The New Generation of Solvents
Developmental Challenges Inspire Creative Solutions

by Cheryl Salerno

Replacement of first-generation solvents, such as CFC-113, led to the introduction of a number of new alternative chemistries for cleaning applications. For those manufacturers that did not or could not embrace aqueous technologies, the search for suitable replacement solvents for their cleaning operations was often a challenging task. Many so-called "second-generation" solvents brought baggage of their own — not only in terms of toxicity and ozone depletion, but also in terms of flammability, potency, odor, separation, recycling, and cost.

Currently, a new wave of solvents is beginning to emerge — ones that address some of the drawbacks relevant to many of the initial replacements. In this article, industry professionals discuss the pros and cons of this new generation of solvents.

Aqueous Inadequacies Open Door for New Solvent Options

Second- and third-generation solvents cover a wide range of chemistries, including:

- Alcohols
- Various hydrocarbons
- Volatile methyl siloxanes
- Terpenes
- Esters (including soy methyl esters)
- Glycol ethers
- New halogens (i.e., *n*-Propyl bromide [*n*PB], hydrochlorofluorocarbons [HCFCs], hydrofluorocarbons [HFCs], perfluorocarbons [PFCs], and hydrofluoroethers [HFEs])
- n-Methyl pyrrole (nMP)
- Ethyl lactate
- t-Butyl acetate

Those interested in exploring the merits of solvent cleaning have a number of companies to which they can turn for answers (see pages 32-33). In fact, some companies represent not one, but many of the alternatives on this list. Mike Jones, vice president of Micro Care Systems, (Bristol, CT), believes that working for a company that packages and sells a wide range of alternatives brings a special understanding of product development and other issues related to these chemistries. According to Jones, more and more manufacturers are becoming aware of the technical limitations of aqueous cleaning technologies, opening the door for a whole new wave of solvent alternatives.

"The axiomatic characteristics of water — surface tension, drying time, energy consumption, and materials compatibility — cannot be changed without extraordinary expense," explains Jones. "Let's face it: the limits of water cleaning are defined at the molecular level, raising barriers that no amount of engineering can cost-effectively surmount."

Conversely, over the past two years, developments in HFE and HFC solvents have drawn attention back to solvent cleaning. Like the CFC and HCFC solvents they are replacing, new HFE and HFC formulations have both the ability to clean under the tightest packaging and the solvency to remove contamination. According to Jones, they are generally easy to handle, nonflammable, fast-drying, safe for technicians, and "easy on the environment."

"Most importantly, their wonderful solvency makes it easy to create new blends that can be tailored to the needs of the marketplace," Jones remarks.

The Long Wait for *n*PB

But while some newer solvent alternatives have sailed smoothly into the marketplace, others have hit what have proven to be significant snags along the way. Jones offered the case of *n*PB as an example.

"This product is a great cleaner, with a high flashpoint and exceptional solvency," states Jones. "It is rather popular and is extremely affordable. However, I have considerable doubts

regarding its continuing success in future years. Problems with [the U.S. Environmental Protection Agency's (EPA)] Significant New Alternatives Program (SNAP) approval, aroma issues, irregular quality, and lingering environmental issues have made this product too complicated for some users. The same is true (although for different reasons) for users of HCFC-225; it's just not a long-term answer."

Dov Shellef, president of Poly Systems USA, (Great Neck, NY), has a very different take on the fate of *n*PB. His company produces and markets brominated solvents, which have replaced chlorinated solvents in many operations due to issues of ozone depletion, toxicity, and hazardous air pollution surrounding the chlorinated forerunners.

"Brominated solvents are different in that they are non-ozone depleting and are not considered hazardous air pollutants," Shellef explains. "There are still issues of toxicity with which to contend, but these solvents offer a big plus in that they do not linger in the environment like the chlorinated and fluorinated versions."

Carrying an even higher toxicity rating than its chlorinated predecessors — 50 to 100 ppm in the working environment — *n*PB remains in limbo in terms of SNAP approval, but, nonetheless, it is currently being employed by many manufacturers. Shellef attributes this to *n*PB's considerable advantages over other solvents in regard to cleaning power. However, the chemistry's ability to clean so aggressively is precisely what has caused EPA officials to wait on long-range test results before granting SNAP approval.

"The hallmark of an exceptional solvent lies in its ability to remain stable and not disintegrate in the machine," Shellef states. "However, this tendency to resist breakdown usually means trouble for the environment. It's the big catch-22 and what was certainly our largest stumbling block in developing our *n*PB formulation."

(For more coverage of the *n*PB issue, see page 42.)

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Other Bumps Along the Road

The challenges involved in producing an effective yet safe product are not unique to those who market *n*PB; in fact, the majority of solvent manufacturers in the industry today face similar dilemmas.

"Most of the new solvent alternatives have some drawbacks, the biggest of which is simply a lack of real solvency," states James A. Mertens,

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development leader for Dow Chemical, (Midland, MI). "Additionally, all of the hydrocarbon products are volatile organic compounds and, to some extent, flammable. The HFCs all bring global warming issues, but some seem to be getting acceptance (Vertrel® and HFEs). Cost is also an issue with many of the newer solvents."

Ken Lobaugh, national sales manager of the Industrial Solvents division of AG Environmental Products, LLC, (Lenexa, KS), agrees that today's regulatory climate poses the greatest challenges for solvent users, but notes that none are insurmountable.

"Most of the regulatory hurdles can be overcome," states Lobaugh, "however, they will typically involve a change in process and often involve capital investment in new equipment. Recycling — as it has traditionally been done — will also change as users make the switch to less volatile chemicals. We will see a lot less distillation for recycling and much more filtration of materials."

Lobaugh works in a unique segment of the marketplace — agricultural-based solvents. "Ag-" or "green-" solvents are derived from crops such as soybeans or corn, and are used in various cleaning and degreasing applications.

"These high-performance green solvents can successfully replace much of the toxic, petroleum-based chemical compounds used in the world today," says Stephen Smith, marketing manager for SOYsolv Industrial Products (Tiffin, OH). "Little by little, the EPA is systematically eliminating cleaning products that industries can use. As they do that, people are scrambling to find products to replace it. Our solvents can serve as a drop-in replacement for mineral spirits, lacquer thinner, xylene, NMP and MEK, and other hydrocarbon degreasing solvents."

Challenges Foster Innovation

But developmental obstacles have

done little to stall the development of new, effective solvents; on the contrary, such challenges seem to have inspired novel ideas and fresh approaches to solvent cleaning.

The Vertrel® C products, developed by DuPont with technical assistance from Micro Care, involved enhancing various blends of HFC-43-10 with the proprietary HFC-365mfc (manufactured by Solvay Fluor und Derivate GmbH of Germany). It was discovered that the flammable but inexpensive HFC-365 easily and flexibly forms nonflammable near-azeotropes with the more expensive HFC-43-10, lowering the cost without degrading performance or safety.

For the wide range of clients who use these solvents in heated cleaning systems, the affordable, nonflammable, azeotrope-like stability of these blends proved to be a crucial technical breakthrough. In fact, for some applications, the necessary blending of newer-generation solvents has proved to be an advantage rather than a burden.

"Because of the limited solubility, these products are blended with other compounds to increase solvency," states Joseph F. Koch, market development supervisor, 3M Performance Materials, (St. Paul, MN). "This can actually be advantageous to end users as manufacturers are often able to formulate blends to remove specific soils while maintaining good materials compatibility. Using azeotropic blends in vapor degreasers ensures that compositions will remain stable in the liquid and vapor phases throughout their use."

For Poly Systems, developing an effective stabilizer is precisely what has enabled them to offer manufacturers the best of both worlds in terms of *n*PB. According to Shellef, this stabilizer allows the solvent to hold up during cleaning — without releasing hydrobrominated acid or sending off an unpleasant odor.

"We faced many challenges in developing our *n*PB-based product," Shellef concedes. "We had to first, answer the issues of stability and, second, ensure that the stabilizer did not bring additional issues of toxicity, flammability, and materials and equipment compatibility. The product that emerged is one that will effectively break down in the environment to a nontoxic substance."

Effective and Responsible Use

In a world of growing environmental awareness, the new generation of solvents provides industrial manufacturers with something invaluable: options. But determining the right solvent for the job is no longer a simple matter of what gets the job done.

As most solvent manufacturers will agree, getting the most from a cleaning operation involves education and diligence.

"There are two key elements to managing a precision cleaning process properly," states Jones. "First and foremost, a responsible engineer will measure every aspect of the system and its performance that can possibly be measured. It's simple: you cannot manage any system if you cannot measure it."

Jones notes several process control attributes that should be included in such measurements, including: solvent consumption, production quantities by part number (different parts will consume solvent at different rates), cleaning cycles versus total cleaning hours, rejects due to improper cleaning, "infant mortality" of products in the field, and warranty repairs (both of which may act as early warnings of cleaning process failures). While this data collection and assimilation might be time-consuming, it need not be expensive and often pays for itself in process improvements.

"Secondly, and a bit bluntly, be skeptical," Jones urges prospective customers. "Every cleaning application is different; your requirements are unique. Demand pre-purchase tests of your circuit boards or assemblies. Test a new solvent on your components, independent of the manufacturer's claims — it may be the cheapest insurance you ever bought. Also, never accept, under any circumstances, a solvent that does not come with a clear, concise, and understandable MSDS. Bet neither the safety of your staff nor the future of your company on unknown ingredients hidden behind 'trade secret' claims."

For More Information

Factors to Consider

Many factors influence — and even dictate — cleaning solvent choices.

- **Cost**
- **Equipment required**
- **Flash point**
- **Level of cleanliness**
- **ODP**
- **Toxicity/worker safety**
- **VOC levels**
- **Compatibility**
- **Effect on other processes**
- **Disposal requirements**
- **Type of contaminant**
- **Geometries of part being cleaned**

Learn more online at:
www.CleanTechCentral.com
www.PartsCleaningWeb.com
www.PrecisionCleaningWeb.com

According to Koch, the secret to getting the most out of solvents goes well beyond simply finding a product that effectively removes the target soils without damaging the part.

"The second part of effective solvent use is to produce efficiently — that is, reduce solvent loss," Koch explains. "New equipment and good operating practices both go a long way toward reducing solvent loss. New vacuum degreasers have improved to the point that costly emissions are extremely low. Even standard degreasers are now designed for better containment."

As many industry professionals pointed out, responsible management of a solvent cleaning operation must be a continuous process. Close scrutiny of chemical manufacturer claims and test results must lead to an equally critical assessment of the purchased product in action. A solid chemical supplier will not drop out of the picture after the transaction is complete.

Until clearance is granted by the EPA for its patented *n*PB formulation, Poly Systems has provided customers their own brand of reassurance in terms of their product's safety and efficiency. Clients are issued monitoring badges, which measure emission exposure limits of technicians who work with *n*PB.

"The badges give our customers a way to responsibly incorporate the chemistry into the working environment," says Shellef. "If it is determined that workers are being exposed to higher levels, we can work with the company to change the environment and/or the machinery to address those issues."

Customers are also provided "acid acceptance" testing kits and trained in their use. The kits are designed to intermittently measure the quality of the solvent, enabling technicians to determine when reclamation or refreshing of the solvent bath is necessary.

The Future of Solvent Cleaning

Most chemical manufacturers envisioned a bright future for solvent cleaning. As new technologies place a greater emphasis on precision cleaning, market demand is rising.

New products on the market — e.g., highly sensitive global-positioning systems, advanced medical products, and ultra-high performance disk drives — are vulnerable to contamination and demand the type of high-performance cleaning provided by solvents. Today's innovative electronic designs are made possible by miniaturized, hard-to-clean components (e.g., BGA, MCM, and flip-chip designs). Many mechanical

Continues on pg. 31

Continued from pg. 29

systems are likewise shrinking and becoming more contamination-prone (e.g., DVD systems and CD-ROM drives).

"Any change in the manufacturing cycle ripples down the production line causing havoc in unforeseen ways," states Jones. "Today's new solvents allow greater versatility and latitude in the production processes, freeing engineers to rectify, experiment, or innovate with new production processes, such as lead-free soldering. As old-style solvents with bad reputations are being phased out, new, affordable solvents are coming to market along with tight, cost-effective machines that can handle them."

"There will always be a place for solvent cleaning," remarks Lobaugh. "As clean water regulations are tightened, the costs of using aqueous cleaners will rise, and some current aqueous users will look back to solvent cleaning for answers."

Koch agrees, stating that today's new alternatives are available, safe, responsible, effective, and economical. He advises users to demand not only the best technical service from solvent manufacturers, but also a commitment to the products. He sees the continued effort toward product development and a commitment to product stewardship as factors that will cement the fate of solvents as safe, effective options in the cleaning industry.

But for end users, the continued success of this new wave of "friendlier" solvents boils down to one very significant factor: performance. With more and more people buying into the idea that today's new breed of solvents can be used safely, legally, and affordably, the question becomes: But do they work?

"The big challenge for this new generation of solvents is not so much to clean more efficiently," explains Shellef, "but to provide the same cleaning power as the older, more hazardous solvents that they replace."

According to Jones, today's new generation of alternatives more than fits the bill.

"New ingredients are offering chemical engineers new tools with which to fashion the new blends that companies require, which has spurred a growth in solvent cleaning," he states. "As products, people, and profits become more sensitive to chemicals in the workplace, solvent cleaning will regain its prominence as the cleaning process of choice for engineers around the world." ■