



Companies Explore Alternatives to Ozone-Depleting HCFC-225 as Global Phase-Out Nears

The phase-out of the last major ozone-depleting solvent, HCFC-225, finally has begun. This is going to be good for the planet but tough for companies with complex cleaning requirements.

“The good news,” reports David Ferguson, Product Manager at MicroCare Corp., “is that the industry is meeting the call to develop new cleaning alternatives. In the past two years we have seen more new chemistries come out of the lab and onto the market than we saw in the entire decade before.”

But none of the alternatives are a “slam-dunk,” according to Barbara Kanegsberg, President of BFK Solutions, a consulting firm specializing in precision cleaning issues. “Anybody who does not have a cleaning alternatives strategy needs to be developing one urgently, and telling his boss to budget for it, right now,” Kanegsberg concludes.

Let’s take a look at the story behind this unusual product, some of the candidates being proposed to replace it, and ways companies can rigorously and systematically develop a plan to make the conversion to ozone-safe cleaning.

Background

Life on this planet is protected from dangerous solar radiation by a thin layer of ozone in the upper atmosphere. This layer is constantly in turmoil, with ozone being

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created and destroyed in relative balance. In the 1970s, it was discovered that man-made synthetic chemicals were depleting this protective barrier faster than nature could restore it. After just a few brief years of debate, more than 100 nations agreed to the Montreal Protocol¹ that set the rules for eliminating ozone-depleting substances around the globe. The first chemicals banned were the refrigerants, aerosol propellants, blowing agents and precision cleaning solvents called CFCs and other "Class I ozone-depleting substances." Now it's time for the less damaging "Class II" solvents to go, and the last among these is HCFC-225.

Thirty-four different HCFCs fluids were developed as interim replacements for the widely popular CFC materials. HCFC-225 was the last of the precision cleaning solvents to be phased-out because it had the lowest projected impact on the ozone layer. This policy was both prudent and practical: HCFC-225 has an ozone depleting impact approximately only 1/25 of the far more popular CFC-113 fluid. HCFC-225 also is a very good cleaner, it was nonflammable and fast-drying, it was VOC-exempt, and it had a relatively low global warming potential². Since companies found the transition from CFCs to HCFCs to be relatively painless they made the change fairly quickly, which helped minimize the damage to the ozone layer.

Was allowing the use of HCFCs ever a smart public policy? Many people disagreed with it; Greenpeace describes "the commercial and political influence of the chemical industry" as a major barrier to environmental improvements.³ But Howard Sidebottom and James Franklin wrote, in the definitive study of the impact of HCFCs on the environment, that "HCFCs have played an essential role, as interim replacement compounds, in ensuring the speedy elimination of CFCs."⁴ So it is a case of the "least bad" answer, and the EPA clearly agreed: one HCFC-225 product,

¹ See: <http://www.epa.gov/ozone/intpol/index.html>

² See: http://www.agc.com/english/chemicals/gas/e_solvents/e_225_6.html

³ See: <http://www.greenpeace.org/international/en/publications/reports/position-paper-on-f-gases/>

⁴ Howard Sidebottom and James Franklin, "The Atmospheric Fate and Impact of HCFCs and Chlorinated Solvents", *Pure and Applied Chemistry*, Vol. 68, No. 9, Pp 1757-1769, 1996. Can be viewed at: <http://pac.iupac.org/publications/pac/pdf/1996/pdf/6809x1757.pdf>. They also noted "HCFCs and chlorinated solvents make a small or insignificant contribution to stratospheric ozone depletion (with the exception of 1,1,1-trichloroethane), global warming, photochemical smog, 'acid rain', or chloride and fluoride levels in precipitation."

under the brand-name “AK-225” received the “Best of the Best” Stratospheric Ozone Protection Award from the Environment Protection Agency in 1997.⁵

This pragmatic approach to protecting the environment is the proper path for future efforts, according to Tom Tattersall, Chief Operating Officer at MicroCare Corp. “The teamwork and collaboration behind the Montreal Protocol is the optimal role-model for government-industry co-ordination,” he said.

Why have companies waited so long to make the change away from HCFC-225? Rob Lee, product manager at DuPont Corp., suspects the main issue is a combination of solvency and materials compatibility.

“They’re hanging on to it from a compatibility perspective,” he thinks. “HCFC-225 is a good cleaner, and it is generally more compatible with materials of construction than the HFC or HFE alternatives. Plus HCFC-225 has been spec’d in on military projects. So it’s hard to change.”

While it has been a long-time coming, this phase-out is important. One expert judges that the reduction in ozone damage and reduced global warming impact may be “the equivalent of removing the climate emissions from 70 million U.S. passenger cars for the next 30 years.”⁷

Cleaning Alternatives to HCFC-225

“As a class, HCFCs were remarkable materials,” said David Ferguson. “They were the last group of cleaners that contained chlorine on the molecule, instead of blending a chlorinated solvent to a fluorocarbon to enhance solvency.” This characteristic gave them broad compatibility with moderate solvency. Duplicating those properties with a different molecule is proving to be a challenging task.

Most companies using HCFC-225 will find the fastest and easiest transition to be to move to another nonflammable, solvent-based product. Even so, this may not be easy.

⁵ Plant Engineering Magazine, 6/12/2003, cited at www.PlantEngineering.com

⁷ See: <http://www.theozonehole.com/recentment.htm>

Almost all of the new cleaning fluids in their pure form are very stable and mild. To kick up their cleaning power, many solvent makers enhance their proprietary ingredients with a chlorinated material called 'trans 1,2 dichloroethylene' along with other ingredients. The resulting formulas may form "azeotropes" which are thermally stable mixtures preferred for their excellent cleaning power, their chemical characteristics, their ease of handling and their compatibility with vapor degreasing.

"But users must do their testing," Kanegsberg explains. "The low-boiling alternatives may need major equipment and process changes. The high-boiling blends may leave residues that are hard to remove. Esters can break down and form acids and alcohols. You have to consider the consequences of switching cleaning agents to assure consistent, cost-effective cleaning."

DuPont's Lee agrees. "The end-user needs to do thorough testing in the lab before they convert; don't expect to buy a couple drums of a new solvent and just dump it into the degreaser. We strongly urge customers to do preliminary screenings and lab tests to eliminate the risk of surprises during the conversion."

Even with this lab work, some end-users are going to find their options to be limited.

"Companies that could go no-clean went no-clean long ago," Lee notes. "Companies that could use water are there already. There are complex reasons why companies have stuck with HCFC-225, and finding a drop-in substitute will not be a walk in the park."

The Contenders, In Alphabetical Order

Novec® HFE Cleaners. For more than 15 years the 'hydrofluoroethers' (HFEs) from 3M Corp. have been available under the "Novec" brand name. Now an aging technology, they are nonflammable, fast-drying and environmentally acceptable. There are a handful of Novec blends, allowing the cleaning to be tailored to some limited degree to suit the contamination and the application. They are effective in vapor degreasers.

Sion® HFO Cleaners. DuPont is fielding a new HFO (hydrofluoro-olefin) alternative under the brand-name "Sion." Pure HFOs are very attractive because they can be candidates for VOC exemption and they have the lowest Global Warming impact. This product looks to be the optimal drop-in replacement for HCFC-225 products,

requiring only modest changes to temperature settings and cycle times. The blended product is a strong cleaner. It has a VOC content higher than 25 g/liter, which may limit its usefulness in areas like Southern California. Long-term, with a profile near HCFC-225 in terms of equipment design, and a superior environmental and toxicity profile, this may be one of the big winners to replace HCFC-225. Available in Asia and Europe now, it is expected to gain final EPA approval for use in the US shortly.

Solstice® HFO Cleaners. Also new on the market is an HFO solvent from Honeywell under the “Solstice” brand name. A mild cleaner used in its pure form, this product is VOC-exempt by the US EPA and has excellent materials compatibility. However, the Solstice fluid has an ultra-low boiling point (66°F) which will require expensive retrofits to existing vapor degreasers to keep the fluid trapped inside the cleaning machine. Nonetheless, in some regions it may be the initial alternative acceptable to some regulatory agencies.

Vertrel® HFC Cleaners. First to the market in the late 1990s, the “Vertrel” brand of hydrofluorocarbons (HFCs) from DuPont Corp. have been widely accepted as worthy successors to CFCs and HCFCs. Interestingly, the DuPont product line includes more than 20 different formulations. This allows DuPont to tackle more varied types of contamination and different regulatory environments than the HFE cleaners. However, HFC products have a slightly higher global warming impact than HFE-based choices.

Choices to Avoid

At this point, one option to seriously study and possibly avoid is any brominated solvent. These products are highly effective precision cleaners with a very attractive price. However, the toxicity standards for these products are being tightened and their use will become problematic. Brominated solvents (also called “nPB” and featuring a cleaner with the CAS number #106-94-5) are marketed under the brand names of Absolv, Bromothane, DrySolv, EnSolv, EnTron, LekSolv, Lenium, Metalnox, Solvon and others.⁸ All of these products feature the exact same chemical and all will probably be the next major class of solvents to be highly regulated or

⁸ This list of brand names was provided by the State of Massachusetts; see: www.turi.org/content/download/7249/132886/file/ for a fairly comprehensive list of brand names.

even phased-out. For most companies, it makes no sense to transition into another cleaner that might only have 18-24 months of useful life on the market.

Many companies also may want to consider aqueous cleaners, because water cleaning is considered very “green.” However, as noted above, most companies that are using vapor degreasers today have already experimented with aqueous options and found the process lacking. Especially with today’s high-end electronics and complex medical devices, water-based cleaning simply will be too costly, too slow, too complex, too energy-intensive, too rough on the components and often not able to get under the parts and get them clean and dry. Solvent cleaning solves all of those issues.

Developing the Cleaning Conversion Plan

First, do your internal research. Companies need to conduct an internal cleaning audit to determine which products in their warehouses and tool cribs contain HCFC-225. HCFC-225 can be found in drums, pails, glass bottles and even in aerosol cleaners. Determine who is using these products and why. Collecting all the details about each cleaning application will help narrow the search for a proper replacement

Companies also should take the time to consider the effectiveness of their current cleaning process. Is the current cleaner doing everything it should? Is it fast enough, reliable enough and is the cost-per-part cleaned affordable? What’s the future of this project – will we still be making this PCB or component in five years? This also is a good time to review the cleanliness specification – how clean is clean enough? Once you have your house in order, it’s time to start reviewing the candidates.

Contact the main vendors to get samples of the new cleaners that meet the cleaning criteria. Vendors should be willing to send small samples at no charge, such as liters and gallons. With samples of this size the effectiveness of the cleaner can be evaluated, and materials compatibility can be tested as well.

Having pruned the list of choices, it’s now time to prepare product samples and send them to the vendors’ labs for cleaning evaluations. Bundle up a significant quantity of soiled parts and package them in clean, air-tight packages for shipment to the cleaning vendors. Be as generous as you can with samples for testing, as a lack of test parts can affect the accuracy of the lab work.

Based on the results from labs, clients might want to fine-tune their expectations with more in-depth cleaning tests, or to vary the cleaning hardware to see if results might shift. Once that's done, you need to work with top management to fund and schedule the transition.

Wrap-Up

With the multiplicity of cleaning choices on the market today, there is no longer any reason to postpone the conversion from HCFC-225 to ozone-safe cleaners. It's not easy and it's not always cheap, but it can be done. The time is right, and it's the right thing to do. Start now.