Questions about MES

1. Is MES an acceptable surfactant for consumer products?

The major detergent players use mixed surfactant systems to balance their cost economics. The use of alternative surfactants to LAS is governed by the prices of the alternative alkylates and their availability on a sustainable basis. ME derived from palm stearin and the MES derived from them, emerge as potential replacements because of the relative cost advantages.

Currently over 40 consumer products containing MES are sold worldwide. MES is used to manufacture detergent powders and is also formulated into both light-duty and heavy-duty liquid detergents. MES is also used in combination soap bars. The commercial success of these products demonstrates that MES has tremendous potential as a consumer product surfactant.

2. What sources can be used to supply ME?

MES can be produced from different ME feedstocks which, in turn, can be derived from vegetable oils such as soybean, rapeseed, canola, coconut oil, palm/palm derivatives, and animal fats such as tallow and lard. The choice of feedstock is cost dependent. Lauric oils (C12 and C14) normally have a higher cost as compared to the palmitics (C16 and C18), which have a lower and relatively stable price. From an economic standpoint, the preferred feed is palm stearin, which is derived when processing palm oil and is in the nonedible category.

3. What is the impact of the biodiesel industry on ME and MES?

The increase in demand for biodiesel has spurred biodiesel production from palm-sourced raw materials such as palm stearin. Malaysia and Indonesia have recently announced that they will set aside 40% of their combined palm oil production for manufacture of biodiesel. Palm-based biodiesel contains a mixture of unsaturated and saturated C16 and C18 ME. The C16 methyl esters are mostly saturated, and biodiesel containing large percentages of C16 ME will not pass the EU biodiesel standard for CFPP (cold filter plugging point). The saturated C16 fraction can be removed by thermal fractionation and, as the production of palm-based biodiesel increases, the supply of C16 ME will be greatly increased. Luckily, C16 ME makes an excellent raw material for manufacture of MES since the resulting surfactant has both excellent surfactant qualities and good cold-water solubility. The fact that removal of the C16 fraction is required means that a large quantity of by-product C16 ME from biodiesel production will be available. The future economics of MES will be tied to the availability of this by-product C16 ME.

Because disposal of large amounts of by-product C16 ME are necessary, C16 ME availability at very competitive prices for manufacture of MES is ensured, and MES use will expand rapidly due to its excellent detergent properties and lower cost.

4. What processes are currently being used to manufacture MES commercially?

Lion Corporation of Japan uses their own patented acid bleaching process to produce approximately 40,000 metric tons/year of MES that is sold as formulated detergent products in Japan and southeast Asia. Stepan Company uses their own acid bleaching technology to produce approximately 50,000 metric tons/year of MES, which is sold for consumer product uses.

5. What are the economics of the MES process?

Currently U.S. LAB costs are US$1490/metric ton while European costs are approximately US$1350/metric ton. In contrast, RBD palm stearin costs less than US$450/metric ton. The cost for processing palm stearin into a distilled, hydrogenated ME feed suitable for manufacture of MES is approximately US$200/metric ton which gives an ME feed cost of approximately US$650/metric ton.

The table below summarizes the raw material consumption norms along with the processing costs. It can be used as a guideline in calculating the surfactant cost given the organic raw material cost.

<table>
<thead>
<tr>
<th>ME</th>
<th>LAB</th>
<th>SLS C1214</th>
<th>AS C1218</th>
<th>AOS C1416</th>
<th>MES C16</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>342</td>
<td>292</td>
<td>312</td>
<td>316</td>
<td>372</td>
</tr>
<tr>
<td>Consumption</td>
<td>720</td>
<td>705</td>
<td>715</td>
<td>700</td>
<td>748</td>
</tr>
</tbody>
</table>

Table 1: Raw material and processing cost
C18 requires higher wash temperatures in cold-water solubility, and the presence of palmitic range, the C16 offers the best detergent manufacturing process. In the powder for use in the post-tower section of the reactor and that can be flaked or ground to a product which solidifies at room temperature and is lightly hydrogenated (IV less than an ME that has been stripped of unsaturates and is very slow and requires storage of material containing both methanol and peroxide for periods of up to 24 hours. For a commercial-scale plant, the risks of storing such a mixture in large tanks with their associated free space containing a potentially flammable vapor are obvious. Thus, all commercially demonstrated MES processes incorporate acid bleaching.

6. What are the quality parameters for MES? What is the significance of each?

The main quality parameters for MES required for detergent use are:

- Product in dry form with low color (for ease of dry mixing and for consumer acceptance of a light-colored product)
- Product with low characteristic fatty odor (for lower fragrance use)
- Product with minimum by-products including di-salts, dimethyl sulfate, and methanol (yield and safety reasons)
- Good solubility in cold water (energy saving)
- Easy biodegradability (environmentally friendly)

These attributes can be met by sulfonating an ME that has been stripped of unsaturates and is lightly hydrogenated (IV less than 0.2%). High-active MES based on lauric oils is in the form of a soft paste. MES produced from the palmitic oil results in a product which solidifies at room temperature and that can be flaked or ground to a powder for use in the post-tower section of the detergent manufacturing process. In the palmitic range, the C16 offers the best cold-water solubility, and the presence of C18 requires higher wash temperatures in dissolving the surfactants.

7. Why have only the acid bleaching MES processes been commercialized?

Acid bleaching processes have demonstrated superior product quality, especially for palm stearin-based products where acid bleaching yields lower color (less than 20 Klett units) products with di-salt levels in the 4% range (100% active basis). Additionally, the acid bleaching process is a rapid reaction that allows a continuous process with a total residence time of less than 2 hours. On the other hand, neutral bleaching is very slow and requires storage of material containing both methanol and peroxide for periods of up to 24 hours. For a commercial-scale plant, the risks of storing such a mixture in large tanks with their associated free space containing a potentially flammable vapor are obvious. Thus, all commercially demonstrated MES processes incorporate acid bleaching.

8. What is di-salt and why are di-salt (NEA) levels in MES a major concern?

Di-salt is formed by hydrolysis of the ester linkage in ME, a process that yields methanol and a carboxylic acid. High or low pH environments promote degradation of ME into methanol and di-salt. Compared to MES, di-salt has very poor surfactant qualities.

Di-salt also has very poor solubility in cold water. This is significant because good cold-water solubility is essential for detergent use in Asia and other regions where room-temperature water is the wash norm. Because of its poor solubility and poor surfactant performance, di-salt represents at best a net loss of ME raw material and in the worst case a limitation on the use of MES in detergent formulations. Since the cost of ME represents more than 70% of the cost of MES, it is apparent that minimizing di-salt has a significant impact on the MES process economics.

Early in the development of the Chemithon patented MES process, we recognized that minimization of di-salt was essential. Years of pilot plant studies demonstrated that only an acid bleaching process would produce low color, low di-salt products from the full range of ME feedstocks. However, even though our acid bleaching process has been a demonstrated large-scale commercial success, Chemithon has continued to work closely with our existing customers to enhance MES product quality. We have recently installed process improvements into one of our customer’s operating plants that have enabled routine manufacture of palm stearin-based MES with di-salt levels in the 4% range (100% active basis) and Klett colors less than 20. The incredible active-to-di-salt ratio of this product (> 23:1) allows wide latitude in formulating MES into a finished detergent product.

9. What by-products are present in MES and what safety concerns do they raise?

The by-products potentially present in MES are di-salt, methanol, dimethyl sulfate, and dimethyl ether. Di-salt as just discussed is a major by-product of MES manufacture.

Methanol is present in the process after sulfonation and has been measured at several tenths of one percent in the digested acid prior to bleaching and prior to any alcohol addition. Additionally, several percent methanol can be released into the system from hydrolysis of MES into di-salt during neutralization since each mole of di-salt that is formed releases a mole of methanol. This hydrolysis is especially severe when little or no alcohol has been added to the process prior to neutralization.

Methanol in the system can form hydrogen methyl sulfate by reaction with free sulfur trioxide, or with the adduct of the methyl ester sulfonic acid and sulfur trioxide. The hydrogen methyl sulfate can then react with methanol to form dimethyl sulfate (DMS). Chemithon has performed extensive evaluations of the formation and presence of DMS in the products. While part per million (ppm) levels of DMS have been detected in the bleached sulfonic acid, extensive testing has verified that none is detectable in neutral MES—even at part per billion levels. This is because DMS is destroyed by the addition of NaOH during the neutralization step.

The DMS can further react with methanol to form hydrogen methyl sulfide and dimethyl ether (DME). DME has been detected in the digested acid prior to bleaching or methanol addition. This chemistry can occur with any alcohol present in the system such as the methanol formed during di-salt formation. In the Chemithon acid bleaching process, DME is removed from the system by an N₂ purge of the bleacher digester.

The safety issues in MES processing involve the presence of flammables and oxygen in the system together. Chemithon has conducted extensive HAZOP studies of its MES process to ensure that it meets the most rigorous safety and environmental protec-
10. Can MES be made in existing sulfonation plants?
The sulfonation reactors in existing air/SO₃ sulfonation plants can be used to sulfonate ME. Further processing steps are required to produce a commercially viable MES. The equipment required to perform these unit operations can be added to the sulfonation unit. Typical costs for add-on MES equipment at an existing sulfonation plant are estimated at:

- 2 TPH – US$ 2.7 million
- 3 TPH – US$ 3.4 million
- 5 TPH – US$ 4.5 million

11. What is the history of the Chemithon MES process?
Chemithon began work on its first MES process in 1983. The initial process was a combination process incorporating both acid and neutral bleaching steps. In 1988 a plant incorporating this dual bleaching process was built for Wuxi Dazhong Chemicals in Wuxi, China. The experience from this plant operation led to the conclusion that a continuous acid bleaching process is preferable to the slow neutral bleaching step.

Further refinements to the Chemithon MES process were made over the next several years. In the mid 1990s, two additional plants incorporating the second generation of Chemithon’s acid bleaching process were commissioned in China. These plants were a technical success but, due to lack of ME feedstock, were not a commercial success. All during this time, Chemithon continued active research on MES, resulting in the filing of patents for the next generation of the Chemithon Acid Bleaching Process.

Between 1996 and 2000 three more MES plants were sold. One of these, for Corporación Cressida in Honduras, was never installed due to damage from Hurricane Mitch. The other two, a semi-works plant (larger than a pilot plant but too small for a commercial unit—usually used to make test marketing samples) for the Malaysian Palm Oil Board and the world’s largest MES plant for Huish Detergents Inc., have been great successes.

Since the Huish plant was commissioned in February 2002, Chemithon has remained actively engaged at the plant site. At its customers’ request, Chemithon has modified the plant to meet new regulatory requirements, improve plant economics, and enhance product quality beyond the level required by contract. Chemithon has incorporated into its present design all of the process and equipment improvements learned during the past four years’ operation of the world’s largest and most advanced MES facility. Continuous collaborative improvement efforts with the Houston plant management and operating personnel have provided Chemithon with the necessary hands-on experience, data, and testing in commercial operation to ensure future success of large-scale MES facilities. New customers will receive the benefits of reduced installed cost, rapid startup, high product quality, lower operating cost, greater plant flexibility, and enhanced reliability.

12. What is the future of MES?
Chemithon believes that use of MES in the world surfactant market is poised for tremendous growth. With hundreds of thousands of tons of new palm-based biodiesel slated to be produced annually, lack of suitable ME feed, one of the major impediments to commercialization of MES, has been eliminated. In this context it is interesting to note that Huish Detergents is also recognized as a supplier of biodiesel.

In early 2006 Chemithon sold a large MES sulfonation plant to a joint venture consisting of Lonkey Industrial Company Ltd., a Chinese surfactant manufacturer, Golden Hope, a vertically integrated Malaysian palm oil producer and Cognis Oleochemicals. Golden Hope will supply ME raw material to Lonkey, who will operate the MES plant. This sale confirms the model of integrating ME manufacture with MES processing and is a portent of the future growth pattern for MES.

Methyl ester sulfonate, photo courtesy Charlie Foster