

Quaternary ammonium compounds

The following look at the use and future of quaternary ammonium compounds was prepared by JAOCS newswriter Anna Gillis.

In the industry, they are considered the ultimate workhorses. They decolorize sugar, kill bacteria growing in waterbeds and help pull the last dribbles of oil from drilling wells. They serve as ingredients in products ranging from underarm deodorants to fiberglass for sailboats. Mostly, they're used to keep the family laundry soft. These jacks-of-all-trades are quaternary ammonium compounds, or quats.

U.S. International Trade Commission statistics estimate American surfactant producers manufactured 187.8 million pounds of petroleum- and fatty acid-derived quaternaries in 1985, compared to 116 million pounds in 1980. Over the same period, sales value rose from \$73 million to \$128 million. Experts in the industry forecast that quaternary usage will continue upward until 1990, but that expansion will not be nearly so great as during the late 1970s to the mid-1980s.

By 1990, about 165 million pounds of fatty acid-derived quats will be consumed yearly by various industries, with approximately 66% of that going into fabric softeners, according to Ellen Donlin, project manager for Hull and Co.'s report, *Fatty Acids and Derivatives: North America 1985-1990*. Figures from the Greenwich, Connecticut, consulting firm indicate total fatty acid quaternary consumption grew from 88 million pounds in 1975 to 149 million pounds in 1986, with the greatest growth between 1975 and 1980. Of the fatty acid-derived quats, more than half have been, and will continue to be, used by fabric softener producers (see Figs. 1 and 2).

"The number one factor in the quat business in the past ten years is the incorporation of quats into the detergent package," James Hartlage, vice-president of technology for Stepan Co., said. "It has been the healthiest thing for the quats business."

Calvin Immel, vice-president of marketing for Sherex Chemical Co.,

said the main growth surge for quats has occurred already. He estimated that U.S. quaternary producers have a fabric softener market of approximately 90-100 million pounds of active material a year. "It [tonnage growth] has been about 7% a year, but it's flattening out now. Growth now will be maybe 3% a year," he said.

The reduction in phosphate-built detergents may have influenced the growth of quaternary ammonium compounds, but it was not a major factor, Immel said. Because phosphate builders promote substantivity while other builders remain neutral, the presence of phosphate builders would require less quats in a formulation. "Quats fill a niche all their own in fabric softeners. Nothing really competes with them in supplying softening and antistatic properties," he added.

What makes quaternary ammonium compounds so valuable to laundry product manufacturers and a host of other industries is their substantivity. Quats, with their positively charged nitrogen atoms, are cationic; they attach themselves to negatively charged surfaces such as fabric or hair to varying degrees depending on the structure of the attached alkyl chains. It's this trait

that prevents fly-away hair and keeps diapers soft.

The three main types of quaternary ammonium compounds used in fabric softening are the dialkyl dimethyl ammonium compounds, the amido alkoxyated ammonium compounds and the imidazolines. The di (hydrogenated tallow) dimethyl ammonium chlorides continue to be the most popular of the quaternary compounds for fabric softeners in both the U.S. and Europe. However, in the U.S., dialkyl dimethyl ammonium methyl sulfates have become increasingly important for dryer cycle products.

Traditionally, tallow has been the primary source of fatty acids for the industry. According to Richard Reck, director of commercial development for Akzo Chemie America, about 80% of all fatty acids are made from tallow, with coconut and palm kernel making up most of the balance. "Tallow is king [in fatty acid quat production]," Immel said. "In terms of price and performance, nothing can beat it."

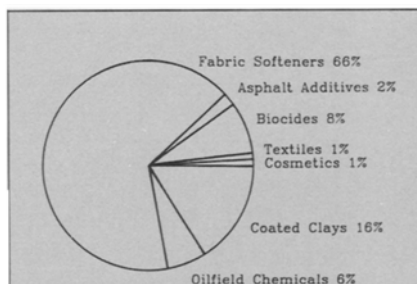


FIG. 1. Fatty acid-derived quaternary ammonium compounds—estimated 1986 U.S. consumption by application. Source: Hull & Co., Greenwich, Ct.

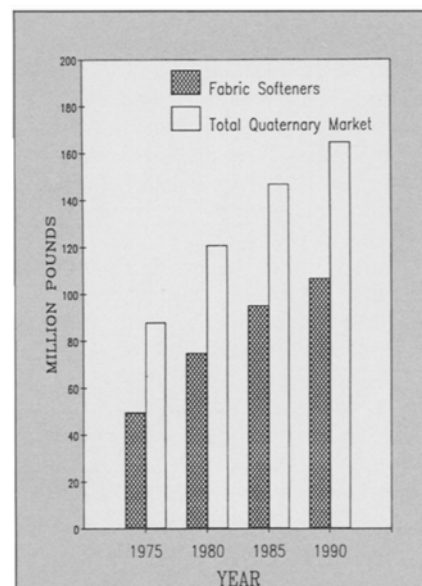


FIG. 2. Fatty acid-derived quaternary ammonium compounds and their use in fabric softeners, 1975 to 1990. Source: Hull & Co., Greenwich, Ct.

Tallow has been described as a compound "practically designed for use in the fabric softener industry." The predominance of stearic and oleic acid (65% C₁₈ content) in tallow is the main reason for its popularity as a feedstock for quats used in laundry and personal care products. For example, distearyl dimethyl ammonium chloride, one of the commonly used quats, has a minimum C₁₈ content of 90%. Industry experts say that quaternaries with two alkyl chains containing 16 to 18 carbons have the best softening properties.

According to Reck, the industry still uses many of the same chemical methods to produce quaternaries as it did in the early 1950s, when the compounds first appeared in home laundry products.

The two main production routes for fatty acid-based quats are (a) conversion of fatty acid to nitrile, to amine, to quat, or (b) fatty acid, to diimidoamine, to imidazoline, to quat. The main alkylating agents are methyl chloride, dimethyl sulfate and benzylchloride. Methyl bromide, diethyl sulfate and ethylbenzochloride are used on a much smaller scale, mainly for specialty quaternaries.

Tallow prices have been below 20 cents a pound and are expected to stay low and stable. With its continued low price and ready availability, it is unlikely the industry will move away from tallow as the primary fatty acid source for quats, although, in some cases, the industry does use soybean, coconut, rapeseed or fish oil, said Richard Marquis, director of marketing for Humko Chemical, a division of Witco Corp.

James Fuller, associate director of applied research for Sherex, described the quaternary business as a "mature business in terms of the chemistry, but very active in applications and end-use work."

Marquis attributes the expansion in applications to "the increased interest on the part of industry in following emerging consumer trends" rather than to factors such as lower prices for fatty acid and petroleum feedstocks. Examples of applications growth include product line extensions by major suppliers in combination detergent/fabric softener products and the trend toward specialty quats with special feel

characteristics by the personal care industry, he said.

Much of the research in formulations has led to "big marketing battles," Reck said.

In their search for the perfect laundry product, the major detergent manufacturers have reformulated existing detergents and created new ones, keeping in mind consumer interest in ease of use.

William E. Broxterman and John C. Dean, in the surfactant section of the May 7, 1986, *Chemical Week*, noted that the \$3.5-billion household laundry detergent business remains the "most active and turbulent field" in the surfactant business, with companies frequently changing their formulations. They cited the increasing popularity of liquid laundry detergents, rather than increases in per capita usage of detergents, as a major factor in the shift in surfactant use. The increase in the use of certain surfactants is partially due to the fact that liquids require more surfactants than powders, Broxterman and Dean said.

With a shift away from laundry softening products for the rinse cycle and dryer toward detergent-softener formulations, quaternary usage will continue to grow, Donlin said. More quats are required in detergent-softener formulations, particularly liquid formulations, so "the shift to increased liquid market share will allow an increase in the sale of quats," she said.

According to Sherex figures presented by Fuller at the Second World Conference on Detergents in October 1986, softener/detergent combinations make up 17% (by volume) of the combined liquid and powder heavy-duty detergent market. The softener/detergent liquids hold 13% (by volume) of the U.S. heavy-duty liquid detergent market. Fuller said the total detergent market is approximately \$3 billion; liquid detergents make up approximately \$1 billion of that.

Although growth has occurred in the formulation of heavy-duty liquid detergents, people in the industry agree that more formulation work is needed. Probably the biggest obstacle to overcome, according to sources at Akzo and Sherex, is the difficulty in formulating a "just-right" combination of softener and

surfactant in a liquid detergent. Current formulations require higher levels of quats in washer combination products to do the same job that softeners do alone. "The trick in liquid detergent formulation is to find a cationic softener compatible with the anion in the detergent, and no one has really come up with the perfect one yet," Reck said.

The heavy-duty liquid softener/detergent combinations fall into two general categories, Fuller said. The ones easier to formulate are those with cationic softeners and nonionic surfactants. The products made from cationic softeners and anionic surfactants require more difficult formulation techniques and a careful selection of raw materials to avoid precipitation of the quat/anionic complex, he said. Other problems also may occur with the addition of components such as brighteners.

John Braunwarth, operations manager of Capital City Products, said that even though the detergent-softener combination appears to be the biggest area of growth and that most of the industry's research in formulation will continue to be in this area, the industry also is looking into other formulation problems. "The industry is particularly interested in working on enhancing agents. One thing of interest is an agent to improve the antistatic performance of softeners for non-garment applications," he said.

According to Broxterman and Dean, multifunctional laundry products that soften, have advanced stain removal systems based on enzymes and include safe oxygen bleaching agents that are activated at lower temperatures will become increasingly popular and will remain a "driving force in the search for the ideal cost-effective surfactant system for ultimate laundry results."

Similar formulation efforts are going into personal care products. Larry Smith, marketing coordinator for Croda Inc., noted that personal care formulations tend to fluctuate more rapidly than detergent formulations. Even with those changes, Smith said, the mainstay of the personal care and cosmetics industry, at least in hair rinses, remains stearylalkonium chloride, because of its price, availability and functional-

Quat's outlook: Japan, Europe

Quaternary ammonium compound production in Japan and Europe will not continue to grow as rapidly as in the past, according to industry experts.

"We expect our production increase through the next decade might be 5% per year, instead of our growth rate of more than 10% in the past five years," Joji Yamaura, Lion Corp.'s associate senior manager for research planning and control, said. He added that growth for the Japanese quaternary industry would probably be approximately 5% per year.

Yamaura estimated Japan's quat capacity at 25,000 metric tons (MT) per year, with most of the quaternary output going to the fabric softener industry. In 1986, approximately 270,000 MT of fabric softener were produced. Kao Corp., Nippon Oil & Fats Co. Ltd. and Lion Akzo, a Lion Corporation-Akzo Chemie venture, are Japan's major producers.

While liquid detergents with softeners are an important market for quats in the U.S. and Europe, those products are not available yet in Japan.

Ellen Donlin, project manager for the consulting firm Hull & Co., said European quat consumption probably doesn't exceed 90,000 MT per year. Of that, 65,000-75,000 MT go into fabric softeners. She predicted volume growth at 2% per year until 1991.

Fabric softener consumption in Europe reached a million tons per year during the early 1980s, according to Hans-Dietrich Winkhaus and Peter Krings of Henkel KGaA. However, fabric softener consumption in West Germany dropped from about 410,000 MT in 1982 to approximately 330,000 MT in 1985, they said. Reasons for the decline are a relatively saturated market and public concern about the environment. "Potential growth in the European market is expected only in the U.K., France, Spain and Italy. A rapid growth of the use of quats in fabric conditioners in West Europe is not expected," Winkhaus and Krings said.

ity. "It provides just the right conditioning for hair rinses, meaning it's not too tacky nor too oily, and it is acceptable for all types of hair," Smith said.

For many of the standby quats used by formulators of personal care products, Smith sees a growth of perhaps two percentage points per year. "The real growth will be in innovative quats. Quats which are milder will experience growth, and if they have dual functionalities—add shine to hair, condition, add manageability—they will also rise in usage," Smith said.

"I would conservatively estimate a 4% to 5% growth rate for quats that are truly new and unique," Smith said, estimating that some of these new quats will cost \$1 to \$5 per pound.

Quats produced from materials that would allow a company to make claims of "natural" are also likely to experience growth, Smith added. He said Croda is looking at a variety of oils, including babassu, olive, chamuga and meadowfoam, as possible quaternary sources.

While quats volume for cosmetics use may be smaller than for large-scale commodity quats used in the laundry detergent business, they offer more profitability, Smith said.

The organophilic clays, the second largest quat market, are a \$30-35 million industry, but are not expected to go up much in the next five years, according to Robert Van Doren of NL Chemicals. "Looking into the future in this market is difficult because the future of the industry depends on the actions of

regulatory agencies over which we have no control," Van Doren said.

The organophilic clays, a mixture of quats with clays such as bentonite, work as thixotropic agents for paint, grease, ink, adhesives, sealants and drilling muds, mixtures used to improve the flow properties of petroleum during drilling. Quaternary ammonium compounds allow the clays to be rheologically functional in organic substances.

While drilling muds have been the major outlet for the organophilic clays, paint and paint-like products now are the more important market. The reason for the shift is the decline in the petroleum industry, Van Doren said. "When oil drilling was booming in the late 1970s and the early 1980s, there was major demand worldwide for drilling muds." The active rig count now is probably less than 1,000, only 20-25% of what it was seven or eight years ago, he added.

Any changes in the drilling mud market will be highly dependent on the price of oil, according to Van Doren. In their surfactant industry outlook, Broxterman and Dean expressed a similar view. "Petroleum production and recovery, thought to be the salvation of the surfactant industry just a few years ago, has fallen far short of early expectations," they wrote. "The enhanced oil recovery prospects are greatly tied to the cost of oil and thus recovery methods are not currently economically feasible. Lower oil prices will prevent this from becoming a dominant surfactant market during the 1980s."

Most future growth would be for highly specialized quats with a high dollar value rather than a high volume, Marquis said.

Industry estimates for organophilic clay consumption, excluding the oil field industry, were in the area of 25 million pounds in the mid-1980s. Two-thirds of that went into paints, 5% into grease and 7-8% into ink. Polyesters and cosmetics each take up 4-5%, Van Doren said.

Van Doren said prices will remain somewhat flat and markets probably won't grow because the paint industry, the major buyer, is under the eye of several regulatory agen-

cies. "Anybody selling to the industry is going to be affected by solvent emission controls and other government action," he said.

Industry sources said government regulation will play a major role in determining the growth potential for the biocidal and germicidal quats, which are registered under a variety of acts including the Federal Insecticide, Fungicide & Rodenticide Act (FIFRA) and the Toxic Substance Control Act (TOSCA).

Approximately 24 million pounds of biocidal quats are produced annually, with most of that from petroleum sources, according to Charlie Tretola, business manager for microbiocides and water treatment for Lonza Inc. "The market is mature," Tretola said. "No one needing biocides is hiding in the woodwork." Biocidal quat sales total \$35-40 million per year; how much those figures will rise will depend on whether producers try to pass on the increased costs of testing to consumers, he added.

"The biggest determinant in how quats will grow is the Environmental Protection Agency's [EPA] data call-in," Robert Huffman, general manager of the chemical division for Huntington Laboratories, said.

The government is asking industry to fill in missing information on the toxicity, carcinogenesis and mutagenesis of a number of compounds. So far, the EPA has asked for information on the common biocidal quat, alkyl dimethyl benzyl ammonium chloride. However, the industry anticipates it will be required to do studies on many more compounds.

Tretola said the studies could cost between \$2 million and \$5 million per quat, depending on the information needed. Quats that come in contact with human skin will be particularly expensive to test. Testing of quats used in swimming pools and hot tubs, where the whole body is immersed, will be especially costly, Tretola said.

As a way to cut the cost of testing

so many compounds, Tretola said the industry is asking the government to cluster similar compounds, accept the data for one or two, then extrapolate to fill in the information on the remaining compounds in the cluster. If the government accepts this proposal, it would decrease costs greatly, he said.

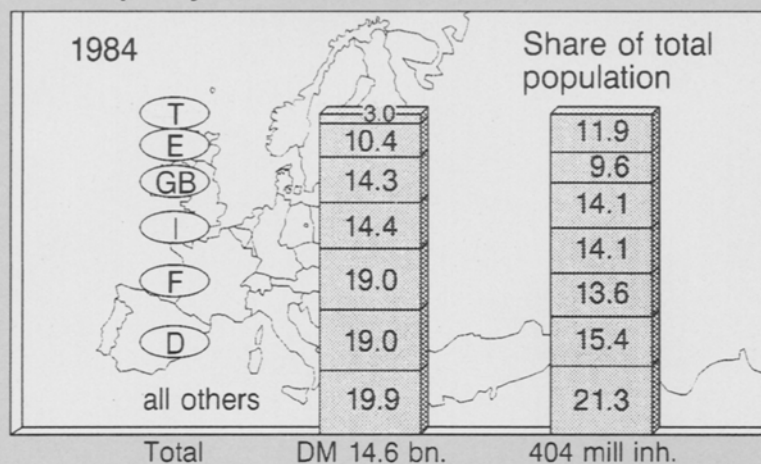
Huffman said the industry has approximately 30 different biocidal quats in use at present, but with the costs of toxicity studies, it is likely the number of available quats will be reduced. Those that are available will have to cover the same range of applications that the 30 now cover. Although the market may continue to grow by 2% to 5% per year, a reduction in the number of quats would quite likely mean a reduction in the number of players in manufacturing, he added.

"If the government accepts clustering, the variety of quats will be less likely to decrease. But if it doesn't, there won't be any choice but to trim the number of quats," Tretola said.

One piece of legislation that concerns biocidal producers is California's Birth Defect Prevention Act, which went into effect in January 1985. The bill requires the California Department of Food and Agriculture to determine the toxicology, mutagenicity, carcinogenicity and teratogenicity of all active ingredients in registered pesticides and biocides. At the end of 1985, after a review period, the Department of Food and Agriculture's Division of Pest Management told many registrants that more tests would be necessary on a number of compounds before risk assessments could be made. The information for that data call-in has to be submitted by March 1, 1991.

Robert Peterson, special assistant in the Division of Pest Management, said there were significant data gaps in the list of approximately 200 active compounds in widespread use that are still under review. However, California has agreed to allow the biocidal quaternary producers to cluster compounds with similar properties. Still, producers are concerned because at least some research will be required on many biocidal quats.

Detergent and Cleanser Market Europe by countries in %



Europe's 404 million inhabitants use 14.6 billion deutsche marks' worth of detergent and cleaning products annually. The chart shows market share percentage for specific countries (left column) compared to their percentage of Europe's total population (right column). The countries listed are (from top) Turkey, Spain, Great Britain, Italy, France and Germany, followed by all others.

—From "The Detergent and Cleanser Market in Europe," presented by Hans-Dietrich Winkhaus, executive vice-president of Henkel KGaA, Dusseldorf, West Germany, during the Second World Conference on Detergents, Oct. 5-10, 1986, Montreux, Switzerland.

"This legislation has caused real consternation in the industry because the industry can't afford the test requirements," Hartlage said, explaining that the legislation asks for considerable safety testing on active materials, yet the industry does not produce enough volume on some products to compensate for testing costs. The industry is concerned because California is an important market for biocides, he added.

Hypothetically, if a company wanted to make a 20% profit on a compound, and it costs \$3 million to test to meet California's requirements, the company would have to make \$15 million in sales to pay for the testing in one year, or \$7.5 million for two years, Huffman said, explaining that actual sales might be insufficient to justify production.

Barry Friedfeld, a senior consultant with Kline and Co., sees the

possibility for some growth. However, during this period, with the industry living in "a legislative-stroke-of-the-pen" environment, he said, it would be difficult to forecast just how much might occur. Friedfeld added that he did not foresee anything new developing in terms of the biocidal quats unless "it's really new and different."

Biocidal quats grew rapidly from 1979 to 1983 because of concerns over using phenolic biocides, Friedfeld said. "If it were not for changes in U.S. regulatory practices, those changes probably would not have occurred.

"What I see is a displacement. Because of the perceived safety of quats over other compounds, quats are displacing some of the more traditional biocidal materials," Friedfeld said.

Hartlage said the biocidal quats are doing well against the backdrop

of phenolic and metal-containing biocides because they've proven themselves safe and biodegradable.

In the biocidal industry, companies are coming out with products to balance product lines, Friedfeld said. For example, if they make a phenolic, they'll formulate a new product with a quaternary. This is particularly important in many household cleaners and disinfectants, where quats have proven themselves less irritating to human skin than phenolic-based disinfectants, he added.

Even with the vagaries of legislation and consumer attitudes, quaternaries generally hold the advantage over other compounds because, in many cases, there may not be adequate substitutes. "Quats will continue to be purchased on the basis of functionality. The cost of the product is small in relation to the job it does," Friedfeld said.

Research areas for detergents

Joel Houston, chemical industry market analyst, told the AOCS Northeast Section he sees several key areas for research and development advances in the detergent industry.

Houston, of the Colin A. Houston & Associates firm, concluded his talk on "Recent Developments in Detergents" at a section meeting earlier this year by listing potential commercially valuable R&D priorities. Among them were

- bleaches for heavy-duty liquid
- slow-temperature bleaches for powder products
- biodegradable detergent polymers
- relatively inexpensive soil-release agents
- more convenience packaging
- lipase enzymes
- further developments in storage-stable liquid automatic dishwashing products

Houston described recent developments in marketing, external factors affecting the industry, consumer factors, ingredient developments and product evolution.



Joel Houston, left, with Paul Sosis, at the Northeast Section meeting.

Recent marketing developments have included the introduction of liquid Tide and similar products, which have grown to about 30% of the market, Houston said. The gain has come at the expense of powder products, he commented, noting that Wisk, a liquid detergent on the market before liquid Tide, has re-

tained its market share. The introduction of Palmolive's liquid product for automatic dishwashers has spawned the launch of similar products by other companies, he said, with about 18-20% of the market now held by liquids. Liquid products store better than the powders, he said, and do not require