

CLEANING UP A SOLVENT PROBLEM

Chemical makers unleash **NEW SOLVENTS** for cleaning industry customers unhappy with current offerings

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ANYONE PULLING a really old bottle of Windex or Formula 409 spray cleaner from the back of the pantry is in for a pleasant surprise. The stuff still works great—perhaps better than a recently purchased bottle—cleaning windows and walls easily and drying quickly with no streaking or smearing.

Until about a decade ago, Windex, Formula 409, and many other hard-surface cleaners owed much of their cleaning power to ethylene glycol monobutyl ether, or EGBE, a glycol ether solvent renowned for its ability to cost-effectively remove both water-soluble soils and water-insoluble oils and greases.

“It is a tremendous solvent. It’s magic,” says Martin Vince, a chemist who runs LizMar, an Ontario-based formulation consultancy.

EGBE came under fire for health reasons, including its ability to cause red blood cell breakage when inhaled, and consumer goods makers largely removed it. But the ingredients substituted for EGBE were often volatile organic compounds (VOCs) or presented other environmental problems. Sometimes they just didn’t clean very well. And EGBE continues to be used in many industrial and institutional cleaning products.

Now, a new round of solvent replacement is taking place in laundry detergents, spray cleaners, and other cleaning products for home and industry. Multiple solvents are being added or removed for performance, environmental, and human health reasons.

For chemical makers, the upheaval means a business boom. Over the past year, companies, often the very ones that make glycol

ethers and other traditional solvents, have come out with a flurry of new products.

They run the gamut from biobased to synthetic, from solvent to surfactant, but they are all intended to help customers in the cleaners business create formulas that are robust, cost-effective, and green. As a result, these are busy times for formulation chemists at cleaning product companies across the U.S.

Last October, two icons of corporate America—Procter & Gamble and DuPont—announced plans to use cellulosic ethanol as a solvent in Tide Coldwater Clean, a member of P&G’s flagship laundry detergent family. The cold-water version of Tide is marketed to consumers seeking to reduce energy consumption.

At present, ethanol derived from corn kernels helps keep Tide Coldwater’s myriad ingredients together in solution. DuPont is building a plant in Iowa that will make ethanol from corn cobs and stalks instead. Blending this cellulosic ethanol into Tide Coldwater will repurpose more than 7,000 tons of agricultural waste a year, the partners say, and in the process save the energy needed to do all the clothes washing in homes across California for a month.



For DuPont, the agreement with P&G is part of a growing focus on the home and fabric care market, according to Simon Herriott, DuPont’s global business director for biomaterials. For about five years the company also has been marketing 1,3-propanediol, another biobased chemical in its portfolio, to the household products industry.

Propanediol’s main use is as a raw material for DuPont’s Sorona brand fiber. One of its next-largest markets, Herriott says, is household care, where it has a lot of room to grow as a solvent, stabilizer, and enzyme carrier. Propanediol is found, for example, in a spray cleaner and a concentrated laundry detergent marketed by Method, a purveyor of environmentally friendly cleaning products.

Herriott is happy with this business, but he sees the potential for DuPont’s solvents to go beyond the niche market served by Method. “Mainstream consumers are increasingly concerned about the impact their own personal actions have on the environment,” he says, and this trend is influencing home care product firms. “We’re at an inflection point between the green pioneers and major mainstream formulators.”

ANOTHER NEW SOLVENT taken up by both Method and Seventh Generation, a competitor in the green consumer goods space, is ethyl levulinate glycerol ketal, manufactured by the biobased chemicals start-up Segetis. The ketal is found in the Method laundry detergent and in specialty spray cleaners from both Method and Seventh Generation.

For Clement Choy, senior director of advanced innovation at Seventh Generation, the ketal is a welcome addition to a woefully small arsenal of solvents his environmentally rigorous company can use. Choy, a chemist, is familiar with the wider world of solvents. Before joining Seventh Generation in 2008 he spent more than a quarter-century at Clorox and P&G, which had more liberal criteria for choosing solvents.

“We are definitely more selective and more restrictive,” Choy says about his current employer. For Seventh Generation, glycol ethers are verboten, and synthetics are avoided whenever possible. The company also won’t use VOCs, a restriction

that eliminates “a fair number of products out there,” Choy says.

Seventh Generation began working with Segetis in 2011. The following year it formulated ethyl levulinate glycerol ketal into a new line of spray cleaners for stone, wood, and stainless steel. Its main role in these products isn’t so much to dissolve soil or grease but to help solubilize fragrance oils and keep the overall cleaning formula stable.

Method hooked up with Segetis even earlier, coming out with the laundry detergent and a ketal-containing tub and tile cleaner in March 2011. In addition to ethyl levulinate glycerol ketal, the bathroom cleaner includes ethyl levulinate propylene glycol ketal. The two solvents work together to dissolve stains and soap scum, according to Kaj Johnson, a product development director at Method who goes by the title green chef.

And for the laundry detergent, which is superconcentrated, Method relies on a system of four solvents: propanediol, ethyl levulinate glycerol ketal, glycerin, and methyl esters. In addition to providing cleaning power, the system makes the formula compatible, flowable, and phase stable under extreme storage conditions.

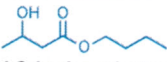

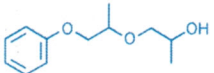
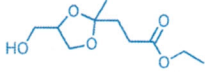


Like Choy, Johnson is happy to have a growing family of sustainable solvents at his disposal when formulating products. But that’s not enough, he cautions.

“If sustainability were all we were concerned about, we would have a very simple task,” Johnson says. In addition, human safety, effective cleaning, compatibility, stability, degradability, and surface safety all need to be considered. To best achieve these goals, he still seeks non-VOC solvents with broad surface safety, a broader portfolio of solubility parameters, and broad pH and heat stability.

Johnson works with non-VOC, biobased ingredients because Method’s upscale, environmentally conscious customers demand it. For Joe Zhou, vice president of R&D at Misco Products, a Pennsylvania-based maker of cleaners for the commercial and industrial markets, the demands aren’t so lofty. His customers are janitorial firms seeking products that clean quickly, effectively, and economically.

That means Misco continues to use EGBE in many of its traditional products, such as its MPC brand concentrated glass cleaner for the maintenance market. “EGBE is a very, very good solvent and very cost-effective,” Zhou says. “It’s like a

PROBLEM SOLVERS New solvents that meet strict VOC standards are proliferating.

Solvent (and structure)	Trade name	Supplier	Select applications
 Butyl 3-hydroxybutyrate	Omnia	Eastman	Industrial cleaners and degreasers
 N,N-Dimethyl-9-decenamide ^a	Steposol MET-10U	Stepan	Household cleaners, adhesive removal, paint strippers
 Dipropylene glycol phenyl ether	Dowanol DiPPH	Dow	Household cleaners
 Ethyl levulinate glycerol ketal	None	Segetis	Detergents, hard-surface cleaners, graffiti removal
 Methyl-9-dodecenoate	Clean 1200	Elevance	Heavy manufacturing, food processing
 1,3-Propanediol	Zemea	DuPont	Laundry detergents, hard-surface cleaners, glass cleaners

^a A surfactant targeted to replace solvents.

Chevrolet—a dependable workhorse.”

But for its Elements glass cleaner, part of a line it calls “environmentally responsible maintenance solutions,” Misco has replaced EGBE with a blend of diethylene glycol monobutyl ether and propylene glycol mono *n*-butyl ether. Unlike EGBE, these glycol ethers aren’t readily absorbed by the skin and aren’t associated with blood cell breakage, the firm says.

Misco is using propylene-based glycol ethers—so-called P-series glycol ethers—to replace EGBE in most of the new products it develops, according to Zhou. The catch, he says, is that there’s no one drop-in replacement for EGBE. The company often must tailor blends out of propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, propylene glycol mono *n*-butyl ether, and dipropylene glycol mono *n*-butyl ether.

Vince, the formulation chemist, also must get creative for customers that come to him seeking to replace EGBE. Sometimes those firms are developing green formulas to appeal to municipal buyers with a mandate to purchase cleaners bearing an eco-label.

Other times, customers need to remove VOCs to make their product comply with Environmental Protection Agency laws

or with state regulations that started in California but are now spreading across the country. Canada, where Vince’s firm is based, will soon enact similar rules.

“In the past, companies would label their products ‘Not for sale in California,’” Vince says. “Now, as more and more states adopt the California standard, having two distribution channels doesn’t wash anymore.”

And soon to affect cleaning product manufacturers is the United Nations Globally Harmonized System of Classification & Labelling of Chemicals, or GHS, which will make chemical hazard information more transparent on product labels and safety data sheets. The Occupational Safety & Health Administration wants U.S. manufacturers to be in compliance by June 1.

Vince notes that GHS requires the use of pictograms to convey hazards. The health hazard symbol, which depicts a human figure with a starlike light on its chest, is particularly forbidding. “It’s something you don’t want on your product,” he says.

For Bob Stahurski, chief executive of the industrial cleaners firm Nyco Products, it was mostly the threat of new VOC regulations that prompted the creation of a line of ready-to-use spray cleaners based on butyl 3-hydroxybutyrate, a cleaning solvent developed by Eastman Chemical.