Peroxygens enter U.S. detergents

As consumers demand more convenient laundry products, peroxygen bleach manufacturers, activator distributors and detergent formulators envision a potentially large U.S. market for bleach systems in detergents. Currently, they are carefully watching consumer reaction to two recently introduced products—Procter & Gam-

ble's Tide With Bleach and Clorox Super Detergent.

Tide With Bleach is the first detergent with an activated perborate bleach system to be introduced into the U.S. market. Clorox Super Detergent, the bleach king's first entry into the detergent market, contains perborate bleach but no activator. If these products succeed, industry experts say other companies also will market detergents with bleach systems, creating a boon for the U.S. peroxygen business.

Approximately 60 million pounds of perborate and 2-4 million pounds of hydrogen peroxide (100% active basis) are used annually in laundry bleach applications in the U.S., according to Bill Eveleth, an analyst with Kline & Company. "If Tide With Bleach gains consumer acceptance and if perborates were added to all standard detergents, the perborate market could really take off. Depending on detergent formulations, it could go as high as 600 million pounds per year in the best possible scenario," Eveleth said. "Any significant growth for hydrogen peroxide will be in the production of perborates.'

Degussa Corp., a major perborate supplier, is more cautious about the outlook. "In the U.S. detergent market, conservative market potential for solid perborate in detergents is two billion pounds of detergent at 5 to 10% perborate content," according to John

Medina, Degussa Corp.'s marketing director for peroxygens. "However, that estimate could further increase assuming greater acceptance by the U.S. consumer and assuming that developments occur which enable the introduction of solid peroxygens into liquid detergents."

What's new in corp ev w

The European detergent market, which is approximately the same size as the U.S. market in terms of volume, uses one billion pounds of peroxygens per year. Although the two markets are of comparable size, DuPont's Market Manager for Cleaning Products Phillip Richardson noted that those levels may be unattainable in the U.S. due to differences between the two markets. "European consumers are accustomed to paying the cost of the bleaching agent while the U.S. consumer is not. Secondly, stable peroxygen systems are not available for liquid detergents which account for 40% of the U.S. market, versus less than 20% for Europe,' he said.

Laundry product sales are big business in the U.S. Consumers spend about \$3 billion for solid and liquid detergents and \$600 million for bleaches, according to Gregory Good, who follows consumer buying patterns in the laundry sector for Kline & Company. He doesn't expect the detergent market to grow much since consumers are spending more to dry clean an increasing array of natural and synthetic fabrics. "However, there is a niche for products with bleach," he said. But market tightness means "detergent formulators will be jockeying more and more for strong positions," Good said.

Formulators who decide to incorporate bleaches into solid (and eventually liquid) detergents will have to spend for every point of market share they wish to gain. "In this business, it is not unusual

for a company to spend \$50 million to \$100 million to launch a product," Good said.

Some industry watchers believe The Clorox Co. and Procter & Gamble have already spent more than \$50 million each to launch their re-

spective products. Tide With Bleach and Clorox Super Detergent were heavily promoted in test markets last year, and both gained market share, according to Kline & Company figures which indicate Tide With Bleach attained about 5% and Clorox Super Detergent earned about 10% of the share in their respective test markets. Figures from Kidder, Peabody & Co. indicate that in the three to six months prior to going national, Tide With Bleach gained 5-7% of the share and Clorox Super Detergent gained 4-5% in their respective test markets.

Good believes the gains by each company are respectable, considering some companies holding less than 3% of total market share are able to market their products profitably. However, he said, the companies "bought" the percentage points they've gained.

Until longer-term figures be-

come available in August, it is difficult to predict how Tide With Bleach and Clorox Super Detergent will do when they compete with each other and every other detergent across the nation, Good said. However, according to Kidder, Peabody's Jay Freedman, early numbers indicate that in areas where Tide With Bleach and Clorox Super Detergent are "head-to-head," the P&G product is outselling Clorox's. "When the companies stop giving the product away, the two products combined could hold 7-8% of the market," Freedman

Good speculated that if Tide With Bleach does as well nationally as it did in test markets, it would push Lever's Surf out of second place and move in behind regular powder Tide, the leader in the detergent powder sector. However, a move into second place might be at the expense of regular powder Tide, which holds more than 25% of the detergent powder market. Good said. "There could be a high percentage of 'cannibalism.' Tide With Bleach could steal market share away from powder Tide." However, according to P&G spokeswoman Jennifer Bailey, "Tide With Bleach is not cannibalizing the parent. Our Denver test market experience showed that Tide With Bleach did not take its growth disproportionately from Tide. The total Tide brand grew in the test market.

The Clorox Co., which holds 55% of the bleach market, is a newcomer to the detergent business. It will be big news if Clorox Super Detergent does as well nationally as it did in test markets, Good said. "There is no 'cannibalism' with Clo-

containing detergent or bleach. In particular, intensive research is aimed at the incorporation of a peroxygen bleach into a liquid detergent. The two primary targets (for this type of detergent) are customers seeking greater convenience and

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rox Super Detergent. It isn't stealing market share from another detergent product in its line. Any points it gains are taken from other companies."

The marketing efforts of the detergent manufacturers, who stress the convenience and fabric safety of peroxygen bleach-containing detergents, have been the driving force that convinced U.S. consumers to move toward detergents with bleaches. Degussa's Medina said. "But it's a real information process.'

If recent market introductions of peroxygen-containing bleaches prove successful, one can assume that other formulators will follow, Medina said. "We believe that all the major detergent and bleach manufacturers are seriously contemplating launching a peroxygen-

customers seeking color- and fabricsafe bleach alternatives," he said.

A look at the patent literature shows that all of the laundry product manufacturers and many of the surfactant and chemical suppliers are developing peroxygen technology, Clorox spokesman Fred Reicker said. "There is a clear recognition in the industry that hypochlorite bleaches are more active cleaning agents than peroxygen bleaches, but that they cannot be used on all dyes.'

Colgate-Palmolive, Dial and Lever are among the companies which have an active interest in the potential of peroxygen bleaches, but they are not currently in the market. "A detergent with bleach is certainly a viable new product option. I see the potential for peroxygen bleaches, but they won't

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convert the entire market," according to Winston Uchiyama, a section head in product development at Colgate-Palmolive.

Meanwhile, Ron Lewis, senior research fellow at the Dial Technical Center, sees incorporation in detergents as the real future for bleaches. However, Dial, which recently released a lemon-scented bleach, "is not doing much with peroxygen bleaches but may in the future."

Even if Tide With Bleach and Clorox's Super Detergent gain a

consumption of auxiliary (separate) bleaches will decline in tonnage by about 1% per year. "The bleaching chemicals used in auxiliaries will decline as a group one to two percent per year despite a better than 12% average annual growth forecast for hydrogen peroxide in this application between 1986 and 2000," she said. "However, the number of wash loads bleached with auxiliaries will grow slightly as more concentrated all-fabric products (particularly liquids) come into wider use."

Overall growth in household bleach consumption will depend largely on the success of detergents that contain bleach.

few percentage points in the scramble for detergent market share and other companies introduce products in the hopes of doing the same, there is no guarantee that the \$15 million, 60 million-pound U.S. peroxygen market will burst open. Industry experts say some detergent powder manufacturers, especially those that produce for the economy market, will be unwilling to formulate with perborates and perborate activators, which are expensive relative to other detergent components.

Another growth-limiting factor for peroxygens is the entrenched partiality for hypochlorite bleaches among U.S. consumers. In 1988, approximately 175 million pounds of sodium hypochlorite (on a 100% active basis)—which translated to about 3 billion pounds of liquid bleach—were consumed in the U.S., according to Eveleth, who noted that peroxygen bleach is not likely to displace hypochlorite bleaches due to the latter's efficacy and low cost.

Overall growth in household bleach consumption will depend largely on the success of detergents that contain bleach, according to Elaine Whitney, a research associate with Colin A. Houston & Associates (CAHA). She predicted U.S.

Formulators want to develop more products such as detergents with bleach to help powders maintain market share, Whitney said. CAHA estimates liquids currently represent nearly 40% of the U.S. household heavy-duty laundry detergent market on a volume basis. Should bleach-containing products not capture a significant share of the heavy-duty powder market, CAHA forecasts heavy-duty liquids could capture as much as 50% of the household laundry detergent market by 2000. "However, if the performance of detergent/bleach powders proves to be noticeable to most consumers, the commonly anticipated continuation of strong market share growth for liquids may well be slowed," Whitney said. She noted that as heavy-duty liquids grow in popularity, increasingly multifunctional powders are being developed to give nonphosphate powders more market parity with liquids.

Capacity

Interox, Degussa and DuPont believe they can meet any increase in peroxygen or hydrogen peroxide demand. DuPont has a worldscale sodium perborate tetrahydrate plant with excess capacity in Memphis, Tennessee, and hydrogen peroxide plants in Memphis and Maitland, Ontario. John Parker, new product development manager for Interox, said Interox operates a facility with 35 million pounds of sodium perborate capacity in Deer Park, Texas, and will go on stream with a 40-millionpound-capacity plant in Longview, Washington, later this year. Sodium perborate monohydrate (used in the production of Tide With Bleach) could be imported from Europe until demand increases, Medina said. There currently is no North American production of sodium perborate monohydrate.

Peroxygen development

In terms of efficacy of stain and soil removal, industry experts say there is very little to match hypochlorite-based bleaches. In standard stain removal and whiteness index testing, hypochlorites are 80% to 90% effective, while perborates are 15% to 20% effective. If a perborate is "activated," efficacy rises to 40% to 50%, Lewis said.

But the high oxidative potential of hypochlorites—the very property that makes them good bleaches—allows them to attack fibers and dyes indiscriminately. Bleaches with a lower oxidative potential, such as peroxygen bleaches, have the advantage of being more fabric- and colorsafe. "Peroxygen bleaches do not cause pinholing like chlorine bleach: they do not affect septic tank systems in a negative way, they do not have an obnoxious chlorine odor, and they do not form chlorinated byproducts," Medina said.

Peroxygen bleaches, in use in Europe since 1907, have traditionally been made from sodium perborate tetrahydrate. Sodium perborate monohydrate, a more recent development, is considered more effective because of its faster dissolution rate. In solution, solid peroxygen bleaches liberate OOH-, the moiety which actually carries out the bleaching.

Peroxygen bleaches worked well when laundry was still being

done at 95°C; in the early 1970s, however, Europe experienced a trend toward lower wash temperatures and peroxygens became less efficient. To work optimally, peroxygens need either high temperatures or an activator compound to compensate for lower temperatures. The activator aids in bleaching by reacting with perborate to form peracids.

Activators

Unilever is recognized as the pioneer in activator incorporation. In the late 1970s, it became the first company to add the activator tetraacetylethylenediamine (TAED) to laundry products.

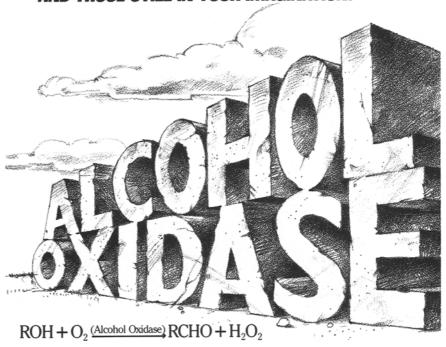
TAED is still the world's most widely used activator. Approximately 40,000 metric tons (MT) of TAED are sold in Europe each year, and in some European countries, as much as 60% of home laundry detergents contain activated oxygen bleaches, according to Pat O'Brien of Focus Chemicals. Focus Chemicals is the U.S. distributor of TAED for Warwick International, a major manufacturer of TAED.

"Miniscule amounts of activator are used in the U.S. relative to the amount of perborate used, but without activators, you don't get much mileage out of perborates," O'Brien said. "Until Tide With Bleach came out, there was no incentive for companies to use activators."

The introduction of Tide With Bleach brought the activator sodium nonanoyloxybenzene sulfonate (SNOBS) into large-scale commercial use. P&G's patent, covering Tide With Bleach-like formula uses, runs until the year 2000. Any P&G competitor wishing to use activators would have to use TAED or develop its own, O'Brien said. "We're looking for spin-off from P&G work. The market is still at ground zero, but it does have almost explosive potential."

If U.S. demand increases, Warwick could expand production capacity at its northern Wales facility, Hoechst, meanwhile, recently expanded TAED capacity to serve growing world demand.

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TAED plus peroxygen above 40°C—the favored wash temperature in Europe—will produce the perfect bleaching system and will work as well as perborate used alone at 95°C, according to Manfred Trautmann, Hoechst Celanese product manager for detergents. "At wash temperatures below 35°C, which are more common in the U.S., and even at 20°C, TAED with perborate shows per-

requires less bleach. P&G is marketing a detergent with SNOBS bleach under the Ariel name in Japan and would consider introducing a product using the SNOBS technology in Europe, he added.

Whitney noted that seven or eight other activators already have seen use, and a number of companies—including BASF, Colgate-Palmolive, Eastman, Ethyl, Monsanto, Shell and Stepan—hold pat-

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ceivable benefits," he said.

David DiGiulio. P&G's director of product development for U.S. laundry products, said P&G is always on the lookout for new activators. "Our testing shows that TAED does not work well enough under U.S. wash conditions. We wanted an activator that would be preferentially drawn to soils by its lipophilic tail. TAED does not have those lipophilic qualities." According to DiGiulio, bleach with SNOBS as the activator concentrates at the fabric surfaces, which means it is more efficient at lower temperatures and the formulation

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300 North Zeeb Road Dept. P.R. Ann Arbor, Mi. 48106 U.S.A. 30-32 Mortimer Street Dept. P.R. London WIN 7RA England ents on SNOBS. But Procter & Gamble is in the strongest patent position for U.S. applications, Whitney said, adding that this strength comes from P&G's patent coverage on SNOBS' use, coating and stabilization. Other companies which hold at least one patent in the activator area are Clorox, Henkel, Unilever, Kao and Lion.

Some researchers said that because P&G's patent position is strong, other companies will be forced to develop alternatives to activators as a method of incorporating bleach into detergents.

Other systems

Uchiyama predicts preformed peracid systems may be a viable option. In preformed peracid systems, the peracid must be coated or chemically modified to maintain stability in the product, Uchiyama explained. In the past, peracids have had limited product stability and have not proven to be economical from a cost/performance standpoint. The advantage of preformed peracids is that they merely dissolve in water to form the active species, whereas activated systems must undergo a second order reaction to form a low-temperature bleach, he added.

Hoechst, meanwhile, has re-

cently developed a preformed peracid system made from the imido peroxycarboxylic acid epsilon-n,nphthaloyl-amino-percaproic acid. According to Trautmann, it has "excellent stability and bleach activity at U.S. washing conditions."

Preformed peracid technology has been used in P&G's Vibrant and in Tide Multi Action Sheets. Both products were test-marketed and subsequently pulled from the market.

The "obvious plum to pick" in the area of detergent development would be a liquid detergent with bleach, according to Lewis. "But nobody has announced the successful incorporation of a preformed peracid or activated peroxygen system into a liquid."

However, P&G has worked on the delivery of peroxy acids in liquid form and recently was granted a European patent for stable, bleach-containing liquid detergents. The patent covers the crystallization of perborate bleach. Meanwhile, Colgate-Palmolive has several patents on liquid detergents that incorporate monohydrate and activator.

The introduction of detergents with bleach into the U.S. does not guarantee the success of peroxygens, hydrogen peroxide or activators, but detergent industry leaders remain optimistic because they believe consumers want an all-inone detergent and bleach. The companies are responding accordingly. 'We usually have an evolution in technology when there is an evoluconsumer tion in needs, Richardson of DuPont said. "Right now, the big search among detergent manufacturers is the search for adequately performing lowtemperature bleaching systems. The market winners will be the companies that develop the technologies that deliver the performance that the consumer wants and can perceive."

This article exploring the latest development in bleaches in the U.S. was written by JAOCS newswriter Anna Gillis.