compound)

Palm oil

Plants (Palm)

Carbon offsetting

CO₂

Plant-Based Detergent (Surfactant)

Domestic sewage water

Biodegradation (Decomposes into CO₂ and H₂O)

H₂O

O₂
Model Formula with MES for Powder Detergent
### Model formula with MES in Powder Detergent

<table>
<thead>
<tr>
<th>Formula</th>
<th>LAS Formula</th>
<th>MES Model formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS-Na</td>
<td>15%</td>
<td>8%</td>
</tr>
<tr>
<td>MES (MIZULAN)</td>
<td>-</td>
<td>5%</td>
</tr>
<tr>
<td>Na2CO3 (Soda Ash)</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Zeolite</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>STPP (Sodium Triphosphate)</td>
<td>4%</td>
<td>2%</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td><strong>Total Surfactant Dosage</strong></td>
<td>15%</td>
<td>13%</td>
</tr>
</tbody>
</table>
Detergency of Proposal formula

**Water Hardness 200ppm**

- **Testing Condition**: water temperature 25°C, bath ratio 30, washing time 10 minutes, detergent dosage 2,000ppm

- **Krefeld 10D**: 50%
- **EMPA 116**: 60%
- **EMPA 101**: 40%
- **Spinach**: 70%

**Control** vs **Proposal**
Detergency of Proposal formula

Testing Condition: water temperature 25°C, bath ratio 30, washing time 10 minutes, detergent dosage 2,000ppm
Application of MES for Liquid Detergent
The mail soil of cloth

Sebum soil composition

- Triglyceride
- Fatty acid
- Others
- Cholesterol ester
- Cholesterol
- Squalene

Soil composition on 1 day worn undershirt

- Sebum soil: 69%
- Protein soil: 18%
- Inorganic soil: 13%

Kashiwa et al., Yukagaku, 19, 35 (1970)

Removing Sebum soil is the key factor to obtain the high detergency products
Substitution for LAS in Liquid Detergent

Detergency increases dramatically with only 25% replacement from LAS to MES

Conditions: Krefeld10D (Pigment, sebum/cotton), Terg-O-Tometer, 25ºC, Dosage:2g/L, CaCO3 100ppm , Formula (%):Surfactant 10, MEA 0.5
Substitution for LAS in Liquid Detergent

Conditions:
- EMPA 101 (Olive oil / cotton), Terg-O-Tometer, 25°C,
- Dosage: 2g/L, CaCO3 100ppm, Formula (%): Surfactant 10, MEA 0.5

Detergency maintains with 50% replacement from LAS to MES.
Substitution for AES in Liquid Detergent

Conditions: Krefeld10D (Pigment, sebum/cotton), Terg-O-ometer, 25°C, Dosage: 2g/L, CaCO3 100ppm, Formula (%): Surfactant 10, MEA 0.5

MES and AES are same Detergency
Substitution for AES in Liquid Detergent

Conditions: EMPA 101 (Olive oil / cotton), Terg-O-Tometer, 25°C, Dosage: 2g/L, CaCO3 100ppm, Formula (%): Surfactant 10, MEA 0.5

MES and AES are same Detergency
MIZULAN Detergency under Soaking Condition

Conditions
- Soaking condition: Surfactant 200ppm, Na2CO3 250ppm, Zeolite 300ppm, Everlase 6T 15ppm, Soaking time 0, 30, 60, 120 min, 25°C Soil: EMPA 116(Protein soil)
- Washing condition: Terg-o-Tometer, Washing 10min., Rinsing 3min.(1 times), 25°, Bath ratio: 30,

MIZULAN has high detergency even shorter soaking time compare to LAS
How to apply the MES flakes into Liquid Detergent

Put MES into main mixing tank directly.

Ingredients:
- Water
- Surfactant
- Stabilizer
- MIZULAN FL 80
- Preservative
- Pigment
- Enzyme
- Perfume
- Preservative

Mixing Process:
1. Put MES into main mixing tank directly.
2. Mix the MES flakes with other ingredients in the mixing tank.
3. The mixture is then packaged for use.
MIZULAN Dissolving Rate

Evaluation condition:
- 1L Flask with baffle plate, Single 4 pieces rake paddle,
- 475rpm (Pv=0.44kw/m3), Scale 500g

MES flake:
- Lot No.20110702-4, Bag No.719-720

Dissolution time:
- With eye

MES dissolves warm water easily
Hydrolysis of MES in Liquid Detergent

MES is stable at pH range 5-9 even under high temp. condition
Hydrolysis Speed of MES Slurry at Various pH

Hydrolysis speed(%/h)

Temperature:
- 80°C
- 60°C
- 40°C
- 20°C

pH

W. Stein, H. Baumann, J. Am. Oil Chemist Soc. 52 (1975) 323
Model Formula with MES for Liquid Detergent
## Model Formula with MES in Liquid Detergent 1

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LAS</strong></td>
<td>9.0%</td>
<td>5.0%</td>
<td>4.0%</td>
<td>3.0%</td>
</tr>
<tr>
<td><strong>MES</strong></td>
<td>0.0%</td>
<td>5.0%</td>
<td>6.0%</td>
<td>7.0%</td>
</tr>
<tr>
<td><strong>AE(EO:7)</strong></td>
<td>9.0%</td>
<td>5.0%</td>
<td>5.0%</td>
<td>5.0%</td>
</tr>
<tr>
<td><strong>SLES</strong></td>
<td>2.5%</td>
<td>2.5%</td>
<td>2.5%</td>
<td>2.5%</td>
</tr>
<tr>
<td><strong>Total Surfactant</strong></td>
<td>20.5%</td>
<td>17.5%</td>
<td>17.5%</td>
<td>17.5%</td>
</tr>
</tbody>
</table>
The amount of LAS in the formulation could be reduced by replacing it with MES while maintaining same detergency.

Conditions: Krefeld 10D, EMPA 101, 116, Terg-O- Timer, 40°C, 10 min, dosage: 7,500 ppm. Water hardness 150 mg/L as CaCO₃.
# Low Temperature Stability of Model Formula

<table>
<thead>
<tr>
<th>(AI%)</th>
<th>Ref.</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
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</thead>
<tbody>
<tr>
<td>LAS</td>
<td>9</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>MES</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>AE(EO=7)</td>
<td>9</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>SLES(EO=2)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mono Ethanol Amine</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Appearance (3 weeks)</th>
<th>50C</th>
<th>25C</th>
<th>5C</th>
<th>0C</th>
<th>-5C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
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<td>Clear</td>
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<tr>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Gel</td>
<td>Gel</td>
</tr>
<tr>
<td>Clear</td>
<td>A little Cloudy</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
</tr>
</tbody>
</table>

We have a know-how for keeping low temp. stability.
## Improve the low temperature stability

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<thead>
<tr>
<th></th>
<th>Control.</th>
<th>Model 1</th>
<th>Model 1’</th>
<th>Model 4</th>
<th>Model 4’</th>
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</thead>
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<tr>
<td>LAS (AI%)</td>
<td>9</td>
<td>5</td>
<td>5</td>
<td>7.5</td>
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<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Mono Ethanol Amine</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ethanol*¹</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

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</tr>
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<td>A little Cloudy</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td></td>
<td>Clear</td>
<td>Gel</td>
<td>Gel</td>
<td>A little cloudy</td>
<td>Clear</td>
</tr>
</tbody>
</table>
# Survey and Analysis of Sebum Soil

<table>
<thead>
<tr>
<th>Survey area</th>
<th>Japan, South Korea</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hong Kong, Malaysia, Thailand</td>
</tr>
<tr>
<td>Test subject</td>
<td>Male (20’s-50’s), n=50</td>
</tr>
<tr>
<td>Material of Shirts</td>
<td>Cotton 100%</td>
</tr>
<tr>
<td>History of Shirts</td>
<td>1) Pre-treated</td>
</tr>
<tr>
<td></td>
<td>2) 10 cycles of Wearing &amp; Washing</td>
</tr>
<tr>
<td>Measurement of remained sebum</td>
<td>1) Solvent extract</td>
</tr>
<tr>
<td></td>
<td>2) Gas, Liquid Chromatography</td>
</tr>
</tbody>
</table>
The ingredient of the residual sebum isn’t much different in each country.