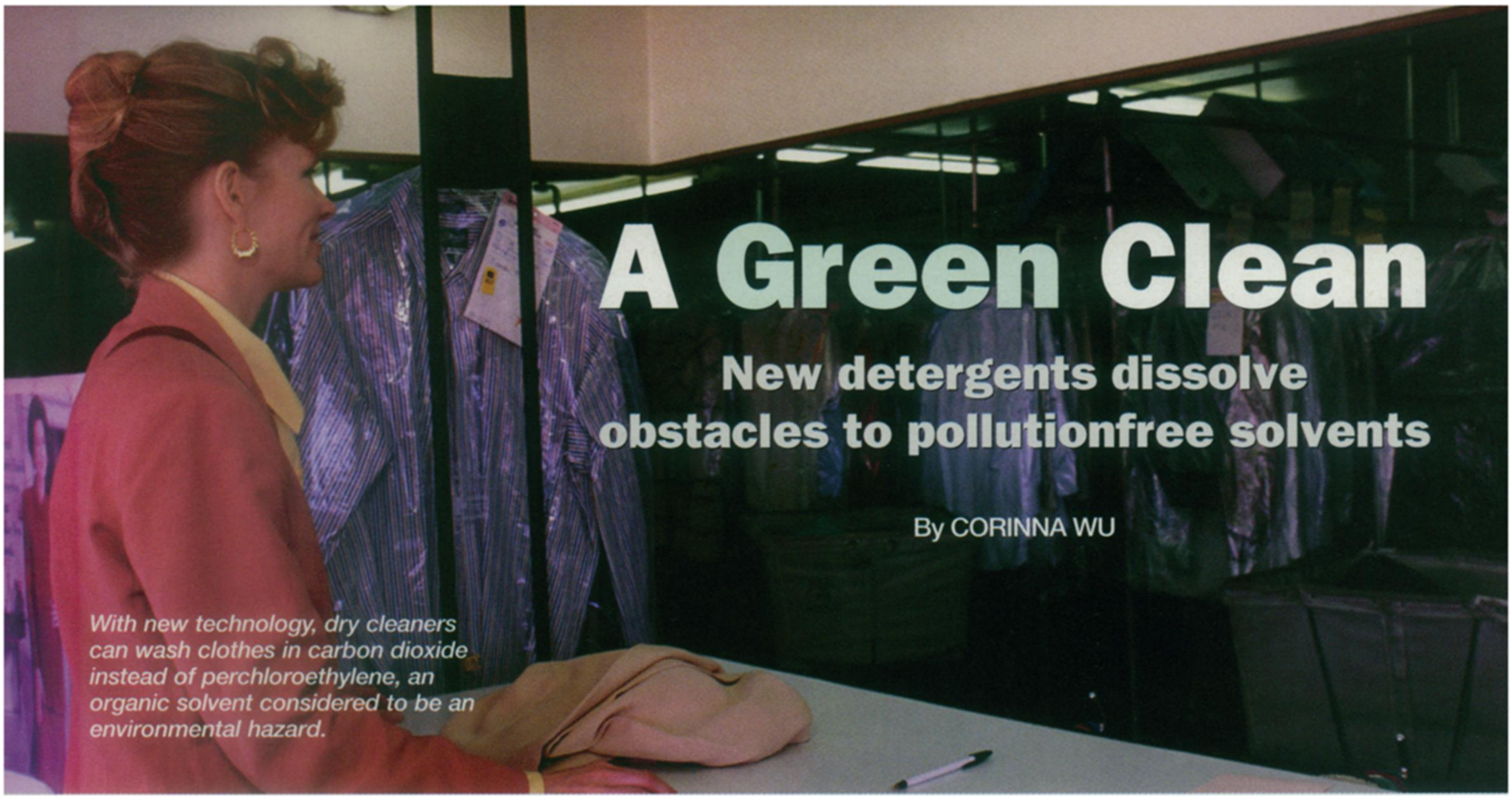

A Green Clean

New detergents dissolve obstacles to pollutionfree solvents

By CORINNA WU

With new technology, dry cleaners can wash clothes in carbon dioxide instead of perchloroethylene, an organic solvent considered to be an environmental hazard.

Water, despite its benign reputation, can wreak havoc on clothing—as anyone who has ever ignored a "dry clean only" label can attest. Consequently, piles of clothing get lugged to the local dry cleaner, for fear of turning another silk dress into a rag or shrinking still more wool sweaters into garments for the family dog.

Dry cleaning involves no water. Instead, clothes are treated for stains, then tumbled in perchloroethylene, a volatile, nonflammable organic liquid.

Concerns that perchloroethylene—or perc, as it's commonly known—may be a human health hazard have inspired tighter controls on its use. Perc is regulated as an air pollutant under the Clean Air Act and constitutes an environmental contaminant when found in soil and water. Dry cleaners and other businesses that use perc must dispose of it as hazardous waste.

Stricter regulation is pushing researchers to find alternatives to perc and other polluting solvents (SN: 6/21/97, p. 391). Recently, a method designed to be less harmful to the environment has been developed. It uses detergents, steam, and precisely controlled temperatures.

Some scientists, though, are taking a different approach. They are dry cleaning with carbon dioxide, the compound that forms dry ice. No one disputes its safety. Carbon dioxide puts the fizz in soda pop, is exhaled in our breath, and is present as a small component of the air around us.

Dry cleaning technology using liquid carbon dioxide made its debut at a recent cleaners' trade show in Las Vegas. Soon, carbon dioxide may prove useful not only as a dry cleaning agent but also as a degreaser for industrial machinery and as an alternative solvent in a variety of manufacturing processes.

About 80 percent of the dry cleaners in the United States use perc, mostly because it works so well. In the 1960s, it replaced petroleum-derived compounds as the cleaning agent of choice. It doesn't burn, and it dissipates from clothes easily.

Perc and chlorofluorocarbons (CFCs) have related industrial uses. They are used to clean metal parts during manufacturing and as solvents for synthesizing chemicals and polymers, an industry that is "ten times bigger than dry cleaning," says Joseph M. DeSimone of the University of North Carolina at Chapel Hill. Thirty billion pounds of these organic solvents are used each year worldwide.

Despite its utility, perc has drawbacks. Studies have linked prolonged perc exposure to liver and kidney damage and cancer. Short-term contact can cause dizziness, headaches, nausea, and irritation of the skin, eyes, nose, and throat.

A person bringing home a load of freshly cleaned clothes isn't exposed to much perc, as long as the clothes have been properly aired. Concern is greater, however, for workers in dry cleaners or factories and even for those who live in urban areas close to dry cleaners. Perc is coming under increasingly strict regulation, says DeSimone, and many states are considering outright bans. "There's lots of writing on the wall." Some companies have already redesigned dry cleaning machines to improve their ability to recapture perc and prevent its release into the environment.

The rapid phasing out of CFCs, which chemically degrade Earth's protective ozone layer, prompted companies to get a head start on their search for alternatives to perc. "Most companies are interested in being good stewards of the environment," says Paul T. Anastas of the Environmental Protection Agency's Office of Pollution Prevention and Toxics. Moreover, companies generally find that developing alternatives is economically beneficial in the long run, he notes.

Many signs point to carbon dioxide as a practical alternative to current solvents. One advantage is that it can be used as a supercritical fluid, a phase that occupies a no-man's-land between liquids and gases. When vapors are compressed, they tend to condense into liquid. If a vapor is heated above a critical temperature, however, it does not condense, no matter how much it's compressed. Carbon dioxide has a low critical temperature, 31°C, that makes its supercritical fluid easy to work with. Moreover, the fluid's properties can be tuned by adjusting temperature and pressure.

When choosing a solvent for a specific application, among the most important characteristics to consider are density and viscosity, says William A. Peters, associate director for fuels and environmental research at the Massachusetts Institute of Technology's Energy Laboratory. "In supercritical carbon dioxide, those properties can be varied greatly by changing temperature and pressure. They give you handles you can turn readily, especially on a commercial scale."

Carbon dioxide's safety makes it a choice solvent for the food industry, which already uses it on a large scale, notably for decaffeinating coffee. As coffee beans move through huge vats filled with supercritical carbon dioxide and a little water, the caffeine leaches out for later extraction and recovery. Carbon dioxide can also remove cholesterol and fat from milk and meat (SN: 7/23/88, p. 63; 4/15/89, p. 238).

For most industrial applications, however, operating at lower temperatures and pressures reduces energy costs, says DeSimone, making liquid carbon dioxide a better option.

Carbon dioxide is cheap and abundant. "There's no shortage of carbon dioxide in the world," says Anastas. Moreover, it can be collected from the waste generated by industrial processes such as ammonia manufacture, DeSimone says. No special disposal procedures are necessary because carbon dioxide can be easily recaptured and reused. In industry, fugitive emissions from leaky valves and gaskets are often difficult to eliminate, but with carbon dioxide, "there are fewer adverse consequences if recovery is less than perfect," says Peters.

Despite its rosy profile, carbon dioxide suffers from some drawbacks that have hampered its usefulness for cleaning. It doesn't dissolve most polymers, oils, waxes, proteins, and salts.

Of course, water doesn't clean everything either, and it needs help from soaps or detergents. The trick, then, is to find detergents that enhance carbon dioxide's ability to dissolve a laundry list of other substances.

DeSimone had been looking at ways of synthesizing polymers in carbon dioxide when he realized that the same techniques could be applied to cleaning. In 1990, he began investigating polymers that could be used as detergents.

Last year, he and his colleagues discovered a class of polymers that work as a detergent. For his efforts, DeSimone was awarded one of the 1997 Presidential Green Chemistry Awards, which recognize new technologies that help to reduce pollution (SN: 7/13/96, p. 22).

Traditional detergents consist of long molecules that stick to dirt and grease on one end and water on the other. They cluster around dirt particles, forming little spheres that water can escort away. The challenge for DeSimone was to find molecules that would form these spheres, called micelles, in carbon dioxide instead of water.

His team met that challenge by synthesizing copolymers, molecules that consist of two polymers joined together. One end needed to be soluble in carbon dioxide, the researchers had reasoned, while the other end should attract oils and waxes. Finding polymers that dissolve in carbon dioxide was the hard part, DeSimone notes, because most polymers shun these molecules.

Fluorinated acrylate polymers are an exception, dissolving well in carbon dioxide. Taking this cue, DeSimone and his colleagues engineered detergent molecules by joining an acrylate with polystyrene, a polymer that binds to oils.

Using a technique called small-angle neutron scattering, the researchers could see that the molecules effectively huddle together to form micelles. In these micelles, the polystyrene segments point toward the core—away from the carbon dioxide—while the acrylate segments hold the spheres suspended in the carbon dioxide.

They tested the would-be detergent further to see if it could suspend dirt particles in supercritical carbon dioxide. In their experiment, short polystyrene molecules served as the dirt.

Sure enough, the newly synthesized detergents surrounded them with micelles. The detergent could take up as much as 20 percent of its own weight in polystyrene. DeSimone and his colleagues described the results in the Dec. 20, 1996 SCIENCE.

MiCELL Technologies in Raleigh, N.C., is marketing the new detergents. Another company, the American Dryer Corp. in Fall River, Mass., has made a 100-gallon dry cleaning machine to use the detergents in liquid carbon dioxide. The machine, which "looks like a bank vault," DeSimone says, cleans about 50 to 70 pounds of clothes at a time. At about 900 pounds per square inch of pressure, the clothes tumble about with the carbon dioxide and about 5 ounces of detergent.

After the wash and rinse cycles, all the carbon dioxide is distilled and re-collected. The process leaves the dirt and grime in a container to be disposed of without any special precautions.

Since the process is carried out at room temperature, there's no need to identify stains before cleaning. Because conventional dry cleaning operates at high temperatures, stains must be pretreated so that the heat won't set them permanently. The lower operating temperature also saves energy.

Leather and suede, which are not amenable to standard dry cleaning, can be cleaned with the new method because liquid carbon dioxide is a milder solvent than perc.

Another research group, at Los Alamos (N.M.) National Laboratory, has also developed a dry cleaning machine based on liquid carbon dioxide. "Preliminary experiments showed that supercritical carbon dioxide was too good a solvent," says Craig M.V. Taylor. He and his colleagues discovered that it dissolves fabric dyes and finishing agents and changes the structure of clothing fibers. Liquid carbon dioxide tends to stay on the surface of the fibers, he says, instead of diffusing in, as the supercritical version does.

What detergents offer, says DeSimone, is "the opportunity to enhance the dissolving power, so what could only be done in supercritical carbon dioxide can be done by dropping the temperature and pressure." The milder conditions avert the problem of dissolving dyes and finishes that should stay in the fabric.

The actual detergents used in the dry cleaning machine are made by joining silicone polymers, which can dissolve in carbon dioxide, and segments that attract either oils or water-soluble dirt.

The Los Alamos group, in conjunction with Hughes Aircraft Co. in El Segundo, Calif., is also investigating detergents. The team combines several substances to attack the dirt on clothes: proteases to break down proteins, agents to mediate the amount of humidity, and soap to move dirt away from the fabric.

Not much detergent is needed to do the job. In powdered products for home washing machines, Taylor says, "70 to 80 percent of it is just filler" because consumers expect to need a cup or so of detergent. Dry cleaners, on the other hand, already subscribe to a less-is-more philosophy.

The power of carbon dioxide is coming to bear on other applications, such as the synthesis of polymers. Many polymer reactions require solvents that don't contain hydrogen because it interrupts the synthesis, leaving short polymer fragments of low molecular weight.

"If you need an organic solvent without hydrogen, what does that leave you with?" DeSimone asks. CFCs, one of the few chemical alternatives, are now banned.

Furthermore, some applications naturally call for benign solvents. For example, organic solvents are used to make contact lenses, Taylor says, but if any solvent remains in the material, it could leach out and irritate the eye.

For these reasons, carbon dioxide seems like an attractive alternative to traditional solvents. Numerous researchers are examining the basic behavior of chemical reactions in carbon dioxide. They hope that carbon dioxide can eventually replace other organic solvents on a large scale in the chemical manufacturing industry, Peters says.

Taylor sees the development of dry cleaning technology as research for "the mom and pop shops" that, unlike large companies, don't have the wherewithal to come up with replacement solvents.

The infrastructure for delivering carbon dioxide is already in place. Many restaurants have large storage reservoirs of carbon dioxide for carbonated beverages; these units are filled from tanks on delivery trucks. Both DeSimone and Taylor envision that such deliveries could easily be made to dry cleaners, too.

With that in mind, what's left is to see if the new, green dry cleaning machines catch on—or fizzle out. □