Zeolites: Gaining ground as replacement for phosphates in detergents

The $5 billion U.S. detergent industry may have found an answer in its search to find an alternative to phosphates.

While no builder matching phosphate's capability has been discovered, zeolite's favorable cost/performance qualities have allowed it to step to the fore as a replacement. Procter & Gamble's zeolite adoption is a major acceptance by industry.

In November 1978 P&G began full-scale marketing of New Extra Action Tide, the first U.S. detergent combining zeolite with a 6.1% level of elemental phosphorous. (This is equivalent to a phosphate level of about 25%, compared to 45+% level in past years.) Since then, a zero-P version of Tide has been test marketed in areas with phosphate bans. No other U.S. manufacturer is advertising a similar product yet.

Why not?

First, there is presently limited availability of detergent zeolites; larger facilities will have to be constructed to satisfy the growing demand. Second, while most soapers have been actively testing zeolite formulas, their evaluations may not be completed. While other manufacturers may choose different builder options, P&G already has incorporated zeolite in Tide, a product which P&G says it has improved by reformulation 25 times since its introduction in 1946.

Zeolite's chemical and physical properties make it compatible in Tide's formulation and processing, but those same properties may hinder its use in other formulations or processes. The zeolite in Tide is Type A, a synthetic particle about 3 microns in size. Structurally, it is a crystalline, hydrated aluminosilicate formed by electron sharing in the oxygens of linked SiO_4 and AlO_4 tetrahedra. (One chemist in the field feels the molecule is more appropriately described as linked AlO_2 and SiO_2.) It functions in wash solutions by ion-exchange in a process that captures hardness ions, mostly Ca^{++}, within the zeolite structure. Type A zeolite is not as effective in removing magnesium ions, the other major contributor to water hardness in some areas. The Union Carbide Corporation (UCC) has commercially available zeolites effective for both Ca^{++} and Mg^{++} hardness. The Ethyl Corporation has reported similar experimentation.

Zeolite's crystalline structure retains its integrity when incorporated into detergent beads produced with a spray-drying process. Zeolite's insolubility in water has prevented its use in liquid detergents, which require less energy to produce than the spray-dried detergents. To date, no stable, suspended solution of liquid and zeolite has been demonstrated to be practical. Liquid detergent makers are therefore less enthusiastic about zeolite's potential, although chemical companies say they are optimistic that a stable solution will be produced.

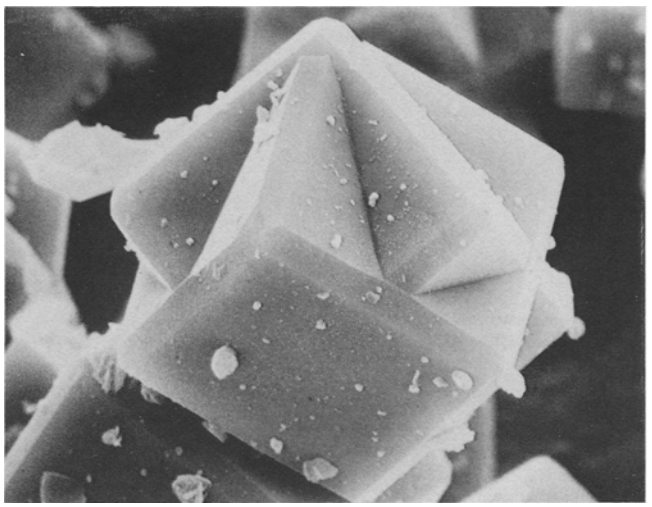
Liquid detergent's main selling points to consumers have been convenience and performance. Now the consumer is also being told one way to save energy costs is by using a liquid detergent in cold water wash. The U.S. Census of Manufactures showed an increase in shipments of liquid detergents to $79.4 million in 1977 from $69.4 million in 1972.

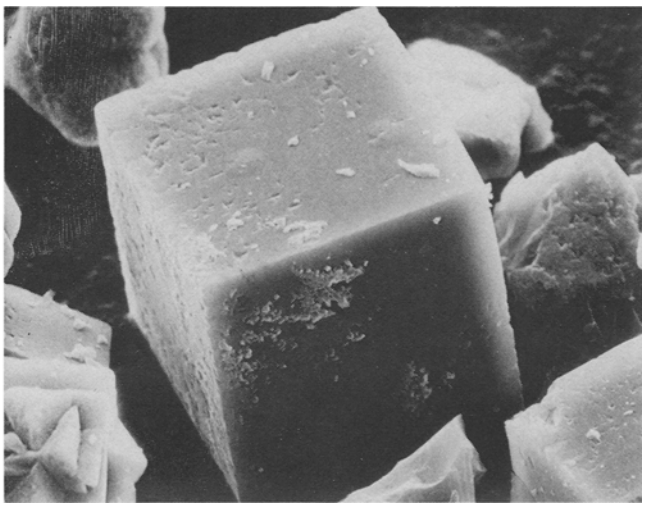
Putting zeolite in a product that meets company standards is only one consideration for soapers. Any new chemical usage faces scrutiny by the EPA and other government agencies for both environmental and health effects. Phosphates came under voluntary and local governmental bans in the U.S. after environmental biologists reported finding super-rapid growth in algae (eutrophication) – linked by some investigators to wastewater phosphates from detergents in certain locations.

Recently, Japan's Shiga prefecture enacted that country's first ban on the sale and use of synthetic detergents containing phosphates, scheduled to go into effect April 1, 1980. In response to the legislation, the Japan-based Lion Fats and Oils Co. will market a zeolite-based detergent. Their product is similar to European zeolite detergents and will be introduced in the near future.

Numerous studies have been completed that tested the environmental safety of zeolites. In a toxicity evaluation, P&G's A.W. Maki and K.J. Macek of Bionomics, Inc., estimated the zeolite concentration in natural waters expected from total detergent industry use to be 0.20 milligrams per liter (mg/L) at low dilutions of sewage effluent upon discharge. Even at very low dilutions where the concentration may reach 1.0 mg/L prior to further dilution, the concentration is two to three orders of magnitude below the point of potential interference with aquatic life – in both marine and freshwater species. Maki and Macek concluded that the zeolite Type A does not enhance algal growth and will have no significant environmental impact. P&G has spent an estimated $5 million testing the safety of zeolite Type A.

While Type A is one of a more than 90 synthetic zeolite forms, over 30 forms occur naturally. The empirical formula for zeolite Type A is similar to that of natural kaolin clay. It may, in fact, be produced from kaolin. G.C. Schweiker of Philadelphia Quartz outlined two methods for producing zeolite at the World Conference on Soaps and Detergents at Montreux in 1977 – first, by superheating kaolin and treating with NaOH, and, second, in a reaction between alumina trihydrate and sodium silicate. Other methods are used commercially, but the manufacturers don't want to divulge them. Schweiker predicted at the Montreux meeting that "zeolite NaA in commercial built detergents will undoubtedly prove to be the largest single use for zeolites in the very near future." He estimated the growth of zeolites to 225-325 thousand metric tons per year (MT/yr) up to 540 thousand tons annually in 1981





Zeolite crystals

worldwide.

UCC developed Type A zeolite but is not the major supplier for the detergent industry. For the past 20 years, UCC has supplied zeolites for use in catalysts, gas drying, dual-pane windows, air conditioners and other antimoisture products. Zeolites are termed "molecular sieves" in many of these commercial markets.

The Ethyl Corporation is probably the No. 1 supplier of detergent zeolites in the U.S. An Ethyl spokesman said the company has an excellent proprietary method for producing detergent-type zeolite on a commercial scale. Ethyl's Raymond Kosakewicz said a multi-million dollar zeolite plant in Pasadena, TX, became fully operational in late 1978. This new facility is estimated to have more than 100 million pounds per year capacity, although exact figures are not available, with additional room for expansion.

Another use for a different type of zeolite may increase industrial demand for these chemicals. Mobil Oil has reported successfully using ZSM-5 zeolites as shape-selective catalyst in making high octane gasoline from methanol, as well as from rubber latex, corn oil, castor oil and jojoba oil.

The soapers who are less enthusiastic about detergent-type zeolite include those experimenting with different methods in phosphate replacement. One such method is to increase the amount of surfactant while proportionately decreasing the builder. Phosphate as a builder may be eliminated altogether. The surfactant level may be increased and a nonphosphorus builder substituted in equal or lower levels, depending on its strength and the surfactant's wetting ability. Phosphate replacement techniques include using, at increased levels, carbonates, sodium silicates, and citrates. These may be used alone or with some phosphate. Lever Brothers patented CMOS (sodium carboxymethyl-tartronate); Colgate Palmolive's Fresh Start has a zero-P version that contains carbonates. A zeolite version of Fresh Start reportedly has been test-marketed in areas where phosphates have been banned.

In Europe, the dominant Henkel Group has opted heavily for zeolite. Four zeolite detergents are offered nationally in Germany: Prodixan, a heavy-duty detergent containing zeolite (Z) and phosphate (P) in a 1:1 ratio; X-Tra, for 60 C laundering (Z:P = 1:1); Fakt, another heavy-duty variety (Z:P = 1:1); and Henkomat, a pre-soaking detergent (Z:P = 1:2). Drs. Werner Stein and P. Berth of Henkel project total zeolite use in Europe at 100-200 thousand tons during the next five years, compared to 16,000 tons total used in 1978-79. Henkel's zeolite products also are available in Holland, Switzerland and Italy. Henkel owns a number of patents covering detergent zeolites.

Despite all the research to find a phosphate replacement there is a sentiment that replacements are not necessary — that phosphate detergents are superior cleaners and, in the long run, removal of phosphate during sewage treatment would be less expensive to the consumer than to use replacements with less cleaning efficiency. SDA President Ted Brenner told HAPPI (Jan. 1979) that if phosphates were completely banned, the money saved in effective sewage treatment would be $2 million — a comparitively small slice of the $250 million spent annually for wastewater plants. U.S. consumers have been absorbing the cost of the search for a phosphate replacement through higher cost detergents and use of additional laundry additives to boost performance of nonphosphate detergents. Critics in Europe have similar doubts about the need for phosphate replacements. However, as the price of energy-intensive phosphate continues to rise and as zeolite production facilities increase, zeolites may become the cheaper builder. Drs. Stein and Berth indicate this is already the case in Europe; there has been no rise in cost for the zeolite detergent. Early Henkel reports indicate zeolite works better without additives than the sodium carbonates.

Meanwhile, the zeolite foothold is already set in its adoption by P&G and Henkel.

Industry News

Soap firm cuts energy use

The Los Angeles Soap Co./White King Corp. in Los Angeles has received an award from the local utility service for reducing natural gas use by 52%.

The conservation program was carried out during 1976-78 and provided a savings of 57.6 million cubic feet of gas, an annual savings of $83,300. The program involved checking more than two miles of steam lines prior to changes in design and replacement of insulation. Use of one boiler was eliminated by converting from an open coil boiling process to a closed process for soap production. Southern California Gas Co. presented the firm with its Concern Award for good energy management. □

Market survey

U.S. manufacturers of household and industrial cleaners will use $1.6 billion worth of raw materials during 1980, according to preliminary results of a market survey by C.H. Kline & Co. (Table I).

Kline says its survey shows about 75 firms market raw materials, with most firms being large, diversified chemical companies. The survey showed an increasing trend toward use of liquid laundry detergents and multi-purpose cleaning products. The full survey is expected to be available in fall of 1980. □

Greenberg heads SCC

AOCS member Stephen M. Greenberg of Lipo Chemicals Inc. is serving as 1980 president of the Society of Cosmetic Chemists. President-elect of the cosmetic group is another AOCS member, Graham Barker of Witco Chemical Corp.

TABLE I

U.S. Consumption of Raw Materials for Household and Industrial Cleaners, 1980

Product class	$ million
Surfactants	$ 925
Builders	
Sodium silicate	115
Sodium hydroxide	90
Phosphates	65
Sodium carbonate	35
Zeolites	25
Total	$ 330
Fragrance compounds	85
Polymers and resins	75
Acids and solvents	60
Biocides	60
Bleaching agents	35
Chelating agents	25
Antiredeposition agents	15
Other	25
Total	$1,635

Meetings

Detergents Eight-O nears

Planners and speakers for the AOCS Short Course on Soaps and Detergents to be held in September will meet during the ISF/AOCS World Congress in New York to discuss plans for meeting.

The meeting, entitled "Detergents Eight-O," will be held at Hershey, Pennsylvania. The first technical session will be Monday morning, Sept.15, on "What Constraints Do We Operate Under?" and will including papers on governmental influence, safety restraints, waste disposal, nonrenewable raw materials, and biodegradability. Chairman will be Helmut Stupel of Shell Chemical.

The second session on raw materials, entitled "What Do We Have To Work With?" will include talks on fatty acids and renewable raw materials, minor ingredients, enzymes, phosphate replacements, and an update on surfactants. Chairman will be Arno Cahn of Lever Brothers.

The third session on Tuesday morning, Sept. 16, will be on "How to Make A Technical Product" with papers on solid and liquid heavy duty detergents, solid and liquid light duty detergents, automatic dishwasher detergents, hard-surface detergents, and miscellaneous products. Chairman will be Ted Matson of Conoco.

The fourth session on Tuesday evening will be "How to Make a Consumer Product" with talks on the role of private label companies, gearing surfactants for use in consumer products, brainstorming, and packaging of consumer products.

The final session on Wednesday morning, Sept. 17, will be entitled "Ask The Expert" with the first panel consisting of the Monday speakers who will answer registrants' questions. After a coffee break, speakers from Tuesday will be available for questioning. Chairman will be Irv Schmolka of BASF Wyandotte, who is also general chairman for the short course.

Social events will include golf and tennis tournaments as well as an informal social event one evening.

Registration forms and full program details are scheduled to be published in the March JAOCS and will be available from the AOCS, 508 S. Sixth St., Champaign, IL 61820. □