Outlook: Competing forces in the industry

The following are highlights from the Chemical Marketing Research Association's meeting on "Competing Materials and Technologies: Outlook for Change," held Feb. 3-6, 1989, in Houston, Texas. This report was prepared with the assistance of Arno Cahn of Arno Cahn Consulting Services Inc., Pearl River, New York, who serves as Associate Editor for JAOCS *News for Surfactants and Detergents.*

Surfactant and detergent sessions at the Chemical Marketing Research Association's meeting on "Competing Materials and Technologies: Outlook for Change" covered such areas as fats and oils—renewable resources for the chemical industry; ethylene and ethylene oxide; alpha sulfomethyl laurate; synthetic versus natural detergent alcohols; linear alkylbenzene sulfonate and alcohol ethoxylates; liquids versus powdered detergents; polyamine-based quaternaries versus conventional quaternaries; alkyl polyglycoside surfactants; phosphate builders; and the impact of human safety and environmental issues.

Papers from the meeting have been published in paperbound form and can be purchased from CMRA, 139 Chestnut Ave., Staten Island, NY 10305-1895. Copies of the 286-page volume cost $35 each.

Fats and oils

Speaking on renewable resources for the chemical industry, Robert J. McCoy of The Procter & Gamble Co. noted that fats and oils are raw materials to be reckoned with. "Natural fats and oils represent a viable feedstock for the chemical industry, with the potential for larger production to meet expanding demands," McCoy said.

He added, "In today's market, many natural fats compete well with their hydrocarbon counterparts, and in some situations, provide better value. Whether or not hydrocarbon prices are higher in the 1990s, the natural fats should provide an acceptable alternative."

Genetic engineering and crop modification offer potential for yielding specific raw materials. Currently under development are high oleic sunflower, cloned oil palm, hybrid coconuts, cuphea domestication, meadowfoam and soybean oil fatty acids. Another advantage is the interchangeability of various seed groups; thus, as price relationships change, manufacturers can choose the least expensive source.

Ethylene and ethylene oxide

In a paper entitled "Ethylene and Ethylene Oxide—From the Barrel to Detergents," coauthors A.W. Godfrey and M.D. Newton of Texaco Chemical Co. pointed to the complex interplay of regulatory factors (such as the mandated decrease in gasoline vapor pressure) and technical demands for pipeline operation, resulting in lower butane content of unleaded gasoline. Butane thus available to the petroleum industry (150,000 barrels per day) needs to be absorbed by the industry, most likely by replacing propane in olefin cracking plants.

Oxygenates with relatively high vapor pressure, such as methyl tert butyl ether (MTBE), have been mandated by several municipalities as gasoline additives to reduce gasoline vapor pressure.

An alternative approach is to blend butane with aromatics. With normal butane prices, toluene and other aromatics are more valuable to a refiner than MTBE. For this reason, continuing higher prices for aromatics seem likely. As more butane is cracked, less ethylene is produced. This will reduce ethylene as well as ethylene oxide supplies; both will be tight until 1992.

Detergent alcohols

The share of $C_{12\text{-}15}$ alcohol surfactant derivatives—alcohol ethoxylates (AE), alcohol ether sulfates (AES), alcohol sulfates (AS) and alkyl glyceryl ether sulfonates (AGES)—has grown from 4% in 1965 to over 30% in 1988, according to a paper on "Detergent Alcohols—Synthetic versus Natural," authored by J.G. Moffett Jr. and J.R. Sandhop Jr. of Shell Chemical Co.

The price of ethylene as a raw material for synthetic alcohols was relatively stable over most of this period; however, recently the situation has changed.

"The prices for natural oils have fallen while the growth of non-alcohol ethylene derivatives and a six-year economic expansion have combined to push ethylene to an all-time high. In conjunction with the development of improved processes for making alcohol from natural oils, this had led to a need to reassess the prospects for the business," the Shell Chemical Co. representatives noted, adding that despite the relative improvement in the cost of natural alcohols, synthetic feedstocks will continue to be the most economical in the early 1990s for the following reasons:

- Investment in current facilities has already been made
- Synthetic alcohol is becoming increasingly a byproduct of alpha olefin manufacture
- Over-capacity does not encourage the addition of new facilities
- The synthetic process is more flexible and can be altered to take advantage of changes in coproduct valuation.

Linear alkylbenzene sulfonates

Linear alkylbenzene sulfonates (LAS) and alcohol ethoxylates (AE) are the most widely used surfactants, according to Cornelia Schirber of Vista Chemical Co., who spoke on "Linear Alkylbenzene Sulfonate and Alcohol Ethoxylates—The Workhorse Surfactant." Schirber noted that both are effective and are to some extent interchangeable, and thus compete with each other. Roughly 80% of both end up in household cleaning products.

LAS is higher foaming than AE and is especially effective in particulate soil removal, effective on cotton,

easier to spray dry but more hardness-sensitive. AE, meanwhile, is especially effective on oily soils on synthetic fabrics.

Performance advantages can be optimized (and drawbacks minimized) by judicious formulation by detergent manufacturers. In fact, most laundry detergents—liquids and solids—are formulated with surfactant systems containing both LAS and AE.

Relative costs of LAS and AE have varied over the years and have affected relative usage. As a result, AE gained market share at the expense of LAS during the 1970s and early 1980s. This trend persisted during 1983–1987 when heavy-duty liquid shares increased and brought a general increase in surfactant usage. During 1988, rapid escalation of ethylene prices resulted in reformulations with higher LAS levels. This trend is expected to continue during 1989.

AE is derived from ethylene; LAS is made from kerosene and benzene. Costs of both generally track crude oil prices. Both could be affected by a large increase in surfactant production from natural oils. If all announced capacity for natural surfactant alcohols were to come on-stream, it would represent 37% of the total alcohol capacity in the U.S. and 53% worldwide. Its impact on the market will depend on the competitiveness of natural oil supplies versus ethylene derived from crude. The best guess is that natural will not replace petroleum-derived AE, but will carve out a market share. Apart from the cost of new plants (compared with amortized existing capacity), the impact of natural alcohols on the AE/LAS intercompetition will be dampened by the larger content of petroleum-derived ethylene oxide in AE, even though the alcohol is derived from natural oils.

Quaternary compounds

Speaking on "Polyamine-based Quaternaries versus Conventional Quaternaries in Laundry Formulations," Robert B. McConnell of Sherex Chemical Co. Inc. noted that the absence of branching in the carbon chain—which results in better softening—is more important than the source of the materials.

He noted that retail sales of softeners are growing 1–2% a year, which is close to the population growth rate. Dryer-added softeners are 41% of the total softener category; detergents with softeners represent 12.1% of the laundry detergent category and are equally split between liquids and powders.

Conventional quaternaries are made from fatty acids via a nitrile intermediate. They also can be made from alcohol precursors which, in turn, can be derived from natural or petrochemical sources.

Polyamine-derived softeners generally start with diethylene triamine or triethylene tetramine. In structure, these quaternaries contain one or more heterocyclic rings (the imidazoline). They also may show an open amide structure and can be modified by the nature of the long chain or by addition of ethylene oxide.

Polyamine-derived quaternaries usually are not quite as effective softeners as the conventional types. However, they provide excellent static control and are generally more compatible with other ingredients in a combination detergent-softener product than the conventional types. Combining the two types in the same formulation, however, can sometimes offer the best of both worlds.

Intercompetitive developments

Noting that "the detergent game is the cleanest game in town," Colin A. Houston of Colin A. Houston & Associates added, "it is also one of the most competitive, with high stakes multimillion dollar chips. These chips are put on the squares of extensive product development and differentiation, creative packaging, advertising and promotion, all in the fight for shelf space and consumer acceptance."

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Houston noted that everything competes with everything else in the detergent business: different raw materials compete for use in the manufacture of surfactants; surfactants compete with each other; surfactants compete with builders; builders compete with each other. Even in secondary functions, there is intercompetition between different foam stabilizers and different bleaching ingredients. Product form is also competitive, most notably liquids versus powders.

He noted that the world market is dominated by six major multinational companies. "For years, Henkel had confined its efforts to Europe and Lion and Kao to the Far East, but now both Henkel and Kao are intensifying their efforts to enter the U.S. market. Henkel has a 26% ownership of Clorox, and Kao recently purchased the Andrew Jergens Co. of Cincinnati." A table compiled by Houston showed Unilever the biggest player in the detergent industry, followed by Procter & Gamble.

Superimposed on these specific intercompetitions are the demands of the environment, which have a major impact on product formulations.

The world market for detergents is very big, totally 17.5 million metric tons per year. Detergents are experiencing the greatest growth in the Far East and in Third World countries.

Alkyl polyglycoside surfactant

Gary W. Granzow of Henkel Corp., speaking on "Alkyl Polyglycoside Surfactant—A New Naturally Derived Surfactant," noted that APG surfactants, a registered trademark of Henkel, are derived from a starch source and a fatty alcohol source and thus are renewable materials.

In the U.S., corn offers the most economical source for starch. However, in Europe, wheat or potato may be the more economical choice. Any number of starch intermediates can be used to provide the basic building

block, glucose; glucose constitutes roughly 60% by weight of the alkyl polyglycoside surfactant molecule.

He noted that although the economics of petroleum-based surfactants are driven by the volatility of a diminishing resource, corn economics are based on population growth and government agricultural policy, and thus are more stable.

Granzow said APG surfactants are nonionic surfactants but possess some unique properties compared with alcohol ethoxylates. "Because the hydrophile is a polyhydric alcohol as opposed to ethylene oxide, higher water solubilities for the same alcohol chain length are found. Our technology allows us to vary the glucose and alcohol chain length to achieve differing hydrophile/lipophile balances," he said.

Approximately 19 billion pounds of soap and detergent products are sold annually.

He noted that alkyl polyglycosides have excellent electrolyte compatibility and good foaming characteristics, and are stable in high caustic environments. They are useful in a wide variety of household and industrial applications, including hand dishwashing, laundry and general purpose cleaners. Used with LAS and AES, they form synergistic mixtures useful in dishwashing liquids, for instance. In laundry applications, synergism is observed with linear alcohol ethoxylates and with LAS.

In hard surface cleaning, Granzow said, developers have found APG surfactants are effective without the use of a solvent, provide non-streaking, nonfilming characteristics and are compatible with builders as well as alkaline and acidic ingredients.

Alpha sulfomethyl laurate

Noting that ethylene supplies are tight throughout the world, Norman Smith of Stepan Co. said alpha sulfomethyl laurate (ASML) offers a new and natural alternative. ASML is produced by distillation of lauric oil methyl esters to produce methyl laurate which is then sulfonated. The supply of lauric-based oils seems to be increasing, thus providing sufficient amounts for use in surfactants.

Smith said ASML is comparable to sulfosuccinates in mildness and biodegradability. Also, it is comparable to ether sulfate and LAS in reducing surface tension although it is not very effective in soft water. ASML is a high foamer, but its foam stability is not as good as that of other surfactants.

It acts as a lime soap dispersant. It also can reduce viscosity of high active pastes of ether sulfate. A 1:1 mixture of ASML and C_{13} looks reasonable in performance and cost, even in very soft water. Similar results are achieved with a 1:1 mixture of ASML and ether sulfate.

In dishwashing liquid formulations, ASML acts as a hydrotrope. ASML potentially has a large number of applications in household, personal care, industrial and institutional formulations.

Builders

In a paper on "Phosphate Builders and Alternative Builder Systems," Jay R. Brummer, Peter P. Carfagno and Bernice A. Murphy of FMC Corp. explored builder systems in laundry products, autodish detergents (ADDs) and in the industrial and institutional (I&I) area.

The paper noted that approximately 19 billion pounds of soap and detergent products are sold annually. Of these, only 11 billion pounds are "built." These include home laundry products (54%), ADDs (6%) and I&I cleaning products (40%).

A builder enhances cleaning performance, doing so by softening water, providing alkalinity and buffering capacity to the wash bath, and mitigating the redeposition of soil removed by the detergent. In terms of performance, the complex phosphates—sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP)—are clearly the most effective. Despite 25 years of R&D, no fully equivalent phosphate substitute has been found.

Today's formulations are more complex than they were 25 years ago. Changing demographics (more women working, resulting in the need for convenience) have spawned multifunctional products (e.g., with softeners) and convenience has contributed to growth of heavy-duty liquids (HDLs).

At the end of 1988, HDLs represented 36% of the laundry market; phosphate powders represented 33%, and nonphosphate powders represented 31%. The market share of HDLs is largest in phosphate-ban areas.

Alternate builders include the following:

- zeolite, which is used generally with co-builders. The drawback is it does not control magnesium hardness.
- sodium carbonate, which precipitates calcium as calcium carbonate in hard water. It now is used at lower levels than those found in the first products introduced as a result of phosphate bans in the early 1970s.
- sodium citrate, used mainly in HDL.
- sodium silicate, effective as a builder but not as a hardness reducer. It is seen as a good corrosion protector.
- polyacrylates, used as co-builders with zeolite and sodium carbonate. These have been used at low levels starting in the 1980s.

ADDs contain complex phosphates, nonionic surfactants, sodium carbonate, sodium silicate, sodium sulfate, a chlorine source and a defoamer. Recently, these ingredients have been slurried into "liquid" products. At the end of 1988, liquids had captured 30% of this category. Sodium tripolyphosphate is even more important in ADDs than in laundry powders—for product performance and as a processing aid.

Although there currently are no bans on phosphate (the industry has explained that no substitutes are available), there are limitations set (e.g., 8.7% as phosphorus, equivalent to about 35% STPP). To optimize

product performance under this limitation, the source of chlorine has changed from chlorinated trisodium phosphate (which contains a phosphate different, and less effective, than STPP) to chlorinated isocyanurates which contain no phosphorus at all. For a given Cl level, therefore, they permit a higher level of the desirable STPP.

The I&I area, which represents 40% of the U.S. detergent industry, is highly complex. Cost and performance are important here, as are ease of use and product safety. These demands have led to changes in products and changes in builders. Builders include those used in laundry detergents, as well as nitrilotriacetic acid (NTA), a strong calcium sequestrant, and sodium hydroxide, an aggressive alkali that is too aggressive for home use.

Liquid versus powdered detergents

Speaking on liquids versus powdered detergents, Paul Sosis of Witco Corp.'s Organics Division concluded that multifunctional powders containing antistats, activated bleaches, enzymes, odor removers and softeners offer better overall performance than liquids and are expected to retain their share of the market.

Liquid detergents are firmly established in the U.S., Europe and Japan. Their advantages of convenience, low temperature solubility, direct application for stain removal and packaging will continue to expand the popularity of this category in other parts of the world.

Also, he predicted, specialty "niche" products designed for specific cleaning jobs are expected to grow.

He noted that higher density concentrated powders containing alkali stable enzymes are widely accepted in Japan and may be expected to show up in other parts of the world.

Safety and environmental issues

One of the major environmental issues faced by the detergent industry in the 1960s was foaming in rivers and streams, Keith A. Booman of The Soap and Detergent Association (SDA) pointed out. This problem prompted the industry to seek more biodegradable products by converting from a branched-chain alkylbenzene sulfonate (ABS), the industry's workhorse anionic surfactant, to linear alkylate sulfonate (LAS). Since that time, there has been a growth of other readily biodegradable surfactants.

During the 1970s, concerns developed over the possible role of detergent fragrances in causing allergic reactions in consumers. Test data collected and published by SDA showed that detergent formulators were selecting and using fragrances responsibly. Still, the industry, aided by the Research Institute for Fragrance Materials, monitors fragrance components to avoid future problems.

Another issue raised was the eutrophication of bodies of water. Although detergents have been blamed, they do not contribute as much as such sources as land run-off and human and food wastes, Booman said. As a result of fears over eutrophication, however, the use of phosphates in detergents became—and remains—controversial. He added that the use of NTA as a phosphate replacement was challenged by New York State "and thus NTA remains unused in laundry detergent formulations in the U.S. today." Canada, however, does allow NTA use.

Booman pointed out that issues keep cropping up that often are not specific to the detergent industry alone. One major problem currently under scrutiny is the disposal of product packages and unused products, particularly as landfills close down and as evidence of groundwater contamination appears at existing and former landfill sites.

"The very complexity of the host of human health and environmental effects that need to be considered in developing a product today suggests that more and more innovation in selecting and combining ingredients into formulations will be called for in the years ahead," he said.

Program announced for industry conference

A joint AOCS/CSMA detergent industry conference on "New Horizons '89" will be held Oct. 29-Nov. 1, 1989, at the Hotel Hershey, Hershey, Pennsylvania. General chairpersons are Ted P. Matson of Vista Chemical Co. and Paul Sosis of Witco Corp. For further information, contact AOCS, PO Box 3489, Champaign, IL 61826-3489, USA. The following outlines the tentative technical program.

SESSION 1 Dinner and Keynote Address
Chairperson: Paul Sosis, Witco Corp.
Sunday evening, Oct. 29

Cocktails and Dinner
Announcements—Paul Sosis
Introduction of session chairpersons—Ted Matson
Introduction of keynote speaker—Paul Sosis
Keynote speaker—William Mahoney, executive vice president, Witco Corp.

SESSION 2 Surface Chemistry
Chairperson: John F. Scamehorn, University of Oklahoma
Monday morning, Oct. 30
Announcements—Ted Matson
Introduction—John F. Scamehorn
Applications of Surfactant Mixtures, Randal M. Hill
Surfactant Precipitation, John F. Scamehorn
Break
Dynamic Surface Tension, Milton J. Rosen
Micelle Formation in Amphoteric Surfactant Systems, James F. Rathman
The Requirements for Optimum Detergency, Herbert L. Benson