

# Methyl Ester Sulfonates

[www.aocs.org](http://www.aocs.org)

a guide to biorenewable resources



Process **Innovation** that goes directly  
to your **Bottom line**

## *The Time is Ripe for MES Production*

### **Global Partners**

#### **IIT Sri**

Europe, Middle East,  
North Africa

#### **Chemithon Engineers Pvt. Ltd.**

South and Southeast Asia

#### **Chemithon Beijing**

Asia Pacific

#### **Mitsui Bussan**

Japan

Since 2002 Chemithon has worked closely with our customers to perfect MES production processes. We provide core technologies for the operation of the world's largest MES plant. And the most profitable. Our patented acid bleaching MES processes are the first to be commercialized on a large scale in the U.S. for liquid and dry products. And the results are stunning! Chemithon's patented process produces a pure white flake with an unmatched 21:1 active/disalt ratio. Our MES process has manufactured more than 250,000 tons of the highest quality MES product on the market today. Less waste and purer end product mean higher profits and easier final product formulation. With huge increases in oil prices and the advent of Palm-based BioDiesel, the time is ripe for MES.

Compare Chemithon processes and equipment with any on the market and you'll discover how our product innovations can impact your bottom line!



**Patented Digestion,  
Bleaching and  
Neutralization Processes**



**Patented Stripper and  
Dryer Processes**



**Purer Product. A 21:1  
active-to-disalt ratio.  
The best in the industry.**



# **CHEMITHON**

The Chemithon Corporation, 5430 West Marginal Way SW, Seattle, WA 98106 USA  
Tel: (206) 937-9954 Fax: (206) 932-3786, (206) 937-9933  
Website: [www.chemithon.com](http://www.chemithon.com) E-mail: [chemoffice@chemithon.com](mailto:chemoffice@chemithon.com)

# Gimme a break! (price, that is)

by Norman Foster, Ph.D., Vice President-Marketing, Chemithon

Is there a way to beat the high cost of detergent feedstock? With the increase in crude oil prices and the resultant rise in the cost of petrochemicals, methyl ester sulfonates (MES) derived from palm and coconut are gaining a great deal of attention.



Linear alkyl benzene (LAB) produced from petrochemical raw materials is under severe price pressure from its key ingredient inputs, i.e., benzene and olefins. Other alternate petrochemical-based feedstocks such as synthetic alcohols and alpha olefins have also seen significant price escalation in the past year and will no doubt continue their

upward climb.

World production of palm oil since 1995 has increased to 33,326,000 metric tons, up 119% for the decade. The rising price of petroleum ensures that the market for much of this growth will now be earmarked for biodiesel production, where the saturated C16 fraction is an undesirable element that must be reduced in motor fuels. Fortuitously, this biodiesel by-prod-

uct is an ideal methyl ester (ME) feed for the manufacture of MES. Refined, bleached, deodorized (RBD) palm stearin at its current price provides MES with a cost to market that is approximately US\$400/metric ton less than the cost of linear alkyl benzene sulfonate (LABS). The strength of the palm-based biodiesel market will ensure that sulfonation-grade ME will continue to be readily available at a price comparable to its fuel value. Thus MES offers a viable cost alternative to the LABS currently used by detergent producers. Additionally, its origin from a renewable oleo-based raw material, its excellent biodegradability, improved calcium hardness tolerance, and excellent detergency are also credited with its rapidly expanding acceptance and use.

The challenges for MES in detergent use include low foam characteristics and formulation constraints when using MES in a high pH liquid form. The issue of low

foam can be addressed by inclusion of co-surfactants, such as a lauric chain length or the addition of foam boosters such as alpha olefin sulfonates (AOS). The availability of MES in recent years as a dry, free flowing powder or in flaked form has overcome most of the manufacturing issues as the product can be directly added to the detergent formulation in a post-addition step. Lion Corporation, Stepan Company and Chemithon Corporation have commercialized acid bleaching technologies for manufacturing MES. MES is produced in Japan by Lion (40,000 metric tons/year) and in the USA by Stepan (50,000 metric tons/year) and Huish Detergents (80,000 metric tons/year). The Huish facility, which began commercial operation in 2002, uses the patented Chemithon Acid Bleaching technology for manufacture of MES. Huish produces MES in a free flowing powder form while both Lion and Stepan produce liquid MES forms. These powder and liquid MES products are being formulated into liquid and powder consumer products that are widely sold throughout North America and Japan. Today MES is used in dozens of commercial detergent formulations and as a co-surfactant premium combination soap bar.

The traditional workhorse surfactant LABS now has a viable challenger. Thanks to its economical manufacture, the increasing supply of feedstock, and high detergency in hard water, the leading position may soon be occupied by the environmentally friendly MES. ■

## Table of Contents

- 3 Introduction:  
Gimme a break! (price, that is)
- 4 Industry poll
- 7 Commercial application of the  
Chemithon MES process
- 9 Questions about MES
- 13 MES overview
- 14 MES in China
- 15 Resource page



### inform Staff

Press Director: Greg Reed ([gregr@aocs.org](mailto:gregr@aocs.org))  
Editor-in-Chief: James B. Rattray ([informeditor@aocs.org](mailto:informeditor@aocs.org))  
Managing Editor: Jeremy Coulter ([jeremyc@aocs.org](mailto:jeremyc@aocs.org))  
Associate Editor: Chelsey D. Hillyer ([chillyer@aocs.org](mailto:chillyer@aocs.org))  
Staff Copy Editor: Marguerite Torrey ([mtorrey@aocs.org](mailto:mtorrey@aocs.org))  
Publications Department Editor: William Gillespie ([williamg@aocs.org](mailto:williamg@aocs.org))  
Advertising Sales: Amie Ziegler-Fernandes ([amiez@aocs.org](mailto:amiez@aocs.org))

### AOCS Officers

President: Howard Knapp, DBC Research Center, Billings, MT, USA  
Vice President: Philip Bollheimer, Bollheimer & Associates Inc.,  
Memphis, TN, USA  
Secretary: Casimir Akoh, University of Georgia, Athens, GA, USA  
Treasurer: Steven Hill, Kraft Foods, Inc., Glenview, IL, USA  
Executive Vice President: Jean Wills, AOCS, Champaign, IL, USA

### AOCS Mission Statement

To be a global forum to promote the exchange of ideas, information, and experience, to enhance personal excellence, and to provide high standards of quality among those with a professional interest in the science and technology of fats, oils, surfactants, and related materials.



Sponsored by Chemithon  
[www.chemithon.com](http://www.chemithon.com)

# Methyl ester sulfonate industry poll

For a cross section of the current state of methyl ester sulfonate worldwide, *inform* asked a variety of experts from the international MES industry to respond to two sets of questions: “In your opinion, what is the state of the MES industry? On a local and global scale? How is it expanding? Any new and exciting developments?” and “Within your discipline, what do you find are the primary challenges to MES development in global markets?”

Yongguo Fu  
CEO  
Lonkey Industrial  
Company, Ltd.  
Guangzhou, China  
[www.lonkey.com.cn](http://www.lonkey.com.cn)



1) Though the MES industry has developed for a long time and has recently undergone rapid improvements, it is still in a local state, established only in the USA and Japan. As a detergent producer in China, we deeply understand the value of MES. For a long time, MES developed slowly because of many problems in manufacture and application. But with improvements in technology, the manufacture and application of MES have become an irresistible trend. MES will take an important part in the surfactant industry and will make a revolution in the detergent industry.

We believe the MES industry will develop more after Lonkey’s MES project and other companies’ similar projects have been put into production. We’re proud to contribute to the development of MES.

2) That people are unfamiliar with MES, though it is not a new product, is the primary challenge to its development. During our study of MES, we encountered many problems and difficulties, such as the risk of manufacturing control ability, the application technique, etc. But in the process of solving these problems, we

became more familiar with MES and fortified our confidence to develop it. We believe MES will have a great future.

Tom Giese  
Business Development  
Manager – MES  
Stepan Company  
Millsdale, Illinois USA  
[www.stepan.com](http://www.stepan.com)



1) MES was first researched by the US Department of Agriculture during the mid 1950s in an effort to find additional uses for tallow. Stepan developed and sold MES as early as 1963. Whereas initial product offerings were plagued by inconsistencies in color and hydrolysis, recent process improvements and control of side reactions have greatly improved product quality. Only recently have high crude oil prices coupled with modest natural fats and oil prices, most specifically palm oil, created a compelling basis for use of MES in consumer products.

The key to successful MES commercialization lies in flexibility. For example, the best raw material for MES use in Brazil, where tallow is abundant, is likely to differ from the most logical starting material in Asia, where palm plantations abound. The Holy Grail lies in having the flexibility to change your MES chemistry based on the evolution of global oleochemical markets.

The most exciting MES development over the past few years has actually been in alternative fuels. Biodiesel, a chemistry based primarily on soybean oil in the US, also can be made from palm oil. Palm oil contains many more C-16s than soybean oil. These C-16s are undesirable in biodiesel but preferable for MES. Biodiesel expansion in Asia offers the possibility for more abundant C-16 ME at reasonable cost. With petroleum, ethylene oxide, linear alkyl benzene, and lauryl alcohol all up between 50 and 70% since 2004, and the biodiesel market growing, never has the outlook been brighter for MES.

Consumers are increasingly desirous of renewable “natural” technologies. A compelling story can be told around the MES life cycle. The chemistry starts with the fruit of a palm tree. The intermediate can be sold as biorenewable fuel (biodiesel) and used to make a safe, biodegradable surfactant with excellent cleansing properties.

“The Holy Grail lies in having the flexibility to change your MES chemistry based on the evolution of global oleochemical markets.”

2) Educating industry how to use MES effectively is paramount. Whereas formulating products with commonly used surfactants such as LAS or ether sulfate is well understood, formulating consumer products with MES can be challenging. MES is not stable in highly alkaline conditions. The challenges can be overcome; it is simply a matter of educating formulators.



Palm fruit, photo courtesy Malaysian Palm Oil Board (MPOB)

## Poll of MES industry leaders

Dr. Salmiah Ahmad  
Director of Advanced  
Oleochemicals  
Technology Division  
Malaysian Palm Oil  
Board (MPOB)  
Selangor, Malaysia  
[www.mpob.gov.my](http://www.mpob.gov.my)



1) Realizing the potential for Malaysia to supply raw material for the production of the surfactant MES, MPOB started promoting the idea, and in 2005 Lonkey Industrial Co. Ltd. in China expressed interest in the production of MES using Malaysian feedstock. MPOB started introducing Lonkey to Malaysian companies. On July 27, 2006, Lonkey Industrial Co. Ltd. in China and Golden Hope Berhad and Cognis Oleochemicals Sdn. Bhd. of Malaysia signed a memorandum of understanding to investigate and promote the development of MES.

Lion Corporation of Japan and Huish Detergent USA have started using MES based on palm oil as active ingredients in their finished products while Stepan USA produced MES based on lauric oils.

Currently there is a lot of interest among companies in China and India. MPOB has been providing services relating to the production of MES and product formulation using MES to local companies, as well as to companies in India and China.

2) MES is suitable as an active ingredient in cleaning products (e.g., powder and liquid detergents). Some markets still prefer the low-density powder. Low-density powder is usually produced *via* spray-drying technique. MES cannot be spray-dried as this will cause the active ingredient to be hydrolyzed and converted to a less active by-product—di-salt.

ME for the production of MES has to be competitively priced in order to create the interest for companies to produce MES to substitute for LAS. However, ME is currently in high demand for biodiesel and the price is therefore high.

MES has better detergency, detergency in hard water, and biodegradation and ecotoxicity characteristics than LAS. MES should therefore fetch a premium price compared to LAS. However, the

majority of the interest is to substitute LAS, and therefore the MES price has to be competitive.

The process to produce MES is complicated compared to sulfation of alcohol and alcohol ethoxylates and sulfonation of alkyl benzene.

Ping Xia  
China Marketing  
Manager  
Chemithon Corp.  
Beijing, China  
[www.chemithon.com](http://www.chemithon.com)



1) A new era for MES is coming. Chemithon stated more than ten years ago that five criteria must be met for any promising new surfactant: plenty of resources, equal or better surfactant properties, demonstrated production technology, demonstrated formulation technology, and competitive cost.

Palm oil has made the very best “magic” in agriculture during the past three decades by increasing oil production rates to 8–10 times per hectare over all other oil plants, such as soybean, peanut, coconut, and rapeseed. The promising biodiesel markets will further ensure that the resources needed for MES-grade ME will reach a level of 1–2 million tons per year in 5–10 years. Considering that the present LAB world consumption is about 3 million tons per year, this amount of ME would make a significant change on the face of the world surfactants and detergents market. There will be no problem for ME to reach the market needs in time and to follow up the progress of MES properly, since the investment for ME is much lower than that required for LAB. ME process technology is mature and readily available anywhere, and the setup schedule for an ME facility is much shorter than that for MES.

MES is not only good, but in fact has excellent characteristics for most aspects of concern to the Chinese market, including hard water detergency, cold water detergency, good detergency in zero or low phosphorus detergents, mildness, biodegradability, and compatibility with other additives in detergents.

It is true that the MES production process is 3–4 times longer than “standard” sulfonation processes and much more sophisticated, with patented re-esterifica-

tion, acid-bleaching, and drying systems to ensure low color and low di-salt. Dedicated engineering, training, and maintenance are absolutely necessary to ensure that the MES plant is run stably, safely, and with high efficiency to ensure the remarkable benefits.

Coincidentally, the soaring petroleum price is another key issue to drive all surfactants/detergents producers to look very closely at MES, whether or not they are going to take action soon. The US\$400-per-ton net production cost difference between LABS and MES cannot be ignored by anyone in this business.

2) There is a real trend to go to MES around the world now. Some top players might appear more conservative because their existing facilities and famous labels might be devalued through this change. However, most of the smaller players, especially those in developing countries such as China, may take the potential benefits more aggressively in the short term since they have little to lose.

---

“MES today is like a brilliant young man at his 18th birthday party, looking forward to a bright future.”

---

MES today is like a brilliant young man at his 18th birthday party, looking forward to a bright future. There are still plenty of challenges ahead, to improve and polish the production process and to enlarge its application. All of these are issues for managers, engineers and chemists in this business to face in the coming decade.

Life is always full of challenges. The more risk, the more benefit. It is always a choice whether to wait for full development and wide application or to be early to claim the opportunity. Based on my conservative judgment, there will be 200,000–400,000 tons of MES produced per year in China within 5–10 years. One 5 tons/hour, or 40,000 tons/year, Chemithon MES plant is under construction at Lonkey Industrial Co., Ltd., Guangzhou, China. This is only the first phase of the project. Its final goal

is to reach 200,000 tons/year within 5–10 years. Some other MES plants are also coming soon in China. Meanwhile, about the same amount of MES will be produced in other Asian countries in this region.

A new era for MES is really coming.

S. N. Trivedi  
Regional Director  
Chemithon Corp.  
Mumbai, India  
[www.chemithon.com](http://www.chemithon.com)



1) The use of MES is increasing. The growth in use of anionic surfactants is driving the growth of MES. In the growing economies of India and China, a strong growth in use of MES as an anionic surfactant for detergent use is projected at 6–7% per year.

The technology challenges for manufacturing MES have been met and the Huish Detergents Inc.'s plant in Houston is proof of this.

A new development is fractionating pure C16 ME from biodiesel produced from palmitic oils. In southeast Asia 2.5 million tonnes of biodiesel capacities have been announced and are under implementation. The availability of C16 ME with a purity greater than 99.5% and an iodine value (IV) less than 0.5 is projected at 1.0 million tonnes per year. The high purity C16 ME does not require hydrogenation and can be used directly for making MES.

2) The primary challenge for use of MES is the ability to formulate it in detergent products.

In Asia the challenge lies in formulating MES in low-cost detergent formulations for consumers who are very price sensitive. In Europe the substitution potential for MES for low suds detergent formulations offers interesting challenges. In the US, the formulation of MES in liquid laundry products has technology challenges.

The growth of MES is not likely to be limited by the tariffs and trade barriers in the different countries. However, competition of alternative surfactants, viz. alcohol sulfates and olefin sulfonates, may pose future challenges.

Southeast Asia will have a significant increase in the natural alcohols capacities (0.8 million tonnes) which will add to competitive pricing pressures for them.

There are two linear alpha olefin plants planned in the Middle East. These plants are based on the use of natural gas, which is significantly discounted in price as compared to the crude oil. Thus, alpha olefins too will be available at competitive pricing and will pose a challenge to the growth of MES for detergent applications.

Asia and Latin America have a large consumption of oils for manufacturing of soaps, which are an alternative to detergents. MES, like the other anionic surfactants, can be added to the oil-based soaps to make combo products and this could add to the growth of the MES business in these regions.

In my view, MES and AOS can be priced aggressively as compared to the other surfactants and will find a nice fit in the alternate surfactants strategy of detergent manufacturers.

Guanglin Sun  
Senior Development  
Manager  
Unilever, Home and  
Personal Care  
Trumbull, Connecticut,  
USA  
[www.unilever.com](http://www.unilever.com)



1) The MES industry is still in an early stage, even though MES has been an interesting anionic surfactant for more than 20 years. With the rapidly rising crude oil price in the last three years, the importance of MES and other surfactants derived from renewable resources has significantly increased. The MES scale in the US has become quite big and is continuously expanding, mainly driven by i) The production of MES feedstock (ME), combined with the biodiesel manufacturing, can provide a scale benefit to drive the ME manufacturing cost down. ii) The substantial progress made in ME sulfonation ensures low di-salt generation. iii) MES has been successfully applied in both powder and liquid laundry detergents in the United States and other parts of the world. iv) Prices continue to rise significantly for conventional anionic surfactants manufactured from crude and natural gas resources.

Unilever has successfully used MES in All/Surf powder detergents. We are interested in expanding the application of MES and other surfactants from renewable resources to other products. As an environ-

mentally friendly surfactant, MES can also provide performance benefits to consumers.

## Geopolitical instability and its impact on crude oil supply provide more incentive for investors to expand MES infrastructure and capacity globally.

2) Further reducing the cost and improving the quality of MES are the primary challenges to MES development in global markets. More cost effective approaches in MES utilization in different product formulations can also aid in MES expansion. The application of MES in laundry and other cleaning products could increase dramatically if the price of MES becomes more attractive and the MES raw material becomes more user friendly. Geopolitical instability and its impact on crude oil supply provide more incentive for investors to expand MES infrastructure and capacity globally. With the growing pressure in environmental protection, the importance of using environmentally friendly surfactants from renewable resources, such as MES, will be recognized by more people, from business leaders to consumers. More strategic partnerships will be formed by the producers covering different stages and the end users, promoted by investors, responsible retailers, and politicians. A new era of MES development and expansion is on the horizon. ■



Huish MES plant in Houston, photo courtesy Chemithon

# Commercial application of the Chemithon MES process

Since 1983, Chemithon Corporation has recognized the importance of MES and has devoted significant resources to developing commercially attractive MES processes. Chemithon's criterion for the process is production of the highest quality MES containing low color, low di-salt and a high level of conversion of ME to MES. Low color is vital for consumer acceptance while low di-salt and high yield are important for process economics. The result of this work has been the development of a patented, continuous acid bleaching process (U.S. 5,723,433, U.S. 5,587,500, U.S. 6,058,623 and corresponding international patents) for making high-quality MES. This process is illustrated in Figure 1 and has been described in numerous publications.

In this process sulfonation is performed in a proprietary Chemithon Annular Falling Film Reactor designed for precise contacting of the ME feedstock with a mixture of sulfur trioxide gas in very dry air. The mole ratio of these primary reactants (moles of SO<sub>3</sub> per mole of ME) is precisely controlled and maintained uniform everywhere in the reactor. Commercial production plants are equipped with air-SO<sub>3</sub> gas generating systems that use molten sulfur as a primary raw material. The gas-liquid reaction mixture discharging from the falling film reactor passes through a high efficiency cyclone, which separates the spent gas stream from the fresh methyl ester sulfonic acid (MESA). The fresh MESA passes through a digester where it is held at an elevated temperature for approximately one hour, allowing the MESA mixture sufficient time for the sulfonation reaction to reach completion.

A side effect of MESA digestion is a significant darkening of the sulfonic acid mixture. In order to reduce the color to a commercially acceptable level, the digested MESA is metered into a continuous acid bleaching system where it is admixed with a controlled flow of methanol and with hydrogen peroxide bleach. The bleaching

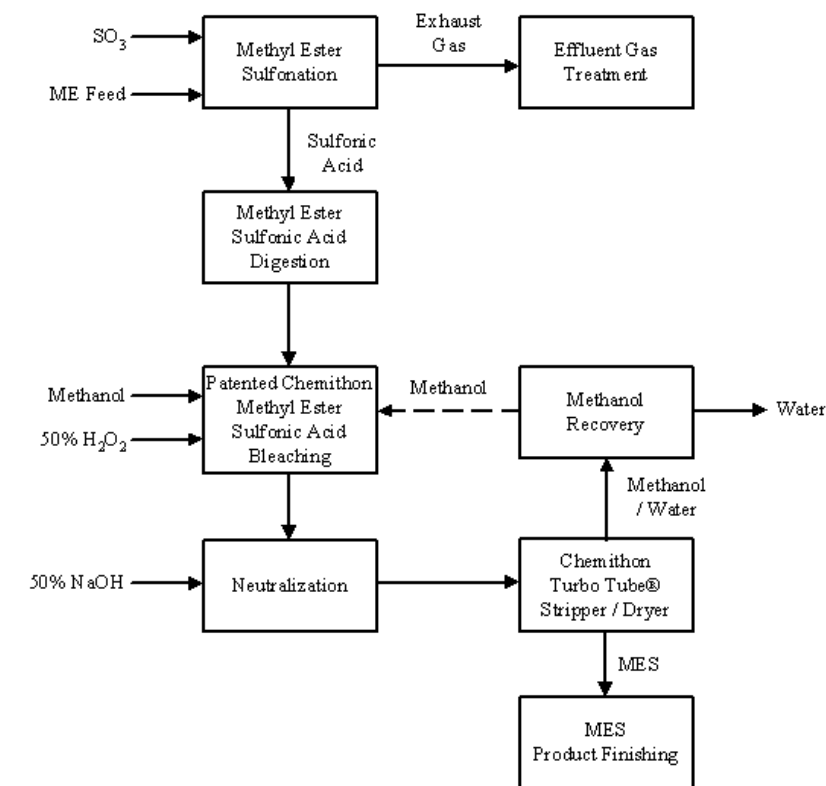


Figure 1: Continuous Process for the Manufacture of Ultra-Pure MES

reaction is carried out with refluxing methanol and precise temperature control. The methanol addition is used to prevent MESA degradation to form undesirable byproducts such as di-salt. The bleached MESA continuously flows through a proprietary bleacher vessel on its way to the neutralizer. The MESA is admixed in the neutralizer with the required flow of 50% caustic soda to produce methyl ester sodium sulfonate in the form of a uniform concentrated paste that contains the residual methanol. The neutralizer operates continuously, maintaining the composition and pH of the paste automatically.

Next, the neutral MES paste is forwarded to a proprietary Turbo Tube® Dryer system where the methanol and excess process water are removed to leave a dry granulated MES product. The recovered

methanol is distilled and recycled back to the bleaching process. The final step is formulating and preparing the MES product into its final composition as a liquid, semi-solid bar, or as a solid granule, using appropriate technology.

## Process safety

Process safety is a basic requirement regardless of the route used to make the MES product. Bleaching technology that uses hydrogen peroxide must be constructed of suitable passive materials to avoid peroxide decomposition into oxygen. Regardless of the level of methanol addition, methanol will be present due to formation of byproduct di-salt, and therefore any vapor space in the process system must be controlled so that a safe, nonflammable

composition is guaranteed. Because the hazards associated with handling flammables are a direct result of the potential presence of flammable mixtures in vessel vapor spaces, processes that minimize the volume of flammable materials are intrinsically safer than those that require large volumes.

Chemithon MES plants have been the subject of extensive Hazard and Operability (HAZOP) studies to ensure that they meet the most rigorous safety and environmental protection standards. The fact that a Chemithon MES plant has been underwritten by Factory Mutual Underwriters speaks volumes about the safety of the process and equipment supplied by Chemithon.

## Economics of MES

The application of MES for detergent and personal care applications requires attractive economics. The current worldwide interest in biodiesel has made ME widely available. The use of palm derivatives, which contain mixtures of saturated and unsaturated C16 and C18 moieties for biodiesel manufacture, means that a portion of the saturated C16 ME must be removed from the biodiesel so that the product will meet biodiesel pour point specifications. As palm-based biodiesel manufacture increases, a continued supply of byproduct C16 ME will be made available.

Currently U.S. LAB costs are US\$1400/metric ton. In contrast, RBD palm stearin costs are currently 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, yielding ME prices of approximately US\$650/metric ton.

Table 1 compares the cost of manufacture of MES and LABS. Even though the operating cost of MES manufacture is higher than that of LABS, the opportunity to use a much less expensive organic raw material results in a savings of approximately US\$400/metric ton of surfactant when MES is substituted for LABS. For a large-scale MES plant with a capacity of 50,000 metric tons/year, the potential annual savings by switching to MES exceeds US\$20,000,000. It is apparent from examination of the table that the feedstock cost represents the major component (70%) of the cost of MES. This critical fact supports the decision to develop and patent a process

		MES		LABS	
Raw Materials	\$/MT	T/T	\$/T	T/T	\$/T
Sulfur	110	0.110	12.10	0.102	11.22
LAB	1400	--	--	0.721	1009.40
ME	650	0.748	486.20	--	--
NaOH	176	0.191	33.62	0.132	23.18
MeOH	192	0.080	15.36	--	--
H <sub>2</sub> O <sub>2</sub>	750	0.060	45.00	--	--
Na <sub>2</sub> SO <sub>4</sub>	100	0.020	2.0	--	--
N <sub>2</sub>	75	0.035	2.63	--	--
<b>Total Raw Materials</b>			<b>596.91</b>		<b>1043.80</b>
<b>Utilities</b>					
Electricity	102/MWH	0.209 MWH	21.35	0.180 MWH	18.36
Steam	8.70/MT	2.05 T	17.83	0.140	1.22
Cooling Water	21.74/KT	0.055 KT	1.20	0.055KT	1.20
<b>Total Utilities</b>			<b>40.38</b>		<b>20.78</b>
Operating Labor			12.00		12.00
Maintenance			10.65		10.65
General OH (50% Op Cost)			6.63		6.63
Tax & Insurance (1% Capital)			1.96		0.88
<b>Operations Costs</b>			<b>31.24</b>		<b>30.16</b>
<b>Total Cost /MT</b>			<b>US\$668.53</b>		<b>US\$1096.64</b>

Table 1: Comparison of the cost of MES and LABS

that minimizes the loss of yield due to formation of di-salt.

## Commercial success

The world's largest MES sulfonation plant (80,000 metric tons/year) was announced in 2001 and started operation in February 2002. Since that time hundreds of thousands of tons of world quality MES have been produced using the Chemithon acid bleaching MES process. This MES has been formulated into more than 30 different consumer products, some of which are illustrated in the picture at the lower right. These products have been highly successful due to their competitive pricing and excellent performance relative to competitive products in the marketplace.

In late July 2006 another large MES sulfonation plant using Chemithon's acid bleaching technology was announced. This plant will be operated by a joint venture consisting of Lonkey Industrial Company Ltd., a Chinese surfactant manufacturer, Golden

Hope, a vertically integrated Malaysian palm oil producer that has recently announced installation of a biodiesel facility, and Cognis Oleochemicals. The plant will manufacture MES from biodiesel byproduct MES supplied by Golden Hope. This project confirms the validity of a business model based on integration of biodiesel and MES manufacture and bodes well for the continued commercial success of MES. ■



Products containing MES

# 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. Huish Detergents Inc. uses the patented Chemithon Acid Bleaching Process (U.S. 5,723,433, U.S. 5,587,500, U.S. 6,058,623 and corresponding international patents) to produce approximately 80,000 metric tons/year of MES in their Pasadena, Texas, USA plant. The output from this plant is formulated into more than 30 different consumer detergent products.

## 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.

Plugging in current raw material costs (US\$650/metric ton for ME and US\$1400/metric ton for LAB), it is apparent that even though the operating cost of MES manufacture is higher than that of LABS, the ability to use a much less expensive organic raw material

	LAB	SLS C <sub>1214</sub>	AS C <sub>1218</sub>	AOS C <sub>1416</sub>	MES C <sub>16</sub>
<b>MW</b>	342	292	312	316	372
<b>Consumption of organic raw material kg/MT of dry form, active ≥ 90%</b>	720	705	715	700	748
<b>Processing cost/ton of AM as sodium salt (dry form)</b>	US\$110	US\$150	US\$155	US\$160	US\$190

Table 1: Raw material and processing cost

results in a savings of approximately US\$400/metric ton of surfactant when MES is substituted for LABS.

## 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 sulfate 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 N<sub>2</sub> 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 pro-

tection standards. A Chemithon MES plant has been underwritten by Factory Mutual Underwriters.

## 10. Can MES be made in existing sulfonation plants?

The sulfonation reactors in existing air/SO<sub>2</sub> 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. ■





5430 West Marginal Way SW, Seattle, WA 98106-1598  
 Tel. (206) 937-9954 • Fax (206) 932-3786  
 E-mail: [chemoffice@chemithon.com](mailto:chemoffice@chemithon.com)  
[www.chemithon.com](http://www.chemithon.com)  
 Celebrating 50 Years 1954 - 2004

**C<sub>16</sub> Sodium Methylester Sulfonate (Feedstock MW 270.2)**

Active (wt %)	93.5 %
Disalt (100% AI basis)	4.1 %
Active/Disalt Ratio	23.4
Color (5% Active Klett)	17
Pet Ether Extractable (wt %, 100% AI)	1.5%
Methanol (wt %)	0.01%
Water (wt %)	2.4%

Methyl ester sulfonate, photo courtesy Charlie Foster

Process **Innovation** that goes directly  
to your **Bottom line**

## *Patented TurboTube® Technology Produces the Highest Grade Dry Surfactants Available Today*

### Global Partners

#### IIT Srl

Europe, Middle East,  
North Africa

#### Chemithon Engineers Pvt. Ltd.

South and Southeast Asia

#### Chemithon Beijing

Asia Pacific

#### Mitsui Bussan

Japan

Dry surfactant products offer versatility, ease of handling and lower shipping cost than high active pastes. Our patented Turbo Tube® Dryer produces dry surfactant actives at lower capital and operating costs than other methods. You can dry high active surfactant pastes without worry of fire, explosion hazards or plumes. Its energy efficient, non-dusting, with no moving parts. The Turbo Tube® Dryer is compact and actually enhances spray tower and agglomerator capacities and efficiencies. It's self cleaning too! An unbeatable set of features and benefits you've come to expect from Chemithon.

Commercial installations on three continents prove the technical and economic benefits of this process. Contact us today to learn how you can lower your surfactant drying costs.



**Alcohol Sulfate Needles**

#### Dry Surfactant Products

Methyl Ester Sulfonates – C<sub>16</sub> C<sub>16/18</sub> C<sub>12/14</sub> C<sub>14/16</sub> C<sub>18</sub>

Fatty Alcohol Sulfates – C<sub>12</sub> C<sub>12/14</sub> C<sub>14/15</sub> C<sub>16/18</sub> C<sub>12/18</sub>

Alpha Olefin Sulfonates – C<sub>14</sub> C<sub>14/16</sub> C<sub>16/18</sub> C<sub>14/18</sub>

Linear Alkylbenzene Sulfonate

Mixed Detergent Actives



**MES Flakes**



# **CHEMITHON**

The Chemithon Corporation, 5430 West Marginal Way SW, Seattle, WA 98106 USA

Tel: (206) 937-9954 Fax: (206) 932-3786, (206) 937-9933

Website: [www.chemithon.com](http://www.chemithon.com) E-mail: [chemoffice@chemithon.com](mailto:chemoffice@chemithon.com)

# MES overview

by Salmiah Ahmad, Director of Advanced Oleochemicals  
Technology Division, Malaysian Palm Oil Board

## What is MES?

An anionic surfactant, MES can be derived from ME through a rather complex process. But it has many advantages, including good detergency, especially C16, C18, and therefore can be derived from palm oil instead of palm kernel oil. MES performances are equivalent to and sometimes better than the well-established surfactants.

MES in the flake form can be ground, then mixed with other powder additives to produce powder detergent, or dissolved and blended with other solid or liquid ingredients to produce liquid detergents.

## MES vs. LAS

The performance of MES, although better than LAS, has not attracted attention due to the low cost of LAS. Petroleum-based products are anticipated to increase in price due to depletion of resources and recent dramatic increases in price. Due to the high cost of linear alkyl benzene (LAB) and therefore linear alkyl benzene sulfonates

(LAS), MES could compete with LAS not only in performance but also in cost.

The performance of powder and liquid detergents derived from MES based on palm stearin ME has been extensively studied by the Malaysian Palm Oil Board, and, in general, MES is found to be better than or comparable to LAS or products based on LAS. Powder detergents based on MES have been tested against different types of stains and in most cases the products formulated with MES are either better than or comparable to the best product available in the Malaysian market.

MES has good calcium tolerance and is more biodegradable than LAS. The toxicity of MES varies according to chain length: the lower the chain length, the lower the toxicity. C16-18 MES exhibits toxicities similar to LAS.

## Biodiesel and MES

The supply of ME used to be a major issue since the majority of the ME producers produced C12- and C14-based and not C16 and C18 ME.



C12 and C14 ME are used as feedstock for the production of fatty alcohols, and they are therefore usually lauric oil-based. These methyl esters can be used for the production of MES but of course the price will be higher due to the high cost of lauric oils.

Production of biodiesel or ME from oils/fats involves conversion of the free fatty acids and oils/fats into ME using methanol and catalyst to produce ME and crude glycerine. The ME is then distilled. If there is a need to produce winter fuel, the ME needs to be fractionated to separate the solid and liquid ME. The biodiesel process therefore produces two co-products: crude glycerine and saturated ME. Saturated ME is a suitable feedstock for the production of MES.

As of July 2006, the number of requests for biodiesel licenses in Malaysia stood at 98, and 42 licenses have been approved. Assuming 100% implementation, then the amount of ME available will be close to 3.9 million tonnes. Assuming that the ME are fractionated to winter fuel and that 30% saturated ME are being produced, implies that about 1 million tonnes of saturate ME will be available for the production of MES.

In the year 2000, CAHA (Colin A. Houston & Associates) projected the world demand for raw materials to produce anionics to grow at 3% annually from 2.5 million tonnes in 1999 to 3.5 million tonnes in 2010. Assuming 30% substitution of LAS with MES, the anticipated ME required is 1 million tonnes. Thus Malaysia will have enough capacity to supply raw material for the production of MES. Malaysian companies producing biodiesel (especially winter fuel) from palm oil will be strategic partners since they can offer ME at a competitive price. ■



Successful precommercial trial of MES plant in China: Malaysian Palm Oil Board (MPOB) with Lonkey Industrial Co. Ltd., photo courtesy MPOB

# History of MES in China

by Ping Xia, China Marketing Manager, Chemithon Corporation

R&D on MES was started at Wuxi Light Industry University, China, in the late 1970s. There were also several small production facilities in the capacity range of 300 tons per year *via* oleum sulfonation in batch processes. Preliminary results were promising and encouraged some companies to go further.

The first wave of MES development in China occurred between 1988 and 1993. During that period, three Chemithon MES plants were imported for Wuxi, Chengdu, and Dalian, with capacities from 1 to 2 tons/hour respectively. A 2,000 tons/year MES plant was also set up at Nantong with a local process. None of those plants made real benefits from MES for different reasons.

Among the four MES plants, Wuxi had made MES paste with acceptable di-salt and color, and successfully made detergent powder with it using a regular spray tower. However, the powder became blocked within a few weeks and lost most of its detergency. A study found that most of the MES in the powder had turned into di-salt. Further, NaClO, applied as the bleaching agent, was found to be unworkable as the end products were skin irritants.

Two lessons were learned from this effort:

1. H<sub>2</sub>O<sub>2</sub> is to be applied as the bleaching agent to replace NaClO.
2. A common spray tower is improper for processing MES into detergent powder, as the pH, water, and temperature in that procedure cause serious hydrolysis of MES. The Chemithon Turbo Tube Dryer® was developed to replace that procedure.

The second wave of MES came to China right after the breakthrough Huish plant was constructed in Houston in 2002, about five to ten years later than expected due to the negative previous experiences. Almost all of the top managers in the Chinese detergent business intended to visit to witness that successful operation and import similar plants. Unfortunately, Huish preferred to keep a low profile and did not permit visits.

However, hundreds and thousands of tons of Huish detergent products containing MES successfully poured into North American

supermarkets over the next three years with equal or better quality and at much lower prices than most competitors. The Chemithon MES technology, and new MES formulations, different from the traditional formulation procedure, were successfully demonstrated.

## Different MES processes in China

*Raw material ME feed specification.* Chemithon's principle is to make top grade MES products from readily available common ME feed, with an IV of 0.5–1.0. The competitor's process requires highly purified and hydrogenated ME feed with an IV under 0.1. As is well known, IV under 0.1 is available from special producers only, while IV between 0.5 and 1.0 is a common market product. The production cost of the two different grades of ME will affect the production cost of the MES significantly.

*Bleaching.* The Chemithon re-esterification and acid bleaching process takes one hour to obtain low color (20–40 Klett units) and di-salt (4–6%), whereas competitors' neutral bleaching needs 24 hours to reach doubled figures of color (50–100 Klett units) and di-salt (8–12%). In addition, bleaching agent is necessary for the neutral bleaching process which has been described by some end-products producers as "improper" or "unacceptable."

*Safety concerns.* As H<sub>2</sub>O<sub>2</sub> and methanol are added in the bleaching loop, there are safety issues that must be taken care of properly. Since most detergent producers in China were old soap makers, at the outset they were not familiar with advanced petrochemical processes and technology and worried about the safety of the process. However, this problem has been solved through professional evaluation and instruction with a better market understanding about the real process and operation. It has been especially verified that, from the explosion-proof point of view, the same safety issues must be overcome whether dealing with acid or neutral bleaching systems as long as methanol and H<sub>2</sub>O<sub>2</sub> are involved.



*Cost.* In order to keep the high performance of H<sub>2</sub>O<sub>2</sub> as a bleaching agent, special construction materials replace stainless steel in the Chemithon bleaching system, which raises the equipment price. After recognizing the great benefit of MES as compared with LABS, and the function of the special materials to ensure high-quality MES production at low consumption of H<sub>2</sub>O<sub>2</sub>, this cost is now considered reasonable.

*Maintenance.* The Turbo Tube Dryer® and Chilled Belt have been considered the best solution thus far for processing MES products into flakes. However, this equipment requires regular maintenance and must be shut down for a few hours every one to two weeks for cleaning.

*Sampling.* After all of the positive and negative experiences, people in China clearly understand that MES process is different from other sulfonation products. A few nice samples do not mean much for MES. On the contrary, it can be claimed as a success only after hundreds and thousands of tons of MES are successfully poured into the market. In addition to the basic process technology, a great number of engineering problems had to be solved properly. It has taken 15 years for Chemithon to fulfill those steps with an extensive R&D program, while WXLIU has not passed that gap yet after 20 years. It is a costly procedure, especially on a commercial scale.

It is quite unusual to have almost no serious competition on the MES market for the time being. As the needs are so strong, some qualified competitors definitely will appear in the near future. Objectively, that would be even more helpful for the development of MES. ■

# Resources page

## Meetings

Sixth World Conference on Detergents. October 9–12, 2006, Montreux, Switzerland

CSPA Annual Meeting, December 3–9, 2006, Ft. Lauderdale, Florida, USA

The Soap and Detergent Association (SDA) Annual Meeting. January 30–February 3, 2007, Boca Raton, Florida, USA

7<sup>th</sup> World Surfactants Congress. June 22–25, 2008, Paris, France

## Presentations

Hovda, K.D., Methyl Ester Sulfonation: Process Optimization, *Proceedings PORIM International Palm Oil Congress*, September 1993.

Hovda, K.D., Effect of Methyl Ester Feedstock on Sulfonate Quality, *Proceedings of 1994 International Seminar on Surfactants and Detergents*, November, 1994.

Hovda, K.D., The Challenge of Methyl Ester Sulfonation, presented at Household '96, São Paulo, Brazil, June 1996.

MacArthur, B.W., B. Brooks, W.B. Sheats, and N.C. Foster, Meeting the Challenge of Methyl Ester Sulfonation, in *Proceedings of the World Conference on Palm and Coconut Oils for the 21st Century*, edited by E.C. Leonard, E.G. Perkins, and A. Cahn, AOCS Press, Champaign, Illinois, 1999.

Sheats, W.B., and B.W. MacArthur, *Methyl Ester Sulfonate Products*, CESIO 2000.

Foster, N.C., Manufacture of C<sub>16</sub> Methyl Ester Sulfonates, presented at Lurgi BioDiesel Operators Conference, Frankfurt, Germany, 2006.

Foster, N.C., Methyl Ester Sulfonates in Commercial Soaps and Detergents, presented at AOCS SODEOPEC, April 2006.

## Books

Cahn, A. (ed.), *Proceedings of the 5th World Conference on Detergents: Reinventing the Industry, Opportunities and Challenges*, AOCS Press, Champaign, Illinois, 2003, 253 pp.

Foster, N.C., Manufacture of Methyl Ester Sulfonates and Other Derivatives, *SODEOPEC: Soaps, Detergents, Oleochemicals, and Personal Care Products*, ed. by L. Spitz, AOCS Press, Champaign, IL, 2004, pp.261–287.

Foster, N.C., Methyl Ester Sulfonates in Commercial Detergents, 6-2004.

2005 World Oleochemical Conference, CD ROM, AOCS Press, Champaign, IL, 2006.

### Surfactant Science Series; Arthur Hubbard, editor

Books in the Surfactant Science Series emphasize surfaces and interfaces, including basic principles, major developments and important applications. The experimental phenomena, behavior and properties, major advances, experimental approaches, essential instrumental methods, theoretical strategies, and important applications are discussed in depth. The authors are distinguished contributors to the specialized fields encompassed by the books. The level of presentation is intended for readers having a basic scientific training, such as advanced science students encountering the topic of the book for the first time, and scientific professionals refreshing their knowledge of the interface science and engineering aspects of the topic. For a complete listing of books in the series, visit [netlink:www.crcpress.com](http://netlink:www.crcpress.com).

## Published Papers

Dishwashing Performance of Mixed Palm Stearin Sulfonated Methyl Esters and Polyoxyethylene Sorbitan Esters [*J. Surfact. Deterg.* 5:33–38 (2002)] by W.H. Lim and S. Ahmad

Methyl Ester Sulfonates in Commercial Detergents (*SÖFW-Journal* 130, June 2004) by N.C. Foster

Meeting the Challenge of Methyl Ester Sulfonation (Chemithon\*) by B.W. MacArthur, B. Brooks, W.B. Sheats, and N.C. Foster

Sulfonation and Sulfation Processes (Chemithon\*) by N.C. Foster

Methyl Ester Sulfonation: Process Optimization (Chemithon\*) by K. Hovda

Concentrated Products from Methyl Ester Sulfonates (Chemithon\*) by W.B. Sheats and N.C. Foster

Methyl Ester Sulfonate Products (Chemithon\*) by W.B. Sheats and B.W. MacArthur

Medium to Very High Active Single Step Neutralization (Chemithon\*) by N.C. Foster and M.W. Rollock

The Challenge of Methyl Ester Sulfonation (Chemithon\*) by K. Hovda

## Patents

Brooks, *et al.*, U.S. Patent No. 3,257,175 (1966)

Brooks, *et al.*, U.S. Patent No. 3,427,342 (1969)

Brooks, *et al.*, U.S. Patent No. 3,350,428 (1967)

Duvall, L.R., B. Brooks, and W. Jessup, U.S. Patent No. 5,723,433 (1995)

Hovda, K.D., U.S. Patent No. 5,587,500 (1996)

Brooks, B., W.A. Jessup, and B.W. MacArthur, U.S. Patent No. 6,058,623 (2000)

\*All listed documents published by Chemithon can be accessed at [netlink:www.chemithon.com/press.html](http://netlink:www.chemithon.com/press.html)

Process **Innovation** that goes directly  
to your **Bottom line**

## When Considering Sulfonation Equipment, Go with the Technology Leader - Chemithon

From our founding in 1954, Chemithon has been the world leader in sulfonation and detergent process technology. Since the issue of our first patents in 1962, Chemithon has continued to reinvest in the development of new technologies. Our customers receive the benefit of more than 50 years of experience and 300 US and corresponding international patents.

### Global Partners

**IIT Srl**  
Europe, Middle East,  
North Africa

**Chemithon Engineers  
Pvt. Ltd.**  
South and Southeast Asia

**Chemithon Beijing**  
Asia Pacific

**Mitsui Bussan**  
Japan

Patent No. 7,008,603	Process and apparatus for quantitatively converting urea to ammonia on demand	Patent No. 4,267,119	Sulfonating method
Patent No. 6,895,983	Method and apparatus for dividing the flow of a gas stream	Patent No. 4,251,456	Method for treating effluent gas from sulfonation process
Patent No. 6,887,449	Method of quantitatively producing ammonia from urea	Patent No. 4,239,035	Solar heating method
Patent No. 6,761,868	Process for quantitatively converting urea to ammonia on demand	Patent No. 4,216,001	Gas scrubbing apparatus
Patent No. 6,572,835	Method and apparatus for producing gaseous sulfur trioxide	Patent No. 4,185,030	Sulfonating method
Patent No. 6,511,644	Method for removing contaminants in reactors	Patent No. 4,171,243	Spray drying method
Patent No. 6,058,623	Apparatus and process for removing volatile components from a composition	Patent No. 4,113,438	Sulfonating apparatus
Patent No. 5,723,433	Solvent removal process	Patent No. 4,096,236	Gas scrubbing method
Patent No. 5,597,403	Flue gas conditioning system for intermittently energized precipitation	Patent No. 4,067,663	Sewage pump priming system
Patent No. 5,591,249	Flue gas conditioning method for intermittently energized precipitation	Patent No. 3,734,109	Spray Cleaning System
Patent No. 5,587,500	Sulfonation of fatty acid esters	Patent No. 3,620,684	Apparatus for Cont. Sulfonation
Patent No. 5,244,642	Method for conditioning flue gas	Patent No. 3,447,732	Integrally Formed Dispensing Containers Having Improved Pouring Methods
Patent No. 5,136,088	Sulfonation process for viscous sulfonic acid	Patent No. 3,363,994	Chemical Digester
Patent No. 4,779,207	SO <sub>2</sub> flue gas conditioning system	Patent No. 4,311,552	Deinking of newsprint
Patent No. 4,587,029	Intermediate product for use in producing a detergent bar	Patent No. 3,279,358	Selling Means
Patent No. 4,347,100	Strength of paper from mechanical or thermomechanical pulp	Patent No. 3,259,645	Continuous Sulfonation Process
Patent No. 4,515,707	Intermediate product and method for use in producing a detergent bar	Patent No. 3,257,175	Sulfonation Apparatus
Patent No. 4,385,593	Introduction of alcohol-water mixture into gasoline-operated engine	Patent No. 3,240,801	Separation of Sulfonic Acid from Excess Sulfonating Agent
Patent No. 4,374,058	Method for producing powdered detergent containing alpha olefin sulfonate	Patent No. 3,091,519	U.S. Reaction Chamber System
		Patent No. 3,069,243	Sulfonation Apparatus
		Patent No. 3,069,242	Sulfonation Apparatus
		Patent No. 3,058,920	Sulfonation Process
		Patent No. 3,024,258	Sulfonation Process



The Chemithon Corporation, 5430 West Marginal Way SW, Seattle, WA 98106 USA  
Tel: (206) 937-9954 Fax: (206) 932-3786, (206) 937-9933  
Website: [www.chemithon.com](http://www.chemithon.com) E-mail: [chemoffice@chemithon.com](mailto:chemoffice@chemithon.com)